Revealing the interface nature of ZDDP tribofilm by X-ray photoelectron spectroscopy and atom probe tomography

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Abstract

Purpose – To decrease wear and friction, zinc dialkyldithiophosphate (ZDDP) has been used in engine oil for several decades, but the mechanism of the tribofilm formation is still unclear. The purpose of this study is to characterize the chemical details of the tribofilm by using high-resolution approaching.

Design/methodology/approach – An ISO VG 100 mineral oil mixed with ZDDP was used in sliding tests on cylindrical roller bearings. Tribofilm formation was observed after 2 h of the sliding test. X-ray photoelectron spectroscopy (XPS) and atom probe tomography (APT) were used for chemical analysis of the tribofilm.

Findings – The results show that the ZDDP tribofilm consists of the common ZDDP elements along with iron oxides. A considerable amount of zinc and a small amount of sulfur were observed. In particular, an oxide interlayer with sulfur enrichment was revealed by APT between the tribofilm and the steel substrate. The depth profile of the chemical composition was obtained, and a tribofilm of approximately 40 nm thickness was identified by XPS.

Originality/value – A sulfur enrichment at the interface is observed by APT, which is beneath an oxygen enrichment. The clear evidence of the S interlayer confirms the hard and soft acids and bases principle.

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1. Introduction

Zinc dialkyldithiophosphate (ZDDP) is a multi-functional additive that has been widely used for formulating lubricants because of its excellent performance and relatively low cost (Spikes, 2004). The addition of ZDDP contributes to the formation of an anti-wear tribofilm, which prevents direct contact between two surfaces acting as a role of a barrier. The tribofilm also has the capability of capturing harmful hard particles such as iron oxide, thus reducing the wear of the sliding surfaces (Minfray *et al.*, 2004b; Onodera *et al.*, 2008). The tribofilm is present as solid-like pads formed in the contact area that is commonly described as blue-colored tribofilm (Kubiak *et al.*, 2012; Onodera *et al.*, 2013; Gachot *et al.*, 2016). It is generally accepted that the presence of a ZDDP tribofilm is correlated with the reduction of wear and friction. ZDDP was used in various applications because of its benefits in tribological performance. However, the usage of ZDDP in engine oil is now facing restrictions, as the phosphorous and sulfur oxides reduce the effective life of exhaust catalysts (Spikes, 2004). To find a proper substitute, several open questions have to be answered.

The formation of ZDDP tribofilm is a complex mechanism induced by thermal activation and tribomechanical reactions (i.e. shearing) (Fujita and Spikes, 2004; Fuller *et al.*, 1997). Shear-induced tribofilms showed a better stability and wear-resistance, according to Bancroft *et al.* (Bancroft *et al.*, 1997). Based on molecular dynamics simulations, it is suggested that the pressure/shear-induced cross-linking is the key mechanism in the formation of anti-wear films (Mosey *et al.*, 2005). In addition, the driving force of the tribochemical reaction of ZDDP is not directly attributed to the temperature but to the entropy mixing contribution (Martin *et al.*, 2012). Gosvami *et al.* (Gosvami *et al.*, 2015) proved by using *in-situ* sliding tests with atomic force microscopy that the formation of the tribofilm is a thermally activated and stress-assisted reaction. Furthermore, it is suggested that nano-crystallization within the material caused by the sliding process enhanced the tribofilm formation.

The composition of the main part of tribofilm, namely, the bulk tribofilm, is based on the ZDDP related elements, such as Zn, P and S. Longer chain of zinc/iron polyphosphates were found at the top of the tribofilm; whereas lower chain at the bottom region (Spikes, 2004). Various methods have been applied to reveal the chemical detail of the ZDDP tribolayer, such as Raman spectroscopy (Berkani *et al.*, 2013), time of flight secondary ion mass spectrometry (Minfray *et al.*, 2004a), auger electron spectroscopy (Martin *et al.*, 2000) and X-ray absorption near edge structure (XANES) (Nicholls *et al.*, 2003). The morphology of the tribofilm can be described as island-like pads, which consists mainly of glassy phosphates (Martin *et al.*, 2001).

A high concentration of oxygen was commonly found in the bulk tribofilm caused by the sliding motion. Martin *et al.* (2001) observed a considerable amount of oxygen in the tribolayer and approximately 4 per cent of sulfur in the top of the bulk tribofilm. Miranda-Medina *et al.* (Miranda-Medina *et al.*, 2019) indicated iron oxide particles captured by the tribolayer in a cross-section observation. Hence, Guo *et al.* (2017) identified a clear iron oxide layer at the bottom of the tribofilm, which revealed that there is an oxygen enrichment at the interface between the bulk tribofilm and the steel substrate.

