# Influence of Additive Chemistry on the Tribological Behavior of Steel/Copper Friction Pairs

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# Abstract

The tribological behavior of boundary lubrication is largely dominated by the anti-wear additives. Here five different anti-wear additives were selected and their tribological properties for a steel-copper contact were investigated. It was found that the tribological performance are highly depending on the anti-wear additive chemistry which determines activity, element compositions of the additive. An amine phosphate anti-wear additive AW 316 exhibit best tribological performance with the lowest mean friction coefficient of 0.082 and smallest wear volume which is more than one order of magnitude smaller than base oil. The friction-reducing order of the tested anti-wear additives are AW 316 > ZDDP > 353 > TCP > $[P_{8888}]$[DEHP] while anti-wear showed similar trend. In addition, the tribological mechanism of AW 316 were also discussed based on surface analysis results, and it was found that an even boundary lubrication film of 10–15 nm which was composed of copper oxides, phosphates, amines was formed on the copper disc and is responsible for its outstanding tribological performances. This study provides fundamental insights of the compatibilities among steel-copper friction pairs and suitable anti-wear additives, which can be beneficial for the development of high performance used for steel-copper friction pairs.


# 1 Introduction

The application of steel and copper alloys as friction materials for sliding machine is very common in modern machinery. Typical applications are worm gears, bearings, spindle drives, hydraulic pumps and various bushing and guiding devices [1]. These components are ordinarily lubricated with oil, therefore, the tribological performance is a significant issue on these friction pairs. Although several studies have been conducted to investigate the friction and wear performances of lubricants for steel/copper friction pairs [2-5], it is still lack basic knowledge about the tribological performance as well as mechanism of copper-based materials when compared with its steel counterpart.

It is well acknowledged that additives play a dominate role in sliding contact under boundary lubrication regimes. Tradition anti-wear additives were designed for steel-steel contact and their compatibility between steel-copper is not well understood. Some previous works related to copper have studied the influences of some additives on the tribological performance for steel/copper contact. Robin Jisa et al [1]. studied the tribological properties of ester-based additives on various type of copper alloys and found that a remarkable variation of tribological behavior with a clear relation to both the chemistry/composition of lubricant and the type of alloy. Recently, ionic liquids as novel lubricant additives for steel/copper contact have been extensively studied [6–8]. Cai et al. [9] reported a multifunctional imidazolium ionic liquid for steel/Cu-Sn alloy and found that a strong interaction between benzotriazole and the surface of the Cu alloy was proposed to account for its outstanding anti-wear and anticorrosion properties. Li et al. [10] studied the corrosion and lubrication properties of 2-Mercaptobenzothiazole functionalized ionic liquids for steel/copper contact and found that synergistic effect of adsorbed ionic liquids film and tribochemical products are responsible for their tribological performances. Our recent study investigated the compatibility between organic friction modifier and various oil soluble ionic liquids for a steel-bronze contact under boundary lubrication regime and found that a protic ionic liquid works well with organic friction modifier in term of both friction reducing and anti-wear performances [1 1]. Very recently, tribological performances of novel nano-lubricants additives such as graphene, nano diamonds for steel/copper pairs were also studied [12]. Although these studies provide valuable insight for the tribological performance of steel-copper friction, the tribological performances of traditional commercial additives on steel/copper were still merely studied and rarely reported.

The aim of this work was to investigate tribological performances of commercial additives under steel/copper friction pairs. Tribological behaviors of several kinds of anti-wear additives with different chemical structures such as zinc dialkyldithiophosphate (ZDDP), ionic liquid (IL), 353, phosphate amines, et al. were studied. The tribological mechanism of these additives were also discussed based on the scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS) analysis. The results offer important guidance for the selection of suitable anti-wear additives for steel/copper friction pairs when formulating high performance lubricants.

## 2 Experiment Section

# 2.1 Materials

A synthetic base oil, poly alpha olefin (PAO4, with a viscosity of around 4 at 100 $^{o}C$) was purchased from Exxon Mobil Corp. Zinc Dioctyl Primary Alkyl Dithiophosphate (ZDDP, trade name: RF203) (Purity98.0%) was provided by Xinxiang Richful Lube Additive Co., ltd. Dialkyl dithiophosphate ester (trade name: Irgalube 353, purity93.0%) was provided by BASF Corporation. Tritolyl phosphate (TCP, purity98.0%) was provided by Zibo Huihua Petroleum Additive Co., Ltd. Phosphate amine (a protic ionic liquid, trade name: AW 316, purity98.0%) was provided by Qingdao Lubemater lubrication materials technology Co., ltd. An aprotic ionic liquid trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate (abbreviated as [$P_{8888}$][DEHP]) was synthesized in our lab according to the procedures reported previously [13].

