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RESEARCH ARTICLE

Combination of diketone and PAO to achieve macroscale oil-based superlubricity at relative high contact pressures

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Abstract: 1-(4-ethylphenyl)-nonane-1,3-dione (0206) is an oil-soluble liquid molecule with rod-like structure. In this study, the chelate (0206-Fe) with octahedral structure was prepared by the reaction of ferric chloride and 1,3-diketone. The experimental results show that when using 0206 and a mixed solution containing 60% 0206-Fe and 40% 0206 (0206-Fe(60%)) as lubricants of the steel friction pairs, superlubricity can be achieved (0.007, 0.006). But their wear scar diameters (WSD) were very large (532 μm, 370 μm), which resulted in the pressure of only 44.3 and 61.8 MPa in the contact areas of the friction pairs. When 0206-Fe(60%) was mixed with PAO6, it was found that the friction coefficient (COF) decreased with increase of 0206-Fe(60%) in the solution. When the ratio of 0206-Fe(60%) to PAO6 was 8:2 (PAO6(20%)), it exhibited better comprehensive tribological properties (232.3 MPa). Subsequent studies have shown that reducing the viscosity of the base oil in the mixed solution helped to reduce COF and increased WSD. Considering the COF, contact pressure, and running-in time, it was found that the mixed lubricant (Oil3(20%)) prepared by the base oil with a viscosity of 19.7 mPa·s (Oil3) and 0206-Fe(60%) exhibited the best tribological properties (0.007, 161.4 MPa, 3,100 s).

Keywords: diketone; oil-based lubricants; chelate; superlubricity

1 Introduction

The phenomenon of friction can be seen everywhere in industrial production. The friction generated by the contact surfaces of these mechanical parts will consume the mechanical energy of the system, and the wear caused by friction will seriously affect the performance and life of the parts [1, 2]. With the development of science and technology, industrial equipment is not only developing in the direction of high speed and heavy load, but also in the direction of precision and miniaturization [3]. The emergence of these two phenomena means that the requirements for reducing friction and wear are more stringent. In order to save energy and improve the durability of materials, it is urgent to reduce the friction between the contact surfaces of moving parts. Since the concept of superlubricity was first proposed by Hirano and Shinjo in the 1990s, a large number of researchers have been inspired to explore superlubricity under macroscopic experimental conditions [4]. Considering the energy dissipation, disturbance, and measurement error in actual measurement, the lubrication state with friction coefficient (COF) lower than 0.01 is usually called superlubricity [5, 6].

Normally, for a friction pair lubricated by an oil-based lubricant, the COF depends largely on the lubrication state. From boundary lubrication (BL) to mixed lubrication (ML) and then to elastohydrodynamic lubrication (EHL), the COF in the contact area of the friction pair decreases accordingly [7]. The minimum COF of oil-based lubricants is usually in the state of

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thin-film lubrication, which is a transition from ML to EHL [8]. The friction pair in this lubricated state is not only completely separated by the liquid film, but also provides very low lubricant shear viscous friction due to the small thickness of the fluid film. However, in practical applications, most of the contact areas of mechanical parts are in a state of ML or even BL [9]. Therefore, it is more practical to carry out experimental research and propose new strategies for reducing friction and anti-wear under the above two lubrication states.

In the ML state, the contact zone is usually composed of solid asperity contact and lubricant. Therefore, the COF in this state can be considered to be composed of solid shear friction and lubricant viscous friction [10]. So, in order to achieve oil-based superlubricity in the ML state, it is necessary to reduce both the solid contact friction and the lubricant viscous friction. Compared with traditional basic lubricants, the rod-shaped liquid crystal molecules have independent viscosity adjustment, so the viscous friction force inside the liquid is smaller during the lubrication process, which is more conducive to reducing the COF between the friction pairs [11]. Nakano et al. conducted tribological experiments with rod-shaped liquid crystal molecules such as alkylcyanobiphenyls and alkoxycyanobiphenyls, and found that compared with aviation oil and vaseline oil, the friction pair lubricated by liquid crystal molecules showed a lower COF [12]. These findings were good agreement with previous studies on the tribological properties of N-(4-methoxybenzylidene)-4-butylaniline (MBBA) and N-(4-ethoxybenzylidene)-4-butylaniline (EBBA) [13]. Chen et al. studied the lubrication characteristics of liquid crystal monolayers sheared between two surfaces by nonequilibrium molecular dynamics simulations [14]. They found that shear flow effects and surface-induced orientation compete with each other. When the shear speed was small, the surface structure controlled the orientation of the liquid crystal molecules, but when the shear speed was high, the liquid crystal was preferentially aligned in the shear flow direction, and the friction force was much smaller than the stick-slip stage at low speed. Amann and Kailer synthesized many rod-like compounds and studied their tribological properties as lubricants. It has been found that an increase in molecular weight correlates with an increase in viscosity [15]. For all compounds, elongation of the alkyl chain also increased viscosity, which was detrimental to the reduction in the COF [16]. In addition to being directly used as a lubricant, considering the cost, the use of rod-like molecules as a base oil additive can also play a good role in reducing friction and anti-wear [17]. Gao et al. added four cholesteric liquid crystals with different tail chain structures to liquid paraffin and found that they all showed good tribological properties [18]. Liquid crystal additives helped to enhance oil film formation and reduce friction. When the liquid crystal contained an ester group, it was easier to adsorb on the surface of the metal friction pair, and when it contained a tail chain, it was more helpful to dissolve in mineral oils [19, 20]. Zhang et al. studied the tribological properties of fluorine-containing liquid crystal compounds with perfluoroalkyl chains as additives for PAO4. The results showed that the COF of PAO4 containing fluorinated liquid crystals (LCs) was significantly reduced (30%), and the wear was reduced (more than 2 times) [21].

In addition to the influence of lubricant on the COF, in the contact area of the asperity, whether a boundary film can be formed to isolate the direct contact of the asperity is also crucial to the reduction of the COF. Zhang found that the formation of protective films of iron oxide and iron fluoride was the main reason for avoiding direct contact between metal surfaces by characterizing the surface of the friction pair [21]. Gao et al. synthesized five kinds of liquid crystals with different molecules, and found that when the liquid crystal molecules contain ester groups, it was easier to adsorb on the metal surface as a lubricant additive to avoid direct contact of metal friction pairs [22]. Thereby, it had the function of reducing friction and anti-wear. Ghosh et al. synthesized multifunctional additives by grafting liquid crystal molecules with lubricating oil viscosity modifier polyacrylate. This can not only increase the viscosity of the lubricating oil, but also facilitate the adsorption of liquid crystal molecules on the metal surface, which improved the anti-wear performance of the lubricating oil [23]. It can be seen from the above that when rod-like molecules containing polar functional groups were selected as lubricants or lubricant additives, they exhibited excellent tribological properties. This provides an idea for the study of oil-based superlubricity.

