Comparison of the Tribological Behavior of Steel–Steel and Si₃N₄–Steel Contacts in Lubricants with ZDDP or Ionic Liquid

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Abstract: This study aims to determine the effects of lubricant anti-wear (AW) additive and base oil viscosity on the tribological behavior of steel–steel and ceramic–steel contacts. Two base oils with the viscosity grades of 15W40 and 0W30 were used. Moreover, two AW additives were compared: a conventional secondary zinc dialkyldithiophosphate (ZDDP) and an oil-miscible phosphonium-phosphate ionic liquid (IL) in 0W30 base oil for both material pairs. Tests were conducted by using reciprocating ball-on-flat sliding at room temperature. The flat material was AISI A2 tool steel, and the ball material was either AISI 52100 bearing steel or silicon nitride. As expected, 0W30 base oil with lower viscosity resulted in a higher wear rate than 15W40 base oil for steel–steel contact. Both ZDDP and IL substantially reduced wear, and the IL-additized 0W30 base oil performed best. For ceramic–steel contact, ZDDP provided moderate wear protection for both ball and flat. By contrast, IL reduced steel flat wear more effectively than ZDDP, but increased ceramic ball wear rate. Cross-sectional transmission electron microscopy examination and X-ray photoelectron spectroscopy chemical analysis were conducted to reveal the thickness, nanostructure, and composition of the tribofilms that were formed by ZDDP and IL on the steel and silicon nitride surfaces.

1. Introduction

The viscosity grade of automotive engine oils has been continuously reduced over the past three decades to improve fuel economy, that is, from SAE 15W40 during the early 1980s to 0W30 in recent years. This reduction in viscosity is made possible through advances in base oils and additive packages, particularly, anti-wear (AW) additives [1,2]. The material composition and microstructure of the contact area at the bearing interface are known to have decisive roles in tribological behavior. A lubricant AW additive is designed to decompose under thermomechanical stresses during the wear process, and the decomposition products subsequently react with wear debris or the contact area to form a protective tribofilm on bearing surfaces [1]. The performance of a tribofilm is determined by its composition, microstructure, and thickness. These properties are influenced by many factors, including the composition and mechanical properties of the contact materials, the rheological behavior of the lubricant, the chemistry of the AW additive, and the experimental conditions (e.g., load, temperature, and speed). Therefore, the characteristics of the tribofilm are important to understand friction and wear performances.

Zinc dialkyldithiophosphate (ZDDP) is the most common AW additive in automotive engine lubricants during the past half century; this additive is known to effectively protect ferrous alloys via tribofilm formation [3,4]. Ionic liquids (ILs) have recently received considerable attention in lubrication research because they are naturally polarized, thermally stable, nonflammable, and nonvolatile, among many other advantages [5,6]. In 2001, Ye et al. [7] first reported the potential of using ILs as lubricants. Since then, the number of published papers on this topic has increased steadily [8]. Although the focus of literature is on using IL neat lubricants, a few dozen reports center on using ILs as oil additives [9–12]. We previously reported an oil-miscible IL trihexyltetradecylphosphoniumbis (2-ethylhexyl) phosphate, noted as $[P_{66614}][DEHP]$, with an excellent anti-scurfing/AW performance when added to PAO base oil to lubricate a Mo-Ni-coated engine piston ring that slides against a gray cast iron cylinder liner [10,11]. However, the AW performance and mechanism of this IL remain unknown when it is used with non-metallic surfaces.

