Impact of surface topography on ZDDP tribofilm formation during running-in stage subject to boundary lubrication

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Abstract: Experimental investigations have been conducted to study the effects of surface topography on ZDDP (zinc dialkyldithiophospahte) chemical tribofilm formation during running-in stage under boundary lubrication conditions. The scope of presented work has been limited and focused on reciprocating motion under boundary lubrication to simulate upper and lower dead center of piston ring movement, which is prone to adhesive wear failure. Several surface topographies were designed and fabricated to measure, compare coefficient of friction and ZDDP time critical tribofilm formation. Rubbing surfaces and their corresponding tribofilms were characterised by SEM and EDX. Mechanisms of surface topography effects on ZDDP time critical tribofilm formation is presented and discussed. Results from this study have demonstrated that the surface topography has a significant influence on the ZDDP time critical tribofilm formation during running-in process and corresponding wear performance. This research provides an opportunity to augment anti-wear performance under boundary lubrication condition. This can be achieved by optimising surface morphology design to influence the formation of anti-wear tribofilms during the running-in stage. In turn, this will result in interacting components' service life enhancement and significant cost savings from mitigated wear.

Key words: ZDDP tribofilm; surface topography; running-in; boundary lubrication

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1 Introduction

Interacting components and complex systems subject to dynamic loading configuration would usually experience boundary lubrication regime especially during the running-in stage. Breaking up of solid-solid interfacial junctions between asperities results in resistance induced friction during boundary lubrication. The strength of asperity junctions must be debilitated, tempered and the intensity of asperities contacts must be lowered to reduce friction, decelerate or reduce wear t [1]. The formation of adsorbed organic films[2] or rubbing induced soft reaction products deposits over metallic surfaces are usually facilitated by lubricant additives. These are generally known as tribofilms and are key elements in reducing interfacial friction[3,4].

Anti-wear zinc dialkyldithiophospahte (ZDDP) additive is one of most commonly employed additives for reducing excessive wear in interacting surfaces by protective layer formation which are commonly referred to as tribofilms[5,6]. In ZDDP molecular formula $Zn[S_2P(OR)_2]_2$, R is an alky- or aryl- group[7]. ZDDP plays a major role in abrasion resistance as an anti-wear additive. Tribological performance of ZDDP tribofilms have been reported in literature to elucidate its anti-wear mechanism[8-19]. It is generally agreed that interfacial tribofilms formed between interacting contacts contribute to anti-wear performance by preventing direct metal-to-metal asperities contact[4,8]. In essence wear would not occur should tribofilms sustain enough thickness. Some studies have reported that once ZDDP tribofilms have formed on the rubbing surfaces, even after substituting ZDDP containing lubricant with base oil, these can sustain for a certain duration of time [17]. Therefore, it can be inferred that during running-in stage accelerated ZDDP tribofilms formation ushers palliating wear and prolonging equipment service life.

The key aim of this study was to attain befitting and apposite methodology to accelerate ZDDP tribofilms formation during running-in stage. Previous studies have shown that contact pressure, temperature, additive concentration, alkyl structure of ZDDP and even voltage could affect ZDDP tribofilms formation and corresponding anti-wear performance[20-22]. In recent years, in addition to increasing application of surface engineering technology, research on the influence of surface topography on tribofilms formation have also attracted significant attention. Previous research has shown that the time required for the formation of ZDDP tribofilms on a rough surface is relatively longer[23]. Surface roughness also affects the removal rate of the formed ZDDP tribofilms. When ZDDP is completely decomposed in the lubricating oil, wear resistance mainly depends on the surface morphology to control the removal rate. In addition to the surface topography which has been formed during machining process, the effect of intentionally designed surface textures on ZDDP tribofilms formation has also attracted the attention of scholars. Rosencrantz & Hsu et al.[24-26] studied the anti-wear performance of ZDDP on bearing washers with dot-like and cross-type textures. The results have shown that the wear quality of textured bearing washers is two orders of magnitude lower than un-textured surfaces and the fatigue life can be increased by a factor of three. Ayerdi et al.[27] conducted friction experiments on the surface of titanium alloy with linear groove textures and found that the wear quality of the textured surface and the non-textured surface is not significantly varied when ZDDP is not added to the lubricant. However, after adding ZDDP additive, the wear of the textured surface is reduced by more than 2500 times than that of non-textured surface. Xu et al.[28] have compared synergistic anti-wear effect of ZDDP and elliptical texture subject to both full and starved lubrication regimes. Results have shown that synergistic anti-wear effect is more significant under starved lubrication conditions. The above research results demonstrate that anti-wear effect of friction pairs can be enhanced by conjoining performance of lubricant additives and surface textures.

An accelerated formation of anti-wear tribofilms on sliding surfaces at the beginning of running-in stage is of utmost importance due to significant influence of surface topography characteristics on ZDDP boundary film. As a result of reduced boundary friction reduced wear is achieved. None of the above mentioned studies have considered the impacts of running-in process. It is known that running-in is the initial stage of relative movement between contacting surfaces, during which the morphology, of initial engineering rough surfaces, changes drastically and will go through a period of high wear rate. Both physical and chemical changes take place at the interface of the interacting surfaces during the running-in stage, including flattening of surface asperities, physical property changes of substrates, boundary film generation and molecular configuration change of adsorption layer. All these changes are aimed at approaching to a relatively stable state of friction and wear. Which infers that useful running-in process can facilitate the contact interface topography to adapt to each other to reduce wear rate[29]. However, wear failure is very facile to occur under such harsh conditions. If the chemical tribofilm can be generated on the surface to help the friction pair to sustain this severe operational phase, it is undoubtedly, helpful to improve the life and reliability of mechanical systems. Therefore, to study the influence of tribofilm formation on the friction and wear performance during the running-in process is momentous.

It is reiterated that the research in this study is limited to reciprocating sliding under boundary lubrication conditions to simulate the upper and lower dead center of piston ring interaction, which are susceptible to severe adhesive wear failure. Under such conditions, rapid generation of ZDDP during running-in stage is beneficial for effectively reducing macroscopic adhesive wear and thus maintaining accuracy of relative motion of interacting surfaces. Rolling contact conditions, which are prone to fatigue wear, the presence of ZDDP additive in lubricating oil may accelerate micro-pitting as tribofilm formation can suppress the asperity smoothing process during running-in stage and increase asperity stresses[21,30,31].

This paper mainly focuses on reciprocating sliding friction, predisposed to adhesive wear, and the study topography influence on tribofilm formation during the running-in stage. The originality of this research lies in the fact that it is intended to fill the knowledge gap in this area. This research provides new findings on how to make use of surface topography to facilitate the formation of ZDDP tribofilms during the running-in stage. The significance of this work is to reduce wear failures during the entire running-in stage in real industrial applications. The outcomes of this research deliver foreseeable impacts such as contributing to energy efficiency due to reduced friction, cost savings because of reduced wear and environmental impacts by enhancing service life.

2 Experimental setup

2.1 Tribometer

Tribological tests were performed by employing Universal Micro-Tribometer (UMT-2, Center for Tribology, Inc.) which is shown in Figure 1. The upper ball is fixed on a fixture and the bottom plate is driven by a reciprocating module with a specified stroke length and reciprocating frequency to simulate reciprocating motion under boundary lubrication. A friction test module and an Electrical Contact Resistance (ECR) module (ECR-100KΩ, Center for Tribology, Inc.) are integrated in the device, therefore friction coefficient and contact resistance between the upper and lower test specimens can be measured simultaneously. It should be noted that the ball fixture remains stationary during the friction experiment, but after the experiment is over, the position of the fixture can be altered by a control modular program to interchange the ball direction from perpendicular to sliding. This allows to conduct various configurations of friction experiments by changing the position on the plate without the need for changing to a new sample.