At present, the research on oil-based superlubricity of metal friction pairs can be divided into two aspects. One is to modify the surface of the friction pair so that it can interact with the lubricant [24, 25]; the other is to select a polar liquid to run-in the friction pair in advance, and then replace the lubricant to achieve superlubricity [26, 27]. Kano and Bouchet et al. achieved superlubricity by coating the metal surface with a tetrahedral amorphous carbon (ta-C) coating and then choosing glycerol monooleate or glycerol as the lubricant [28, 29]. Nitinol 60/steel can achieve superlubricity by the lubrication of castor oil under boundary lubrication state. However, due to the poor oxidative stability of castor oil, superlubricity cannot be achieved at high speeds [30]. Ge et al. achieved superlubricity with both polar (polyalkylene glycols) and non-polar (PAO) oils between a steel/steel tribopair by pre-treating the interface with PEG(aq) [31]. Chen et al. found that the COF of the metal friction pair after running-in with acetylacetone was reduced by 80% under the lubrication of 4-cyano-4-pentyl biphenyl (5CB) [32]. The analysis showed that the tribo-chemical reaction between acetylacetone and the steel surface during the running-in process and the unique structure of liquid crystal were the reasons for the extremely low COF.

The emergence of 1,3-diketone provides a new method for the study of oil-based superlubricity [33–35]. Tribological experiments were performed by preparing 1-4(ethylphenyl)-butane-1,3-dione (EPBD-0201). It was found that the chelation reaction of diketone molecules on the metal surface to form a tribochemical adsorption layer played an important role in the realization of superlubricity [36]. Recently, by mixing 1,3-diketone and chelate in a ratio of 4:6, our team found that the mixed solution can not only achieve superlubricity compared with pure diketone, but also increase the contact pressure from 24.7 to 105.2 MPa [37]. Studies on 1,3-diketones as additives to improve the tribological properties of basic lubricants have been carried out by researchers [38]. However, most researchers only focused on the improvement of the tribological properties of base oils by adding diketones. There were relatively few studies on whether superlubricity can be achieved after adding 1,3-diketone to the base oil, and what kind of ratio can achieve superlubricity.

Previous studies on 1,3-diketone were carried out under a load of 1 N, in this study, the tribological properties of 1,3-diketone, chelate, and PAO were first explored at 5 N. Then focuse on the tribological properties of 1,3-diketone, chelate, and PAO in different proportions. And evaluate the effect of different viscosity PAO on whether the mixed lubricant can achieve superlubricity. Through the analysis of surface characterization and lubrication state, the effects of different components in the lubricant on the realization of superlubricity were determined, which provided a reference for the application of 1,3-diketone in base oils.

2 Experimental

2.1 Materials and lubricants

The preparation of 1-(4-ethylphenyl)-nonane-1,3-dione (0206) was based on the Claisen condensation method, and the detailed synthesis procedure was described in our prior work [37]. 0206 shows a rod-shaped molecular structure, which consists of a rigid center and two flexible alkyl chains (shown in Fig. 1(a)). The reaction product of 1,3-diketone and iron is called chelate (0206-Fe), which has the structure of regular octahedron (shown in Fig. 1(b)). To investigate the effect of viscosity, we selected three base oils

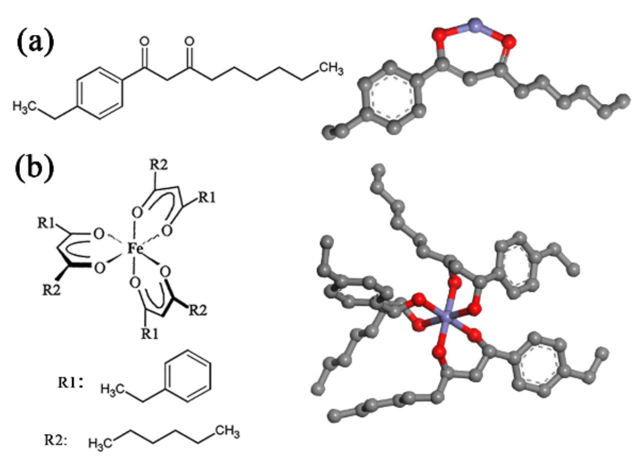

Fig. 1 Molecular structure of (a) 1,3-diketone (0206) and (b) chelate (0206-Fe).

of different viscosities, PAO2, PAO4, and PAO6. A commercial lubricant 4129A for precision bearing lubrication was also selected.

2.2 Tribological tests

The tribological tests were carried out on a UMT-5 tester (UMT TriboLab Bruker Nano Inc, Germany) using a ball-on-disc configuration. The materials of the steel balls and steel discs used in the experiments were GCr15. The steel ball was purchased from Shanghai Steel Ball Plant CO., Ltd. with a diameter of 12.7 mm and a surface roughness of 5 nm. The plate provided by Shenzhen Chengyang Metal Materials Co., Ltd. had been quenched and the rockwell hardness was around 60 HRC, and the roughness was about 5 nm after uniform polishing. The tested contacts were steel/steel under lubrication conditions with base oils (PAO2, PAO4, PAO6) and the mixtures of the base oils with 1,3-diketone and chelate at 25 °C. Before the tribological tests, all samples were ultrasonically cleaned with acetone and alcohol, then were dried in stream of air. The same amount of oil (10 μL) was added on the surface of the disc for each test. All the tests were repeated at least three times. The normal load was 5 N, resulting in an initial contact pressure of 683.6 MPa. The experiment was carried out from low speed (62.8 mm/s for 5 min) to high speed (314.2 mm/s). Each test lasted for 8,400 s so that the COF became stabilized.

2.3 Characterization

The wear scar diameters and the worn surface on the friction pairs were measured using an optical microscope (VHX-5000). The viscosity of lubricants was tested through a rheometer (MCR302, Anton P, Austria). The three-dimensional topography and cross-sectional profile of the friction pair after wear were obtained by a three-dimensional white light interferometer (ZYGO NexView). The scanning electron microscope (SEM, FEI, Quanta 200 FEG) was used to characterize the details of the worn surface of the friction pair at high magnification. The surface chemical composition was explored by X-ray photoelectron spectroscopy (XPS, Ulvac-Phi lnc. PHI Quantera II, using monochromatic Al Kα irradiation) with an accelerating voltage of 15 kV and a power of 25 W. Before starting the analysis, 500 V argon ions were used to sputter the surface to remove the hydrocarbon contaminants adsorbed in the air after the surface was cleaned. A binding energy value of 284.6 eV for C 1s was used to calibrate binding energies.

The oil film thickness of different lubricants at different speeds under point contact was measured by a film thickness measuring instrument with relative optical interference intensity (TFM-150) [39, 40]. The device had a vertical resolution of about 0.5 nm and a horizontal resolution of about 1 μm. The diameter of the ultra-polished GCr15 alloy balls was about 22.225 mm, and the surface roughness was 5 nm. The surface roughness of the glass disc with chromium semi-reflective layer was 0.56 nm. The load was set to 40 N. Experimental speeds ranged from 10 to 1,000 mm/s.