# 2.2 Tribological tests

Boundary lubrication tests were conducted on SRV IV oscillating reciprocating friction and wear tester under ball-on-flat configuration. A bronze plate (25.37 × 25.37 × 6.35 mm) was sliding against AISI 52100 bearing steel ball (mm diameter). The chemical composition of the test materials was summarized in Table 1. Tests were carried out under a 50 N load and an oscillation frequency of 25 Hz, with a stroke of 1 mm, at 100 $^{o}C$ and for a duration of 1 hour. After tests, contact surfaces were cleaned with ethanol and petroleum ether.

Table 1
Chemical composition of sliding materials

| Materials | Composition |
|---|---|
| AISI 52100 | C, 1.04%; Mn, 0.11%; Si, 0.25%; Cr, 1.58%; Fe-balance |
| H62 Brass | Cu, 60.5–63.5%; Fe, 0.15%; Pb, 0.8%; Sb, 0.005%; Bi, 0.002%; P, 0.01%; Zn-balance |

# 2.3 Surface characterizations

Wear volume of lower disc was measured using a MicroXAM-800 3D noncontact surface mapping profiler. A Hitachi S-3500N scanning electron microscope (SEM) coupled with an energy-dispersive X-ray spectroscopy was used to examine the morphology and chemical composition of the worn brass surface. X-ray photoelectron spectroscope (XPS). Al Kα X-rays, focused to a 250 μm spot, were used to excite photoelectrons that were measured with a hemispherical electron energy analyzer and 128 channel detectors. Cross-sectional lamellae of the tribofilms were obtained by using a focused ion beam (FIB) in a DualBeam SEM/ FIB instrument for further HR-TEM investigation. In order to protect the tribofilms, the aera was coated with Au and Pt cap layer before cutting cross-sectional lamellae.

## 3 Results And Discussion

# 3.1 Friction-reducing behaviors

Mean coefficient of friction (COF) and worn surface roughness of each tests were summarized in Table 2. Variation of COF with test duration were also displayed in Fig. 2. It is observed that COF of base oil PAO4 experienced a drastic fluctuation during test and give the highest mean COF of 0.349. The introduction of anti-wear additives greatly alleviated severe friction conditions on the metal interfaces. Among which, AW 316, a phosphate amine anti-wear additive achieved the lowest mean COF of 0.082, that is almost 76% reduction of COF compared with base oil. Besides, COF of ZDDP was 0.093 which indicates that ZDDP works very well on the steel-copper friction pair. 353, an ashless anti-wear additive with typical DDP (dialkyldithiophosphate) group also showed a relatively low COF of 0.118. All of these three additives share a common characteristic that they all chemically active additives and have a relatively high total acid number (TAN). TAN of of AW 316, ZDDP and 353 were 260 mgKOH/g, 140 mgKOH/g and 136 mgKOH/g, respectively. High acid value indicates these additives need less active energy to initial tribochemical reaction, on other words, they are more prone to take part into the tribochemical reactions during sliding. By contrast, mean COF of TCP and [$P_{8888}$][DEHP] were 0.170 and 0.199, respectively, which are much higher than their counterparts. TAN of TCP and [$P_{8888}$][DEHP] are around 0.1 mgKOH/g which are much lower than above active additives means that they are chemically inert. Overall, the friction-reducing order of the tested anti-wear additives are AW 316 > ZDDP > 353 > TCP > [$P_{8888}$][DEHP]. What's more, worn surface roughness of copper plate also display a similar order which is consistent with friction reducing performances, demonstrating COF is closely related with the surface roughness.

Table 2
Mean coefficient of friction and worn surface roughness of copper flat

| Item number | Composition | Mean Coefficient of friction | Worn Surface roughness |
|---|---|---|---|
| a | PAO4 base oil | 0.349 | 0.155 |
| b | PAO4 + 0.8% ZDDP | 0.093 | 0.049 |
| c | PAO4 + 0.8% AW316 | 0.082 | 0.042 |
| d | PAO4 + 0.8% [$P_{8888}$][DEHP] | 0.199 | 0.124 |
| e | PAO4 + 0.8% 353 | 0.118 | 0.048 |
| f | PAO4 + 0.8% TCP | 0.170 | 0.161 |

# 3.2 Anti-wear performances

Figure 3 showed the wear volume of copper plate after tribological tests of different lubricants. PAO4 yield the highest wear volume of 72.9 × $10^{-3}$ $mm^3$. The addition of anti-wear additives greatly enhances the wear protection performance of base oil. It's worth to mention that AW 316 produce the lowest wear volume of 6.15 × $10^{-3}$ $mm^3$ which is more than an order of magnitude smaller than base oil. Other anti-wear additives also reduce the wear volume to a great level. The wear protection properties of the selected additive follow the order of AW 316 > ZDDP > 353 > [$P_{8888}$][DEHP] > TCP. The general trend of anti-wear behaviors is similar to their friction reducing performances.