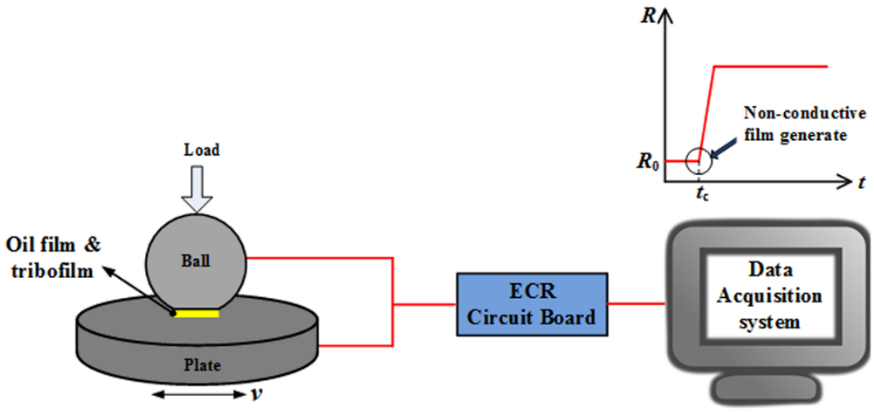


Fig.1 Schematic of test rig

ECR method [32,33] can monitor ZDDP tribofilms formation in-situ as opposed to alternative offline techniques such as Energy Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). This is due to the fact that ZDDP tribofilm is non-conductive and the contact resistance between metals is fairly dissimilar to ZDDP tribofilms. When ZDDP tribofilms are formed at the interface of ball and plate, ECR signal will transform significantly from a low ECR value of R_0 for the metallic contacts to a high ECR value as shown in Fig.1. It is to be emphasised here that ECR is a qualitative method which can only monitor whether there is a non-conductive film between the contacting interfaces, however there is no direct correspondence between ECR value and the film thickness. In this research, the ECR method is limited to monitor the initial running-in stage of ZDDP tribofilms generation.

2.2 Sample preparation

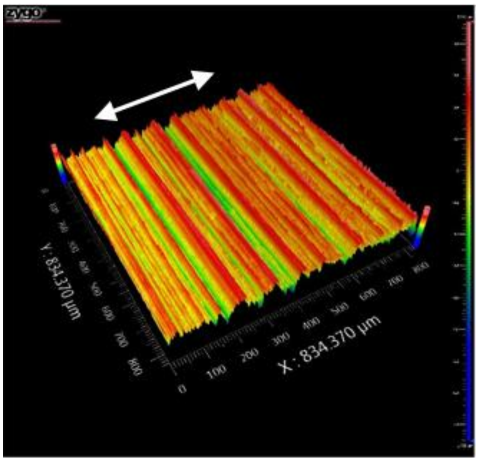
(1) Friction pairs

Table.1 provides a list of ball and plate test samples parameters which were used in this study. Surface roughness of ball elements is Ra = 20nm. Two sets of surface finishing, texture-free and textured, were fabricated for plate samples. Fig.2.(a)~(e) are 3D surfaces with various roughness ranging from R_a = 242nm to R_a = 8.2nm by grinding and were conditioned by polishing with several grades (#120, #400, #600 and #4000) of emery papers. These are termed as 120# polished surface, ground surface, 400# polished surface, 600# polished surface, 4000# polished surface, and noted as No.1, No. 2, No. 3, No. 4 and No.5 respectively. Two-dimensional topography is shown in Figure

3.

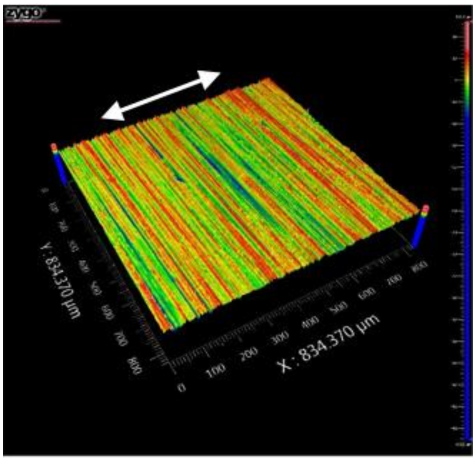
Table 1 Sample parameters

	Material	Dimension (mm)	Hardness (HV @ 300g, 10s)	Elastic-modulus (GPa)	Poisson's ratio
Ball	52100 steel	$\phi 5$	826	210	0.3
Plate	52100 steel	$\phi 24\times 8$	719	210	0.3



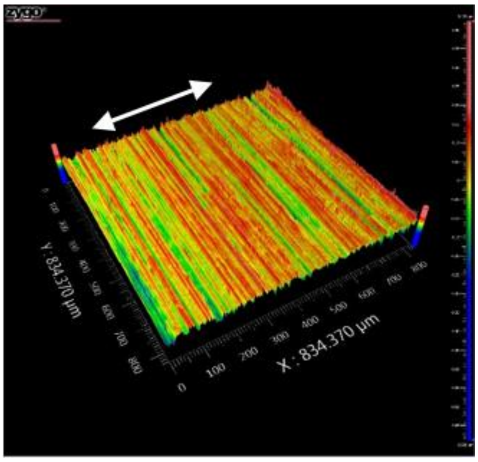
120# polished surface, Ra=242nm

(No.1)



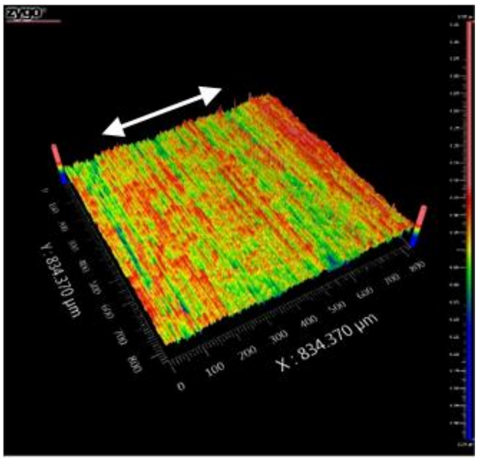
original ground surface, Ra=176.2nm

(No.2)



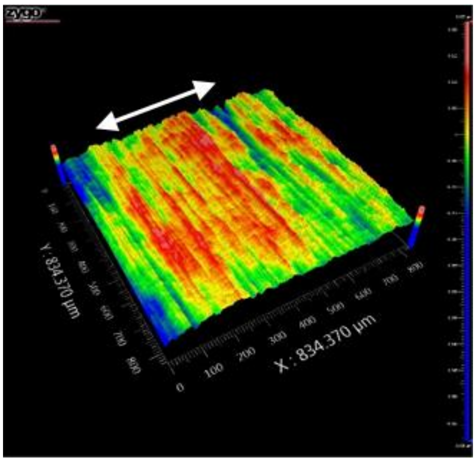
400# polished surface, Ra=62.7nm

(No.3)



600# polished surface, Ra=28.3nm

(No.4)



4000# polished surface, Ra=8.2nm

(No.5)

Fig.2 3D topography profiles of plate surfaces (white arrow depicts the sliding direction)