3 Results

3.1 Tribological properties of based oils

The viscosity and rheological properties of lubricant will affect the actual lubrication effect. The dynamic viscosity curves of seven lubricants at shear rates of 0.1 to 1,000 s^{-1} are shown in Fig. 2(a). The viscosity values of base oils (PAO2, PAO4, PAO6) and commercial lubricant (4129A) were 5.8, 30.2, 46.4, and 106.5 mPa·s, respectively. In the dynamic viscosity test, the viscosity of the above four lubricants did not change significantly with the shear rate, indicating that the lubricants were Newtonian fluids. For the prepared diketone (0206), its viscosity showed obvious shear orientation. At low shear rate, the viscosity was as high as 120 mPa·s. With the increase of shear rate, the viscosity decreased and finally stabilized at 9.5 mPa·s. This phenomenon can be explained by the molecular orientation of its rod-shaped structure [37]. As for the chelate (0206-Fe), its viscosity also decreased slightly with the shear rate, which can be attributed to the fact that the formed octahedral structure molecules were also composed of rod-shaped diketone molecules. 0206-Fe(60%) represented a mixed lubricant in which the proportions of 0206 and 0206-Fe are 40% and 60%, respectively. This lubricant did not exhibit shear

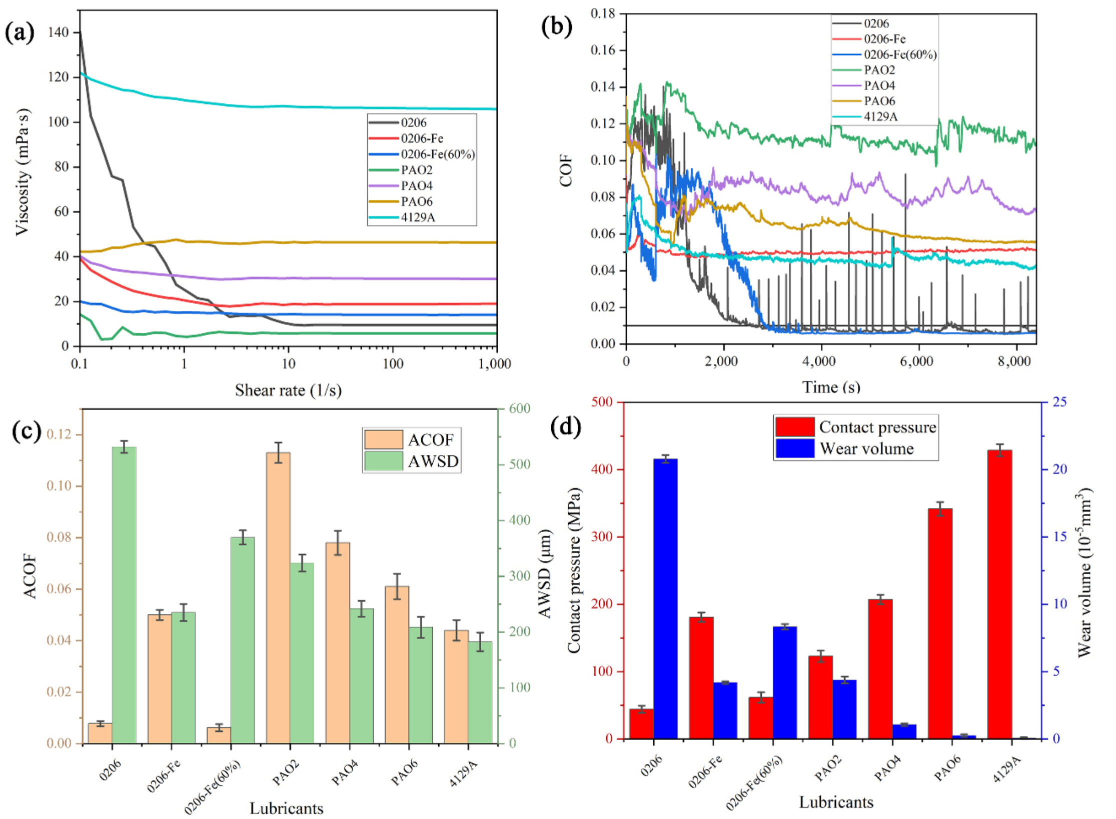

Fig. 2 (a) Viscosity of seven different lubricants as a function of shear rate; (b) COF curve; (c) ACOF and AWSD; (d) contact pressure and wear volume value of friction pairs lubricated by 0206, 0206-Fe, 0206-Fe(60%), PAO2, PAO4, PAO6, and 4129A. 0206-Fe(60%) represents a mixed lubricant in which the proportions of 0206 and 0206-Fe are 40% and 60%, respectively.

thinning properties, and its viscosity value (14.1 mPa·s) was between 0206 and 0206-Fe.

The tribological properties of 0206, 0206-Fe, 0206-Fe(60%), PAO2, PAO4, PAO6, and 4129A as lubricants were investigated. As shown in Fig. 2(b), the friction pair lubricated by 0206 and 0206-Fe(60%) can enter superlubricity (0.007 and 0.006) after 2,500 s and 2,800 s, respectively. And the superlubricity state can be maintained until the end of the experiments. However, the COF curve of the friction pair lubricated by 0206 appeared regular noise after entering superlubricity. Figures 2 and 3 show that the steel ball lubricated by 0206 had the largest wear scar diameter (WSD) and wear volume. Under the load of 5 N, the lower viscosity of 0206 made the steel ball more prone to wear, and its reactivity further promoted the wear during the lubrication process. Although the running-in period of the friction pair lubricated by 0206-Fe(60%) was slightly prolonged, the COF curve was relatively stable after entering the superlubricity. The friction pair lubricated by 0206-Fe(60%) had a significant improvement in WSD, wear scar depth, and wear volume compared with 0206. This result can be attributed to the addition of 0206-Fe, which increased the viscosity and reduced the reactivity of the lubricant. On the other hand, the octahedral structure of 0206-Fe increased the bearing capacity of the lubricant. As for the friction pairs lubricated by 0206-Fe, PAO2, PAO4, PAO6, and 4129A, superlubricity can not be achieved. It can be seen from Fig. 2(b) that the COF decreased and the COF curve was more stable with the increase of the viscosity of the base oils. The experimental results also showed that as the viscosity of the lubricant increased, the contact pressure between the friction pairs increased, and the wear of the friction pairs decreased. For the friction pair lubricated by 0206-Fe, there was an obvious exception. The viscosity of 0206-Fe is only was 9.0 mPa·s, much lower than that of PAO4, PAO6, and 4129A. However, the COF of the friction pair lubricated by 0206-Fe was 0.05, which was only slightly larger than that of 4129A. The WSD

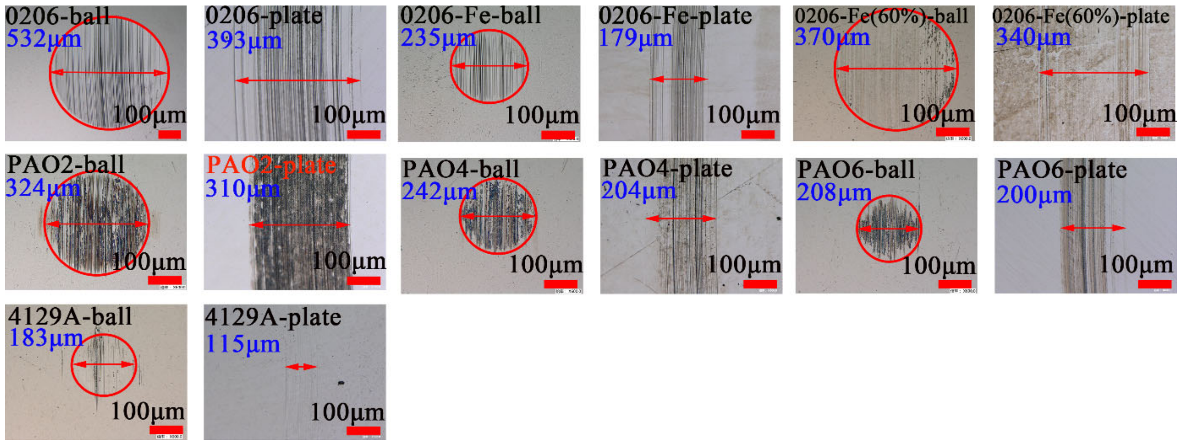

Fig. 3 Optical images of the wear scar on the surface of friction pairs lubricated by different lubricants.

was even smaller than that of PAO4. The above results can be explained by its shear thinning phenomenon and its octahedral structure containing a large number of benzene ring rigid groups [37].

