The preparation and tribological properties of surface modified zinc borate ultrafine powder as a lubricant additive in liquid paraffin

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Abstract

This paper investigates the effects of surface modification of zinc borate ultrafine powders (ZB UFPs) on their tribological properties as lubricant additives in liquid paraffin (LP). ZB UFPs were successfully modified by hexadecyltrimethoxysilane (HDTMOS) and oleic acid (OA). It is evident that HDTMOS modified zinc borate ultrafine powder (HDTMOS-ZB UFP) delivered a small conglomerate size, good stability in the organic solvent and sound anti-wear property. It has been observed that a continuous and tenacious tribo-film on the worn surface generated from HDTMOS modified ZB UFP as a lubricant additive in LP plays an important role in the outstanding anti-wear property. It is suggested that HDTMOS modified ZB UFP as a lubricant additive in LP has a great potential.

Keywords: Zinc Borate Ultrafine Powder; surface modification; dispersibility; lubricant oil

1 Introduction

Metal borates as an important group of engineering additives have always been the focus of extensive researches [1-4]. Zinc borate, in particular, has been widely employed as an additive in a broad range of industrial products due to its flame resistant, smoke suppressive character as well as its interesting optical properties [5-7]. The utilisation of zinc borate nanoparticles as an inorganic lubricant additive has also raised much attention over recent years owing to their outstanding tribological properties and good environmental friendly feature compared with the traditional organic lubricant additives that contain P, S and Cl elements [8-10]. There was a report regarding zinc borate nanparticles in liquid paraffin with assistance of dispersing agent sorbitol monostearate where an up to 50% reduction of friction coefficient and a 10% drop of wear scar diameter were observed [8]. However, without a direct evidence of testing zinc borate additive alone in the base oil, the true property of zinc borate particles in liquid paraffin cannot be identified and an actual level of contribution from either zinc borate nanoparticles or dispersing agent (sorbitol monostearate) to such improved tribological properties is still not clear. In fact, it has also been reported that without dispersing agent zinc borate powder did

not demonstrate noticeable friction reduction behaviour [9]. All the zinc borate particles studied in the past as a lubricant additive are in the size of nanometer although a majority of the available commercial zinc borate powders are submicron particles. Compared with nanoparticles, submicron size particles have relatively low cost and simple preparation process which has guaranteed their domination in industrial application although submicron size particles are more thermodynamically unstable in liquid media.

The stable dispersion of solid lubricant additive in base oil has always been a great challenge, and the intrinsic poor stability of solid additives in polymers and a lubricant system has considerably restrained from their applications. Modification of particle surfaces using suitable modification agents is one of the widely applied approaches to improve the dispersibility of solid additive particles in lubricant base oil. Surface modified Al_2O_3 [11], SiO_2[12, 13], Fe_3O_4[14], MoS_2[15, 16], ZnO [17], and LaF_3[18, 19] have all been synthesized successfully, and the improved tribological performances achieved by using these surface modified additives in lubricant base oils have also been reported. In the case of the surface modification of zinc borate particles, oleic acid is the most commonly used modification agent [9]. However the information on the surface modification of zinc borate particles using alternative agents is very limited.

In this study, zinc borate ultrafine powder functionalised with oleic acid (OA) and hexadecyltrimethoxysilane (HDTMOS) coupling agent was synthesized. Anti-wear properties of liquid paraffin with original and modified zinc borate ultrafine powders were investigated and compared using a Pin-on-disc tribotester. Conglomerate size and stability of the original and modified samples in hexane were studied with zeta-potential. The morphology and mechanical properties of worn surface were studied using atomic force microscopy (AFM), scanning electron microscopy (SEM) and nano-indentation facilities. The elemental analysis on the worn surfaces was also conducted with energy-dispersive X-ray spectroscopy (EDS). A significant wear reduction was achieved when the HDTMOS modified zinc borate ultrafine powder was used as the lubricant additive in liquid paraffin. A continuous and tenacious tribo-film generated on the wear scar was observed and considered to be the reason for the enhanced anti-wear performance.

2 Materials and experimental apparatus

2.1 Materials

Analytically pure liquid paraffin (LP) (Kerax Ltd, UK) was employed as lubricant base oil, which has a flash point of 220^{o}C, a viscosity of 24 mPa·s at 40 ^{o}C and 4.8 mPa·s at 100^{o}C. Oleic acid (OA) (*Sigma-Aldrich, Inc.*) and Hexadecyltrimethoxysilane (HDTMOS) (*Gelest, Inc.*) were used as surface modification agents and lubricant additives. Commercial zinc borate ultrafine powder (ZB UFPs) with 99.5% purity and the particle size

of 500-800nm (*Shandong Jiqing Chemical Co.,Ltd, China*) were employed (Molecular Formula:2ZnO .$3B_2O_3$ $3.5H_2O$). Fig.1 shows a typical particle size and shape of the employed ZB UFPs.

2.2 Surface modification of zinc borate ultrafine powder

The OA modified zinc borate ultrafine powder (OA-ZB UFPs) and HDTMOS modified zinc borate ultrafine powder (HDTMOS-ZB UFPs) were synthesized in this study. ZB UFPs of 2.78 g were firstly dispersed in 40mL mixed solution of ethanol and water (volume ratio 1:1) using a high shear homogenizer at a rotary speed of 15K rpm for 10 minutes. A suitable amount of modifier (either OA or HDTMOS) dissolved in 10 mL of absolute alcohol was then added into the first dispersion. Subsequently, the mixture was heated to 70^{o}C and maintained at this temperature with vigorous stirring for 4 hours. Then, the suspension was centrifuged at a speed of 8000 rpm for 10 minutes and the white precipitate was collected. The obtained precipitate was rinsed with distilled water and ethanol alternately and centrifuged repeatedly in order to remove the excessive modifier. Finally the thoroughly washed precipitate was dried in a vacuum oven at 40^{o}C for 6 hours and the modified ZB UFPs were obtained.

2.3 Characterisation of surface modified zinc borate ultrafine powder

Infrared spectroscopy measurements were conducted using a Perkin-Elmer Spectrum 100 FTIR Spectrometer. Samples were prepared as powder-pressed KBr pellets. The spectra were collected in the wave range from 600 to 4000 cm^{-1} with a resolution of 4cm^{-1} in a transmission mode.

Thermo gravimetric analysis (TGA) was carried out with a SETARAM TG-DSC 1600 instrument. For each test, approximately 10mg sample placed in an aluminium crucible was tested with a heating rate of 5 °C/min from 80 to 500 °C in atmosphere.