The current study investigated the effects of oil viscosity with AW additives (ZDDP and IL) on the friction and wear characteristics of two common ball bearing material pairs: steel–steel and silicon nitride (Si_3N_4)–steel. Various surface imaging and chemical analysis techniques were performed for tribofilm characterization [13,14] to reveal the wear protection mechanisms; these techniques include

scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

2. Materials and experimental method

Tribological tests were conducted on a PLINT TE-77 tribometer using a ball-on-flat reciprocating sliding configuration at room temperature (23 ± 2 °C). We understand that the normal temperature range of an engine oil is 80-140 °C. On the other hand, the engine oil also experiences cold start (room temperature). In this study, we intend to investigate the friction and wear performance at room temperature and to gain some fundamental understanding of the material-additive interactions. The focus of this study is not to simulate an actual application, but to investigate the tribochemical interactions for ferrous and ceramic surfaces with conventional and candidate anti-wear additives. Since such tribochemical reactions are rather instantaneous, we do not expect the tribofilm formation mechanisms to be much different between reciprocating and unidirectional sliding.

Two common ball bearing material pairs, steel–steel and silicon nitride–steel, were selected to study. The flat was a hardened AISI A2 tool steel plate, and the work surface had a roughness of 0.18 μm (R_q). The steel ball was a grade 25 AISI 52100 bearing steel ball with a diameter of 10 mm and a roughness of 0.05 μm (R_q), and the ceramic ball was a grade 10 hot isostatically pressed Si_3N_4 bearing ball (NBD-100, Cerbec Corporation, East Granby, CT) with a 9.525 mm diameter and a highly polished surface finish. Table 1 summarizes the composition and microindentation hardness of the test materials. Roughness was measured by using a Mahr Perthometer M2 profiler. Vickers hardness was determined by using a Buehler Micromet® 2100™ microindenter.

Two base oils with SAE viscosity grades of 15W40 and 0W30 (supplied by Chevron Corporation, USA), and two AW additives, i.e., secondary ZDDP (provided by Lubrizol Corporation, USA) and an IL [P_{66614}] [DEHP] developed by the Oak Ridge National Laboratory (USA), were used in this study. The molecular structures of the two AW compounds are illustrated in Fig. 1. Two oil–AW blends were prepared: 0W30 base oil plus 1 wt% ZDDP (0W30+1%ZDDP) and 0W30 base oil plus 1 wt% [P_{66614}] [DEHP] (0W30+1%IL). Viscosity was measured with a falling ball viscometer (PETROLAB MINIVIS II). Table 2 presents the densities and viscosities of the four lubricants at various temperatures. Adding either of the two AW additives only marginally increased oil viscosity.

The reciprocating sliding tests were conducted at an oscillation frequency of 10 Hz with a stroke of

10 mm. For the 52100 steel ball against the A2 steel plate (steel–steel) tribo-pair, tests were conducted under a normal load of 54 N for a sliding distance of 1000 m. A higher load of 104 N and a longer sliding distance of 10,000 m were applied for the Si_3N_4 ball against the A2 steel plate (Si_3N_4 –steel) tribo-pair to generate a measurable wear. At least two repeat tests were conducted for each condition.

The maximum (stroke midpoint) central lubricant film thickness (h_c) was estimated for each lubricant by using the Hamrock and Dowson formula [15]; the results are listed in Table 3. The composite roughness $S = \sqrt{R_{q,ring}^2 + R_{q,liner}^2}$ values were 0.19 μm and 0.18 μm for the steel–steel and ceramic–steel contacts, respectively. The calculated maximum λ (ratio of h_c/σ) ranged from 0.2 to 0.7, as shown in Table 3. This result indicates that all tests were operating within boundary lubrication ($\lambda < 1$).

The friction force was measured in situ with a piezoelectric load sensor. The worn surfaces of the plate and ball were cleaned with isopropanol before wear volume measurements and surface characterization were conducted. Wear volume, as well as scar depth and width, was quantified by using a Wyko NT9100 optical profiler.