# 3.2 Worn surfaces analysis

Worn surfaces of copper plates were ultrasonically cleaned with petroleum ether after tribological tests. Both steel ball and copper plate were examined with SEM. Figure 4 showed the top view images and 3D morphologies of worn surfaces. As observed, PAO4 ($a_1$, $a_2$, $a_3$) showed the largest and deepest wear scar among these lubricants. Deep and large grooves and large bumps were clearly detected on the wear scar of PAO4 indicating server tribology and both abrasive wear and adhesive wear occurred on the rubbing surfaces. For PAO4 with 0.8% ZDDP, the wear scar is much narrow and shallow and clear separate patches can be seen on the surfaces which is similar to the tribofilm (pad-like structure) formed on steel-steel interfaces. AW 316 exhibited best tribological properties among these additives, worn surfaces of AW 316 is much smoother than pure PAO4 and PAO4 with ZDDP. Although the wear scar of AW 316 is a litter wider than ZDDP, the depth of wear scar is much shallow than ZDDP. The wider and smoother wear scar usually means a larger contact area and explained the lowest COF of PAO with AW 316.

Element composition on the copper worn surfaces were also examined using EDS and listed in Table 3. It can be seen in the table that besides oxygen and copper, a substantial amount of Fe (4.46 %) were found on the worn surface lubricate with pure PAO4 proves that abrasive wear occurred during sliding. Element mappings on steel ball (see supporting information S1) also confirm the transfer of Cu and Fe. Notably, 31.95 % Zn were detected on the worn surfaces lubricated by PAO4 with ZDDP demonstrates the formation of zinc rich boundary lubrication films. All of the signature elements of AW 316 were found on the worn surfaces. Distinguished from steel-steel contacts where little or no N were observed for amine phosphate anti-wear additives, worn surface of copper exists abundant nitrogen. Due to the high reactivity between sulfur and copper, 353 showed the highest sulfur content among these additives indicating sulfur plays a dominate role on the formation of boundary film. For TCP and [$P_{8888}$][DEHP], only few phosphorus (around 1 %) were detected on the worn surfaces suggests that limited or inadequate tribochemical reaction took place on the interfaces which explains their poor tribological performances.

Table 3
Elements composition on worn surfaces of copper plates obtained from EDS analysis

| Elements (wt.%) | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| O | 7.45 | 10.26 | 8.73 | 6.00 | 6.96 | 6.18 |
| Fe | 4.46 | 1.38 | 4.88 | 2.30 | 3.09 | 1.24 |
| Cu | 88.08 | 54.02 | 81.24 | 90.72 | 83.36 | 91.45 |
| P | - | 2.04 | 2.62 | 0.99 | 1.57 | 1.12 |
| S | - | 0.36 | - | - | 5.02 | - |
| N | - | - | 2.52 | - | - | - |
| Zn | - | 31.95 | - | - | - | - |
| Total | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% |

## 3.4 FIB-TEM analysis

In order to further understand the tribological mechanism of lubricants, FIB-TEM technique was applied to analysis the tribofilm generated with the lubrication of PAO4 + AW 316. It is identified that a white tribofilm with a thickness of 10–15 nm is formed the worn surface as shown in Fig. 5. Underneath the tribofilm is a subsurface plastic deformation zone with a thickness of about 250 nm. It is observed that the tribofilm is even and flat which is consistence with the SEM results (Fig. 4 $c_2$). It was this tribofilm protected the rubbing pair by separating the direct contact of the friction pairs. Figure 5f depicts the phosphorus content along the surface depth. It is clearly shown that the phosphorus content decrease with the depth of surface, when the depth is higher than about 12 nm the phosphorus become almost 0, which further demonstrates the film thickness of the boundary lubrication film.