2.4 Wear tests

The tribological properties of all lubricant samples were evaluated using a POD 2 Pin-on-disc tester (Teer Coatings Ltd.). All the tests were carried out with a 10N load and a sliding speed of 50mm/s for a testing period of 60 minutes and under the experimental environment that has ambient temperature of 22°C and humidity of 45%. A bearing ball of 5mm diameter used as the pin in a test was made of AISI52100 chrome steel with HRC of 59-61. The disc was made of the identical material, with 27mm diameter and 3mm thickness. Prior to each test, the discs were grounded and polished to a mirror finish and a uniform surface roughness Ra of 15nm was achieved. Before each test, both the pins (bearing balls) and the discs were cleaned with toluene in an ultrasonic water bath for five minutes to eliminate any potential grease on the surface, and then a further cleaning with acetone was carried out for five minutes. In this study, a uniform concentration of 0.5% in weight fraction was applied for all friction and wear tests when the additive powders were employed. Some surfactants have

excellent tribological properties when they were used as lubricant additives [20-22]. To eliminate the effects of applying surfactants on the anti-wear results of surface modified particles, OA and HDTMOS were combined with LP separately and tested on pin-on-disc rig as well. When either OA or HDTMOS was added into LP alone as an additive, the concentration of additive is 0.1% in weight. All additives (either particles or modifiers) were dispersed in LP with an ultrahigh shear homogenizer at the speed of 20k rpm for 20 minutes. The lubricants prepared in this study are presented in Table 1.

Table 1 The lubricants prepared for the tests

Sample code	Constituent
LP	Liquid paraffin
LP + OA	Liquid paraffin with 0.1 wt% oleic acid
LP + HDTMOS	Liquid paraffin with 0.1 wt% hexadecyltrimethoxysilane
LP + ZB UFPs	Liquid paraffin with 0.5 wt% original zinc borate ultrafine powders
LP + OA-ZB UFPs	Liquid paraffin with 0.5 wt% oleic acid modified zinc borate ultrafine powders
LP + HDTMOS-ZB UFPs	Liquid paraffin with 0.5 wt% hexadecyltrimethoxysilane modified zinc borate ultrafine powders

2.5 Characterisation of the worn surfaces

Wear scars on the pins used in the pin-on-disc tests were observed using optical microscopy and scanning electron microscopy (SEM). Wear scar diameter of each pin was measured to the accuracy of 1μm. The topography of the wear scar surface was studied with atomic force microscopy (AFM). Energy dispersive X-ray spectroscopy (EDS) were conducted to examine the chemical features and elemental composition of the tribo-film generated on the worn surfaces of the pin.

Mechanical properties of the tribo-film were determined using a Nano indentation facility (Micro Material Ltd). A Berkervich indenter with a tip diameter of 50nm was employed for the measurement. A maximal indentation load of 5mN was applied with a loading/unloading duration of 15 seconds, and the initial load was set to be 0.05mN.

3 Experimental results and discussion

3.1 Sample characterisation

Fig.2 shows the SEM images of the surface structure and morphology of the original and surface modified ZB UFPs. It can be seen that ZB UFPs modified by OA shown in Fig.2(b) share a similar particle size and morphology to the original ZB UFPs shown in Fig.2(a). However, compared with the unmodified specimen, more complicated surface texture with less sharp edges can be observed from the OA-ZB UFPs. The HDTMOS-ZB UFPs shown in Fig.2(c) demonstrate the smallest particle size.

The conglomerate size and zeta-potential of the original and surface modified ZB UFPs in non-polar solvent, hexane, are shown in Table 2. The samples of 0.05wt% were dispersed in hexane with an ultrasonic homogeniser (KINEMATICA PT 10-35 GT) running for 5 minutes. It can be seen that the average conglomerate size of original ZB UFPs measured in hexane was 2611nm in diameter. Under the identical condition, OA-ZB UFPs demonstrated a similar value of 2350nm in diameter. By contrast, the conglomerate size of HDTMOS-ZB UFPs was reduced to 857nm when HDTMOS was employed as the modification agent. Zeta-potential of the original ZB UFPs dispersed in hexane was measured to be 3.2 mV. In comparison, both OA-ZB UFPs and HDTMOS-ZB UFPs demonstrated the higher values of 7.8mV and 11.5mV respectively. It is well known that surface charges of the particles caused by absorption of ions and molecules generate an electrostatic repulsion force between two particles. This electrostatic repulsion force can partially counteract gravitation and reduce agglomeration and sedimentation of particles. The physical stability of a colloidal system can be determined by the balance between the repulsive and attractive forces that are described quantitatively by the Deryaguin–Landau–Verwey–Overbeek (DLVO) theory [23]. Therefore, a higher absolute value of zeta-potential of a suspension presents a better stability. The Zeta potential results from this study shown in Table 2 suggest that surface modifications of the ZB UFPs carried out with OA and HDTMOS have effectively improved the stability of ZB UFPs in organic solvent. The highest zeta-potential value of HDTMOS-ZB UFPs also suggests that it has better stability than OA-ZB UFPs in hexane.

Table 2 Conglomerate size and Zeta-potential of zinc borate powders despersed in hexane

	Zinc borate ultrafine powders		
	Original	OA-ZB UFPs	HDTMOS-ZB UFPs
Conglomerate size (in hexane)	2611nm	2350nm	857nm
Zeta-potential	3.2 mV	7.8mV	11.5mV

The composition and structure of the OA-ZB UFPs and HDTMOS-ZB UFPs were characterised with FT-IR spectroscopy as shown in Fig.3. In the infrared spectrum of original ZB UFPs shown in Fig.3(a), the band at 3458cm^{-1} is assigned to stretching of –OH. The band at 1650 cm^{-1} is attributed to the H–O–H bending mode, which indicates the existence of crystal water. The peaks observed between 1450–1300 cm^{-1} and 1200–1000 cm^{-1} are related to asymmetric stretching vibrations of trihedral borate (BO_3) and tetrahedral borate (BO_4) groups respectively, and the peaks between 960–740 cm^{-1} are related to the symmetric stretching vibrations of (BO_3) and (BO_4) groups [24]. In the spectra of OA and HDTMOS displayed in Figs.3(b-c), two sharp peaks at 2923 and 2856 cm^{-1} are attributed to the asymmetric and symmetric $–CH_2$ stretching vibrations respectively. The peaks with lower intensity at the same range of wavenumber can also be found in the spectra of OA-ZB UFPs and HDTMOS-ZB UFPs shown in Figs.3 (d-e). It is evident that the positions of peaks for the distinctive functional groups observed in the spectra of OA-ZB UFPs and HDTMOS-ZB UFPs are identical with the pure modification agent OA and HDTMOS. The infrared spectra result indicates that the surface of ZB UFPs has been successfully modified with OA and HDTMOS.