In addition to oxygen, sulfur has also been identified in the tribofilm; however, it is still unclear whether there is an enrichment at the interface. Based on the hard and soft acids and bases (HSAB) principle, the chemical reaction between sulfur and nascent steel substrate has been proposed as an initial step of film formation (Martin, 1999). Bell *et al.* (1992), Smith and Bell (1999) found an enrichment of S/O at the interface with about 5-10 per cent of sulfur content. Some recent works present the existence of the sulfur-enriched layer differently by various methods, Shimizu and Spikes (2016) found the enrichment of S at the initial state of sliding, but it was afterward pushed to the edge of the contact zone and transformed to be P- and Zn-enriched. Soltanahmadi *et al.* (2017) have made the sulfide interlayer visualized by using transmission electron microscopy (TEM)/energy dispersive X-ray spectroscopy (EDS). Moreover, X-ray photoelectron spectroscopy (XPS) identified a sulfur/oxygen enrichment at the bottom side of the bulk tribofilm (Heuberger *et al.*, 2007; Dorgham *et al.*, 2018). However, there are some studies claimed that no sulfur interlayer was identified (Martin, 1999; Martin *et al.*, 2001; Zhou *et al.*, 2017). According to the literature mentioned above, the S enrichment at the interface is still ambiguous. The thinness and the mixture of oxygen and sulfur increase the difficulty of identifying the interface nature of the tribofilm.

Atom probe tomography (APT) is a high-resolution analytical technique, which provides three-dimensional (3D) chemical compositional analysis at the nanometer scale (Kelly and Miller, 2007; Miller and Forbes, 2009). The chemical sensitivity limit of APT is around 10 ppm, and it is accordingly an ideal tool to reveal quantitative chemical information of segregation and near interfaces. The spatial resolution limit of this technique is approximately 0.1 nm in *z*-direction (depth) and 0.2 nm in *xy*-directions (lateral), which takes a longer time for the sample preparation, but gives a prominent three-dimensional representation of the elemental distribution at high-resolution. So far, there are only a few APT studies aiming at tribofilms. Kim *et al.* (2016) applied APT to prove the little content of boron in the tribofilm formed by boron added lubricants. Guo *et al.* (2017), Zhou *et al.* (2017) identified the existence of an iron oxide interlayer, but no sulfur enrichment was found. Therefore, APT was used in this study to examine the interface region between the ZDDP tribofilm and the steel substrate.

2. Experiments

2.1 Zinc dialkyldithiophosphate tribofilm formation

Tribofilm was formed after a tribological sliding test operated by a modified FE8 test rig according to DIN 51819-3. Cylindrical roller thrust bearings (Type 81212) comprised of two washers, a cage, and 15 cylindrical rollers made of 100Cr6 bearing steel (AISI 52100) were tested in lubricated conditions. The bearings were installed in the vertical plane, i.e. with a horizontal axis of rotation. The test was run with a rotational speed of 20 rpm and an axial load of 80 kN for 2 h. A mineral oil of class ISO VG 100 was used as a base oil and mixed with a secondary ZDDP additive in a concentration of 0.02 Wt.% of phosphorous. Sufficient lubricant was fed to the contact area by a pumping system. The working temperature was 80°C. The maximum contact pressure according to Hertzian calculation was 1.92 GPa. More experimental details can be found in Table 1. In addition, the minimum oil film thickness was estimated according to the Dowson-Higginson equation (Dowson *et al.*, 1962) as boundary lubrication. After the sliding test, the surface was cleaned by benzene and isopropanol to remove the residual lubricant, abrasives and contaminants.

2.2 X-ray photoelectron spectroscopy

The depth profile of the tribofilm was examined by XPS. The instrument is equipped with a monochromatic Al Kα (1486.6 eV) source based on a 500 mm circle geometry, a delay-line detector (DLD), a 165 mm mean radius hemispherical analyzer plus spherical mirror analyzer (SMA) for parallel chemical imaging and runs under ultra-high vacuum conditions with a working pressure below 10^{-8} mbar in the main chamber. The spectrometer was used in small spot spectroscopy mode, where the virtual probe on the surface of the samples is defined by choosing a suited aperture inside the electrostatic column of the detector. The place of measurement was set to a size of 0.3 x 0.7 mm, matching the tribofilm regions within the wear track. Congruence of the region of interest and place of measurement was controlled by parallel chemical imaging. The chemical composition of the surface of the sample was analyzed by XPS survey spectra with a typical information depth of less than 5 nm. Elemental concentrations in atomic percentages for the detected elements were calculated from the peak areas of photoelectron lines. Depth information of the tribofilm was obtained by XPS sputter profiles. All ZDDP tribofilm related elements including zinc, phosphorus, sulfur, oxygen and iron were considered. For sputter etching, the standard Argon ion gun was used with a raster size of 2 x 2 mm and an ion energy of 2 keV. The depth scale is given in regard to a Ta_2O_5 reference sample, which would be sputtered up to this deep with the same adjustments of the ion gun.

2.3 Atom probe tomography

Sample preparation for APT was processed in a dual beam scanning electron microscope/focused ion beam workstation (SEM/FIB). A 200 nm Cr sacrificial capping layer was deposited above the ZDDP tribofilm by physical vapor deposition (PVD). The specimens were prepared by the lift-out technique described in (Thompson *et al.*, 2007). The last step of low energy milling at 2 kV was performed to minimize Ga induced damage. Laser pulsed APT measurements were performed at a repetition rate of 100 kHz, specimen temperature of about 60 K, a pressure lower than $1 \times 10\ -10$ Torr (1.33×10^{-8} Pa) and a laser pulse energy of 0.7 nJ. The evaporation rate was set to 2 atoms per 1,000 pulses. Data sets were reconstructed and analyzed by a computational analysis software.