## 3.5 XPS analysis

To get a further insight of chemical composition of tribofilm on copper disc, XPS spectra of key elements of PAO + ZDDP and PAO + AW316 were analyzed. The $Cu_{2p}$ peaks at 932 eV and 951.8 eV can be ascribed to CuS for PAO + ZDDP while peak at 932.6 can be assigned to $Cu_2O$ for PAO + AW316 [14–15]. $P_{2p}$ of PAO + ZDDP exhibit a binding energy at 134.4 eV, indicating that the phosphorus in the worn surface exists in the pentavalent oxidation state and possibly apparently as P-O bond species. A typical peak near 132.8 eV in the high-resolution spectra of $P_{2p}$ of PAO + AW316 (Fig. 6d) can be assigned to P-C bond [16–18]. It is seen that the binding energy of $S_{2p}$ is 160.89 eV for PAO + ZDDP which corresponds to S-C compounds [19, 20]. Figure 6h shows $N_{1s}$ of PAO + AW316 give a strong peak appears at 399.8 eV and 398.5eV, which is most possibly identified as Cu-N [21, 22]. The O1s peak of PAO4 + AW316 (Fig. 6d) at approximately 531.6 eV can be assigned to C–O bonding. Above XPS results suggest that tribo-chemical reactions occurred between anti-wear additives and copper during the tests. These processes generate metal oxides, phosphate and sulfur or nitrogen oxides or amide. These boundary films can effectively protect against the direct contact of rubbing surface and reduce the friction coefficient of the tribology system and resulting a better tribological properties.

## 4 Conclusions

Five typical anti-wear additives were studied as lubricant additives for steel-copper friction pairs. The tribological performance were investigated and their tribological mechanism were discussed. The main findings are summarized as below:

(1) Tribological behavior were highly determined by the chemical structure of anti-wear additives. Higher chemical activity (high polarity and high acid value) are favorite to achieve a better tribological performance.

(2) Amine phosphates was found the best anti-wear additive for steel-copper sliding, which achieves the lowest mean friction coefficient (0.083) and smallest wear volume ($6.15 \times 10^{-3}$ $mm^3$).

(3) The superior tribological performance of AW316 can be explained by the rapid formation of an even boundary lubrication film which is 10–15 nm thick and composed with copper oxides, phosphates, amines.

Overall, carefully screen of additives are essential for steel-copper friction pairs since the tribological are highly influenced with additive type and chemistry. This study provides a significant guidance on choosing suitable anti-wear additive when developing lubricants for steel-copper friction pairs.