3.2 Tribological properies of all kinds of lubricants

Although the friction pair lubricated by 0206-Fe(60%) can achieve superlubricity, the contact pressure was only 61 MPa, while the contact pressure of the friction pair lubricated by PAO6 was 341 MPa. This result showed that high viscosity PAO6 effectively increased the contact pressure by reducing the wear of the friction pair. How to balance the realization of oil-based superlubricity and the increase of contact pressure was the focus of the following.

The lubricants shown in Fig. 4 were prepared by mixing PAO6 and 0206-Fe(60%). Lubricants with different proportions were represented by the content of PAO6. In Fig. 4, 95% represented the content of PAO6 in the mixed lubricant is 95%. The tribological properties of lubricants with different PAO6 and 0206-Fe(60%) mixing ratios will be further verified by experiments. The purpose was to try to find the optimal mixing ratio of PAO6 and 0206-Fe(60%). Ten mixed solutions with different content of PAO6 were prepared: from 95% to 5%. Figure 4 shows the COF curves, ACOF, AWSD, contact pressure, and wear volume of the friction pairs lubricated by ten different lubricants at ambient temperature. It can be seen that the COF decreased with the decrease of PAO6 content in the mixed solution. When the PAO6 content was 70%, 60%, and 50%, the COF was maintained at about 0.045. On the other hand, it was found that with the decrease of PAO6 content in the mixed lubricant, the WSD of the steel ball decreased first and then increased. The 0206-Fe(60%) in the mixed solution can reduce the wear of the steel ball by forming a frictional adsorption film on the metal surface and the bearing capacity formed by the molecular structure of the regular octahedron. When the content of 0206-Fe(60%) in the mixed solution was too much, the viscosity of the oil was significantly reduced, the thickness of the oil film was reduced, and the wear of the steel ball was increased. The interaction of the above two factors made the contact pressure between the friction pairs increase and then decrease with the decreased of PAO6 in the mixed lubricant.

From Fig. 4(a), it can be seen that only the friction pair lubricated by 5% (PAO6) barely enters the superlubricity at the end of the experiment (7,900 s). The contact pressure was 166 MPa when the friction pair achieved superlubricity, which was greatly improved compared with the friction pair lubricated by 0206-Fe(60%) (61 MPa). However, the WSD and wear volume of the friction pair lubricated by 5% (PAO6) were significantly larger than those of the friction pairs lubricated by 30%, 20%, and 10% (PAO6).

In order to further study the effect of base lubricants with different viscosities on the tribological properties of mixed lubricants, we replaced PAO6 with 4129A, PAO4, and PAO2, respectively. The contents of base oils in the mixed solution were 30%, 20%, and 10%.

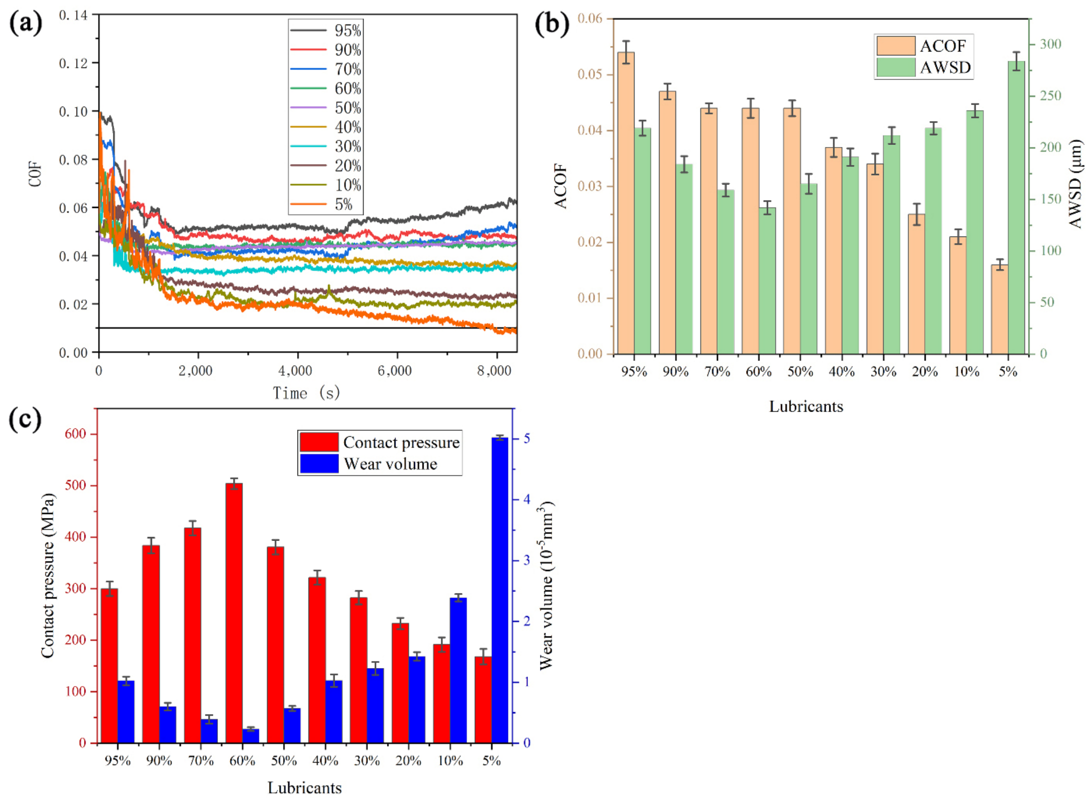

Fig. 4 (a) COF curve; (b) ACOF and AWSD; (c) contact pressure and wear volume value of friction pairs lubricated by 95%, 90%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, and 5%. These ten lubricants are mixed solutions composed of PAO6 and 0206-Fe(60%). The values in the figure represent the content of PAO6 in the mixed solutions.