Wear scars were first inspected by using an optical microscope (Nikon Labophot-2), and then they were examined by using a field-emission scanning electron microscope (Hitachi S-4800) equipped with EDS. Further tribofilm characterization was conducted through TEM and XPS to investigate the wear mechanism. The TEM samples were prepared by using the FEI Nova 200 dual-beam focused ion beam (FIB) system with a Ga source to extract a thin cross section of the near-surface zone from the wear scar. A C film and a W layer were deposited on the sample surface before the FIB process to protect the tribofilm. Figure 2 shows the surface crater after FIB extraction. It also indicates that the electron beam-thinned TEM sample of the A2 steel plate slid against the Si_3N_4 ball in 0W30+1%IL. Each TEM sample was attached to a Cu half-grid. The TEM system used was an aberration-corrected FEI Titan S 80-300 TEM/STEM equipped with a Gatan Image Filter Quantum-865. XPS analysis was performed on a Thermo Scientific TM K-Alpha XPS instrument. The X-rays used were monochromatic Al- $\text{K}\alpha$ photons, and the photo-emitted electrons were analyzed with a hemispherical energy analyzer. Wide survey scans were collected from 0 eV to 1350 eV at a pass energy of 200 eV to determine overall elemental composition. Depth profiling was performed by using a 3 kV Ar-ion sputter beam that was rastered over an area of 1 mm $\times$ 2 mm. The base pressure in the analysis chamber was

approximately 10^{-9} Pa.

3. Results and Discussion

3.1 Friction

Traces of the coefficients of friction (COF) for the two tribo-pairs in the four lubricants are compared in Figs. 3a and 3b. Each curve is an average of two repeat tests. The COF of the steel–steel contact in most oils (except the IL-additized oil) decreased gradually during testing (Fig. 3a). A decreasing COF is commonly observed in constant load sliding and may be attributed to the following: (a) a substantially reduced contact stress resulting from an enlarged contact area (e.g., a flattened ball cap) in the wear processor, and (b) debris accumulation at the contact interface that introduces low-friction localized rolling to the otherwise high-friction two-body abrasion. Compared with the other base oils, 15W40 exhibited a more pronounced friction decline, possibly because its higher viscosity allows it to trap more debris at the contact interface. By contrast, the COF in 0W30+IL maintained a relatively stable value of 0.11 from beginning to end.

The friction traces of Si_3N_4 –steel contact are shown in Fig. 3b. For a given lubricant, the COF was generally lower than that for steel–steel contact probably because adhesion at the ceramic–steel contact (a similar material pair tends to have stronger adhesion than a dissimilar material pair) was weak. In the 0W30 base oil, the COF decreased rapidly from the initial value of 0.085 to 0.076 early in the test (which suggests a fast wear-in process), and then remained at the lower level throughout the rest of the test. The friction behavior of the 0W30+1%ZDDP or 15W40 base oil was similar to that of the 0W30 base oil, but the COF decreased less at the beginning of the test and stabilized at a higher level, which is a behavior that corresponds to lower wear rates (Section 3.2). Again, the outlier was 0W30+1%IL, which showed an increasing COF during wear-in and a continuously decreasing COF for the rest of the test. This behavior is related to the (unexpectedly) high ball wear of 0W30+1%IL (Section 3.2).

3.2 Wear

3.2.1 Steel–steel contact

Material loss of the tested A2 plate could not be precisely quantified because wear scar depth was too shallow and had the same order of magnitude as roughness; however, the worn surface morphology was distinct, as shown in Fig. 4. The wear scar from the testing with 15W40 base oil was largely covered by patches of deposited materials (Fig. 4b), whereas the worn surface from the testing with

0W30 base oil appeared cleaner, with signs of abrasion and plastic deformation (Fig. 4c). On the plates lubricated by the two oils with AWs, the contact area slightly changed in morphology, except for some high plateaus that appeared to be covered by isolated small patches of dark films (Figs. 4d and 4e), which were later found to be AW tribofilms, as described in Section 3.3.

