Tribology Properties of Synthesized Multiscale Lamellar WS\textsubscript{2} and Their Synergistic Effect with Anti-Wear Agent ZDDP

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Abstract: The microscale/nanoscale lamellar-structure WS\textsubscript{2} particles with sizes of 2 µm and 500 nm were synthesized by solid-phase reaction method and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The synergies between microscale/nanoscale WS\textsubscript{2} particles and ZDDP as lubricating oil additives was evaluated by means of UMT-2 tribometer at room temperature. The wear scars were examined with SEM and electron-probe micro-analyzer (EPMA). The results show that the anti-wear properties were improved and the friction coefficient was greatly decreased with the simultaneous addition of WS\textsubscript{2} particles and ZDDP, and the largest reduction of friction coefficient was 47.2% compared with that in base oil. Moreover, the presence of ZDDP additive in the lubricant further enhances the friction-reduction and anti-wear effect of microscale/nanoscale WS\textsubscript{2}. This confirms that there is a synergistic effect between WS\textsubscript{2} particles and ZDDP.

Keywords: multiscale lamellar WS\textsubscript{2} particles; ZDDP; additives; synergistic effect; friction; wear properties

1. Introduction

It is well-known that the energy loss caused by friction is enormous and staggering, accounting for about 1/3–1/2 of the energy consumption in the world [1]. This is the reason why tribological research particularly focuses on the development of low-friction materials and high-performance lubricants. In recent years, with the emergence and rapid development of nanotechnology, more and more new lubricated nanomaterials have been successfully synthesized and widely used for their excellent lubricating properties. The nanoparticles as lubricant additives have steadily gained attention during the last few years [2,3]. Nanoparticles of transition metal dichalcogenides (TMD) (e.g., MoS\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, and WSe\textsubscript{2}) are considered to hold great prospect as lubricating additives for improving the friction and wear on the surface of the friction pairs [4]. In recent years, the preparation methods of MoS\textsubscript{2}/WS\textsubscript{2} nanoparticles have been extensively studied. The researchers have successfully prepared MoS\textsubscript{2}/WS\textsubscript{2} nanoparticles through various synthetic methods and discussed their tribological properties under different experimental environments [5–7]. Among them, inorganic fullerene-like (IF) MoS\textsubscript{2}/WS\textsubscript{2} nanoparticles seem to be the most widely explored ones, probably because of their low surface energy, fine chemical stability, and spherical shape, which allow them to play an active role in a variety of tribological applications [8–10]. The lamellar-structure WS\textsubscript{2} particle (which hereafter will be referred to as 2H-WS\textsubscript{2}) is an independent research object in relatively few studies. In fact, within
a lamella, the tungsten atoms and the sulfur atoms are bonded by strong covalent forces, whereas inter-laminar binding made by weak Van der Waals forces, which results in low inter-lamellar shear, and therefore, this material exhibits low sliding friction [11]. Moreover, the surface of 2H-WS₂ particles is very smooth, the length and width are far larger than the thickness, and the surface area is large. The slippage easily occurs between the layers, so that the friction coefficient is particularly small [12]. Therefore, the 2H-WS₂ particle also has a great research prospect.

It is worth noting that the current commercial lubricants are a mixture of base oil with lots of conventional additives. Thus, it is essential to understand the interaction of nanoparticles with conventional additives used in lubricants. Zinc dialkyl dithiophosphate (ZDDP), as a common anti-wear additive for lubricating oils, has been used for more than 70 years and is still the critical component of almost all modern gasoline and diesel engine lubricants [13]. Therefore, it is meaningful to study the interaction between WS₂ nanoparticles and ZDDP. It is now recognized that ZDDP can form reaction film on rubbing surfaces, which consists primarily of amorphous zinc phosphate [14–16]. The reaction film called “tribofilm” is considered to control wear by limiting direct contact of the two rubbing surfaces, thereby preventing the surfaces’ adhesion and reducing the transient contact stresses in the course of sliding [13].