Thermal gravimetric (TG) analysis of OA-ZB UFPs and HDTMOS-ZB UFPs was carried out to clarify if the surface modification of the particles has made any particle change in weight due to coverage of organic groups. As shown in curve (a) of Fig.4, the dashed line shows a change of temperature versus time. It can be seen that the weight of the original ZB UFPs reduced sharply with an increase of temperature (time) due to the loss of crystal water. The decrease on sample weight started at 140 °C, and a weight loss of 15% was observed when the reduction stopped at 230 °C. Curves b-c in Fig.4 show the TGA results of HDTMOS-ZB UFPs and OA-ZB UFPs respectively when they were heated from 80 °C - 500 °C. It can be seen that the weight of both samples began to reduce at almost the same temperature about 95 °C and the reduction completed accordingly at 480 °C and 445 °C. Compared with the original ZB UFPs, HDTMOS-ZB UFPs and OA-ZB UFPs have a higher ratio of weight loss of 20% and 25% respectively because of the decomposition of the organic groups covered on the surface of the modified samples. The results of TG analysis confirm that ZB UFPs have been successfully covered with organic groups of HDTMOS and OA modification agents. Based upon the fact that OA-ZB UFPs have a higher weight loss in TG analysis compared with HDTMOS-ZB UFPs, it is suggested that a bigger coverage of organic groups on the particle surfaces of ZB UFPs is achieved when OA is employed as the modification agent.

3.2 Particle stability in liquid paraffin

Stability of the modified and unmodified ZB UFPs dispersed in base oil liquid paraffin has also been investigated. Fig.5 shows the status of the sedimentation of unmodified ZB UFPs, OA-modified ZB UFPs, and HDTMOS-modified ZB UFPs at the different periods after the preparation, respectively. As shown in Fig.5(c1),

when all the suspensions are well dispersed at t=0, LP + HDTMOS-ZB UFPs has demonstrated the best transparency, while LP + OA-ZB UFPs (Fig.5(a1)) and LP + ZB UFPs (Fig.5(b1)) has illustrated a more cloudy colour tone. This is possibly due to the smaller cluster size of HDTMOS-ZB UFPs dispersed in liquid paraffin.

At the 48th hour from the preparation, a significant sedimentation in LP + ZB UFPs was observed and the clear supernatant liquid paraffin indicated a complete deposition of the solid contents. Noticeable settling of additive in LP + OA-ZB UFPs was also observed. Compared with LP + ZB UFPs, a much softer accumulation of solid particles appeared at the bottom of the container and no clear boundary between the deposition and supernatant liquid was found. Moreover, a cloudy colloidal transition layer emerged above the solid sedimentation. However, no sign of solid deposition in LP + HDTMOS-ZB UFPs was identified, as shown in Fig.5(c2). A stable colloidal system with higher concentration of HDTMOS-ZB UFPs was formed at the lower half of the sample flask. Based upon the aforementioned observations, it is suggested that the dispersibility of ZB UFPs can be greatly improved with the surface modification of HDTMOS.

3.3 Anti-wear behaviour

Wear scars of the pins (bearing balls) used in pin-on-disc tests were firstly assessed using an optical microscope. The morphology and wear scar diameter (WSD) of each individual tested pin are shown in Fig.6. A smaller WSD implies a less material loss and therefore the superior wear resistance. It is evident that with the employment of HDTMOS-ZB UFPs, WSDs of the pins have been reduced. Particularly, a WSD as small as 123μm was obtained when LP with HDTMOS-ZB UFPs was used as the lubricant, which has the smallest value of WSD compare with other samples. Compared with HDTMOS modified ZB UFPs, OA modified additive particles did not demonstrate comparable anti-wear performance. A WSD of 226μm was received when the LP with OA-ZB UFPs was used as the lubricant. Very often, surface modification agents could also contribute to the improvement of the tribological properties of a lubricant therefore it is essential to identify the performance of the surface modification agent when they are employed in the lubricant base oil alone. Without ZB UFPs, HDTMOS failed to deliver a noticeable anti-wear property, a WSD of 242.5μm was obtained. On the other hand, in comparison with OA modified ZB UFPs, smaller WSD is found when OA was added in LP alone. This is possibly due to the abrasive effect of ZB UFPs solid additive with inadequate dispersibility. A uniform and tenacious tribo-film was found on the wear scar lubricated with LP with HDTMOS-ZB UFPs, as shown in Fig.6(d), and the formation of this tribo-film appears to have played an important role in the outstanding anti-wear property.

The volume losses of the pins lubricated by different lubricant samples were also illustrated in Fig.7. The volume loss due to wear was calculated geometrically based on the assumption that wear scar is a flat surface. Fig.7 shows that the maximum value of fluctuation in volume loss due to WSD measurement is marginal and

acceptable. As shown in Fig.7, the addition of 0.5% HDTMOS-ZB UFPs in LP has led to a more than 15 times decrease on wear loss of the upper pin.

3.4 Characterisation of the tribo-film

3.4.1 Physical and mechanical properties

Fig.8(a) shows a magnified optical photo of the wear scar on the worn surface of a bin lubricated by LP with HDTMOS-ZB UFPs. Figs.8(b-c) present the AFM images of tribo-film generated on wear scar surface as marked in Fig.8(a). Clearly a uniform and complete tribo-film was observed. The thickness of the tribo-film was measured to be around 170nm as shown in Fig.8(c). The mechanical property of the tribo-film has also been measured with nano-indentation. Indentations were made on both the tribo-film and the substrate steel. Fig.9(a) shows the patch of tribo-film that had the indentation on. The corresponding load–depth curves are illustrated in Fig.9(b). Mechanical properties of the worn surface on the tested bearing balls can be derived from a further analysis of the load–depth curves. With a maximum indentation load of 5mN, the value of indentation depth on tribo-film reached 155nm (curve (ii) in Fig.9(b)) which is not higher than the thickness value of the tribo-film. Under this condition the mechanical properties of the tribo-film measured may result in some interference from the substrate; therefore the surface hardness and reduced modulus derived from this load-depth curve as shown in Table 3 can only represent a relative difference between the tribo-film and substrate steel. It can be suggested that the observed tribo-film is made of a softer material with lower stiffness compared with substrate steel.