The cross-section profiles of the wear scars (after subtracting the original ball curvatures) of the 52100 steel balls were compared in Fig. 5a. The normalized ball wear rate and lubricant viscosity were compared in Fig. 5b. Viscosity had an obvious influence between the two base oils, i.e., the thinner 0W30 base oil (26.6 cP) resulted in a wear rate that was approximately 20 times higher ($335 \mu\text{m}^3/\text{Nm}$ vs. $17 \mu\text{m}^3/\text{Nm}$) than that of the thicker 15W40 base oil (95.5 cP). Even in boundary lubrication, oil viscosity can still significantly affect wear performance. Although the entire oil film collapsed at the contact area in BL, the oil absorption layer on the surface asperities still significantly prevented asperity collisions. In general, base oils with high viscosity have long hydrocarbon chains, and thus, produce a thick oil surface absorption layer for efficient wear protection. With only a minimal change in oil viscosity that was induced by adding ZDDP or IL at the 1.0 wt%, both additives substantially reduced wear rate to $53 \mu\text{m}^3/\text{Nm}$ and $11 \mu\text{m}^3/\text{Nm}$, respectively. Notably, 0W30+1%IL performed better than the more viscous 15W40 base oil, and IL demonstrated superior wear protection compared with the conventional ZDDP for steel–steel contact.

Figure 6 presents the optical images, 3D and 2D profiles, and EDS spectra of the steel ball wear scars. The wear scar on the ball lubricated by 15W40 base oil was relatively small, rough, and covered by a layer of wear debris (Fig. 6a). By contrast, the wear scar on the ball lubricated by the thinner 0W30 base oil was significantly larger and smoother, with less debris deposited on the surface (Fig. 6b). Moreover, its higher oxygen content, which was detected by EDS (Fig. 6e), suggests the presence of more oxides on the worn surface. For the two base oils, the morphologies of the ball scars correlate well with those of the plates (Fig. 6). The presence of more debris on the worn surfaces tested with the 15W40 base oil may be explained by the higher viscosity of this base oil compared with 0W30, which allows it to trap more wear debris on the interface, as discussed in Section 3.3.

When added to 0W30 base oil, both ZDDP and IL effectively reduced ball scar size and introduced a film of dark patches on the scar (Figs. 6c and 6d). The EDS spectrum in Fig. 6e indicates the presence of Zn, P, and S on the worn surface tested in 0W30+1%ZDDP, which suggests a ZDDP-induced AW tribofilm. Similarly, P was detected on the worn surface generated in the tests with 0W30+1%IL.

Furthermore, TEM cross-sectional examination and XPS surface chemical analysis confirmed the formation of an IL-induced tribofilm (Section 3.3).

3.2.2 Si₃N₄-steel contact

For Si₃N₄-steel contact, the A2 steel plates exhibited more wears than the ceramic balls, as shown in Fig. 7. Note that the range of wear rate for the ceramic-steel contact (even at a high load) was two orders of magnitude lower than that for the steel-steel contact (Fig. 5b), which was probably due to the significantly reduced adhesion for the ceramic-steel contact. The relatively rough surface of the steel plates ($R_a = 0.17 \mu\text{m}$) made measurement of small wear volumes difficult and was partly responsible for the relatively large deviation, particularly in the case of the plate lubricated with 15W40 oil.

The wear results of the steel plates were as expected. The thinner 0W30 base oil resulted in a higher wear rate on the steel plate than the 15W40 base oil. Moreover, both AW additives reduced wear on the steel plate to a certain extent. IL provided better protection, although it was insufficient to overcome the effect of the lower viscosity of 0W30 base oil than that of 15W40 oil. The worn plates tested in all the lubricants exhibited similar morphologies, as shown in Fig. 8.

The results of Si₃N₄ ball wear presented a couple of revelations (Fig. 9). (1) Ball wear was less with 0W30 base oil than with 15W40 base oil. (2) Adding IL to the base oil substantially increased wear on the ceramic ball.