In this paper, the synthesized 2H-WS₂ with different sizes and ZDDP are the research object, and the aims of this study were the following:

- To characterize the synthesized multiscale 2H-WS₂ and investigate the lubricating performances of 2H-WS₂ particles under four sliding velocities.
- To evaluate the synergistic effect between multiscale 2H-WS₂ and ZDDP in base oil and study the effect of additives on the chemical and structural characteristics of the tribofilm formed in the course of sliding.

2. Experimental

2.1. Synthesis

The multiscale WS₂ particles used in this experiment were synthesized by solid-phase reaction method [17]. According to the Chemical formula W+2S→WS₂, tungsten disulfide can be synthesized by sintering tungsten powders and sulfur powders at high temperature. The tungsten powders used in the experiment were purchased from China Metallurgical Research Institute. Two different sizes of tungsten powders were obtained, namely microscale 2 µm and nanoscale 500 nm. Tungsten powders and sulfur powders were mixed at a mass ratio of 1:3; the reason for the higher amount of sulfur powders is that it is easy to volatilize in the high temperature environment. The mixed powders were synthesized by high-energy ball milling in a planetary ball mill for 1 h, which contributed to completely mixing the powders. Then, the fully mixed powders were put into a stainless-steel autoclave and placed in a high-temperature vacuum tube furnace. The tube furnace was heated to 750 °C at a heating rate of 10 °C/min, under the protection of N₂, and then heat preservation at 750 °C for 3 h. Finally, the black powders were obtained when the tube furnace was cooled to room temperature. Based on this method, two sizes 2H-WS₂ particles were synthesized, respectively.

2.2. Preparation of Sample Oil Containing 2H-WS₂ Particles and ZDDP

The sample oils used in the experiments were additive-free PAO, PAO with 2H-WS₂, and PAO with 2H-WS₂ and ZDDP. The base oil used in this study has a low viscosity poly alpha olefin (PAO6), which is the common base oil for various industrial synthetic lubricants. The kinematic viscosities of PAO6 are 31 mm²/s at 40 °C and 5.8 mm²/s at 100 °C. According to the previous studies, it was shown that 1 wt.% nano-WS₂ particles in the base oil have the most positive effect on the tribological properties of the lubricant [18]. Thus, the 2H-WS₂ was blended in a concentration of 1 wt.% in the base oil. The ZDDP has a primary alkyl structure with 99% purity and was used at 1 wt.% concentration in sample oil containing WS₂ particles. The reason for using 1 wt.% ZDDP is that the optimum
anti-wear effect can be obtained when the addition amount of ZDDP is 1 wt.% [19]. Then, the base oil and additives were thoroughly mixed, using ultrasound bath for 1 h, to obtain their suspension. The contents of 2H-WS2 and ZDDP as lubricant additives in the sample oil are shown in Table 1.

### Table 1. Contents of 2H-WS2 and ZDDP as lubricant additives.

| Particle Size | WS2/PAO6 (wt.%) | ZDDP/PAO6 (wt.%) |
|---------------|-----------------|------------------|
| 500 nm        | 1%              | /                |
| 500 nm        | 1%              | 1%               |
| 2 µm          | 1%              | /                |
| 2 µm          | 1%              | 1%               |