3. Results and discussions

A ZDDP anti-wear tribofilm was formed at the contact area after 2 h of the sliding test. The surface overview of the bearing washer obtained by optical microscopy is shown in Figure 1(a) and (b). In the wear track area, a tribofilm with brown and blue coloration was found along the wear track. The correlation between the Slide-Roll Ratio (SRR) and the thickness of the tribofilm on roller bearings has been presented previously (Stratmann *et al.*, 2017). By means of the formation of the anti-wear tribofilm, no severe wear damage was observed. The presence of the ZDDP tribofilm enhances the tribological performance and prolongs the lifetime of the thrust bearings (Hsu *et al.*, 2017; Rosenkranz *et al.*, 2016). Furthermore, it has been proven by Gachot *et al.* (2016) that the blue regions are enriched in phosphates, whereas the brown-colored film fractions show significant amounts of iron oxides. As a consequence, the blue region at SRR +7 per cent was selected for further investigation by XPS and APT. In addition, the cross-section profile obtained by SEM is shown in Figure 2. The thickness of the tribofilm is up to a maximum of 80 nm. It can be observed that the average thickness is around 40 nm. The inhomogeneity of the tribofilm can be attributed to the complex tribochemical reaction, which is in good agreement with the literature (Kalin, 2004; Topolovec-Miklozic *et al.*, 2007).

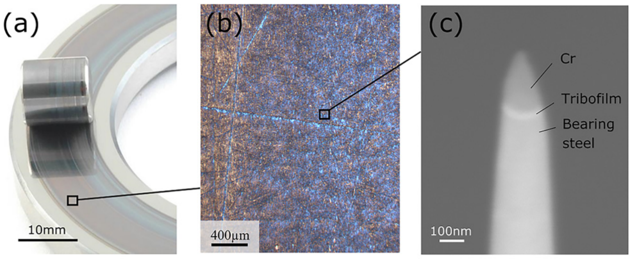
XPS analysis presents the chemical composition of the ZDDP tribofilm at its surface and by sputtering along with the depth. In Figure 3(a), the depth profile shows the concentration of the elements identified, and Figure 3(b) shows the concentration profile of the uppermost 100 nm. According to the depth profile, the tribofilm was approximately 40 nm in thickness. The tribofilm was composed of the ZDDP related elements, including 11 Wt.% of P, 2 Wt.% of S and 24 Wt.% of Zn; meanwhile around 50 Wt.% of oxygen was found. The analysis reveals a considerable amount of oxygen in the tribofilm, which could be composed of the products of the decomposition of ZDDP itself, iron oxides from the wear debris, or even caused by the exposure to ambient air after testing. In addition, iron has been detected in the tribofilm. This can be attributed either to the diffusion of Fe from the iron-based substrate, or to the deposition of wear debris (Martin, 1999; Martin *et al.*, 2001). For further examination into the interface, the tribofilm was cut and shaped into the form of a tip by SEM/FIB lift-out process. An SEM image of an APT tip specimen from the respective sample is shown in Figure 1(c).

APT atom maps are shown in Figure 4. The data set shows the spatial distribution of the elements in the specimen, including the Cr capping layer, anti-wear tribofilm and steel substrate (Figure 4(a)). Figure 4(b) shows the spatial distribution of single ions as well as some complex ions. The Cr capping layer can be observed at the top of the specimen, whereas the tribofilm and its related elements such as P, S, Zn and O are dominant in the region below. Fe atoms are located mainly beneath the region of tribofilm (steel substrate) but also

Table 1. Lubricant properties and lubrication conditions for tribofilm growth in sliding test

	Oil properties at 80°C		Sliding and lubrication condition		
Kinematic Viscosity	**Density**	**Pressure-viscosity coefficient**	**Rolling speed**	**Max. pressure**	**Temp.**
18.4 mm^2/s	856.9 kg/m^3	1.59×10^{-8} Pa^{-1}	0.04 m/s	1.92 GPa	80°C

Figure 1 General view of the sample preparation



Notes: (a) Overview of the wear track on the surface of thrust ring with a cylindrical roller; (b) the ZDDP tribofilm in the wear track obtained by optic microscopy; (c) the shaped tip specimen of the tribofilm for APT analysis

Figure 2 STEM image showing the cross-section of the tribofilm in the wear track. From top to bottom are Pt protective layer, ZDDP tribofilm and Fe substrate

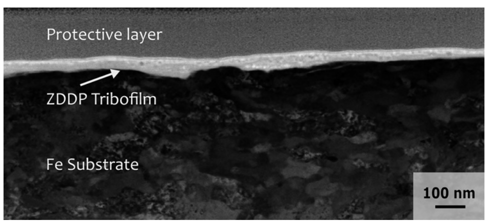


Figure 3 (a) Chemical composition profile of the ZDDP tribofilm by XPS, sputtering from the top of the film to the steel substrate and (b) a concentration profile for the uppermost 100 nm