Table 3 A comparison of mechanical properties of the tribo-film and the substrate

Indentation position	Indentation depth	Hardness	Reduced modulus
Tribo-film	155nm	7.2Gpa	228Gpa
Substrate	132nm	9.8Gpa	260Gpa

Fig.10 shows the AFM morphologies of the worn surfaces of the pins lubricated with different lubricants. Changes of residual materials on the worn surface were discovered when the different lubricants shown in Table 1 were used. When pure paraffin was used as the lubricant, as shown in Figs.10(a-b), no complete film but only small patchy pieces scattering over the worn surface were found, and some ploughings were also seen clearly. Similar phenomenon was also observed when LP with the original ZB UFPs was employed, as shown in Figs.10(c-d). Very fine fragments of patchy pieces can be seen spreading over the examined area. The key change is that a partial tribo-film started to appears on the wear scar lubricated by LP with OA-ZB UFPs, as shown in Figs.10(e-f). Furthermore the tribo-film generated on the worn surface of a bin by LP with HDTMOS-ZB UFPs has widespread across the contact surfaces. Almost the whole scanned surface is covered with the tribo-film, and the thickness of the tribo-film is fairly uniform across the area. As marked in Fig.10(h), the main

part of the tribo-film is continuous and smooth, while the other areas shown in Fig.10(f) demonstrates the trace of disintegrating of the tribo-film. Cracks can be seen propagating in the tribo-film in this area and gradually break a complete piece of tribo-film into small fragments. No outstanding change of film thickness was found on a disintegrating part of the tribo-film compared with the other completely covered area. The results suggest that the employment of HDTMOS-ZB UFPs in LP enables to generate a more complete and durable tribo-film on the contact surface and this tribo-film can effectively protect the surface from significant wear damage.

3.4.2 SEM morphology and EDS analysis

The worn surfaces lubricated by LP with HDTMOS-ZB UFPs were analysed under a scanning electronic microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Typical SEM images and EDS analyses are shown in Fig.11. Distinctive topographical differences of the tribo-film and substrate can be seen clearly. The tribo-film displayed in Fig.11(a) appears in dark colour with a complex topography which makes a good contrast with the substrate displayed in brighter colour with smoother surface texture. The EDS patterns of the region highlighted on the tribo-film and the substrate are shown in Fig.11(**b**) and Fig.11(**c**) accordingly.

Table 4 Quantified elemental analysis on worn surface shown in Fig.11

Element	Spectrum (b) (At%)	Spectrum (c) (At%)
B	24.53	26.54
C	25.10	22.78
O	15.67	12.11
Zn	4.63	1.78
Cr	0.62	0.77
Fe	29.45	36.02

Quantified elemental analysis results are also given in Table 4. A considerable increase of Oxygen and Zinc contents was found on the tribo-film compared with the element distribution on the substrate. The Oxygen is possibly derived from ZB UFPs and metal oxides. The Zinc is attributed to the ZB UFPs. An obvious increase of Boron content was not detected since it is generally difficult to achieve an accurate Boron quantity by EDS due to its low atom weight. It is evident that HDTMOS-ZB UFPs are an important ingredient of the formation of the tribo-film. These results suggest that some tribochemical reactions may have taken place during the sliding process due to the local high pressure and flash temperature caused by the collision and rupture of the asperities between the mating surfaces.

3.5 Discussion on the tribo-film

Experimental data from the current study have demonstrated the excellent tribological properties of surface modified ZB UFPs employed as lubricant additives in LP. HDTMOS-ZB UFPs have revealed a superior anti-wear property to conventional OA-ZB UFPs. Under a friction force, zinc borate lubricant additive is firstly entrapped and then deposited on to contact interfaces due to shear effect. The third body effect of the ultrafine

particles between the contact surfaces can reduce a direct metal contact and consequently adhesion [25]. Reduction of adhesion is directly responsible for the reduction of wear. As the sliding continues, ploughings take place and debris are also resulted. A tribo-film is formed on the contact surfaces as a result of interaction between chemical components of the lubricant with the lubricated surface. The formation of tribo-film is associated with the decrease of wear. At all times the high wear loss was associated with small and patchy tribo-film fragments observed on the worn surface. On the contrary, the low wear loss was obtained when more complete tribo-films were formed. The test results suggest that a formation of tribo-film is greatly influenced by the dispersibility of ZB UFPs in LP. Solid lubricant additives with large particle size may sometime behave like abrasive particles, which will encourage the generation of debris and destruction of tribo-film, and eventually increase wear. As a result, original ZB UFPs demonstrated the highest wear loss due to its poor dispersibility in LP.

When HDTMOS-ZB UFPs were employed as the lubricant additive in LP, the best anti-wear result was achieved due to the formation of a complete and tenacious tribo-film with a lower hardness and reduced modulus than substrate steel, as shown in Table 3. This outstanding anti-wear property can be explained with *the delamination theory of wear* [26]. When a thin layer of tribo-film with low hardness and reduced modulus is generated on the hard substrate, the dislocations due to fatigue fracture will pile up at the interface between the tribo-film and the substrate. As the sliding continues, these dislocations escape through the surface of the tribo-film due to its very small thickness [27]. For a surface without tribo-film, the dislocations will be transferred and generated within the substrate material as a result of very high stresses, on the other hand, the transfer of dislocations from tribo-film to substrate metal will be considerably less owing to the lower tangential force transmitted. Therefore the wear of material protected by tribo-film will be remarkably reduced or delayed.

EDS analysis suggests that zinc borate additive is a critical component for the formation of a robust tribo-film. Therefore, the stability of additive particles in base oil plays an important role in the formation of tribo-film. Compared with original ZB UFPs, OA-ZB UFPs have better stability in LP although the original particle size is unchanged by this modification. HDTMOS-ZB UFPs have demonstrated the best stability and the smallest conglomerate size in organic solvent, which suggests that HDTMOS-ZB UFPs may have better integration with base oil and easier access to the contact interface. Therefore, the film forming ability and completeness of the tribofilm can be improved when HDTMOS-ZB UFPs are used as a lubricant additive.