## Declarations

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# Figures

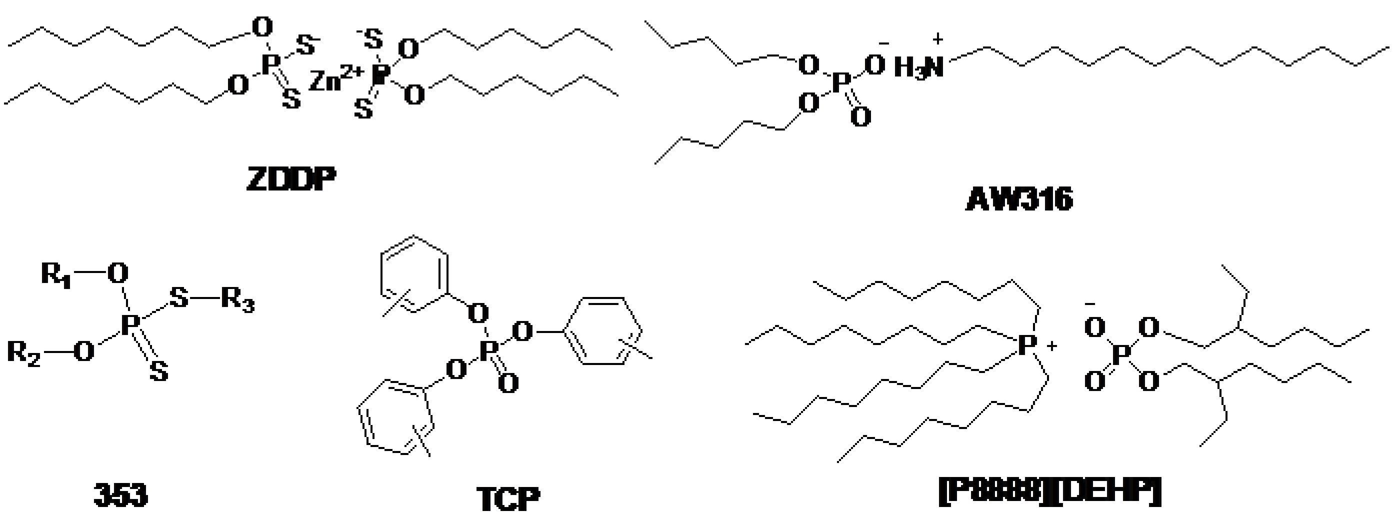