2.3. Tribological Tests

The tribological properties of four sample oils were tested by UMT-2 tribometer at room temperature. In the experiment, the contact type of the friction pairs was ball-on-disc, and the kinematic form is reciprocating linear motion. The balls were made of a polished bearing steel sphere with a diameter of 10 mm and a roughness of 0.02 µm. The polished steel disc with a diameter of 25 mm was used for the experiment, having a surface roughness inferior to 0.05 µm. The steel disc and balls were cleaned in an ultrasonic bath for 15 min, in absolute ethanol, before the experiments. Four sliding velocities were set for the tests, 10, 20, 30, and 40 mm/s respectively, and with a constant load of 20 N. The magnified contact diagram of frictional pair of UMT-2 tribometer is shown in Figure 1. The length of experiment time was 30 min for each sample. After the experiment, the wear tracks on disc were straight, and each wear track length was 15 mm. The lubrication performance of the sample oil containing 2H-WS2 particles was first evaluated under four sliding velocities. The results were compared with the results when lubricating with PAO alone under the same test conditions. Then, the tribological behavior of 2H-WS2 in presence of ZDDP additive in PAO was also evaluated under the same test conditions. In addition, drop lubrication was applied in the test, which was lubricated at a rate of 3 drops/min and a total amount of about 5 mL. Three drops of lubricant were deposited on the plate before starting the experiment. The friction experiments were repeated three times in order to ensure reproducibility of the results and that the average value was calculated.

![Figure 1. The magnified contact diagram of frictional pair.](image)

The wear scars on the steel disc after the test were analyzed with scanning electron microscopy (SEM) and an electron-probe micro-analyzer (EPMA), to determine the anti-wear properties of lubricating oil. The anti-wear properties of additives can be determined according to the size of wear scar, wear depth, and material loss. The wear scars on the steel disc after tests can be seen clearly by means of SEM. In addition, in order to know the distribution of the main elements on the friction surface after the tests, EPMA analysis was carried out on the rubbed surface lubricated with the sample oil containing additives. Some elements on the surface of the steel were revealed, such as iron, carbon, oxygen, tungsten, sulfur, zinc, and phosphorus.
3. Results and Discussion

3.1. Nanoparticles Characterization

Standard characterization procedures were used for the synthesized WS2 particles. The microscale/nanoscale 2H-WS2 powder was characterized through X-ray diffraction (XRD) and SEM to obtain its physical and chemical properties. Figure 2 shows the XRD images of the synthesized WS2 particles. The diffraction peaks in Figure 2 correspond to the PDF#08-0237 in the powder diffraction file, with lattice parameters of $a = 3.154$ Å, $b = 3.154$ Å, and $c = 12.362$ Å. Because of no impurity peaks in the figure, it can be determined that the purity of synthesized WS2 is relatively high. The SEM images of synthesized WS2 particles at different magnifications are shown in Figures 3 and 4. The thickness of WS2 particles in Figure 3 is about 500 nm, and the lateral dimension is between 1 and 5 µm. The thickness of WS2 particles in Figure 4 is about 2 µm, and the lateral dimension is between 5 and 10 µm. As can be seen from the figures, the WS2 particles are mostly lamellar structure with different orientations, disordered arrangement, and irregular shapes. In addition, it can be clearly seen that the large WS2 particles are formed by the close packing and agglomeration of some lamellas. Among them, most of these stacked particles have obvious delaminations on the edges, and the other parts have blurred edges and have a tendency to fuse. This is because the high-temperature calcination is conducive to the conversion of stacked multilayer lamellas into disordered single lamellas; this conversion is limited by the size of the particles and therefore cannot be fully conducted. Therefore, the lamellar-structure WS2 particles with sizes of 2 µm and 500 nm were successfully synthesized by solid-phase reaction method.

![Figure 2. XRD images of the synthesized WS2 particles.](image)

![Figure 3. SEM images of nano-WS2 at different magnifications, (a) 5000×; (b) 10,000×.](image)
3.2. Tribological Results

3.2.1. Friction-Reduction Properties

The friction coefficient curves of PAO and two sizes of 2H-WS₂ particles at four sliding velocities are plotted in Figure 5. The purpose of the test is to investigate the lubricating properties of the synthesized 2H-WS₂ in PAO. The tribological behavior of 2H-WS₂ in the presence of the ZDDP additive in PAO was also evaluated, and the results are shown in Figure 6. Moreover, the important fluctuations in friction experiments can be observed in Figures 5 and 6. In addition, in order to reflect the friction coefficients more intuitively at different sliding velocities, the average friction coefficients and the variances of all sample oils are reported in Figure 7. It shows that the friction coefficient increases gradually with the increase of the sliding velocity. Friction coefficients ranged from 0.138 to 0.175 when only PAO was added, whereas the friction coefficients of sample oils containing additives are all lower than that of base oil under the same test conditions. Therefore, the frictional benefits of the 2H-WS₂ and ZDDP are observed compared to PAO alone in Figure 7.