4 Conclusions

The tribological properties of the original and modified zinc borate ultrafine powders (ZB UFPs) employed as lubricant additives in liquid paraffin (LP) were investigated. Based on the above results and discussion, the following conclusions can be drawn:

i. Oleic acid (OA) and hexadecyltrimethoxysilane (HDTMOS) modified UFPs were successfully prepared. Without surface modification, original ZB UFPs did not demonstrate any anti-wear performance.

ii. The HDTMOS modified ZB UFPs as lubricant additives in LP displayed superior anti-wear property to LP and LP with other additives. Compared with OA-ZB UFPs, the HDTMOS-ZB UFPs demonstrated much greater improvement on anti-wear property when it was used in LP, and it also exhibited better stability and smaller conglomerate size in the base oil.

iii. The outstanding anti-wear property of HDTMOS-ZB UFPs is attributed to the formation of a complete and tenacious tribo-film on worn surface. This tribo-film with content of Fe, O, C, Zn, and B elements has a smaller hardness and reduced modulus than the substrate material.

iv. The changes on the size and profile of the tribo-films were discovered when different lubricant samples were employed. It is evident that the coverage of the tribo-films on the worn surfaces has a good consistence with intensity of wear. A good coverage of tribo-film can protect the surface from wear effectively. Only small patchy pieces of film were found on the worn surfaces lubricated by LP, LP with surfactants and LP with ZB UFPs. The larger fragments with elongated shape were observed on the worn surface when LP with OA-ZB was used. The best coverage by tribo-film was achieved by using LP with HDTMOS-ZB as the lubricant.

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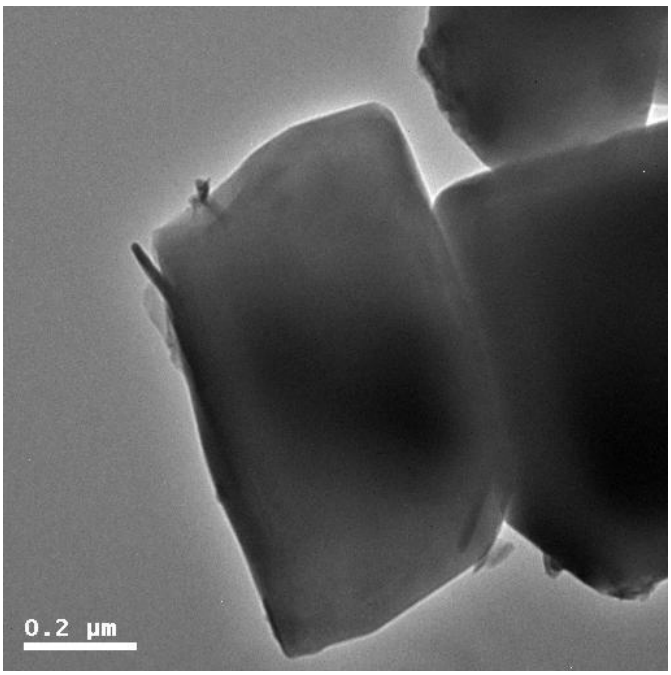

Fig. 1 Typical particle size and shape of the employed ZB UFPs under TEM

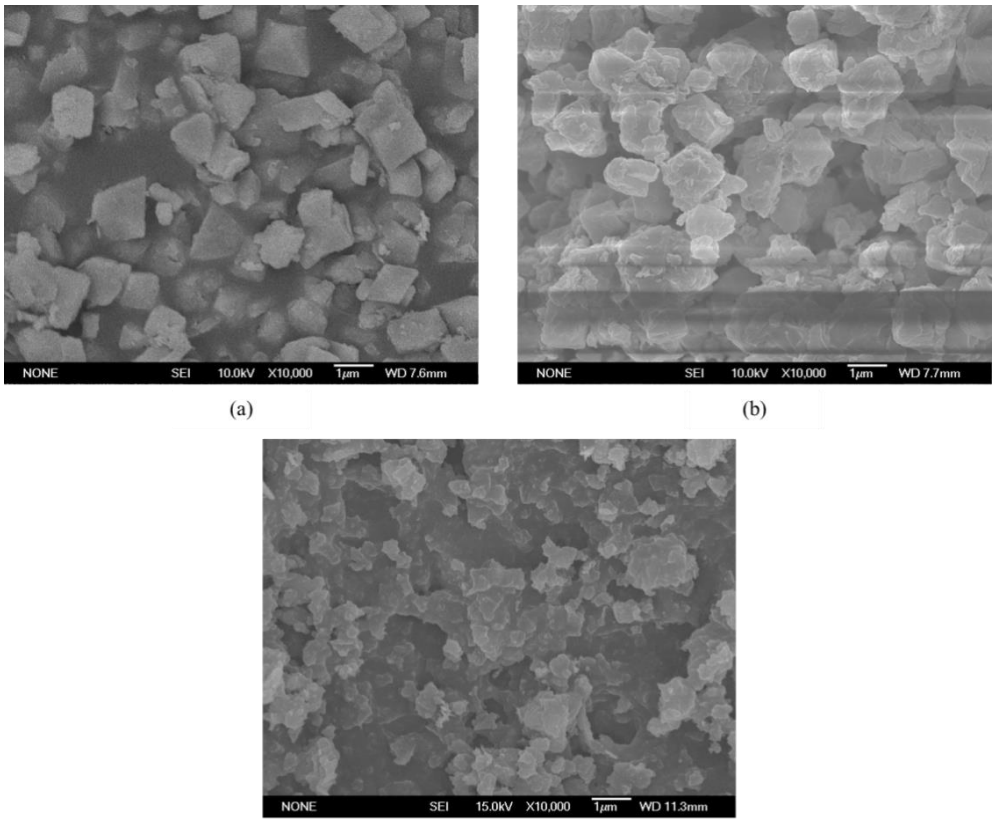

Fig. 2 Morphology of the powders: (a) the original ZB UFPs, (b) OA-ZB UFPs, (c) HDTMOS-ZB UFPs