**Figure 1**

Schematic chemical structures of different anti-wear additives

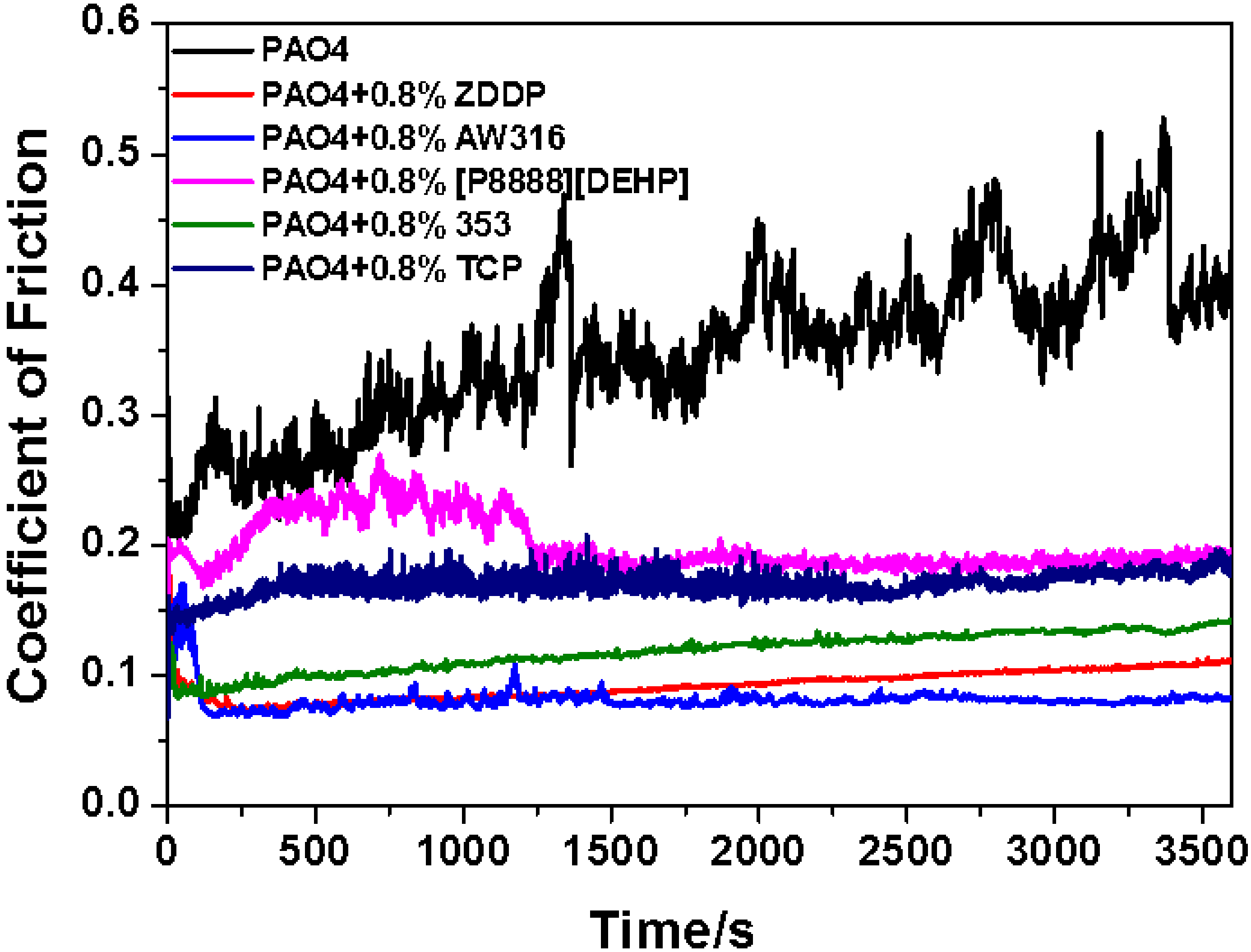
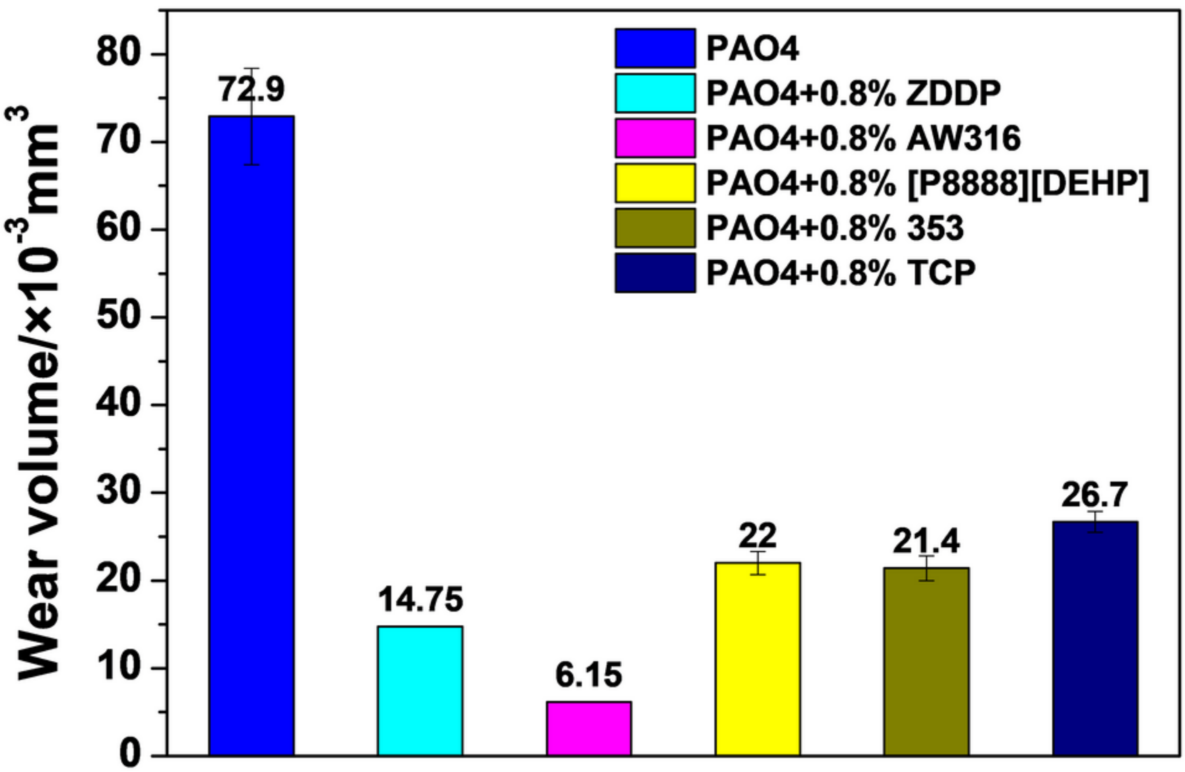