The worn ball surface that resulted from the tests with the 0W30 base oil clearly presented more transfer materials (probably because of debris adhesion) than the ball tested in 15W40 base oil, as shown in Fig. 9. The ball wear scar that resulted from the tests with 0W30+1%ZDDP was also covered by a deposit layer but its morphology was different from those observed in the tests with base oils (Fig. 9c). SEM/EDS examination (Fig. 10) indicates that the aforementioned layer is a ZDDP tribofilm. The Si₃N₄ ball surface tested in 0W30+IL appeared significantly cleaner, with minimal evidence of a surface film, under both optical (Fig. 9d) and electron (Fig. 10) microscope examination, compared with the wear scars tested in the other lubricants (Note: The small P peak was likely from the lubricant residue that was trapped on the worn surface and capped by a C layer that was deposited for SEM examination. XPS examination is presented in Section 3.3.). The preceding result suggests that IL additive prevents adhesion. Similarly, adhesion reduction was observed for another type of IL in our previous work [16]. A surface film, regardless of whether it is a debris layer similar to that formed in base oils or a

tribochemically developed tribofilm similar to that formed in ZDDP-additized oil, offers protection by reducing surface exposure.

To understand wear progression on Si_3N_4 balls, experiments were performed with a short sliding distance (1000 m). The 2D profiles (after subtracting the original ball curvature) of the ball scars generated by different sliding distances in the four lubricants were compared (Fig. 11). In the two base oils and 0W+1%ZDDP, ball wear rate decreased by 80% or higher as sliding distance increased from 1000 m to 10,000 m. By contrast, ball wear rate in 0W30+IL oil remained at or near the same level. This finding is probably attributed to the lack of surface film protection, as observed in Figs. 9 and 11. Notably, all Si_3N_4 ball scars presented a “central-peak crater” shape, which is the “W” profile in the cross section.

3.3 Tribofilm characterization

3.3.1 Steel–steel contact

0W30+1%IL performed best among the four lubricants in terms of wear protection during steel–steel contact, as shown in Figs. 5 and 6. Therefore, the wear scars generated in 0W30+1%IL were selected for further characterization to help understand the wear protection mechanism of the IL additive.

Figure 12 shows the cross-section TEM images of the near-surface zone of the worn A2 steel plate that was rubbed against a 52100 steel ball in 0W30+1%IL. The TEM images clearly show a 20 nm to 25 nm thick tribofilm, and the electron diffraction pattern suggests an amorphous phase. The tribofilm appears to have no porosity or cracking and is well bonded with the substrate. However, the film thickness in this sample is considerably thinner than that on the gray cast iron (60 nm to 180 nm) lubricated by PAO base oil additized with the same IL [10,11]. Steel is known to form thinner tribofilms than cast iron because of its lower reactivity and higher wear resistance (less wear debris supplied for tribochemical reactions with IL).

Aided by ion sputtering, an XPS composition–depth profile was generated for the plate (Fig. 13a). *(The depth was converted from the sputtering time assuming a constant sputtering rate of 10 nm/min based on the calibration of solid silica. The actual sputtering rate of the tribofilm is unknown. The uncertainty of the sputtering rate is believed to be in part responsible to the discrepancy in tribofilm thickness observed by XPS and TEM.)* Figure 13b is a magnified chart for concentrations of up to

10 at. %, with detailed information for critical elements. For the worn A2 steel plate, the P content (solely from IL) started at 5 at. % near the surface and decreased gradually with depth until it eventually faded off at approximately 30 nm, which indicates the maximum thickness of the tribofilm within the XPS inspection area. The magnified chart in Fig. 13b clearly shows the Fe (ion), Cr (ion), O (phosphate), O (oxide), and P, which exhibit a similar trend. This finding suggests that the tribofilm is largely composed of phosphates and oxides of Fe and Cr. Note that (ion) refers to an oxidation state of Fe or Cr higher than the metal. Peak fitting of the Fe and Cr depth profile data allowed the identification of these higher oxidation states of Fe and Cr which were consistent with mixed valence oxides, i.e. Fe_xO_y and Cr_xO_y . The binding energies for these components were ~710 eV for iron and ~577 eV for Cr, compared to ~707 and ~574 eV for the corresponding metals. During the Ar-ion depth profiling two distinct O features were observed: one at ~530 eV which is primarily associated with Fe (and to a lesser extent Cr) oxide; and another at ~532 eV which is primarily associated with O-bonding to P. Indeed, the P binding energy at 133-134 eV is consistent with P bound to O as in a phosphate-like species.