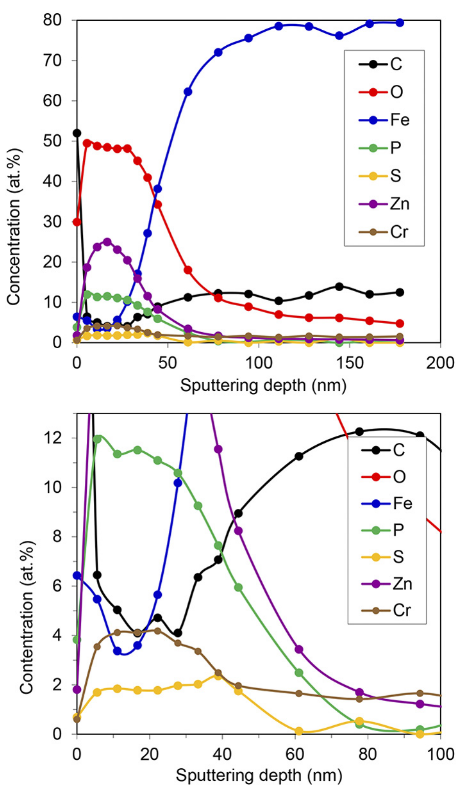
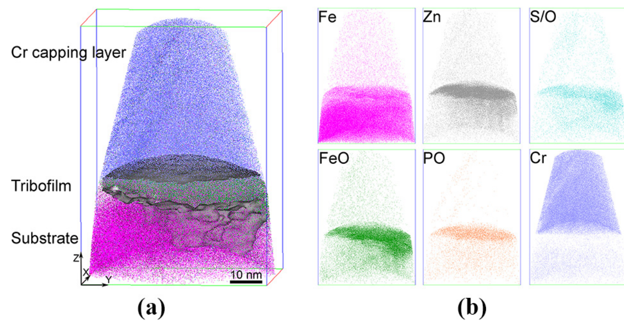


Figure 4 (a) 3 D APT reconstruction showing the Cr capping layer, ZDDP tribofilm and steel substrate. A 5 Wt.% of Zn iso-concentration surface (grey) is used to delimitate the tribofilm and (b) spatial distribution of Fe, Zn, S/O, FeO, PO and Cr atoms in the reconstruction



found in the tribofilm. Several peak-overlaps exist in the APT mass-to-charge-state ratio spectrum such as Zn^{2+} (m/n = 32-35) with SiO_2^{2+} (m/n = 30-33), FeO^{2+} (m/n = 35-38) and CrO^{2+} (m/n = 33-36). Furthermore, the overlap in the mass spectrum between O^{+1} and S^{+2} at m/n = 16 and between O_2^{+1} and S^{+1} at m/n = 32, makes it difficult to differentiate these elements in the spatial maps clearly. A peak decomposition algorithm was used to correct the overlaps based on the natural isotopic abundance (Gault *et al.*, 2012).

Table 2 shows the average composition of the tribofilm measured by APT. The tribofilm was delimited by a 5 Wt.% of Zn iso-concentration surface [Figure 4(a)], and the composition was calculated considering the atoms inside this volume. The compositions of the Cr-capping layer and the steel substrate are therefore excluded from such analysis. The results show that the tribofilm was composed of approximately 26 Wt.% of Zn and approximately 3 Wt.% of S, which is similar to the results of XPS. On the contrary, a higher amount of Fe and a lower amount of O and P were identified. The differences between these two methods could be attributed to the inhomogeneity of the tribofilm, which was also found in the previous study by TEM (Gachot *et al.*, 2016). Additionally, APT analysis required high-level cleanliness of sample preparation. The organic phosphate layer could have been partially removed by solvent cleaning before APT sample preparation (Smith and Bell, 1999). However, the interlayer covered by the inorganic layer was fully conserved. A clear insight into the interface between the tribofilm and the substrate was then obtained.