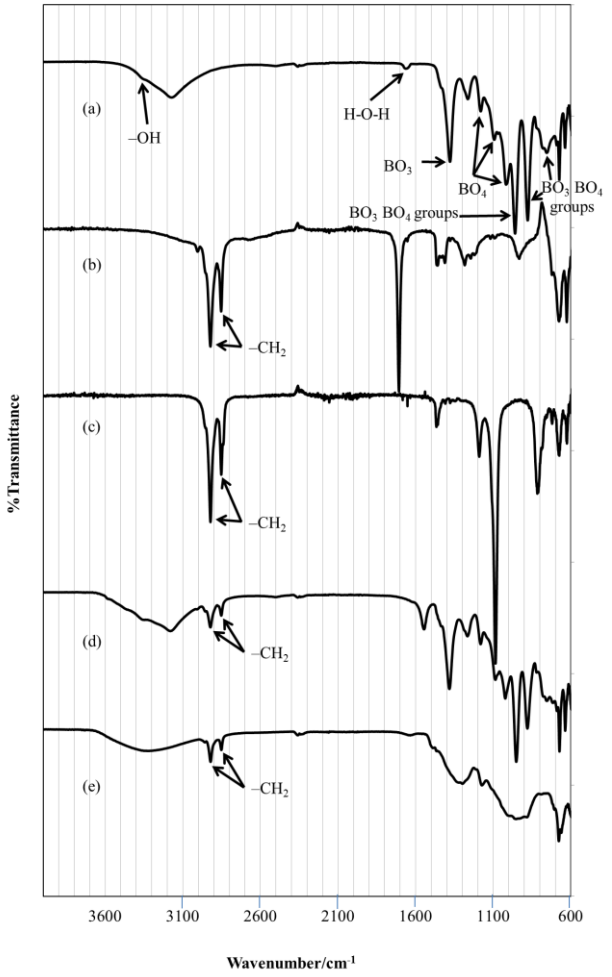

Fig. 3 FT-IR spectra of (a) original ZB UFPs, (b) OA, (c) HDTMOS, (d) OA-ZB UFPs, (e) HDTMOS-ZB UFPs

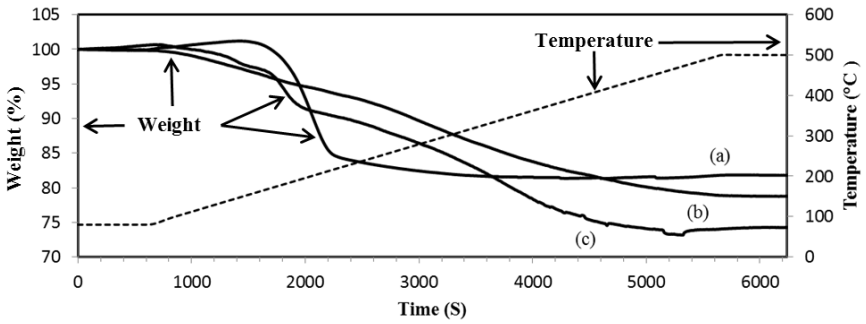

Fig. 4 Thermal gravimetric analysis (TGA) of (a) original ZB UFPs, (b) HDTMOS-ZB UFPs, (c) OA-ZB UFPs

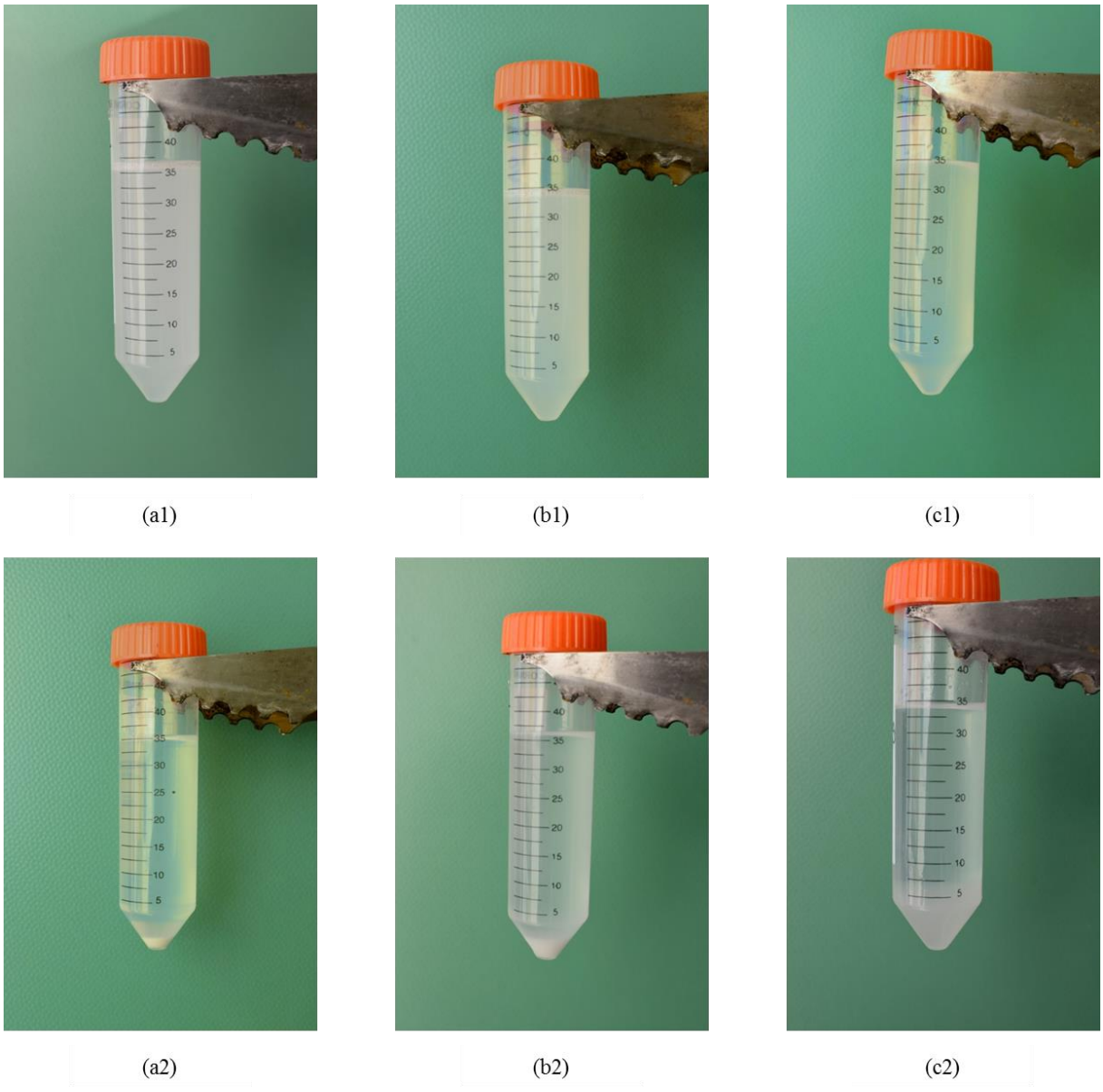

Fig. 5 Status of the sedimentation of the lubricant systems in the different periods after the lubricant preparation: at zero hour: (a1) LP + ZB UFPs, (b1)LP + OA-ZB UFPs, (c1) LP +HDTMOS-ZB UFPs, and at the 48th hour: (a2) LP + ZB UFPs, (b2)LP + OA-ZB UFPs, (c2) LP +HDTMOS-ZB UFPs