Figure 5 shows the COF curves, ACOF, AWSD, contact pressure, and wear volume of the friction pairs lubricated by nine different lubricants. The values in parentheses in Fig. 5 represented the content of base oil in the mixed solution. The experimental results show that when 4129A was selected, the friction pairs under three lubrication states cannot achieve superlubricity. With the decrease of the viscosity of the lubricant, the friction pair can not only achieve superlubricity but also the running-in time was significantly reduced. The running-in period of the friction pair lubricated by PAO4(10%) was 4,900 s, which was 2,000 s earlier than that of PAO4(20%) lubricated friction pair. The contact pressures of friction pairs lubricated by PAO4(20%) and PAO4(10%) were 178 and 160 MPa respectively. Since the viscosity of PAO2 was only 5.8 mPa·s, the WSD and wear volume of the friction pair were larger than those of the friction pair lubricated by 0206-Fe(60%) when the mixed solution contains PAO2.

It can be seen from Fig. 2(a) that the viscosities of 0206, 0206-Fe(60%), and 0206-Fe were just between the viscosities of PAO2 and PAO4. And the viscosity difference between PAO2 and PAO4 was large. Therefore, in order to fully study the influence of the viscosity of the base oil, base oils with viscosity between PAO2 and PAO4 must be selected for tribological experiments. By mixing PAO2 and PAO4 in different proportions, base oils with different viscosities were prepared and named Oil1 (8.9 mPa·s), Oil2 (13.9 mPa·s), and Oil3(18.9 mPa·s), respectively. The above base oils were mixed with 0206-Fe(60%) at a ratio of 2:8 to prepare lubricants, named Oil1(20%), Oil2(20%), and Oil3(20%). The experimental results show that the running-in times of the friction pairs lubricated by Oil1(20%), Oil2(20%), and Oil3(20%) were significantly reduced compared with PAO4(20%). It can be found from Fig. 6 that the friction pair lubricated by Oil3(20%) had the smallest WSD, the smallest wear volume, and the largest contact pressure (161 MPa) compared with the other two lubrication states.

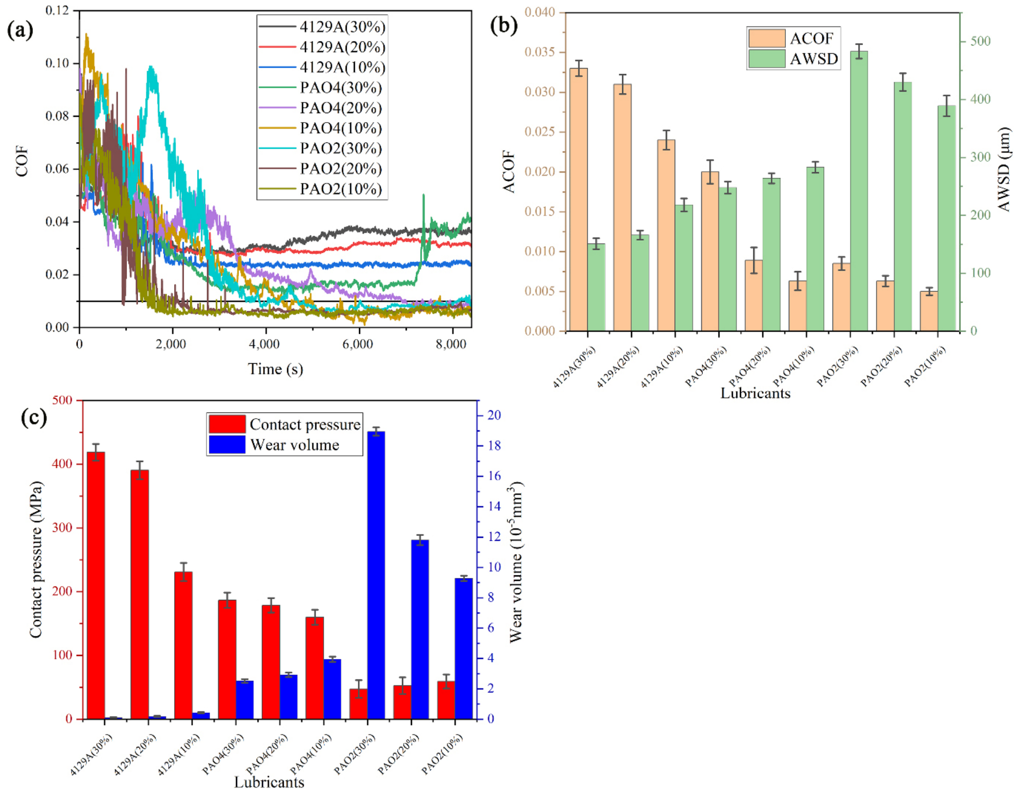

Fig. 5 (a) COF curve; (b) ACOF and AWSD; (c) contact pressure and wear volume value of friction pairs lubricated by 4129A(30%), 4129A(20%), 4129A(10%), PAO4(30%), PAO4(20%), PAO4(10%), PAO2(30%), PAO2(20%), and PAO2(10%). The values in parentheses represent the content of the lubricant in the mixed solutions with 0206-Fe(60%).

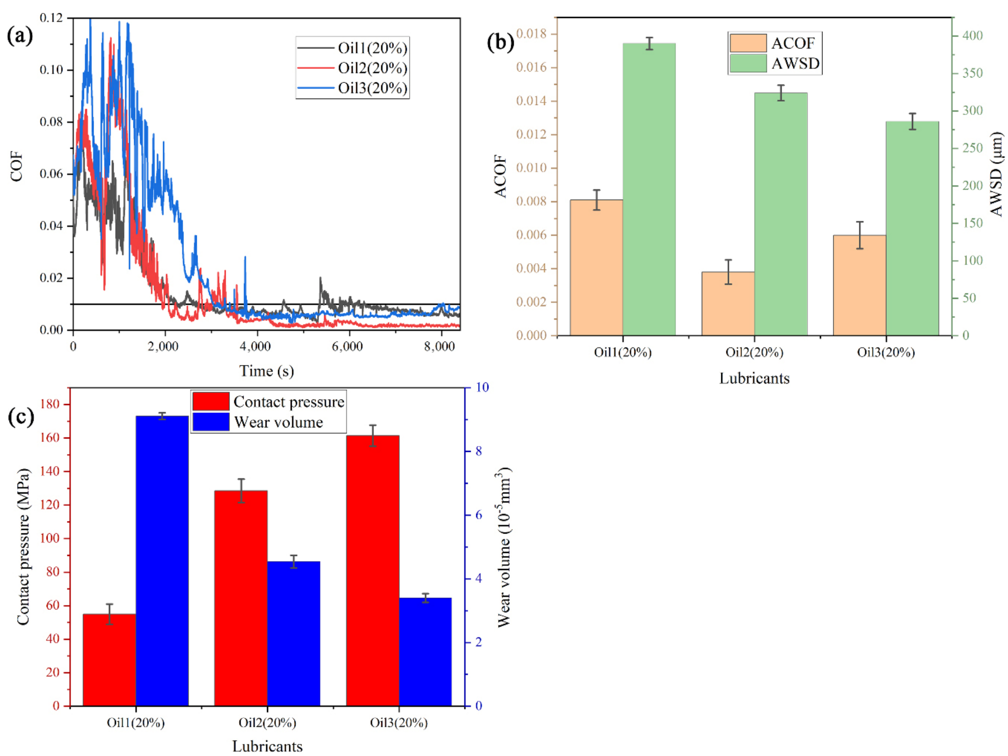

Fig. 6 (a) COF curve; (b) ACOF and AWSD; (c) contact pressure and wear volume value of friction pairs lubricated by Oil1(20%), Oil2(20%), and Oil3(20%). Oil1, Oil2, and Oil3 are base oils with viscosity of 8.9, 13.9, and 18.9 mPa·s, respectively.