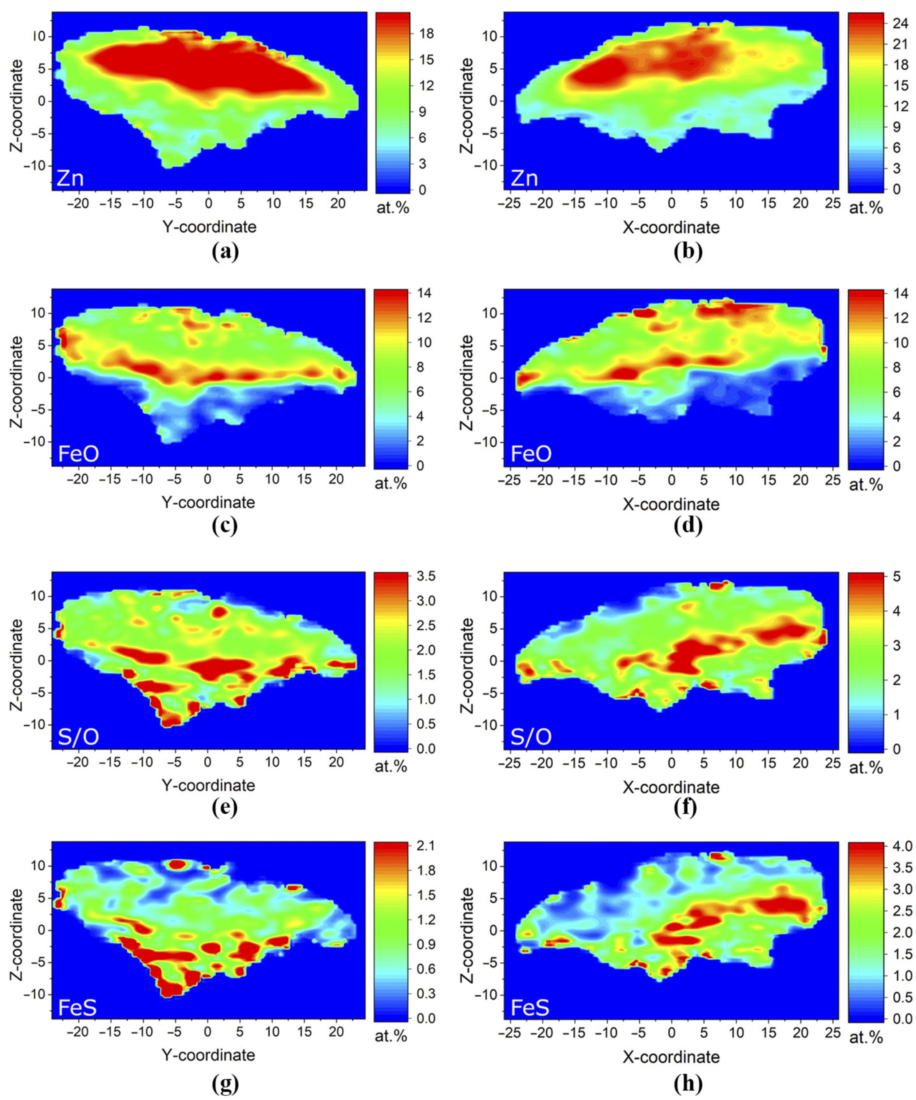
Table 2. Chemical composition of the tribofilm measured by APT, calculated from within a volume enclosed by iso-concentration surfaces of 5 Wt.% Zn

	Composition Wt.%		
Zn	25.74	±	0.08
P	0.73	±	0.01
S	2.79	±	0.02
O	15.08	±	0.01
Cr	3.98	±	0.03
Fe	48.33	±	0.09
C	0.61	±	0.01

In Figure 5, two-dimensional (2D) contour plots highlight the elemental distributions and compositions within two mutually perpendicular 5 nm thick slices through the APT data set at the tribofilm, namely, *x-z* and *y-z* planes [correlated to Figure 4 (a)]. From top to bottom, Zn enrichment at the upper part of the tribofilm is presented in Figure 5(a) and (b), and the enrichment of FeO underneath the Zn-rich region is shown in Figure 5(c) and (d). Finally, enrichment of S/O at the bottom of the substrate is shown in Figure 5(e) and (f). The disambiguation between S and O was done by the FeS complex ion peaks, showing the presence of S in the lowest part of the tribofilm [Figure 5(g) and (h)].

At the upper part of the tribofilm, a higher amount of Zn was found, which was mixed with iron and oxygen. The composition of the tribofilm shows the participation of ZDDP elements, which can be attributed to the aforementioned shearing influence by sliding. Moreover, an iron oxide layer was formed beneath the Zn-rich area, which can be attributed to the entrapment of wear debris. The observation of the oxygen enrichment is in good agreement with the literature, which suggested that the shearing causes the oxidation of the surface and the tribofilm (Zhang *et al.*, 2005). Wear particles removed from the steel surface by mechanical motion were first carried into the lubricant; the particles would then be embedded into

Figure 5 Two-dimensional (2 D) contour plots showing the elemental distribution and composition profiles at two mutually perpendicular slices through the tribofilm (*x-z* and *y-z* planes)



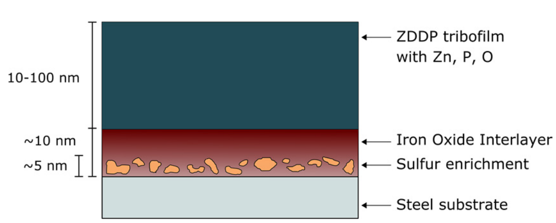
Notes: (a,b) Zn enrichment at the upper part of the tribofilm; (c,d) enrichment of FeO underneath the Zn rich region; (e,f) enrichment of S/O on the substrate. The overlap in the mass spectrum between O+1 and S+2 at m/n = 16 makes it difficult to clearly differentiate the e elements. the presence of S on the substrate is then confirmed by the separate plot of the distribution and concentration of FeS in the film (g,h)

the tribofilm because of the "digestion" mechanism (Martin, 1999; Minfray *et al.*, 2006; Spikes, 2004).
The specific observation of the sulfur enrichment by APT dedicates to understanding the structure of the ZDDP tribofilm. According to the HSAB principle, a thin sulfur layer (FeS) would be formed at the nascent steel surface by following the soft reaction, which happens at the beginning of sliding tests (Martin, 1999). Although some aforementioned studies found no S enrichment at the interface, the present study supports its existence with a high-resolution insight. By separating the mass-to-charge peaks based on the abundance of isotopes, the correlation between the distribution of sulfur and oxygen was distinguished.