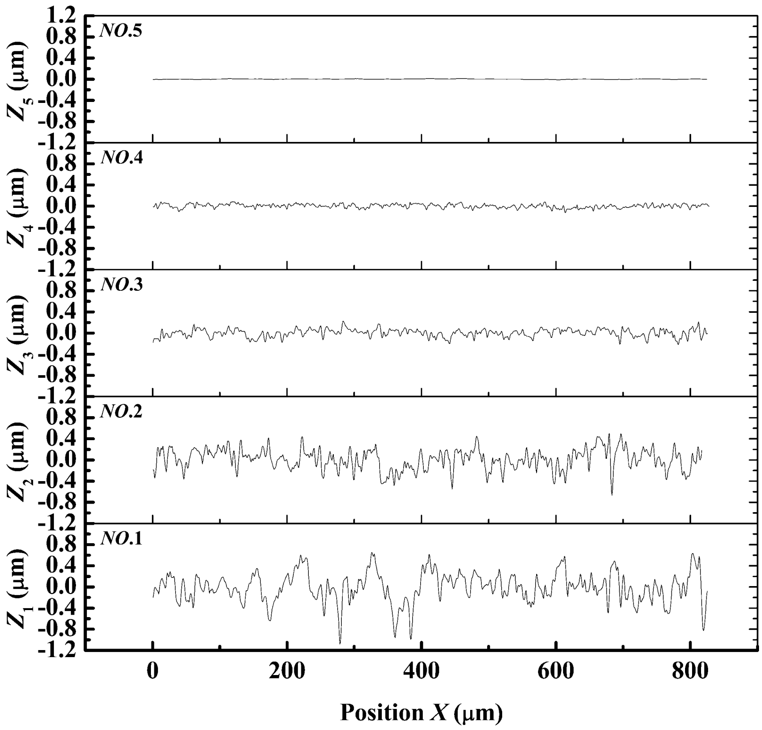
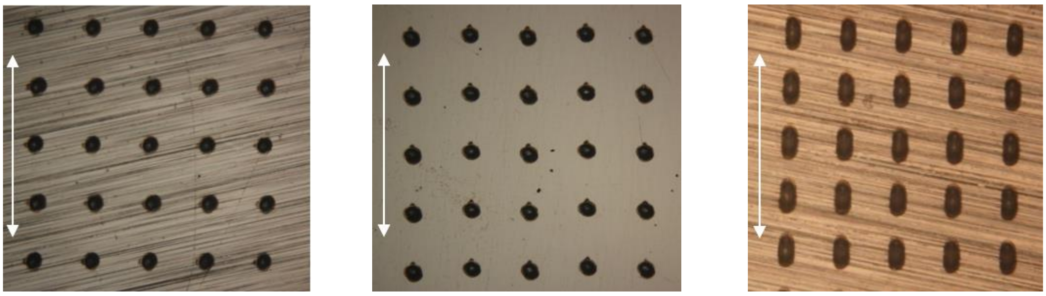


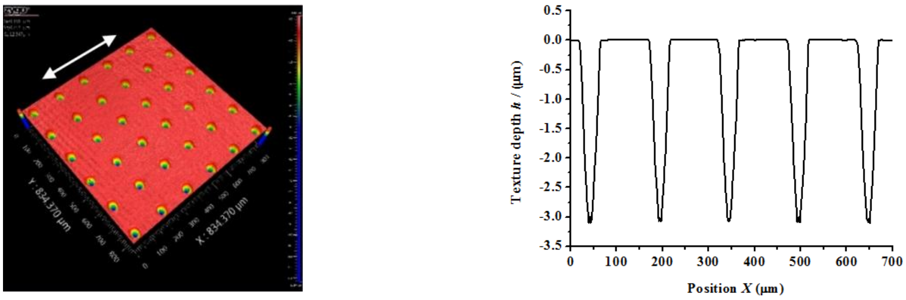
Fig.3 2D profiles of texture-free plate surfaces (along sliding direction)

To study the synergistic effects of surface texture and anti-wear additive ZDDP, two commonly used surface textures; circular and elliptical dimples were fabricated on ground/polished sample surfaces. Picosecond laser with 532nm wavelength and 100KHZ pulse frequency was used to achieve the desired surface textures. During the texture machining process, laser energy and scanning speed were set as 0.3W and 100mm/s respectively to ensure processing quality and efficiency. Post laser processing, no further processing, such as removing burrs, was performed on the surface. Fig.4 shows optical images of textured surfaces. Fig.4.(a) and Fig.4.(b) are ‘circular dimple’ surfaces with various substrate roughness, denoted as ground -‘circular dimple’ surface (No.6) and 4000# polished - ‘circular dimple’ surface(No.7). Fig.4.(c) shows ‘ellipse dimple’ fabricated on ground surface, denoted as ground -‘ellipse dimple’ surface (No.8). Fig.5(a)~(b) shows an example of 3D topography and cross-sectional profile of a typical circular dimple surface No.6. Texture parameters are presented in Fig.5. (c) ~ (d).

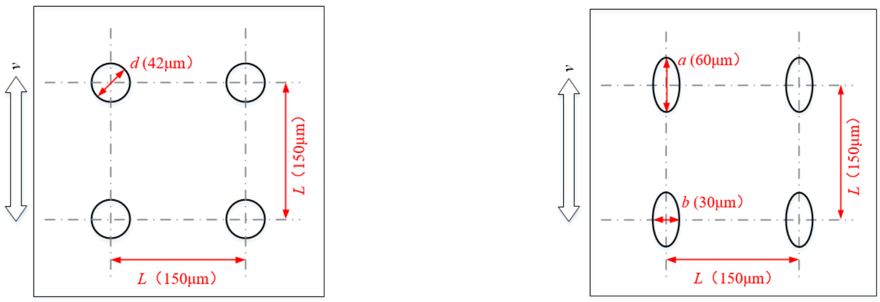


(a) ground circular-dimple (No.6) (b) polished circular-dimple (No.7) (c) ground ellipse-dimple (No.8)

Fig.4 Optical image of textured surfaces (arrow depicts the sliding direction)



(a) 3D profile of surface NO.6 (b) Cross-section profile of surface NO.6



(c) Circular-dimple textured surface (NO.6, NO.7) (d) Elliptical-dimple textured surface (NO.8)

Fig.5 Topography profiles of textured surface（arrow depicts the sliding direction）

(2) Lubricant

Synthetic base oil GTL8 (provided by Shell (Shanghai) Technology Ltd., China). GTL8 has been mixed with 1.0wt% commercial anti-wear additive ZDDP (referred to as mixed lubricant, ML) were used as lubricant for experimentation. Molecular formula of ZDDP and the contents of its characteristic elements are presented in Fig.6 and Table 2. Viscosities of GTL8 and ML during the experiments are almost the same as about 78mPa·s at 20℃. Therefore, the effect of ZDDP on lubricant viscosity and viscous friction is assumed to be negligible.

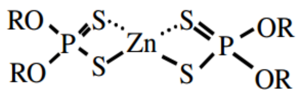


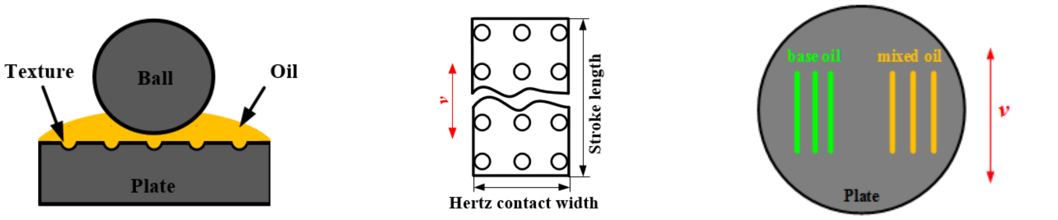
Fig.6 The molecular formula of ZDDP (R = alkyl group)

Table 2 Content of characteristic elements (*wt*%)

Element	**Zn**	**S**	**P**
***wt*%**	8.6	17.2	8.1

2.3 Testing procedure

Prior to testing, 500μL of lubricant was fed between the ball and plate to ensure sufficient oil supply. Schematic diagram of contact area is shown in Fig.7. Experimental conditions are shown in Table 3. Under these experimental conditions, maximum Hertz contact pressure of the ball and plate is 2.57GPa and the contact radius is 167μm. When one test was completed, the ball was replaced by a new sample. One plate was used for base oil and ZDDP contained mixed oil in a set of comparative experiments to ensure the same roughness of the plate in repeated experiments. The position of the wear marks was artificially changed after each experiment to make sure that a new surface was used each time as shown in Fig.7(c).