3.3 Wear scar surface analyses

In order to further analyze the mechanism of superlubricity realized by the mixed solution of base oil and 0206-Fe(60%), the friction pairs lubricated by PAO2, 0206, 0206-Fe(60%), and Oil3(20%) were analyzed. To observe and compare the anti-wear properties of these samples, their wear scars were measured, and the results are shown in Fig. 7. The images of the wear scars were obtained using a 3D white light interferometer (Figs. 7(a)–7(d)), and the microscopic images of friction pair surface were obtained using a SEM (Figs. 7(i)–7(l)). Figures 7(e)–7(h) show the cross-section profile curve after the balls were worn. The experimental results show that although the viscosity of PAO2 was lower than that of 0206, the WSD of steel ball lubricated by PAO2 was lower than that of 0206, and the roughness of wear scar area was larger than that of 0206. This phenomenon can be attributed to the reactivity of 0206 with metal. During the friction process, the metal friction pair material was removed in large quantities, and the generated abrasive particles were consumed in combination with 0206 molecules, so the surface roughness did not increase with the increase of wear volume. Figures 7(g), 7(h), 7(k), and 7(l) show that when base oil was added to 0206-Fe(60%), the WSD became smaller, and the wear scar showed no indication of furrows. Of the three samples with 0206, the ball tested with Oil3(20%) sample had the smallest wear scar.

Previous studies have confirmed that the reason for the superlubricity of the friction pair lubricated by 0206-Fe(60%) was that 0206 was adsorbed on the metal surface and formed synergistic lubrication with 0206-Fe in the solution [37]. In order to further understand the chemical composition of the friction film on the surface of the friction pair lubricated by the above four lubricating oils, we performed XPS characterization. XPS spectrum was used to analysis

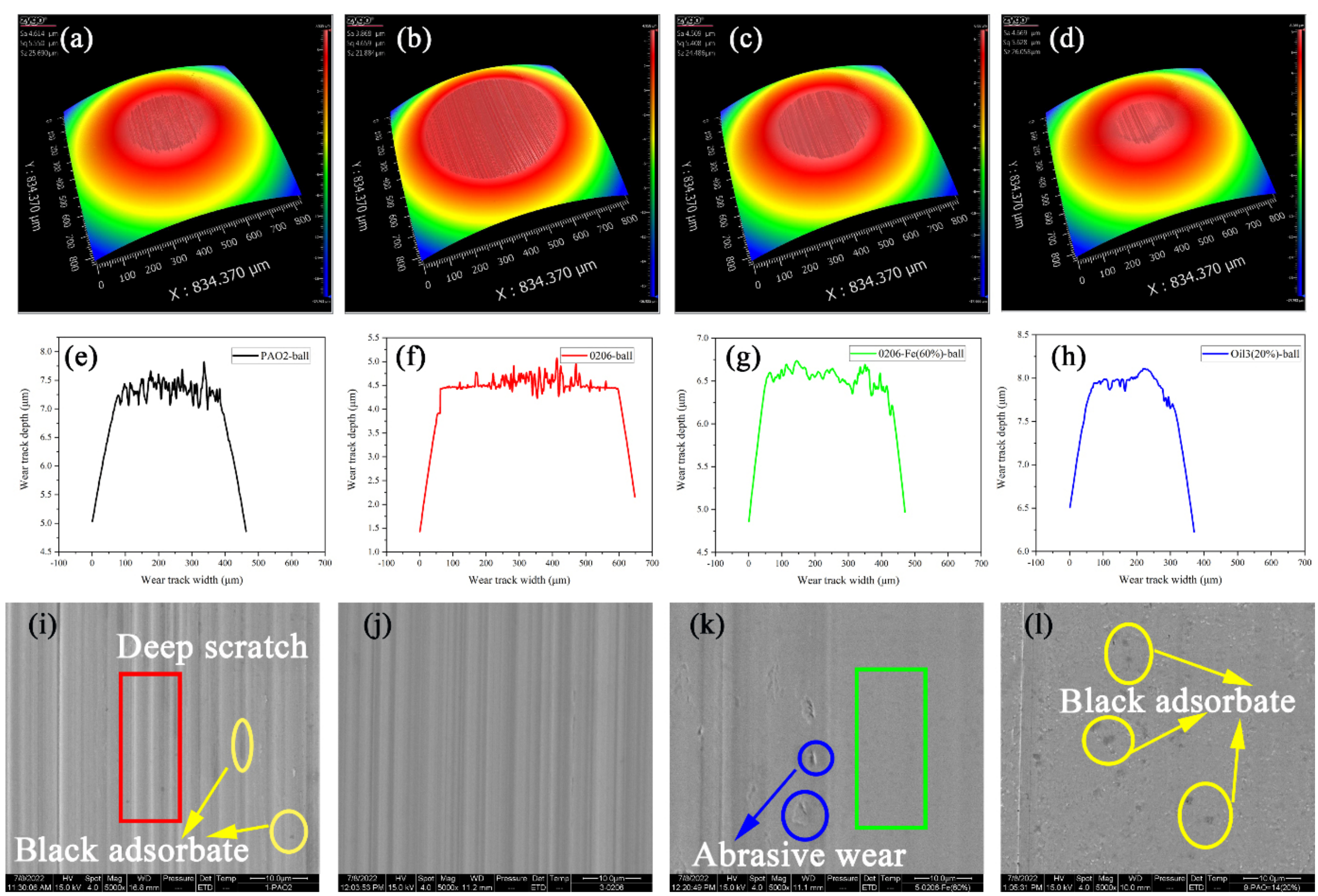

Fig. 7 (a)–(d) 3D morphologies, (e)–(h) the line scans, and (i)–(l) SEM images of the wear scars on the ball lubricated by (a, e, i) PAO2, (b, f, j) 0206, (c, g, k) 0206-Fe(60%), and (d, h, l) Oil3(20%). Among them, (i)–(l) were 5,000 times magnified images.

the parameters of C 1s and O 1s. Two samples were prepared under each lubrication condition. The first sample was wiped off the residual lubricating oil on the surface before XPS characterization (the left two columns of Fig. 8). The second sample was ultrasonically cleaned before XPS characterization (the right two columns of Fig. 8).