A hypothetical construction of the ZDDP anti-wear tribofilm is illustrated in Figure 6 based on the observation from XPS and APT. The construction of the tribofilm is generally corresponding to the Schmaltz model (Schmaltz, 1936). From top to bottom, it comprises a tribofilm, an oxide interlayer, a sulfur enrichment and the steel substrate. Zinc dominated in the tribofilm and mixed with a considerable amount of iron and oxide. Beneath the tribofilm, an oxide interlayer and a sulfur enrichment at the bottom appeared. The oxide layer was attributed to the mixture of oxides, which mainly came from wear debris because of the severe sliding conditions. Furthermore, the sulfur enrichment was formed by the tribochemical reaction that nascent iron surfaces react with sulfur species (De Barros *et al.*, 2003).

Two different methods, XPS and APT, were both used for chemical analyses. In this study, XPS is used as a kind of fast preparatory screening technique for APT analysis. Regarding the complex load situation of macroscopic technical samples and its roughness, the tribofilm formation is understood to be inhomogeneous, at least on a micro-scale. The XPS depth profiles cover a representative area of the tribofilm and give a first impression of the chemistry concerning the average depth distribution of its components. Based on these results, including STEM lamella, the best-suited sites for APT analysis, with a high probability of matching locally pronounced tribolayer and the relevant depth scale, could be selected. In the next step, the introduction of APT revealed the tribofilm at the nanometer scale that provided further details of the tribofilm composition, which would be difficult to obtain by using other analytical techniques. Consequently, adequate preliminary examinations should be manipulated prior to running in an APT experiment in future studies for a better insight of characterization (Kelly *et al.*, 2007).

Figure 6 Schematic representation of the ZDDP anti-wear tribofilm. From top to bottom are Fe/Zn polyphosphate tribofilm (10-100 nm), oxide layer (≅ 10 nm), sulfur enrichment (≅ 5 nm) and steel substrate. The sulfur enrichment is shown to be unevenly distributed according to the findings by APT (Figure 5)



4. Conclusions

In the present study, ZDDP anti-wear tribofilms formed on the surface of a cylindrical roller thrust bearing have been analyzed by XPS and APT. The chemical composition and constituents of the tribofilm are revealed. The findings show:

- Analysis from both the XPS and APT demonstrate a well-established tribofilm formed under high pressure, including a Zn-rich tribofilm, an oxide layer, and S enrichment. Higher content of Zn was found at the upper part of the tribofilm; in contrast, a more massive amount of Fe can be found at the lower part of the tribofilm.
- Sulfur enrichment was found between the tribofilm and the steel substrate. The sulfur-rich region distributed heterogeneously beneath the oxide layer in a range of approximately 5 nm. With the advantage of using APT, it is the first time that clear evidence has proven the existence of a sulfur enrichment covered by ZDDP tribofilm.
- The finding of sulfur enrichment supports the predictions according to the HSAB principle. The reaction between sulfide ions and nascent iron substrate, namely the soft reaction, triggers the formation of the tribofilm.

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References

Bancroft, G.M., Kasrai, M., Fuller, M., Yin, Z., Fyfe, K. and Tan, K.H. (1997), "Mechanisms of tribochemical film formation: stability of tribo- and thermally-generated ZDDP films", *Tribology Letters*, Vol. 3 No. 1, pp. 47-51.

Bell, J.C., Delargy, K.M. and Seeney, A.M. (1992), "The removal of substrate material through thick zinc dithiophosphate anti-Wear films", *Tribology Series*, Vol. 21, pp. 387-396.

Berkani, S., Dassenoy, F., Minfray, C., Martin, J.M., Cardon, H., Montagnac, G. and Reynard, B. (2013), "Structural changes in tribo-stressed zinc polyphosphates", *Tribology Letters*, Vol. 51 No. 3, pp. 489-498.

De Barros, M.I.I., Bouchet, J., Raoult, I., Le Mogne, T., Martin, J.M.M., Kasrai, M. and Yamada, Y. (2003), "Friction reduction by metal sulfides in boundary lubrication studied by XPS and XANES analyses", *Wear*, Vol. 254 No. 9, pp. 863-870.

Dorgham, A., Azam, A., Morina, A. and Neville, A. (2018), "On the transient decomposition and reaction kinetics of zinc dialkyldithiophosphate", *ACS Applied Materials & Interfaces*, Vol. 10 No. 51, pp. 44803-44814.