For the worn surface on the 52100 steel ball, the XPS composition–depth profile in Fig. 14 suggested a tribofilm of up to ~125 nm thick, with a P content as high as 11 at. %. The thicker film may be attributed to the constant contact of a small confined area on the ball compared with the periodic contact of a relatively long scar on the plate. With a similar overall energy input (normal contact stress, shear stress, and frictional heating) between the ball and the plate, the small ball scar possessed high energy density, and consequently, grew into a thick tribofilm. The magnified chart in Fig. 14b shows Fe(ion, BE~710 eV), O(phosphate, BE~532 eV), O(oxide, BE~530 eV), and P (BE~133 eV) exhibiting a similar trend, which suggests that the tribofilm on the steel ball primarily consists of Fe phosphates and Fe oxides. The Cr content of the tribofilm is low because the 52100 steel contains significantly less Cr than A2 tool steel.

3.3.2 Si_3N_4 –steel contact

During Si_3N_4 –steel contact, the total material losses (ball+plate) for the two oil–AW blends were comparable, whereas wear distribution between the ball and the plate was distinct for ZDDP and IL. With ZDDP-additized oil, wear on the steel plate was two orders of magnitude higher than that on the Si_3N_4 ball. By contrast, a similar wear was observed on the ceramic ball and the steel plate with IL-additized oil. Among the four lubricants, 0W30+1% IL produced the lowest steel plate wear and the

highest Si_3N_4 ball wear. To further investigate the difference in the wear protection behavior of ZDDP and IL additives during Si_3N_4 -steel contact, the tribofilms formed in 0W30+1%ZDDP and 0W30+1%IL were examined through TEM and XPS.

(a) 0W30+1%ZDDP

Figure 15 shows the cross-section TEM images under two magnifications, and the electron diffraction pattern for the tribofilm on the worn steel plate against the Si_3N_4 ball in 0W30+1%ZDDP. The tribofilm is amorphous and ~20 nm thick in the TEM image. It presents no porosity or cracking and bonds well with the substrate.

The XPS composition-depth profiles of the steel plate and Si_3N_4 ball worn surfaces are shown in Figs. 16 and 17, respectively. The near-surface region of the plate contained up to 20 at.% P, 6 at.% Zn, and 5 at.% S, which confirmed the formation of a ZDDP tribofilm. ZDDP elements did not fade until ~125 nm of the surface material was sputtered off, which suggests a film thickness of up to 125 nm. Thus, this film is significantly thicker than the ~20 nm film that was observed on the TEM sample (Fig. 15). A tribofilm frequently forms on a contact area in patches, where asperity contact occurs, and film thickness varies in each location. While XPS data reflect an average effect over a relatively large area (400 μm in diameter), TEM images only show a slice of less than 0.5 μm . This could be another reason (in addition to the uncertainty in ion sputtering rate) for the discrepancy in film thickness between XPS and TEM observations. The tribofilm was presumably composed of Zn/Fe phosphates, sulfides, and oxides, as suggested by the detailed XPS analysis in Fig. 16b. Nearly no ion-phase chromium (i.e. Cr with a valence > 0) was detected in the tribofilm, which was probably because Zn and Fe have lower reduction potentials than Cr, and thus, dominated tribofilm formation. The S content of the tribofilm was noticeably lower than the P content, although four S atoms and two P atoms were present in each ZDDP molecule, and S was more sensitive than P in XPS analysis. This finding suggested that P has a more important role in tribofilm formation than S under the particular test conditions of this work.