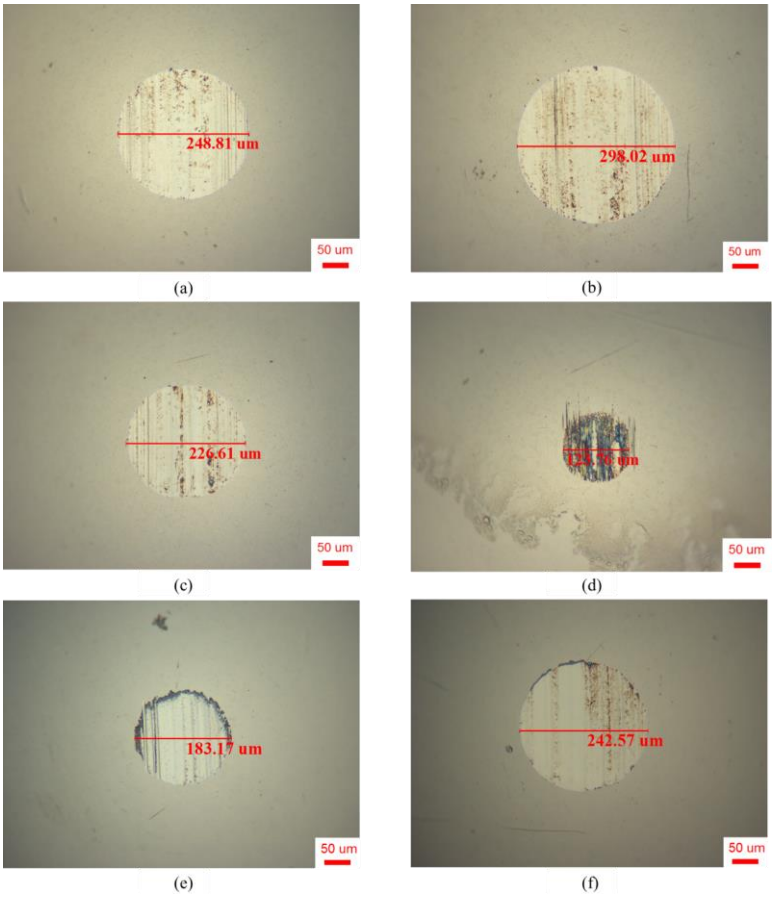

Fig. 6 Optical micrographs of wear scars lubricated with: (a) LP, (b) LP with ZB UFPs, (c) LP with OA-ZB UFPs, (d) LP with HDTMOS-ZB UFPs, (e) LP with OA (f) LP with HDTMOS

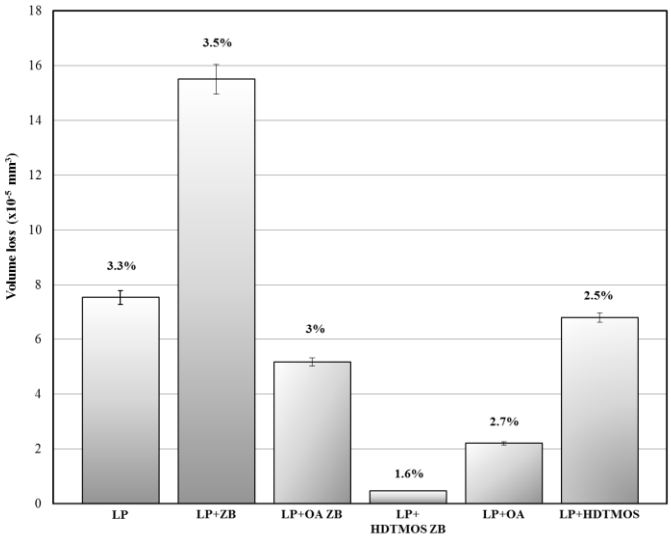

Fig. 7 Effect of different lubricant additives on volume loss of the bearing balls

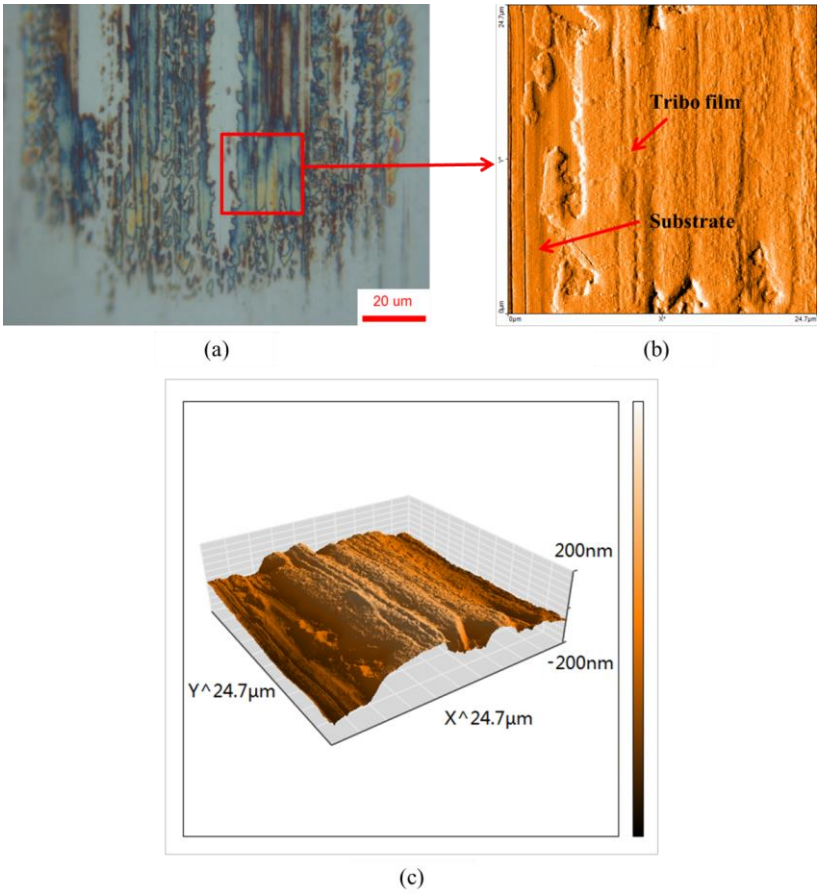

Fig. 8 Morphologies of the tribo-film generated by LP with HDTMOS-ZB UFPs:

a) optical image, (b) AFM surface topographic image, (c) 3D AFM surface topographic image