Dowson, D., Higginson, G.R. and Whitaker, A.V. (1962), "Elasto-hydrodynamic lubrication: a survey of isothermal solutions", *Journal of Mechanical Engineering Science*, Vol. 4 No. 2, pp. 121-126.

Fujita, H. and Spikes, H.A. (2004), "The formation of zinc dithiophosphate antiwear films', proceedings of the institution of mechanical engineers", *Part J: Journal of Engineering Tribology*, Vol. 218 No. 4, pp. 265-278.

Fuller, M., Yin, Z., Kasrai, M., Bancroft, G.M., Yamaguchi, E. S., Ryason, P.R., Willermet, P.A. and Tan, K.H., (1997), "Chemical characterization of tribochemical and thermal films generated from neutral and basic ZDDPs using X-ray absorption spectroscopy", *Tribology International*, Vol. 30 No. 4, pp. 305-315.

Gachot, C., Hsu, C., Suárez, S., Grützmacher, P., Rosenkranz, A., Stratmann, A. and Jacobs, G. (2016), "Microstructural and chemical characterization of the tribolayer formation in highly loaded cylindrical roller thrust bearings", *Lubricants*, Vol. 4 No. 2, pp. 1-11.

Gault, B., Moody, M.P., Cairney, J.M. and Ringer, S.P. (2012), "Atom probe crystallography", *Materials Today*., Vol. 15 No. 9.

Gosvami, N.N., Bares, J.A., Mangolini, F., Konicek, A.R., Yablon, D.G. and Carpick, R.W. (2015), "Mechanisms of antiwear tribofilm growth revealed in situ by single-asperity sliding contacts", *Science*, Vol. 348 No. 6230, pp. 102-106.

Guo, W., Zhou, Y., Sang, X., Leonard, D.N., Qu, J. and Poplawsky, J.D. (2017), "Atom probe tomography unveils formation mechanisms of wear-protective tribofilms by ZDDP, ionic liquid, and their combination", *ACS Applied Materials & Interfaces*, Vol. 9 No. 27, pp. 23152-23163.

Heuberger, R., Rossi, A. and Spencer, N.D. (2007), "XPS study of the influence of temperature on ZnDTP tribofilm composition", *Tribology Letters*, Vol. 25 No. 3, pp. 185-196.

Hsu, C.-J., Stratmann, A., Rosenkranz, A. and Gachot, C. (2017), "Enhanced growth of ZDDP-Based tribofilms on Laser-Interference patterned cylinder roller bearings", *Lubricants*, Vol. 5 No. 4, p. 39.

Kalin, M. (2004), "Influence of flash temperatures on the tribological behaviour in low-speed sliding: a review", *Materials Science and Engineering: A*, Vol. 374 Nos 1/2, pp. 390-397.

Kelly, T.F., Larson, D.J., Thompson, K., Alvis, R.L., Bunton, J.H., Olson, J.D. and Gorman, B.P. (2007), "Atom probe tomography of electronic materials", *Annual Review of Materials Research*, Vol. 37 No. 1, pp. 681-727.

Kelly, T.F. and Miller, M.K. (2007), "Invited review article: atom probe tomography", *Review of Scientific Instruments*, Vol. 78 No. 3, doi: 10.1063/1.2709758.

Kim, Y.J., Baik, S., Il, Bertolucci-Coelho, L., Mazzaferro, L., Ramirez, G., Erdermir, A. and Seidman, D.N. (2016), "Atom-probe tomography of tribological boundary films resulting from boron-based oil additives", *Scripta Materialia*, Vol. 111, pp. 64-67.

Kubiak, K.J., Mathia, T.G. and Bigerelle, M. (2012), "Influence of roughness on ZDDP tribofilm formation in boundary lubricated fretting", *Tribology - Materials Surfaces & Interfaces*, Vol. 6 No. 4, pp. 182-188.

Martin, J.M. (1999), "Antiwear mechanisms of zinc dithiophosphate: a chemical hardness approach", *Tribology Letters*, Vol. 6 No. 1, pp. 1-8.

Martin, J.M., Grossiord, C., Le Mogne, T., Bec, S. and Tonck, A. (2001), "The two-layer structure of zndtp tribofilms, part I: AES, XPS and XANES analyses", *Tribology International*, Vol. 34 No. 8, pp. 523-530.

Martin, J.M., Grossiord, C., Le Mogne, T. and Igarashi, J. (2000), "Transfer films and friction under boundary lubrication", *Wear*, Vol. 245 Nos 1-2, pp. 107-115.

Martin, J.M., Onodera, T., Minfray, C., Dassenoy, F. and Miyamoto, A. (2012), "The origin of anti-wear chemistry of ZDDP", *Faraday Discussions*, Vol. 156, p. 311.

Miller, M.K. and Forbes, R.G. (2009), "Atom probe tomography", *Materials Characterization*, doi: 10.1016/j.matchar.2009.02.007.