(a)sufficient lubricant (b) contact region (c) contact positions on plate

Fig.7 Schematic diagram of contact condition

Table 3 Test conditions

Load	Stroke	Sliding frequency	Temperature	Test time
150N	5mm	5Hz	20℃	20min

2.4 Lubrication state

The ratio between composite root-mean-square (RMS) roughness and average film thickness is equal to film thickness ratio λ, this is usually used for estimating the state of lubrication within a rough point contact, so in this case, Hamrock-Dowson formula, Eq. (1), has been employed to compute the minimum lubricant film thickness hence h_{min}[34].

$$\mathrm{H}_{min}^{*} = 3.63R\frac{G^{*0.49}U^{*0.68}}{W^{*0.073}}(1-e^{-0.68}) \quad (1)$$

where, $\mathrm{H}_{min}^{*} = \frac{h_{min}}{R}$, $\mathrm{H}_{min}^{*} = \frac{h_{min}}{R}$, $\mathrm{G}^{*} = \alpha E'$, $\mathrm{U}^{*} = \frac{\eta_0 U}{E'R}$, $\mathrm{W}^{*} = \frac{\mathrm{W}}{\mathrm{E'R^2}}$. R is the radius of the ball, U is the relative sliding speed, η_0 is the oil viscosity, E' is the equivalent-elastic-modulus, W is the applied load. The pressure-viscosity coefficient is $\alpha = 2.2 \times 10^{-8} m^2/N$. So, the film thickness calculated with Eq. (1) is $h_{min} = 8.24nm$.

The RMS roughness of the ball and the plate are 20nm and 8.2~242nm respectively, so the composite RMS roughness is σ = 21.6~242.8nm. Therefore, the film thickness ratio $\lambda = h_{\mathrm{min}} / \sigma < 1$, this implies that the friction pair has been operated within the boundary lubrication regime.

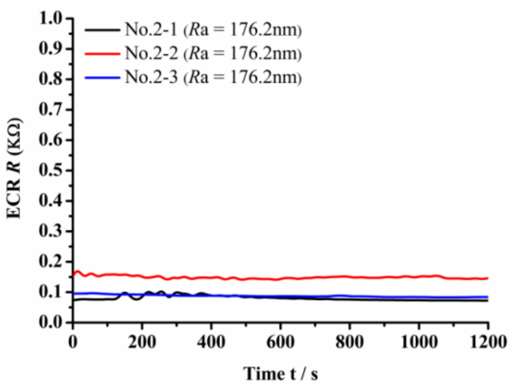
3 Experimental Results

3.1 Repeat Test and Definition of Critical Time of ZDDP Tribofilm Formation

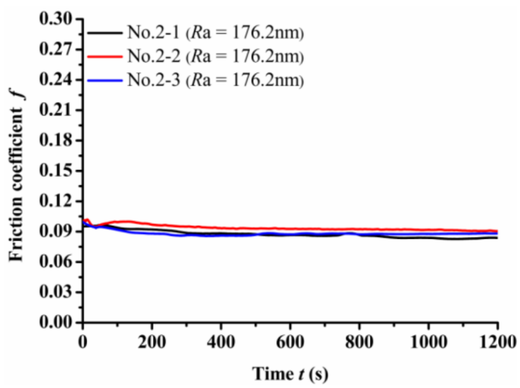
During experiments, each test was repeated up to three times. Fig.8 shows a set of experimental results of original ground surface (No.2) when base oil and ML were used as lubricant. For GTL8 base oil, the friction coefficients of three repeated test were almost the same as presented in Fig.8(b1). The ECR values remain low between 0.05-0.15 (Fig.8(a1)) through the entire testing schedule. This suggests that there is no obvious non-conducting hydrodynamic oil film or ZDDP tribofilm generated between the ball and plate, otherwise the electrical contact resistance would sharply rise. The small ECR values between 0.05-0.15 through the entire testing period are probably from the conductor resistance. For ML, though the values of friction coefficient show good repeatability through the whole tests (Fig.8(a2)), ECR values are more spread out (Fig.8(b2)).

As described in ***Section 2.1***, *ECR* is a method for qualitatively monitoring the generation of ZDDP tribofilms. Its value is only used to judge whether there is a sufficiently thick non-conductive film formed between two surfaces instead of computing the film thickness. In order to characterise the time needed for effective tribofilms formation, a parameter, t_c, termed as the critical time of ZDDP tribofilm formation, is defined here, as the duration from the beginning of test to the moment at which *ECR* value increases abruptly (see Fig.1). As shown in Fig.8(a2), although the magnitudes of *ECR* values in three repeat tests are not identical, the critical time of ZDDP tribofilm formation t_c shows a small gradient between 200s to 280s. Therefore, the experimental results still demonstrate good repeatability. The test curve with critical time t_c in the middle was selected to compare the influences of surface topography on the critical time of ZDDP tribofilm formation.

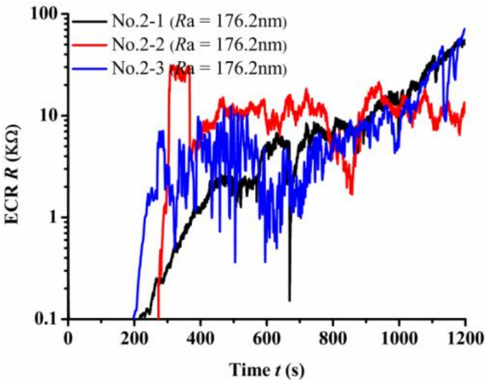
It also should be noted that the critical time of ZDDP tribofilm formation t_c is just a characteristic time, which does not mean that no tribofilm is generated when running time is less than t_c. As discussed later in ***Section 4***, in fact, ZDDP tribofilms can be generated in a much shorter time than t_c, however, the *ECR* signal registers a small value until the tribofilm growths are thick enough at t_c.

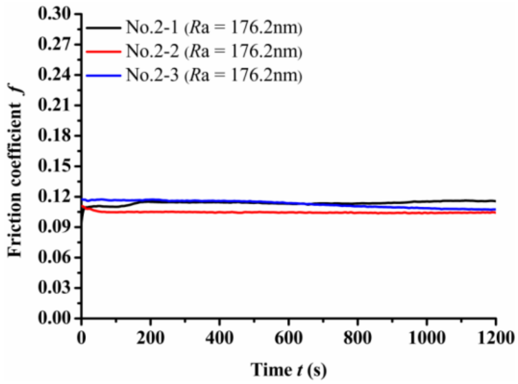


(a1) base oil-GTL8



(b1) base oil-GTL8





(a2) ML-GTL8+1wt%ZDDP (b2) ML-GTL8+1wt%ZDDP

(a) contact resistance *ECR* (b) friction coefficient *f*

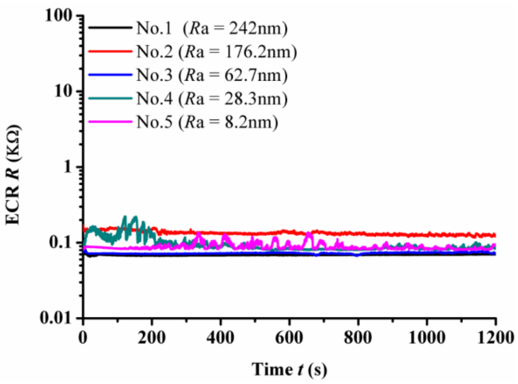
Fig.8 Repeatability of tests (No.2)

3.2 Influence of Surface Roughness on the critical time of ZDDP tribofilm formation

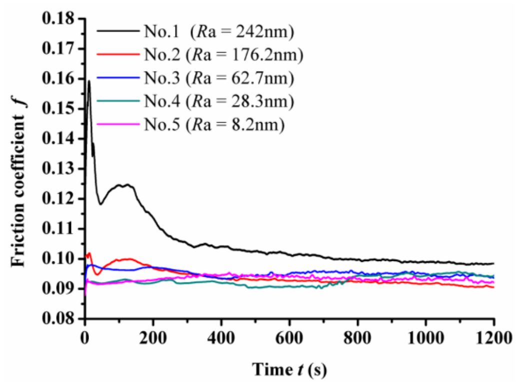
To study the influence of surface roughness on the critical time of ZDDP tribofilm formation and corresponding friction performance, the contact resistance value *ECR* and friction coefficient *f* of surface No.1~No.5 were monitored in real time. Rough peaks and valleys distribution of No.1~No.5 along the sliding direction is shown in Fig.3. The roughness of surface No.1~No.5 are R_a = 242nm, 176.2nm, 62.7nm, 28.3nm and 8.2nm respectively.