In Figure 5, the lubrication performance becomes more stable as the sliding velocity increases. Figure 7 reveals that the maximum reduction of friction coefficient is 31.3% when the 500 nm of 2H-WS₂ was added to base oil, and the maximum reduction of friction coefficient is 27.4% in the case of adding 2 µm of 2H-WS₂ compared with that of base oil. Thus, the following conclusions can be drawn according to the experimental results: Firstly, the addition of 2H-WS₂ in base oil resulted in a significant reduction in the friction coefficient under appropriate working conditions. Secondly, in general, the sample oil containing smaller size 2H-WS₂ particles showed a better lubricating effect.

Figure 6 shows the friction curves of the sample oil containing both ZDDP and 2H-WS₂, and then compares them to the curve with better lubrication effect in Figure 5. The addition of ZDDP further reduces the friction coefficient compared to the addition of 2H-WS₂ alone, as shown in Figure 6. When we combine this with Figure 7, we can see that the maximum reduction in friction coefficient was 35.4% when the 500 nm of 2H-WS₂ and ZDDP were both present, and the maximum reduction of friction coefficient was 47.2% in the case of adding both 2 µm of 2H-WS₂ and ZDDP. Therefore, some conclusions can be drawn: Firstly, the presence of 2H-WS₂ and ZDDP in PAO can cause greater reduction of friction coefficient and exhibit a better lubricating performance, and there is a positive interaction between the two additives. Secondly, in the presence of ZDDP, the 2H-WS₂ particles with larger size have the better friction-reduction performance compared with that of other sample oils.
Friction curves obtained for the reference sample oil (PAO) and the microscale/nanoscale 2H-WS$_2$ in PAO, both with respect to four sliding velocities: (a) 10 mm/s; (b) 20 mm/s; (c) 30 mm/s; and (d) 40 mm/s.

Figure 5. Cont.
was 15 mm. Based on the anti-friction results mentioned above, in Figure 7, a few wear scars were
more and more obvious with the increase of velocity. What’s more, it can be concluded that the
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was different at four sliding velocities. Some of them had a poor friction-reduction effect, while others had a very
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Friction curves of microscale/nanoscale 2H-WS2 in the presence of ZDDP additive: (a) 10 mm/s;
(b) 20 mm/s; (c) 30 mm/s; and (d) 40 mm/s.
Figure 7. Average friction coefficient measured for all sample oils and their variances.
The average friction coefficient and its variance of each sample oil at four sliding velocities are
shown in Figure 7. The friction-reduction effect of the sample oil containing additives was different at
four sliding velocities. Some of them had a poor friction-reduction effect, while others had a very good
one. For example, at the sliding velocity of 20 mm/s, the anti-friction effect was not prominent, as the friction coefficients were reduced only by 4.9–15.3% compared with that of PAO alone. However, at 30
and 40 mm/s sliding velocities, the additives apparently played a positive role in reducing friction, as the friction coefficients were greatly reduced by 22.7–47.2%. Thus, the friction-reduction effect was more and more obvious with the increase of velocity. What’s more, it can be concluded that the friction-reduction properties of the multiscale 2H-WS2 not only can be preserved in presence of the ZDDP additive, but also that the ZDDP allows a stabilization of the friction coefficient, as well as lower values.
3.2.2. Anti-Wear Properties
After the experiment, the wear tracks on the disc were straight, and each wear track length
was 15 mm. Based on the anti-friction results mentioned above, in Figure 7, a few wear scars were
selected for comparison. Figure 8 shows the SEM micrographs of disc surfaces after rubbing at
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3.2.2. Anti-Wear Properties

After the experiment, the wear tracks on the disc were straight, and each wear track length was 15 mm. Based on the anti-friction results mentioned above, in Figure 7, a few wear scars were selected for comparison. Figure 8 shows the SEM micrographs of disc surfaces after rubbing at different velocities.