Figure 2

Variation of coefficient of friction with test duration




### Figure 3

Wear volumes of copper plate after tribological tests

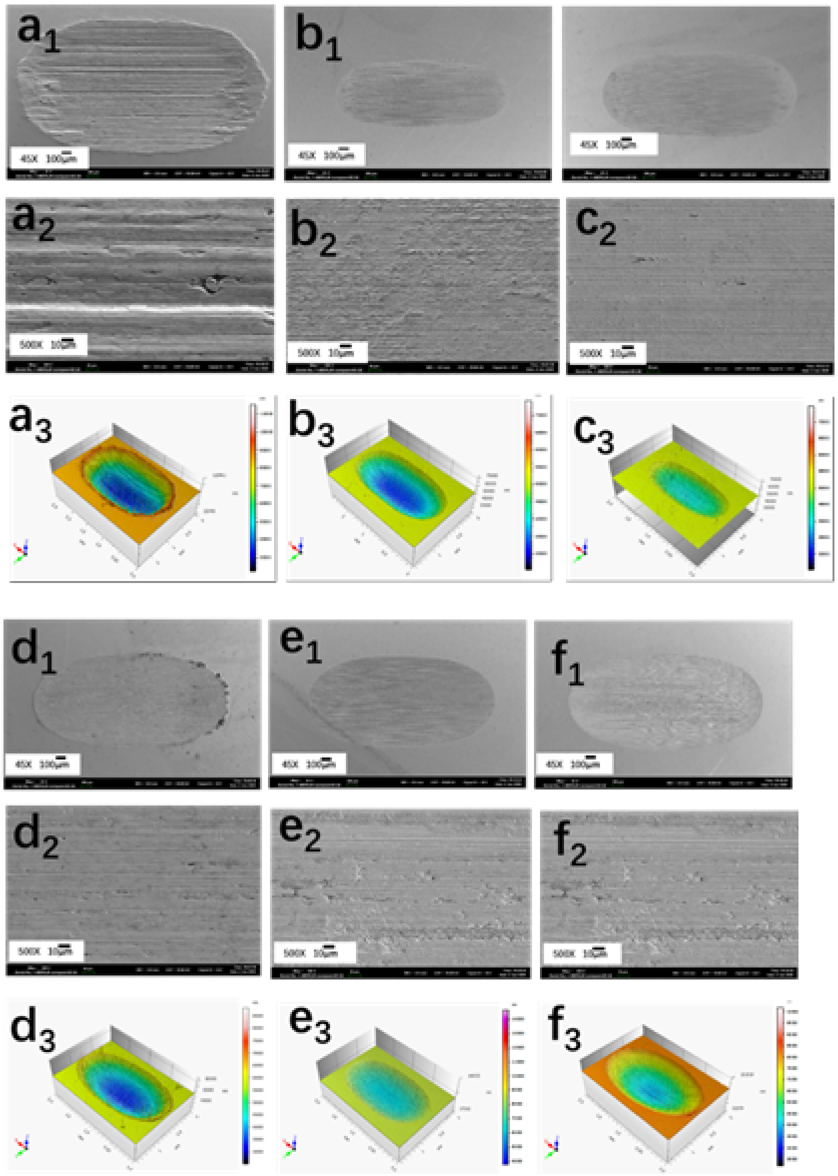
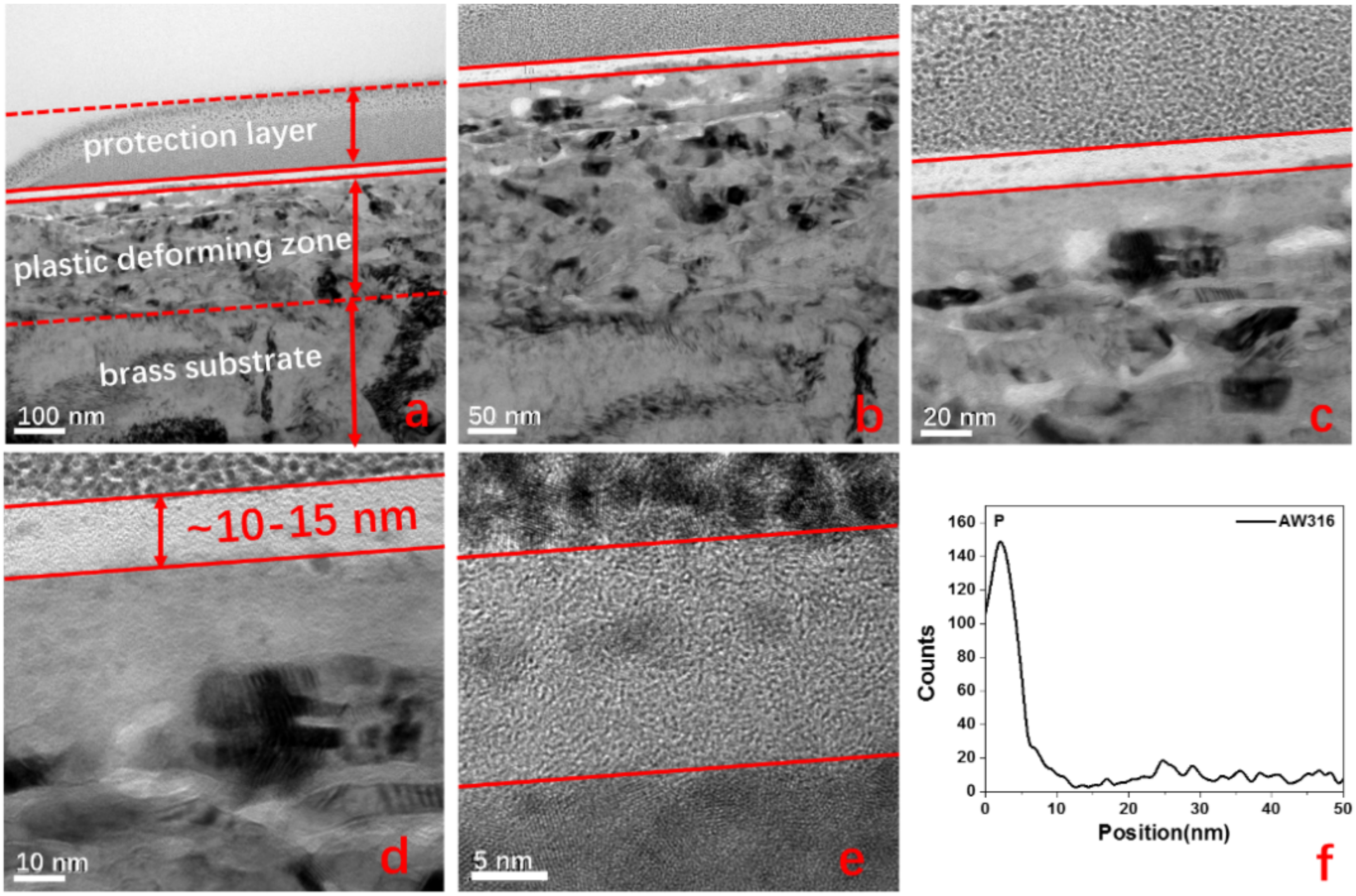