It can be seen from Fig.9 (a1) that the *ECR* values remain low between 0.06-0.2 through the whole testing period when GTL8 was used as a lubricant and there is a little difference of *ECR* values between surfaces No.1 to No.5. The low ECR values through the whole testing schedule are probably from the wire resistance. To eliminate the influence of wire resistance, non-conducting film formation can only be arbitrated when the *ECR* value is greater than 0.2. Fig.9(a2) shows the friction coefficient of surface No.1~No.5. For surface No.1, the friction coefficient is relatively high at the beginning, and then decreases from 0.16 to about 0.10. While for surface No.2~No.5, the friction coefficient values are narrowly distributed between 0.0.9-0.10 and are comparable. This means that except for surface No.1, the difference of friction coefficient caused by surface roughness is not apparent when base oil is used as a lubricant.

Fig.9(b1) shows the *ECR* values of friction pairs when ML was used as a lubricant. It can be seen that when ZDDP is contained in the lubricant, the *ECR* values are much higher and become unstable. It should be noted that under this contact condition, no hydrodynamic pressure film is formed, so the change in contact resistance is entirely due to the formation of non-conductive ZDDP tribofilm. Under the operating conditions used in this experiment, the critical time of ZDDP tribofilm formation t_c for surface No.1 with roughness of 242nm, No.2 with roughness of 126.2nm and No.5 with roughness of 8.2nm is narrowly distributed between 200~300s and are comparable. While, for surface No.3 with roughness of 62.7nm and No.4 with roughness of 28.3nm the critical time of ZDDP tribofilm formation t_c increases to 1000s and 450s respectively. This means that during running-in process, the time needed for effective tribofilm formation first increases and then decreases as the surface roughness decreases. The specific reasons and mechanisms are analysed and discussed in ***Section 4***. The friction coefficient values are shown in Fig.9(b2). They have varying distributions as compared to Fig.9(b1). For surface No.1, the friction coefficient decreases from 0.12 to 0.11. While for surface No.2~No.5, the friction coefficient values are distributed between 0.0.9-0.12. This is a quite large range compared to Fig.9(b1). This means that except for surface No.1, the gradient of friction coefficient caused by surface roughness is more apparent when ZDDP is used as a lubricant. This difference will be discussed later in the following sections.

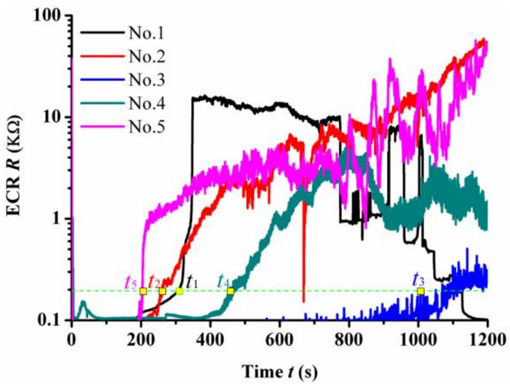


(a1) contact resistance *ECR*

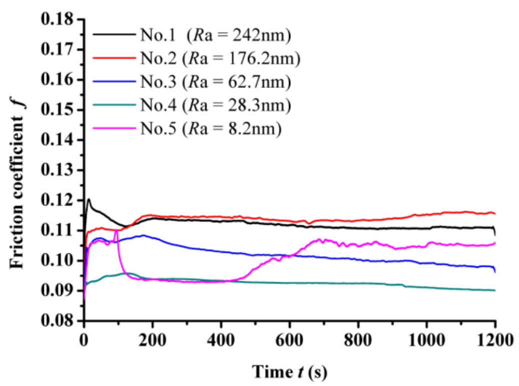


(a2) friction coefficient *f*

(a) GTL8



(b1) contact resistance *ECR*



(b2) friction coefficient *f*

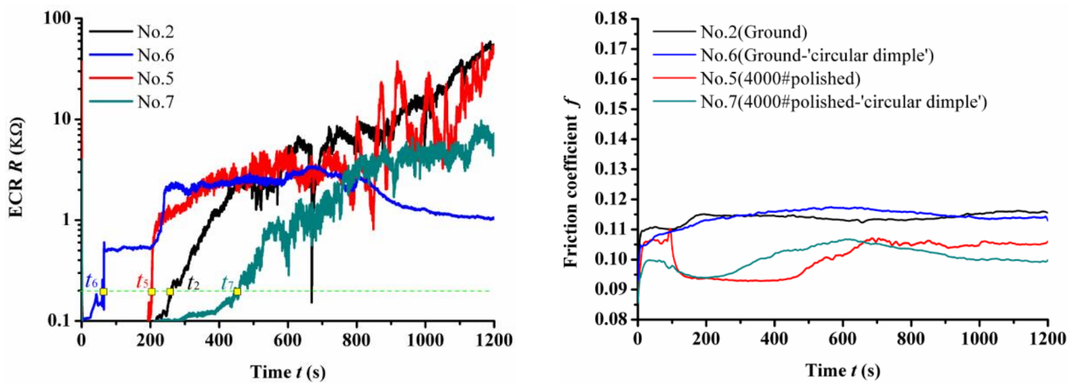
(b) GTL8+1wt%ZDDP

Fig.9 Influence of surface roughness

3.3 Effect of Surface Texture on the Critical Time of ZDDP Tribofilm Formation

The contact resistance and friction coefficient of textured surfaces No.6 and No.7 are presented in Fig.10. As described in ***Part 2.2***, dimples fabricated on surfaces No.6 and No.7 have the same profile, diameter and depth. The only difference lies in the surface roughness of the substrate. For surface No.6, circular dimples are fabricated on ground surface No.2. While for No.7, circular dimples are fabricated on 4000# polished surface No.5. As shown in Fig.10.(a), the critical time of ZDDP tribofilm formation for textured surfaces and corresponding substrate surfaces are 70s (No.6), 260s (No.2), 450s (No.7) and 200s (No.5) respectively. This means that for original ground surface, both fabricating dimples and polishing to decrease the roughness from 176.2to 8.2nm are useful methods to decreases the critical time of ZDDP tribofilm formation. Furthermore, fabricating dimples on the ground surface is more effective than complex polishing process from the perspective of promoting ZDDP tribofilm formation during running-in stage. However, for the 4000# polished surface, circles play no improving effect because the critical time of ZDDP tribofilm formation increases from 200s (No.5) to 450s (No.7). This is because the two textured surfaces are not deburred after laser textured processing. The bulge damage effect of the texture edge on surface No.7 is greater than the texture promotion effect. While for surface No.5, the burrs are hidden in the rough peaks, therefore the damage effect is not apparent.

Fig.10(b) shows the friction coefficient of surfaces No.2, No.6, No.5 and No.7. As the figure shows, the friction coefficient of ground surface (No.2, No.6) is larger than 4000# polishing surface (No.5, No.7) no matter if circular dimples are fabricated on the surface. This is because the friction pair were sliding under boundary lubrication regime and even textures cannot promote the formation of hydrodynamic film to separate the contact surfaces. Therefore, the surface contact state is the main factor which affects the friction coefficient. The contact stress between surfaces No.2, No.6 and their corresponding ball elements are much higher than that of surfaces No.5 and No.7, leading to higher friction coefficient values.



(a) contact resistance *ECR*　　　　　　　　(b) friction coefficient *f*

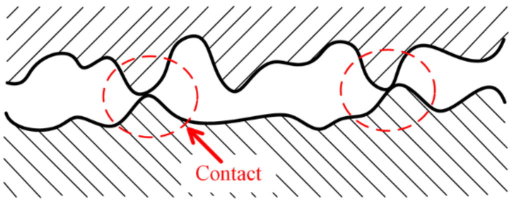
Fig.10 Influence of surface textures

4 Discussions

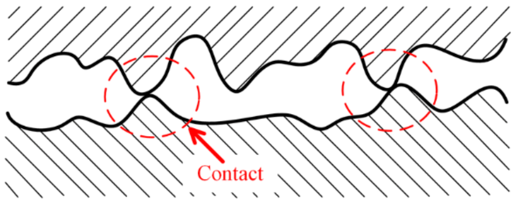
In this study, the influence of surface morphology on ZDDP tribofilm generation during running-in stage was experimentally studied. It is worth noting that the ZDDP chemical film formation process is only part of the running-in process. Although only the influence of ZDDP tribofilm formation in the running-in process is studied, this does not imply that other functions are not important. It is emphasised that all presented work has been focused on reciprocating motion under boundary lubrication to simulate upper and lower dead center of piston ring movement, which is prone to adhesive wear failure. The mechanism of ZDDP tribofilm formation on steel surfaces with various morphologies during running-in are analysed and discussed below.