A ZDDP-induced tribofilm on the wear scar of the Si_3N_4 ball was implied by the SEM morphology and EDS spectrum and confirmed by XPS analysis, as shown in Fig. 17. The tribofilm appeared to be a product of oxidized ZDDP (high oxygen content) with a slight involvement of metallic wear debris from the steel counterface (the Fe content, which is not shown here, was less than 0.2 at. %). Film thickness was less than 25 nm, which was considerably thinner than on the steel counterface. This

difference is attributed to the chemical inertness of the Si_3N_4 ball.

(b) 0W30+1%IL

Figure 18 shows the TEM cross-section images of the steel plate that slid against the Si_3N_4 ball lubricated by 0W30+1%IL. A tribofilm with a thickness of < 25 nm was detected at the spot sampled by the FIB mill.

Figure 19 shows the XPS composition–depth profile of the worn steel plate against the Si_3N_4 ball lubricated with 0W30+1%IL. The IL tribofilm thickness appeared to reach as much as 100 nm (where P fades off), and again thicker than observed via TEM. Such a discrepancy has been discussed in Section 3.2.1 for the ZDDP tribofilm. In particular, the IL tribofilm on the plate that slid against the ceramic ball is evidently considerably thicker than that (< 30 nm thick) on the plate against the steel ball (Fig. 13). The P concentration in the tribofilm reached up to 15 at. % on the plate that slid against the Si_3N_4 ball, which was three times higher than that in the film produced when sliding against a steel ball. The thicker tribofilm and higher P content could be attributed to the higher contact stress in the ceramic–steel contact, which was caused by a higher load on a smaller contact area (the wear scar on the ceramic ball was significantly smaller than that on the steel ball). The magnified chart in Fig. 19b suggests that the tribofilm on the steel plate contained Fe/Cr phosphates and oxides.

The XPS composition–depth profile of the worn Si_3N_4 ball in 0W30+1%IL is shown in Fig. 10. No IL tribofilm was found (no P was detected) and minimal Fe (< 0.2 at.%) was transferred from the plate. The lack of an IL tribofilm or transfer layer was believed to be responsible for the increased wear of the Si_3N_4 ball when IL additive was used (Fig. 7).

4. Discussion on wear mechanisms

Figure 21 illustrates the wear mechanisms of different oils and tribo-pairs. For steel–steel contact in 0W30 base oil, the wear rate was high because of the thin lubricant film and the lack of surface protection (Fig. 21a). In 15W40 base oil, the wear debris at the contact interface was not too mobile because of high viscosity, and thus, was somewhat trapped. Viscosity has been reported to create resistance to the flow and movement of agglomerated particulates, e.g., an ISO 320 (320 cSt at 40 °C) VG oil-resisted movement, and mixing 10 times more than an ISO 32 (32 cSt at 40 °C) VG oil [17]. A wear debris layer (Figs. 6, 17, and 19) at the contact interface bed may reduce direct metal–metal

contact and consequently reduce wear. Figure 21b illustrates the formation of a tribofilm by the AW additive to protect the contact area. The wear debris may be difficult to wash away from the contact zone in a thick oil, and thus, improving wear protection to a certain extent. The schematics in Figs. 21c and 21d illustrate the debris dispersion behavior in oils with low and high viscosities, respectively.