**Figure 8.** SEM micrographs of disc surfaces after rubbing in (a) 30 mm/s PAO; (b) 40 mm/s PAO; (c) 30 mm/s PAO+2H-WS₂; (d) 40 mm/s PAO+2H-WS₂; (e) 30 mm/s PAO+2H-WS₂+ZDDP; and (f) 40 mm/s PAO+2H-WS₂+ZDDP.

In Figure 8, the wear scars at 30 mm/s are not as clear as the wear scars at 40 mm/s in the case of the same additives, and the furrow depths are not as pronounced as the latter. It is clear that the wear becomes more serious with the increase in sliding velocities. This is because the increase of velocity is bound to increase the total sliding length of the steel ball at the same experimental time. Therefore, under the same test conditions, the greater the velocity, the more obvious the wear.

As a reference, the wear scars with additive-free PAO are shown in Figure 8a,b. There are lots of obvious furrows and a slight spalling on the friction surface. It can be speculated that the friction pairs mainly undergo microploughing and adhesive wear during the friction process due to the fact that it is difficult to avoid the direct contact between many asperities of the friction pair. The friction surface is prone to plastic deformation under a certain positive pressure, and the friction and wear is further aggravated when the abrasive particles enter the lubricating medium during the friction process. Compared with this, the abrasive wear is relatively light, and the furrows are shallow in the wear scars with adding 2H-WS₂, and the surface is more smooth (Figure 8c,d). This shows that the addition of 2H-WS₂ has a positive effect on reducing wear. The 2H-WS₂ are most likely to form a protective film on the friction surface, thereby reducing the direct contact between the friction pairs.
These results confirm that the anti-wear performance is greatly enhanced under the combined action of 2H-WS and ZDDP, indicating that the additives played a role in reducing wear. At a sliding speed of 10 mm/s, the wear volume at 10 mm/s is much larger than that at 10 mm/s, almost 3–5 times more than that at 10 mm/s. At the same sliding speed, the wear volume decreases with the increase of 2H-WS and ZDDP, indicating that the additives played a role in reducing wear. At a sliding speed of 10 mm/s, the wear volume of PAO was 0.117 mm$^3$. Compared with this, the maximum wear volume of the sample oil containing WS$_2$ was reduced by 61.16%, while the maximum wear volume of the sample oil with 2H-WS$_2$ and ZDDP was reduced by 74.38%.

![Three-dimensional topography of wear scar.](image)

**Figure 9.** Three-dimensional topography of wear scar.

The wear scars were characterized with a three-dimensional topography instrument, and the results are shown in Figure 9, from which the wear volume can be obtained. The wear volume of the wear scars of the sample oil at 10 mm/s and 30 mm/s are shown in Figure 10. In terms of sliding speed, the wear volume at 30 mm/s is much larger than that at 10 mm/s, almost 3–5 times more than that at 10 mm/s. At the same sliding speed, the wear volume decreases with the increase of 2H-WS$_2$ and ZDDP, indicating that the additives played a role in reducing wear. At a sliding speed of 10 mm/s, the wear volume of PAO was 0.117 mm$^3$. Compared with this, the maximum wear volume of the sample oil containing WS$_2$ was reduced by 61.16%, while the maximum wear volume of the sample oil with 2H-WS$_2$ and ZDDP was reduced by 74.38%.