4.1 Roughness

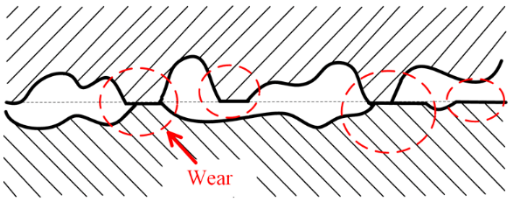
Surface roughness mainly affects the real contact area and stress under a given normal load. For the rough surface, the actual contact area accounts for only a miniscule part of the nominal contact area, therefore, the majority of contact pressure is sustained by the asperities, especially under boundary lubrication conditions as there is almost no hydrodynamic lubrication exist. Fig.11 compares the evolution of rough contact surface when only base oil is used as well as anti-wear additive ZDDP are contained in the lubricant. As shown in Fig.11(a), when two rough surfaces are sliding relatively under high contact pressure, the top of the contact asperities will be worn off effortlessly to form mild wear on the contact surfaces. As the sliding continues, the worn area on asperities increases and severe wear such as adhesion wear may occur as only limited number of base oil molecules can be brought into the sliding interface. However, if anti-wear ZDDP additive are contained in the lubricant then ZDDP molecules decompose under high contact pressure and the breakdown products will react with the fresh metal surface when mild wear occurs to form anti-wear tribofilms which can prevent direct contact and adhesion wear between the asperities staves off (Fig.11(b)). The role of tribofilm in the reduction of adhesive wear can be explained with the reduced work of adhesion of the interface rather without an intervening tribofilm [35]. As the sliding continues, more tribofilms will form on the surface to prevent severe wear.



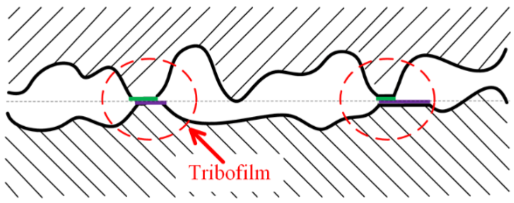
(a1) High contact pressure



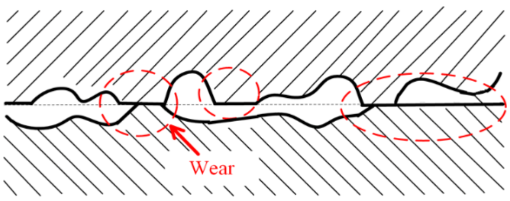
(b1) High contact pressure



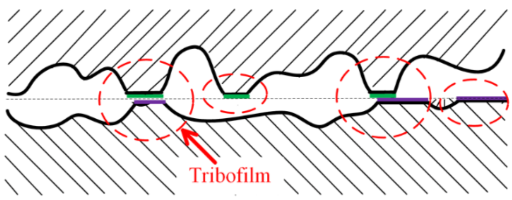
(a2) Mild wear



(b2) Mild wear and tribofilms formed



(a3) Severe wear



(b3) More tribofilms formed

(a) base oil-GTL8

(b) mixed lubricant-GTL8+1%ZDDP

Fig.11 The evolution of contact surfaces

There are three main factors which affect ZDDP tribofilms formation during running-in process. (1) The contact stress: ZDDP tribofilm growth rate increases exponentially with applied pressure subject to a single-asperity contact[18]. The larger the surface roughness, the sharper the asperities in turn the greater the asperity contact stress. From this point, the ZDDP tribofilms form more easily on the rough surface. (2) The removal rate: the formation of anti-wear film is a process containing tribofilms generation and removal. Some researchers have pointed out that the tribofilms formed on the rough surface are easily penetrated by asperity[19]. Therefore, the larger surface roughness is not conducive to long-term maintenance of the tribofilms. (3) The additive supply: it is crucial to ensure adequate additive can be brought into the contact region during running-in process because ZDDP is a kind of consumable additive. For rough surfaces, more lubricant can be stored in the valleys between rough peaks and will provide more additive molecules or decomposition products to the contact region during sliding process. Ying[36] proposed an entropy model to analyse tribochemical reaction rate of tribofilm formation on coin blanks during a burnishing process. According to the model, the larger the amount of reactive chemicals, ZDDP molecules in this case, the faster the tribofilm formation.

Since ZDDP tribofilm formation is a dynamic process which contains generation and removal. Which is a process with the aim to form effective chemical tribofilms during running-in stage on the rubbing surface. ZDDP tribofilm formation is affected by the above mentioned three factors. Therefore, setting appropriate operation conditions is critical in forming effective anti-wear tribofilms during running-in process for a given surface. Similarly, processing surface with corresponding surface roughness to promote effective anti-wear tribofilms formation is also an appropriate method in the case of a constant load.

As shown in Fig.9, the critical time of ZDDP tribofilm formation first increases and then decreases as surface roughness increases. This may be because there is almost no tribofilm removal during running-in process when the roughness is small (Ra = 8.2nm and Ra = 28.3nm). When the surface is rough (Ra = 176.2nm and Ra = 242nm), the contact pressure is large enough to make sure that the generation rate is larger than the removal rate and adequate additive can be brought into the contact region since more lubricant can be stored in the valleys between rough peaks, and the critical time of ZDDP tribofilm formation is also less. When the surface roughness is 62.7nm, the generation rate may be almost the same as the removal rate at first, then the removal rate decreases as the asperities wear off, so the effective tribofilms are formed. It can be inferred that under various contact pressures, the surface roughness with the longest time of ZDDP tribofilm formation is different and is related to the rough peak contact conditions.

It should be noted that typical elements of ZDDP tribofilm (Zn, P, S) are detected by EDX even after only 1min running in for surfaces No.1~ No.6. *ECR* experiments have shown that at least 200s running in time is needed for effective tribofilms formation. This variance is caused by different detection methods. *ECR* value increases sharply from a very small value to a high *ECR* value when two rubbing surfaces are completely separated by non-conducting ZDDP tribofilms. In

EDX analysis, the tribofilms can be detected if the reaction film is formed, regardless of whether the two sliding surfaces are completely separated by tribofilms. However, the main purpose of this study mainly focusses on forming effective anti-wear tribofilms on various surfaces to ensure that the two sliding surfaces separated completely. The *ECR* values are the main results and the EDX analyses are used only as auxiliary results in these experiments.

In addition to contact resistance, the distribution of friction coefficient also varied depending on whether the lubricant contains ZDDP. As mentioned in section 2.4, the friction pairs slide under harsh boundary lubrication conditions which makes contact surfaces more prone to wear. As shown in Fig.9(a2), when only base oil is used as a lubricant, obvious wear occurs at the beginning of the experiment for surface No.1 and the friction coefficient is relatively high due to large initial roughness. As the sliding continues, the height of rough surface peaks decreases and the friction coefficient decreases. For surfaces No.2~No.5, the initial surface roughness is not particularly large as surface No.1. The surface become rougher and the roughness becomes similar after wear, resulting in lower friction coefficient gradients. ZDDP protective film is formed on the surface after a period of sliding time when the lubricant contains ZDDP. This protective film can maintain the surface as original as possible, such hat the difference between the surface topographies is larger compared to when base oil is used as a lubricant. Therefor the distribution of friction coefficient is relatively dispersed as shown in Fig.9(b2).