In the ceramic–steel contact, the ball wear scar profiles in all lubricants had similar characteristic “W” shapes (Fig. 11), which are different from the regular “U” shapes observed on 52100 steel balls (Fig. 5). A W-shaped wear scar is usually observed in fretting wear, that is, either in linear (reciprocating tangential fretting) or rotational (torsional fretting) models [18,19]. In fretting, the contact center sticks and the outside slides. These movements lead to faster material loss in the outside sliding zone than in the center sticking zone, which has no relative motion. Under our test conditions, the sliding stroke was long (10 mm); therefore, the stick–slip mechanism in fretting wear is not applicable to the phenomenon in this work. According to the Hertz contact model, the outer part of the contact zone exhibits maximum shear stress during the ball-on-flat contact. Ceramics are known to have a high compressive strength, but weak shear strength, and thus, cracks may be initiated on the Si_3N_4 ball surface at the outer contact zone that experiences high shear stress. Evidently, the Fe oxide wear debris contained (Fig. 20) soft nanoscale particles [20], and thus, it was different from the hard, brittle Si_3N_4 wear debris. The ceramic wear particles then functioned as abrasives at the contact interface to accelerate wearing process on the ball. Given that the central contact zone was pressed tightly, minimal debris could reach the center. However, the debris remained at the outer ring of the contact zone, accelerated wear, and resulted in the W-shaped wear scar.

5. Conclusions

Two base oils of different viscosity grades (SAE 0W30 and 15W40) and two AW additives (ZDDP and IL in 0W30 base oil only) were used to explore the effects of viscosity and AW additives on the tribological behavior of steel–steel (AISI 52100–A2 steel) and ceramic–steel (Si_3N_4 –A2 steel) contacts. For steel–steel contact, plate wear was minimal in all lubricants, and a low oil viscosity led to a high ball wear rate. Both AWs were effective in wear protection, with IL outperforming ZDDP. For ceramic–steel contact, oil viscosity had a more important role in the wear performance of the steel plate. Although IL reduced wear to a greater degree for the steel flat than ZDDP, IL generated a higher wear rate for the ceramic ball.

Cross-sectional TEM examination and XPS chemical analysis helped reveal the thickness, nanostructure, and composition of tribofilms. The results suggested that both ZDDP and IL-formed tribofilms were amorphous. The IL tribofilms contained metal phosphates and oxides, whereas the ZDDP tribofilms had additional Zn and S compounds. The tribofilm on the steel plate was thicker after sliding against the ceramic ball as a result of the higher contact stress compared with that after sliding against the steel ball. For the Si_3N_4 ball, lubrication by the neat base oil generated a wear debris layer, and ZDDP produced a tribofilm on the wear scar. Both films may reduce surface exposure and, consequently, material loss. In contrast, the ceramic ball surface lubricated by the IL-additized oil was rather clean without such a protective layer and, as a result, experienced a higher wear rate.

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Fig. 21. Schematic of the wear mechanism.

Table 1. Composition and microindentation hardness of the test materials

Materials	Hardness (HV), 100 g-f	Composition (wt%)
AISI A2	976	1.0 C, 1.0 Mn, 5.3 Cr, 0.6 Mn, 1.1 Mo, 0.3 V, bal-Fe
AISI 52100	872	1.04 C, 0.11 Mn, 0.25 Si, 1.58 Cr, bal-Fe
Si ₃ N ₄	1700	1.0 MgO, 99.0 Si ₃ N ₄

Table 2. Physical properties of the lubricants

Lubricant	Density (g/mL, 23 °C)	Viscosity (cP)		
		23 °C	40 °C	100 °C
15W40 base oil	0.85	95.49	41.17	5.86
0W30 base oil	0.82	26.59	13.78	3.12
0W30 base oil+1%ZDDP	0.86	26.61	13.84	3.13
0W30 base oil+1%IL	0.86	26.81	13.91	3.13

Table 3. Estimated lubricant film thickness and λ ratio

Lubricant	Steel–steel		Si ₃ N ₄ –steel	
	Max h_c (μm)	Max λ	Max h_c (μm)	Max λ
15W40 base oil	0.13	0.7	0.09	0.5
0W30 base oil	0.06	0.3	0.03	0.2
0W30 base oil+1%ZDDP	0.06	0.3	0.03	0.2
0W30 base oil+1%IL	0.06	0.3	0.03	0.2