![Wear-volume histogram of all sample oils at 10 and 30 mm/s.](image)

**Figure 10.** Wear-volume histogram of all sample oils at 10 and 30 mm/s.

However, when the 2H-WS$_2$ and ZDDP are added at the same time, the wear is the lightest, and there are no obvious furrows. In addition, as can be seen from Figures 9 and 10, the wear width is much smaller than the addition of 2H-WS$_2$ alone at the same magnification. It can be inferred that the fatigue wear and galling are the main wear forms between friction pairs. The rubbed surfaces are separated by the friction-reaction film and deposition film during the friction process. Therefore, it can be concluded that the presence of 2H-WS$_2$ in lubricating oil can reduce wear and play a certain role in anti-wear. Moreover, the presence of ZDDP greatly improves the anti-wear properties of lubricating. These results confirm that the anti-wear performance is greatly enhanced under the combined action of 2H-WS$_2$ and ZDDP.
3.2.3. EPMA Characterization of Wear Scars

The chemical mapping by EPMA of the wear tracks (40 mm/s, PAO+2H-WS₂) is reported in Figure 11. The survey reveals the presence of iron, carbon, oxygen, tungsten, sulfur, zinc, and phosphorus on the steel surface. The iron and oxygen elements can clearly show the wear track in Figure 11, so it can be speculated that the iron oxide friction film has formed on rubbed surface. The content of tungsten and sulfur is not very much, and the traces are basically the same, so we can guess that these could be residual WS₂. The image shown in Figure 12(a) suggests that a small amount of 2H-WS₂ was trapped in the grooves of the flat surface, which can also prove the above conjecture. The phosphorus and zinc elements are evenly distributed throughout the surface, so there is no marked wear track.

![Chemical mapping by EPMA of the wear track obtained when using 2H-WS₂ in oil to lubricate the rubbed surfaces (40 mm/s, PAO+2H-WS₂). (a) abrasion trace; (b) Fe; (c) C; (d) O; (e) W; (f) S; (g) P; (h) Zn.](image1)

![Figure 11.](image2)

![Figure 12. (a) the enlargement of the SEM images in Figure 11; (b) the enlargement of the SEM images in Figure 13.](image3)
Therefore, at room temperature, the 2H-WS$_2$ proves that a tribofilm has been formed on the steel surface. The scratch width in Figure 13a is relatively narrow compared with Figure 11a. It can be concluded that the presence of ZDDP improves the anti-wear ability of the lubricant under the same experimental conditions. The wear track can be seen from the elemental graphs of zinc and phosphorus. Thus, the worn surface is likely to form a reaction tribofilm, which is mainly composed of zinc phosphate compounds. The amount of oxygen element is obviously lower, and because the ZDDP additive is known for its antioxidant properties, it can be guessed that the ZDDP may play a key role in the protection of the metal surfaces against oxidation. The distribution of tungsten and sulfur elements is less than that in Figure 11, and Figure 12b shows that these may be a small amount of residual WS$_2$.

3.3. Lubrication Mechanism of WS$_2$

From the experimental results, compared with the base oil PAO6, the addition of 2H-WS$_2$ particles can reduce the friction coefficient, the maximum can be reduced by 35.4%, and the wear scar is relatively light and the furrows are shallow. The lubrication mechanism discussed below when multiscale 2H-WS$_2$ as additives are added alone in base oil. The schematic illustration of the lubrication mechanism under lubrication conditions of containing 2H-WS$_2$ is shown in Figure 14a. When the two friction surfaces were in contact, 2H-WS$_2$ deposited on the concave surface of the metal surface to fill the surface, thereby reducing the relative surface roughness and friction between sliding surfaces. The deposited 2H-WS$_2$ particles on the worn surface can also decrease the shearing stress, and hence reduce friction and wear. With the increase of friction time, the metal surface undergoes a chemical action to produce an iron oxide film that can effectively prevent direct contact between the metal surfaces, thereby significantly reducing wear between the metal surfaces. However, no obvious tungsten oxide or iron sulfide appeared during the whole friction process the Figure 11, and this is different from the results of the reference [20]. In this reference, Ratoi et al. found that small quantities of WO$_3$ and iron sulfides were formed in the tribofilm. The reason for the different results may be due to the fact that the reaction temperature or load in this test cannot meet the reaction requirements. Therefore, at room temperature, the 2H-WS$_2$ used as a lubricant additive has friction-reduction and anti-wear effects mainly in the form of deposited films, and there is no oxidation reaction of the 2H-WS$_2$, and the chemical film is mainly composed of iron oxide in the process of friction. Moreover, the 2H-WS$_2$ with different sizes have different results under the same experimental conditions. In view
of the friction coefficient, small-sized 2H-WS₂ exhibit better friction-reducing properties, probably because small-sized 2H-WS₂ are more easily deposited on the concave surface, filling the surface, thereby reducing the relative surface roughness and the friction between sliding surfaces. In addition, small-sized 2H-WS₂ are more easily embedded, and they repaired the metal surface after scratched.