4.2 Surface textures

Fig.12 shows contact between ball element and textured surface. Blue dotted line and purple solid line indicate pressure distribution of contact area when plate is un-textured and textured respectively. Textures can affect friction performance by storing oil, capturing abrasive particles and changing stress distribution under boundary lubrication condition. These factors will also influence the effective ZDDP tribofilms formation during running-in process. (1) Store lubricant: for point contact, the most important role of textures is storing lubricant and then providing oil "secondary" to the contact area when there is not enough lubricant in the contact area. This role of textures ensures adequate additive can be brought into the contact region during running-in process. (2) Capture abrasive particles: contact pressures between asperities of two sliding surfaces are large during running-in process, leading to form abrasive and/or adhesive wear and then scratch tribofilms.

However, the existence of textured dimples produce some grits embedded in textures and reduce tribofilms scratching to a certain extent. (3) Change stress distribution: texture edge causes contact pressure surge [37] which promotes the generation of ZDDP tribofilms. Simultaneously, some very small metal burr and flashing are formed at the edge of the textures during laser processing, which will exist as hard iron oxide particles between the ball element and plate. These particle burrs work as grinds to block the tribofilms formation and scratch tribofilms during running in process leading to abrasive wear since the beginning of sliding.

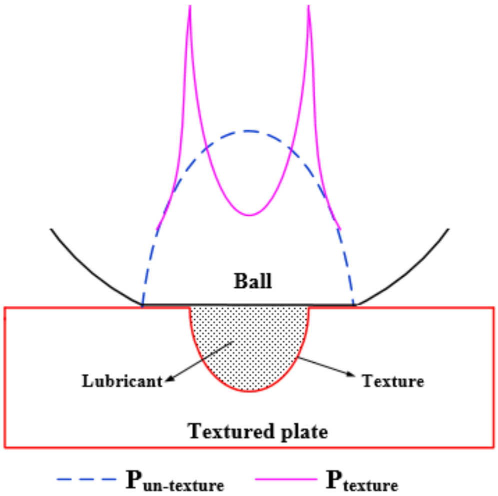


Fig.12 The contact between ball and textured plate

Fig.13 shows critical time of ZDDP tribofilm formation of surfaces with and without textures. For surface No.7, fabricating dimples play no improving role in effective tribofilms formation during running in process. For surface No.6 the time from start to obvious tribofilm generation has decreased as compared to non-textured ground surface No.2. Circular dimples on 4000# polished surface and ground surface have the same geometrical parameters such as circle diameters, depth and center distance, which determine the effects of storing of lubricant, capturing abrasive particles and stress distribution caused by circles. The only difference between surface No.6 and surface No.7 is the roughness of the substrates. Metal burrs at the edge of the textures on surface No.7 are much higher than the asperities of the substrate, these metal burrs will be easily crumpled during the loading process before sliding and then scratch tribofilms during the sliding process. On surface No.6, the height of the metal burrs is smaller than the asperities on the substrate. Therefore, these burrs have almost no influence on the tribofilms generation and removal. This is the main reason for the different critical time of ZDDP tribofilm formation. Therefore, if the surface texture is processed to promote ZDDP tribofilm formation, it is recommended to use a laser with a shorter wavelength for processing, or the surface should be polished after the laser texture is processed to remove the burrs around the pits.

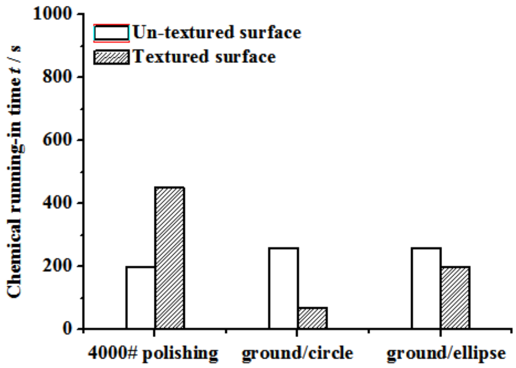


Fig.13 The critical time of ZDDP tribofilm formation for surfaces with different textures

4.3 Wear performance

The purpose of researching the critical time of ZDDP tribofilm formation is to reduce wear of sliding contact parts. In order to analyse wear resistance performance, worn surfaces were examined by using SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-ray) after friction tests. Worn morphology of original grinding surface No.2 and ground-‘circular dimple’ surface No.6 is shown in Fig.14 and Fig.15. As Fig.14(a) shows, for the original ground surface, severe wear scar can be observed if GTL8 is used as a lubricant. When 1*wt*% ZDDP is added to GTL8, only a slight wear scar can be seen and the original grinding grain is still clearly visible as shown in Fig.14(b).

For ground-‘circular dimple’ surface No.6, when the lubricant is GTL8, the original grinding grain is also worn away, however, the degree of wear is lower than non-textured surface No.2. This shows that under boundary lubrication conditions the circular texture can reduce wear if the lubricant is base oil. Zn, P, and S are the ZDDP reaction film constituents. EDX analysis result of the wear scar in Fig. 14(b) shows that when the lubricant is GTL8+1wt% ZDDP, the ZDDP tribofilm is formed during the friction process.

Fig.15 shows SEM images of circles in the wear scar. Diameters of the circles in wear scar decrease after friction experiments because the debris accumulate in pits when only base oil GTL8 was used as a lubricant (Fig.15(a)). However, when 1wt% ZDDP is added to GTL8 almost no visible wear marks in the contact area can be seen and the circles remained almost as if untested (Fig.15(b)). It can be deduced from comparing Fig.15(b) and Fig.14(b) that by shortening the time of ZDDP tribofilm formation by fabricating textures on ground surface can indeed reduce wear. Furthermore, in practical applications the dimple edge is susceptible to peeling off and exacerbates wear under heavy load, counteracting initial beneficial effects of lubricating oil and wear debris storage. The experimental results, however, show that ZDDP additive can effectively reduce further metal flaking on the dimple edge. This means that although the circular dimples have good performance in reducing wear, the combination of circular dimple and ZDDP shows better anti-wear performance.