As shown in Fig. 8, the C 1s spectrum of the steel surface lubricated by 0206 could be differentiated into four peaks due to the different chemical environments of C atoms. The binding energy of each component were 283.1, 284.8, 286.2, and 289.0 eV, which corresponded to the peak of metal carbide, C–C, O=C–C–C=O, and C=O. The O 1s binding energy of each component were 529.8, 530.6, 531.7, and 532.9 eV, which corresponded to metal oxide,

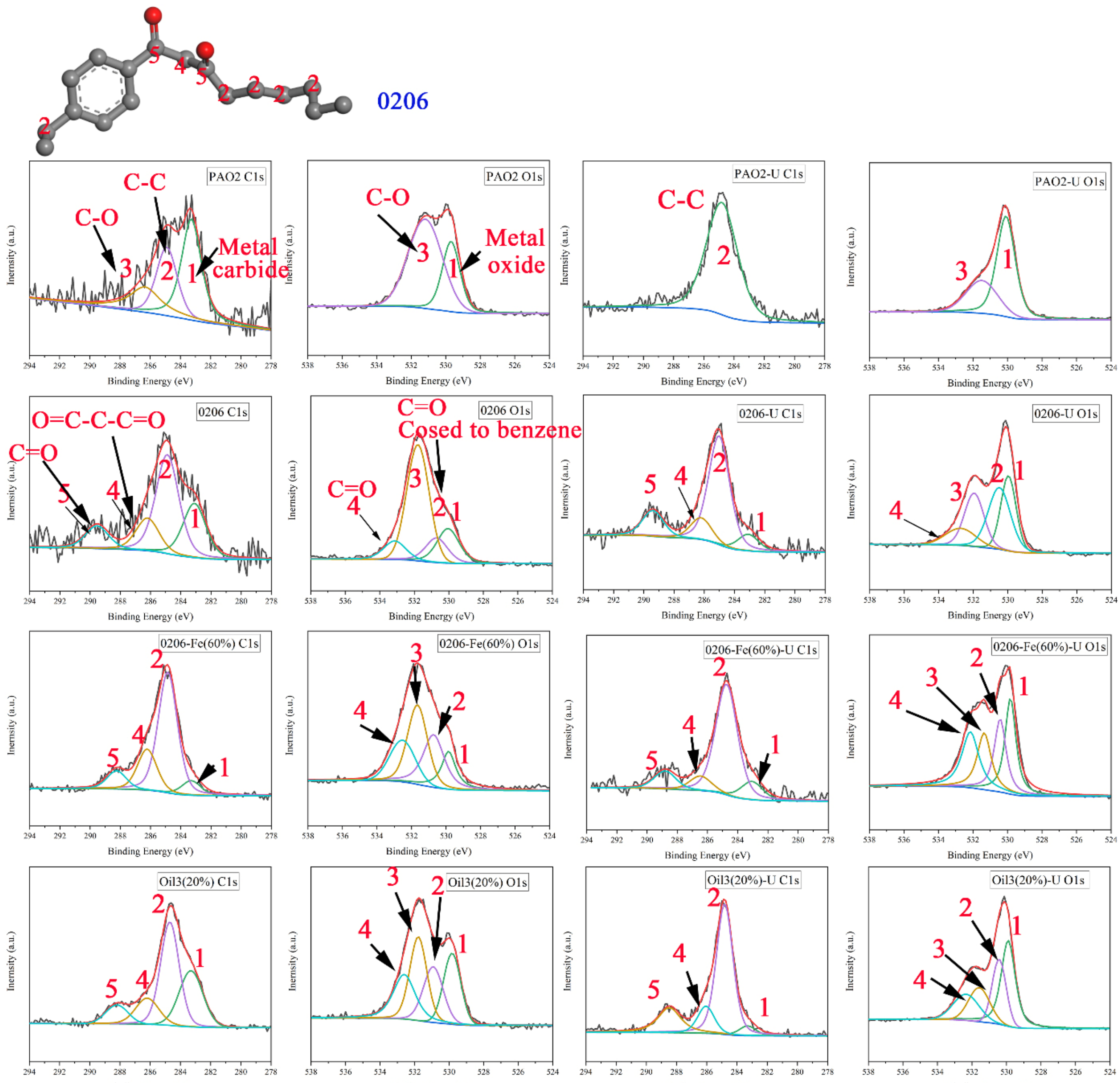

Fig. 8 XPS spectra of the C 1s and O 1s on the surface of the friction pairs lubricated by PAO2, 0206, 0206-Fe(60%), and Oil3(20%). The left two columns were characterized by XPS by wiping the surface, and the right two columns were characterized by ultrasonic cleaning.

C=O (closed to benzene), C–O, and C=O. These absorption peaks were also found on the friction pair lubricated by Oil3(20%), which proved that there was an absorbed film of 0206 on the friction pair. The C 1s spectrums of the surfaces lubricated by PAO2 only had one peak. Its binding energy was 284.5 eV, and the existing binding mode was carbon-carbon single bond. The friction pair lubricated by PAO2 had no absorption peak of metal carbide on its surface after ultrasonic cleaning, while the friction pairs lubricated by 0206, 0206-Fe(60%), and Oil3(20%) still had the characteristic absorption peaks (4 of C 1s and 2 of O1s) of diketone molecule on their surfaces after ultrasonic cleaning. This proved that the friction chemical adsorption film formed by 0206 and metal surface was not easy to fall off.

4 Discussion

According to the Hamrock-Dowson theory of point contacts, the minimum film thickness ($h_{\min}$) and central film thickness can be obtained by Eqs. (1) and (2) [41]:

$$h_{\min} = 3.63\frac{G^{*0.49}U^{*0.68}}{W^{*0.073}}(1-\mathrm{e}^{-0.68k})R \tag{1}$$

$$h_{\mathrm{c}} = 2.69\frac{G^{*0.53}U^{*0.67}}{W^{*0.067}}(1-0.61\mathrm{e}^{-0.73k})R \tag{2}$$

where $G^* = \alpha E'$, $U^* = \eta_0 U / E'R$, $W^* = W / E'R^2$, $k = 1.03(R_x / R_y)^{0.64} = 1.03$. In addition, α is the viscosity–pressure coefficient, E' is the comprehensive elastic modulus of friction pairs, η_0 is the dynamic viscosity of the lubricating oil. Substitute $h_{\min}$ obtained from Eq. (1) into Eq. (3) to determine the lubrication state of the contact area:

$$\lambda = h_{\min} / \sqrt{R_{a,\mathrm{ball}}^2 + R_{a,\mathrm{disc}}^2} \tag{3}$$

Here, R_a represents the surface roughness of friction pair. When λ is less than 1, the friction pair works on the conditions of boundary lubrication; when λ ranges from 1 to 3, mixed lubrication occurs; when λ is greater than 3, the friction pair enters the elastic hydrodynamic lubrication (EHL). In order to determine the viscosity-pressure coefficient of lubricating oil, the oil film thickness curve of lubricating oil at different speeds was measured by TFM-150. As shown in Fig. 9, the curve of the oil film thickness of the lubricating oil with the change of the speed was nonlinearly fitted according to the Eq. (2), and the viscosity-pressure coefficient of each lubricating oils at room temperature can be obtained as shown in Table 1. In addition, when the lubricant contains 0206 or 0206-Fe, the oil film thickness of the lubricant at low speed was higher than the theoretical fitting value (shown in Fig. 9). This result proved again that the rod-shaped structure of 0206 molecules had shear orientation.