The presence of 2H-WS₂ particles and ZDDP in PAO produce a greater reduction of friction coefficient and exhibit a better lubricating performance, according to the experimental results, and the maximum reduction is 47.2% compared with that of the base oil. In addition, the wear is the lightest, and there are no obvious furrows. When 2H-WS₂ and ZDDP are both added as additives into the base oil, the anti-wear and anti-friction properties of the lubricating oil are improved again, and the lubrication mechanism is discussed as follows. The schematic illustration of the lubrication mechanism under lubrication conditions of containing both 2H-WS₂ and ZDDP is shown in Figure 14b. Due to the presence of ZDDP, the rubbed surface will quickly form a tribofilm composed of zinc phosphate compounds [21,22]. The chemical tribofilm formed by ZDDP could also have acted as a spacer to keep metal surfaces separated, which can also prevent oxidation of the metal surfaces and 2H-WS₂ because of its excellent oxidation resistance. Thereby, the metal surface is well protected, and the wear is reduced. The content of oxygen element in Figure 13d is obviously smaller than that in Figure 11d, indicating that the existence of ZDDP greatly reduces the formation of iron oxide film. Therefore, only a small amount of iron oxide exists on the friction surface. Additionally, the 2H-WS₂ particles are deposited on the rubbed surface, to form a deposited film; the deposition of 2H-WS₂ on the worn surface can decrease the shearing stress and friction force, which can reduce the friction coefficient. The friction coefficient and the wear are both reduced by the combination of the chemical tribofilm and the physical deposition film. These results clearly emphasize the synergetic effects between the 2H-WS₂ and the ZDDP anti-wear additive.

Figure 14. Schematic illustration of the lubrication mechanisms under lubrication conditions of containing (a) 2H-WS₂ and (b) 2H-WS₂ and ZDDP.
4. Conclusions

In this work, the multiscale lamellar-structure WS$_2$ particles with sizes of 2 µm and 500 nm were successfully synthesized by solid-phase reaction method. Then, the tribological properties of multiscale 2H-WS$_2$ and ZDDP as additives in PAO at four sliding velocities were investigated at room temperature. The conclusions are as follows.

The tribological properties of microscale/nanoscale 2H-WS$_2$ in PAO were tested first. The results show that the friction coefficient can be reduced by approximately 30%, and the wear scars are relatively shallow compared to the results of the base oil. The friction-reduction and anti-wear properties are improved due to a layer of oxide film formed on the rubbing surface and the 2H-WS$_2$ trapped in the surface grooves. Therefore, the multiscale 2H-WS$_2$ particles can play a role in friction-reduction and anti-wear when used as a single additive, according to the experimental results.

The friction-reduction and anti-wear properties of the base oil are enhanced when the 2H-WS$_2$ particles and ZDDP work as additives at the same time. A strong reduction of the friction coefficient and slight wear of the surfaces were observed from the results. The friction coefficient can be reduced by up to 47.2%. The wear-scar width is narrower, the wear scar is shallower, and the rubbing surface is relatively smooth. The better results found with the use of ZDDP are explained by its antioxidant properties and a tribofilm composed of zinc phosphate compounds, which protects metal surfaces from oxidation and contact. Therefore, the positive synergistic effect between multiscale 2H-WS$_2$ and ZDDP can be verified from the above conclusions.

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