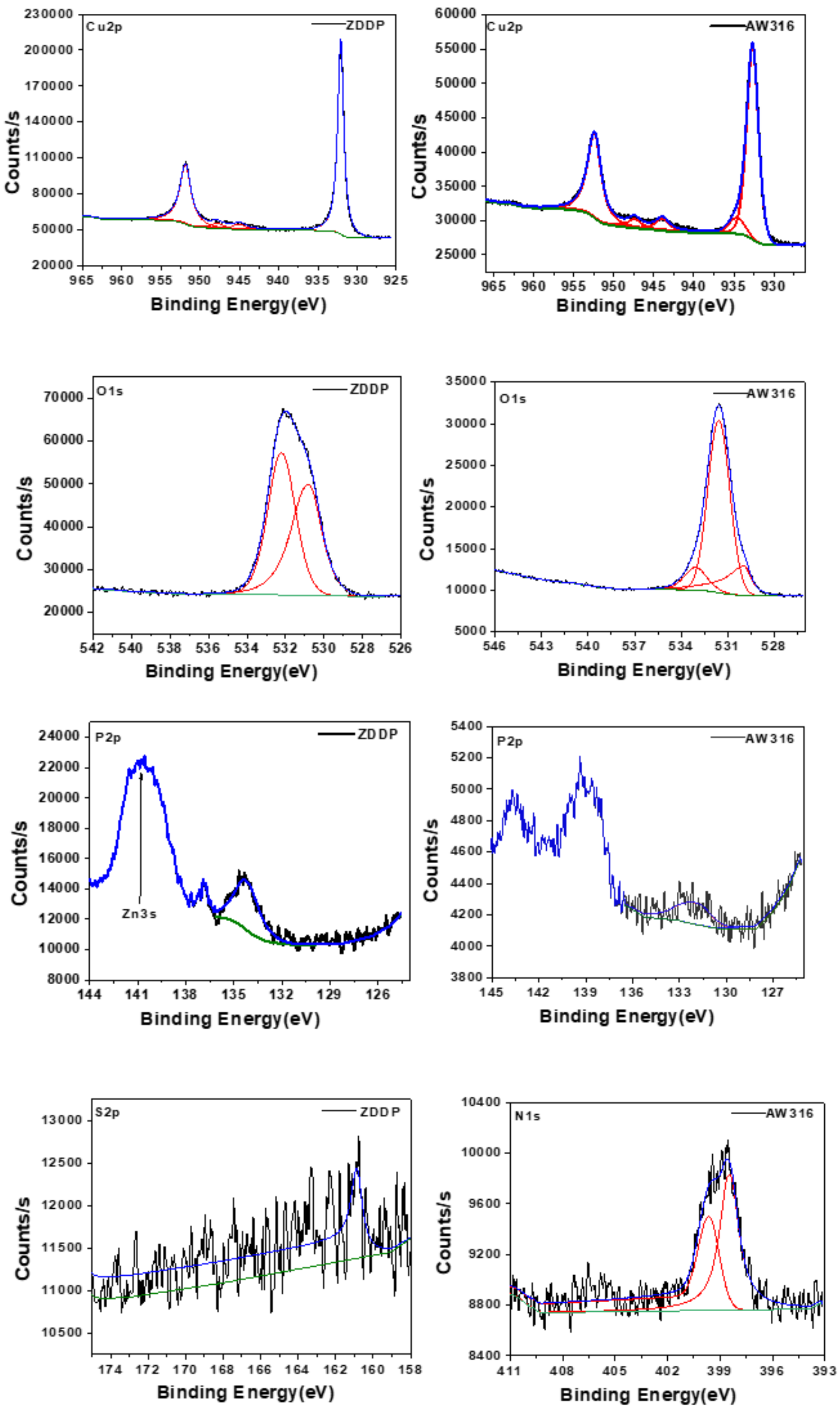

**Figure 4**

SEM images and 3D morphologies of copper worn surfaces




## Figure 5

(a, b, c, d, e) Overview of TEM graph of FIB-cut cross-section of the tribofilm formed on the brass disk lubricated by PAO4+AW316, (f) EDS line (phosphorus) analyses along the brass disc




## Figure 6

XPS spectra of Cu2p, O1s, P2p and S2p on the brass disk lubricated with PAO+ZDDP (left side), XPS spectra of Cu2p, O1s, P2p and N1s on the brass disk lubricated with PAO+AW316 (right side)