Substituting the obtained viscosity pressure coefficient values of different lubricants in Table 1 into Eq. (1) and Eq. (3), respectively, λ of different lubricants at the beginning and ending of the experiment can be obtained. Considering the setting

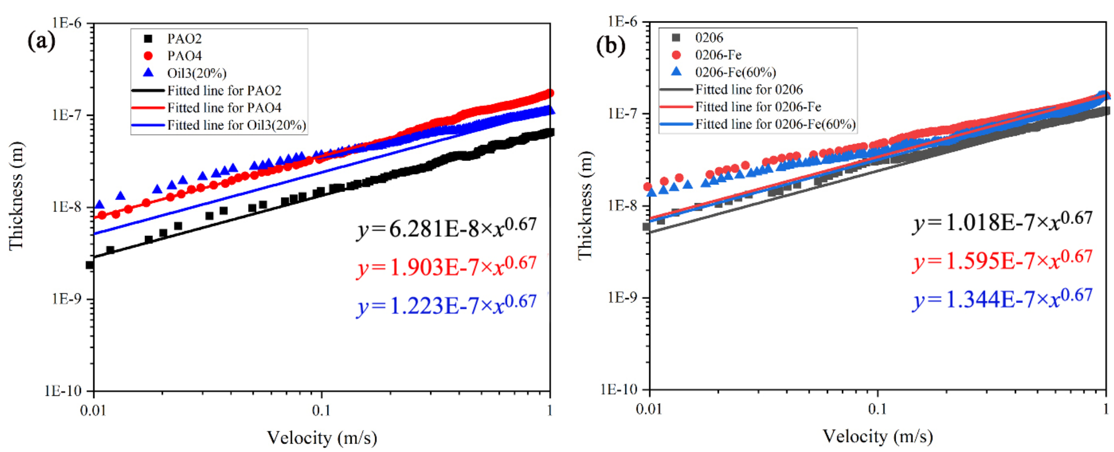

Fig. 9 Evolution of lubrication film thickness of (a) PAO2, PAO4, Oil3(20%), and (b) 0206, 0206-Fe, 0206-Fe(60%) as a function of rolling speed.

of experimental parameters, the speed was 62.8 mm/s in the initial stage and 314.2 mm/s in the end stage. Following the friction test, a circular flat worn surface was produced. Moreover, the surface roughness of the ball-disc friction pair also changed. Therefore, it was necessary to measure the surface roughness of the friction pair after wear and the radius of curvature of the steel ball to calculate the lubrication state of the friction pair at the end of the experiment, as shown in Table 2.

λ was calculated to be 0.661 of the friction pair lubricated by PAO2, and it can be concluded that the contact zone in the initial stage was in the boundary lubrication state, which indicated that the initial wear was severe. In addition, due to the low viscosity of PAO2, the carrying capacity of lubricating oil was poor, and it cannot react with the metal friction pair to form a strong adsorption film, resulting in serious wear of the friction pair. The smaller λ value was calculated after the experiment confirmed this conclusion. For PAO4 and 0206-Fe, the load-bearing performance of high viscosity lubricating oils was satisfied, but the conditions for tribo-chemical reaction were not satisfied, so both of them were in boundary lubrication state at the end of the experiment. The result of 0206 was opposite to them. Although 0206 can react with friction pair, the high wear made the friction pair still in the boundary lubrication state. This result can be attributed to the high reactivity and low viscosity of 0206, which increased the wear of the friction pair, and the resulting abrasive particles caused an increase in the surface roughness of the friction pair. By mixing 0206 with 0206-Fe, 0206-Fe(60%) not only had the ability to react with metal friction pair, but also had a certain bearing capacity. The friction pair lubricated by 0206-Fe(60%) can not only achieve superlubricity, but also remain in mixed lubrication at the end of the experiment due to the small surface roughness. The addition of PAO in Oil3(20%) reduced the content of 0206 in the lubricant, thereby reducing the consumption of the friction pair. On the other hand, the increase of the viscosity of the lubricating oil was also beneficial to the improvement of its bearing capacity and the reduction of the wear scar diameter. This also explained why the friction pair lubricated by Oil3(20%) had lower surface roughness and higher contact pressure. And the friction pair was in mixed lubrication state during the experiment.

5 Conclusions

In summary, an oil-soluble liquid molecule 1,3-diketone (0206) with rod-shaped structure was used as a lubricant in this study, and it was used to react with ferric chloride to prepare octahedral chelate (0206-Fe). Then the synergistic lubrication effect of 0206, 0206-Fe, and base oil was explored. The following conclusions can be drawn:

Table 1 Viscosity-pressure coefficients of different lubricants obtained by calculation.

Lubricant	PAO2	PAO4	0206	0206-Fe(60%)	0206-Fe	Oil3(20%)
Viscosity−pressure coefficients (Pa^{-1})	1.390E-8	1.403E-8	1.903E-8	1.893E-8	1.787E-8	1.470E-8

Table 2 h_{min}, lubrication state (λ), and lubrication state between the friction pairs in the initial stage and the end stage of the experiment, as well as the roughness of the friction pairs and the radius of curvature of the steel balls after the experiment (boundary lubrication abbreviated as BL, mixed lubrication abbreviated as ML).

Parameter / Lubricant	h_{min} (nm)		Roughness (nm) (end stage)		λ		Lubrication state		Radius of curvature (mm)
	Initial stage	End stage	ball	disc	Initial stage	End stage	Initial stage	End stage	End stage
PAO2	4.67	34.80	110	109	0.661	0.225	BL	BL	45.098
PAO4	14.38	85.60	65	88	2.034	0.782	ML	BL	26.694
0206	7.51	112.75	100	125	1.062	0.704	ML	BL	209.330
0206-Fe	11.89	67.66	85	89	1.681	0.550	ML	BL	25.355
0206-Fe(60%)	9.55	120.04	51	66	1.406	1.439	ML	ML	127.078
Oil3(20%)	9.16	66.04	38	41	1.296	1.181	ML	ML	38.246

(1) The steel friction pairs lubricated by 0206 and 0206-Fe(60%) can achieve superlubricity after running-in for 2,500 s and 2,800 s. However, 0206 had a low viscosity and can react with the metal, resulting in serious wear of the friction pair lubricated by 0206, and the contact pressure was only 44.3 MPa. For 0206-Fe(60%), the decrease of 0206 content contributed to the decrease of wear and the increase of contact pressure, and the presence of 0206-Fe helped the friction pair to achieve superlubricity.

(2) When 0206-Fe(60%) was mixed with PAO6, it was found that the COF decreased with the increase of 0206-Fe(60%) content in the solution. When the ratio of 0206-Fe(60%) to PAO6 was 8:2 (PAO6(20%)), it exhibited better tribological properties (0.023, 232.3 MPa).

(3) When the viscosity of the base oil in the mixed solution was reduced, the COF and contact pressure were reduced and the WSD was increased.

(4) Considering the COF, contact pressure, and running-in time, it was found that the mixed lubricant (Oil3(20%)) prepared by the base oil with a viscosity of 19.7 mPa·s (Oil3) and 0206-Fe(60%) exhibited the best tribological properties (0.007, 161.4 MPa, 3,100 s).

(5) The surface characterization of the friction pair lubricated by Oil3(20%) showed that there was a friction chemical adsorption layer of 0206 on the surface. Through the analysis of the lubrication state, it was found that the friction pair was in a mixed lubrication state in the initial stage and the end stage.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article. The author Chenhui ZHANG is the Editorial Board Member of this journal.

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