Minfray, C., Le Mogne, T., Lubrecht, AA. and Martin, J.M. (2006), "Experimental simulation of chemical reactions between ZDDP tribofilms and steel surfaces during friction processes", *Tribology Letters*, Vol. 21 No. 1, pp. 65-76.

Minfray, C., Martin, J.M., De Barros, M.I., Le Mogne, T., Kersting, R. and Hagenhoff, B. (2004a), "Chemistry of ZDDP tribofilm by ToF-SIMS", *Tribology Letters*, Vol. 17 No. 3, pp. 351-357.

Minfray, C., Martin, J.M., Esnouf, C., Le Mogne, T., Kersting, R. and Hagenhoff, B. (2004b), "A multi-technique approach of tribofilm characterisation", *Thin Solid Films*, Vols 447/448, pp. 272-277.

Miranda-Medina, M. de, L. Tomastik, C. Truglas, T. Groiss, H. and Jech, M. (2019), "Effect of engine oil additives reduction on the tribofilm structure of a cylinder liner model surface", *Industrial Lubrication and Tribology*, doi: 10.1108/ilt-05-2019-0193.

Mosey, N.J., Müser, M.H. and Woo, T.K. (2005), "Molecular mechanisms for the functionality of lubricant additives", *Science*, Vol. 307 No. 5715, pp. 1612-1615.

Nicholls, M.A., Do, T., Norton, P.R., Bancroft, G.M., Kasrai, M., Capehart, T.W., Cheng, Y.T. and Perry, T., (2003), "Chemical and mechanical properties of ZDDP antiwear films on steel and thermal spray coatings studied by XANES spectroscopy and nanoindentation techniques", *Tribology Letters*, Vol. 15 No. 3, pp. 241-248.

Onodera, T., Martin, J.M., Minfray, C., Dassenoy, F. and Miyamoto, A. (2013), "Antiwear chemistry of ZDDP: coupling classical MD and tight-binding quantum chemical MD methods (TB-QCMD)", *Tribology Letters*, Vol. 50 No. 1, pp. 31-39.

Onodera, T., Morita, Y., Suzuki, A., Sahnoun, R., Koyama, M., Tsuboi, H., Hatakeyama, N., Endou, A., Takaba, H., Kubo, M. and Del Carpio, C.A., (2008), "A theoretical investigation on the abrasive wear prevention mechanism of ZDDP and ZP tribofilms", *Applied Surface Science*, Vol. 254 No. 23, pp. 7976-7979.

Rosenkranz, A., Stratmann, A., Gachot, C., Burghardt, G., Jacobs, G., Mücklich, F., Rosenkranz, B.A. (2016), "Improved wear behavior of cylindrical roller thrust bearings by three-beam laser interference", *Advanced Engineering Materials*, Vol. 18 No. 5, pp. 854-862.

Schmaltz, G. (1936), *Technische Oberflächenkunde, Technische Oberflächenkunde*, Springer Berlin, doi: 10.1007/978-3-642-51820-1.

Shimizu, Y. and Spikes, H.A. (2016), "The tribofilm formation of ZDDP under reciprocating pure sliding conditions", *Tribology Letters*, Vol. 64 No. 3, pp. 1-11.

Smith, G.C. and Bell, J.C. (1999), "Multi-technique surface analytical studies of automotive anti-wear films", *Applied Surface Science*, Vols 144/145, pp. 222-227.

Soltanahmadi, S., Morina, A., van Eijk, M.C.P., Nedelcu, I. and Neville, A. (2017), "Experimental observation of zinc dialkyl dithiophosphate (ZDDP)-induced iron sulphide formation", *Applied Surface Science*, Vol. 414, pp. 41-51.

Spikes, H. (2004), "The history and mechanisms of ZDDP", *Tribology Letters*, Vol. 17 No. 3, pp. 469-489.

Stratmann, A., Jacobs, G., Hsu, C.-J., Gachot, C. and Burghardt, G. (2017), "Antiwear tribofilm growth in rolling bearings under boundary lubrication conditions", *Tribology International*, Vol. 113, pp. 43-49.

Thompson, K., Lawrence, D., Larson, D.J., Olson, J.D., Kelly, T.F. and Gorman, B. (2007), "In situ site-specific specimen preparation for atom probe tomography", *Ultramicroscopy*, Vol. 107 Nos 2/3, pp. 131-139.

Topolovec-Miklozic, K., Forbus, T.R. and Spikes, H.A. (2007), "Film thickness and roughness of ZDDP antiwear films", *Tribology Letters*, Vol. 26 No. 2, pp. 161-171.

Zhang, Z., Yamaguchi, E.S., Kasrai, M. and Bancroft, G.M. (2005), "Tribofilms generated from ZDDP and DDP on steel surfaces: part 1, growth, wear and morphology", *Tribology Letters*, Vol. 19 No. 3, pp. 211-220.

Zhou, Y., Leonard, D.N., Guo, W. and Qu, J. (2017), "Understanding tribofilm formation mechanisms in ionic liquid lubrication", *Scientific Reports*, Vol. 7 No. 1, pp. 1-8.

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