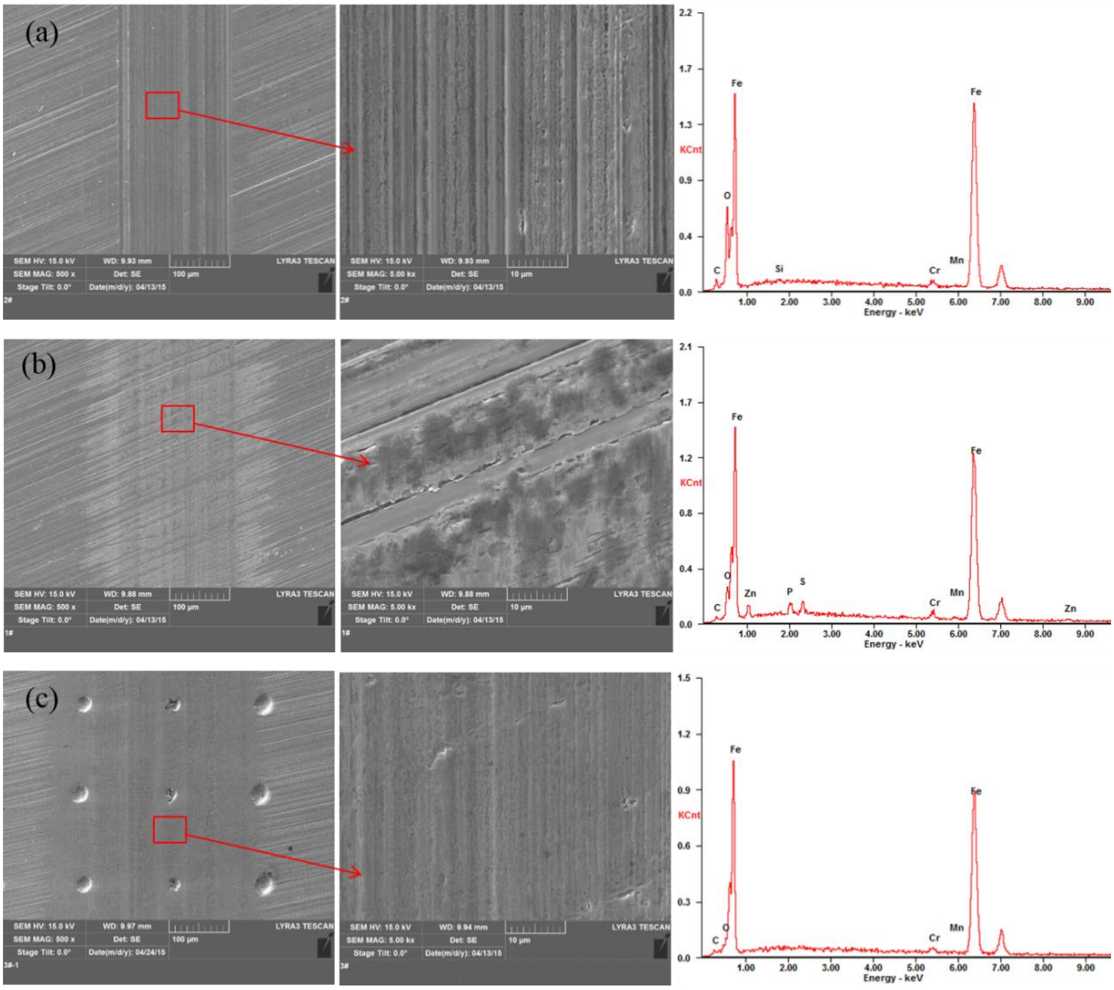


Fig.14 SEM+EDX images of wear scar

(a) ground-GTL8； (b) ground-GTL8+1wt%ZDDP; (c) ground+circle-texutred-GTL8

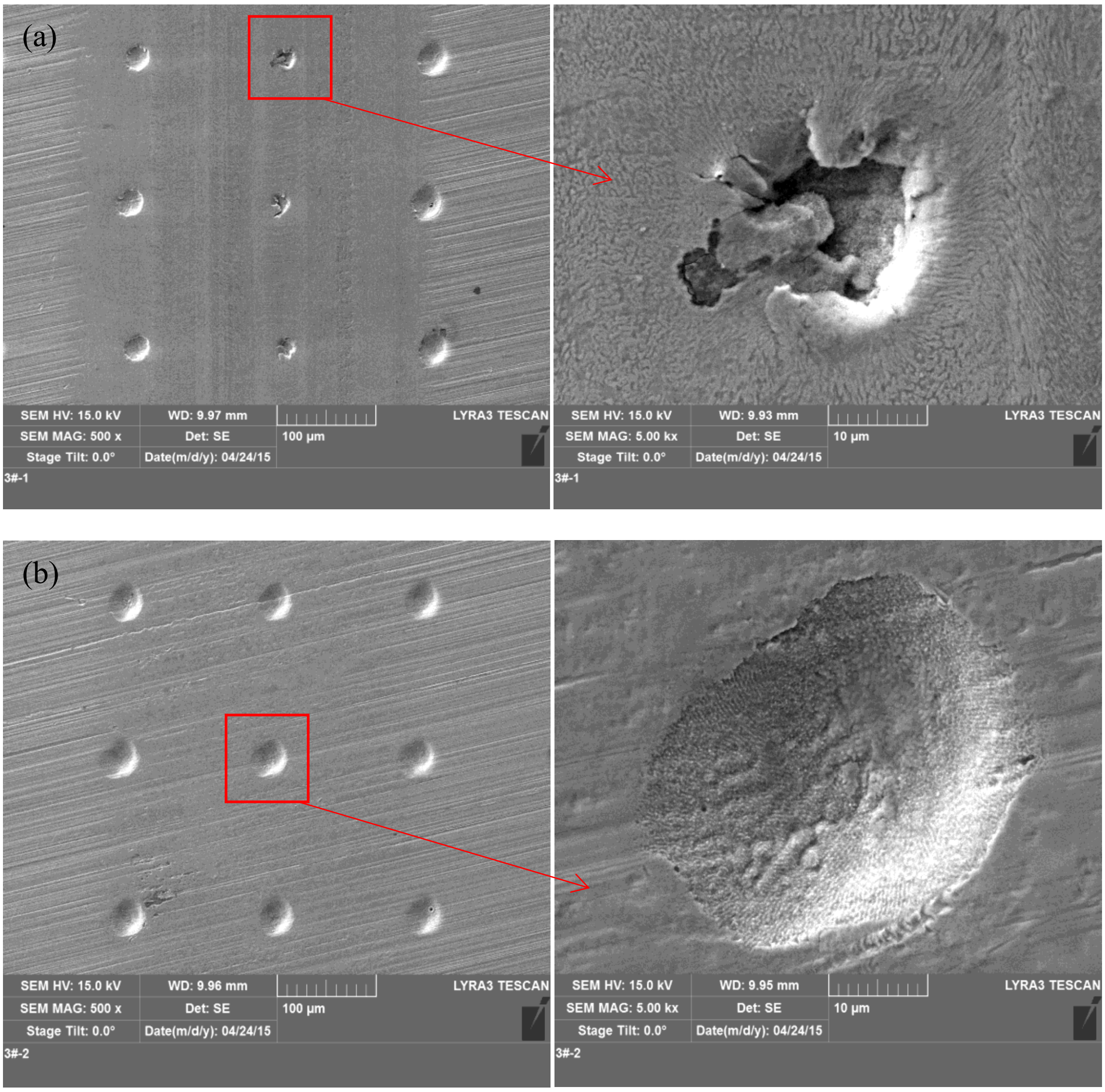


Fig.15 SEM images of wear scar(ground+circle-textured)

(a) GTL8； (b) GTL8+1wt%ZDDP

5 Conclusions

In this paper, the influence of surface roughness and textures on the critical time of ZDDP tribofilm formation under boundary lubrication condition during running in stage associated with reciprocating motion are studied and discussed. This research has provided an insight into the influence of surface roughness and textures on ZDDP tribofilm formation during running in process. The following conclusions can be reached from the presented results.

(1) Surface roughness influences ZDDP tribofilm formation during running in process. Rough surface can promote the formation of ZDDP tribofilms from the point of increasing contact pressure and providing more lubricant. At the same time, the tribofilms formed on the rough surface are

easily penetrated by asperity. Therefore, running in process with the purpose of forming effective tribofilms as quickly as possible is significantly affected by these two aspects. Surface with roughness of 8.2nm is the best to form anti-wear ZDDP tribofilms as quickly as possible.

(2) Circular dimples on ground surface have better performance in promoting tribofilms formation than non-textured surface, however fabricated dimples play no improving role in case of 4000# polished surface. Textured surface is a unique rough surface with more apparent and regular textures fabricated on the substrate. Tribofilms formation is also influenced by contact pressures and lubricant supply in case of non-textured surface. As the size of textures are much larger than the valleys of rough peaks, they can absorb the abrasive particles to prevent tribofilms penetration by asperities. Roughness of the substrates also influences the formation of tribofilms because the metal burrs at the edge of the textures are easily creased during the loading process and then scratch the tribofilms during the sliding process when the height of the metal burrs are larger than the asperities. Conversely, if the height of the metal burrs is smaller than the asperities on the substrate, they have almost no influence on the tribofilms generation and removal. In these experiments, fabricating dimples on 4000# polished surface induces no improving effect on effective tribofilms formation during running in process. While, for ground-'circular dimple' surface, the time from start to obvious tribofilm generation decreased as compared to non-textured ground surface.

(3) Textured surface has better anti-wear performance than non-textured surface under boundary lubrication conditions during this study even only base oil was used as a lubricant. The diameters of the circles in wear scar decrease after friction experiments because the debris accumulate in the pit. Dimples remain almost as the new ones until the end of the friction experiments when 1wt% ZDDP was added to the base oil. This means that although the circular dimples have good performance in reducing wear, the combination of circular dimples and ZDDP additive shows better anti-wear performance.

Acknowledgments

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