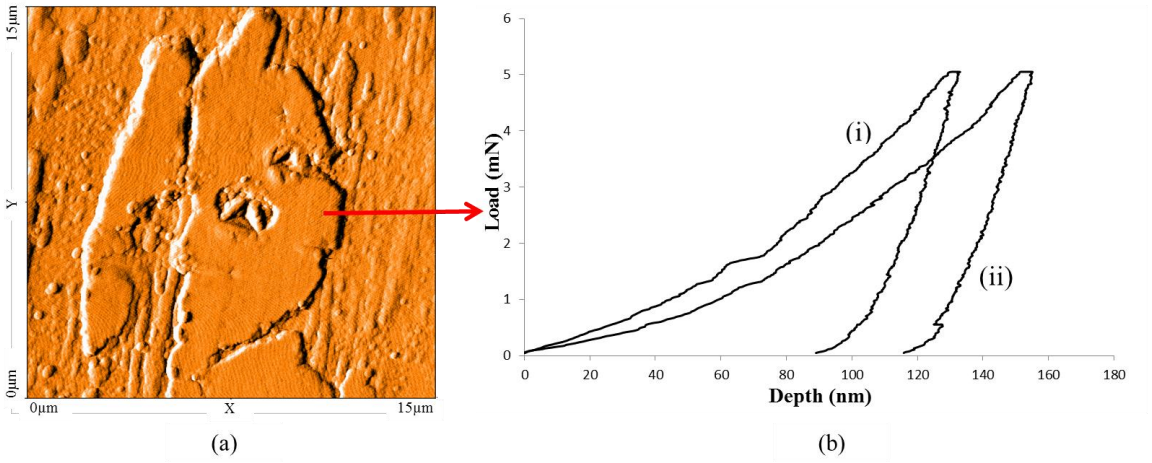

Fig. 9 Morphology of a piece of tribo-film generated by LP + HDTMOS-ZB UFPs and corresponding indentation curves obtained from different domains: (i) on substrate, (ii) on tribo-film

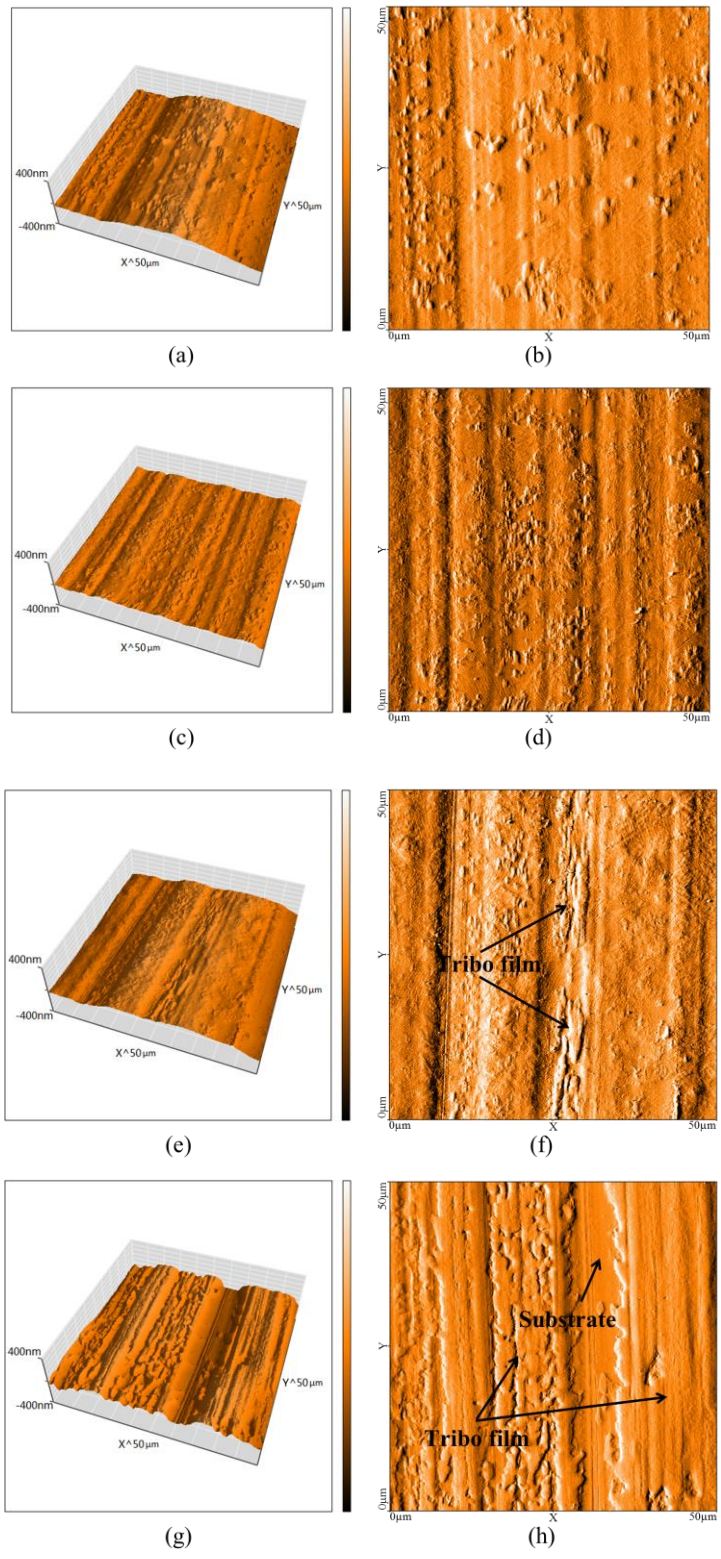

Fig. 10 AFM surface topographic images of the worn surfaces lubricated with different Lubricants: (a-b) LP, (c-d) LP with ZB UFPs, (e- f) LP with OA-ZB UFPs, (g-h) LP with HDTMOS-ZB UFPs

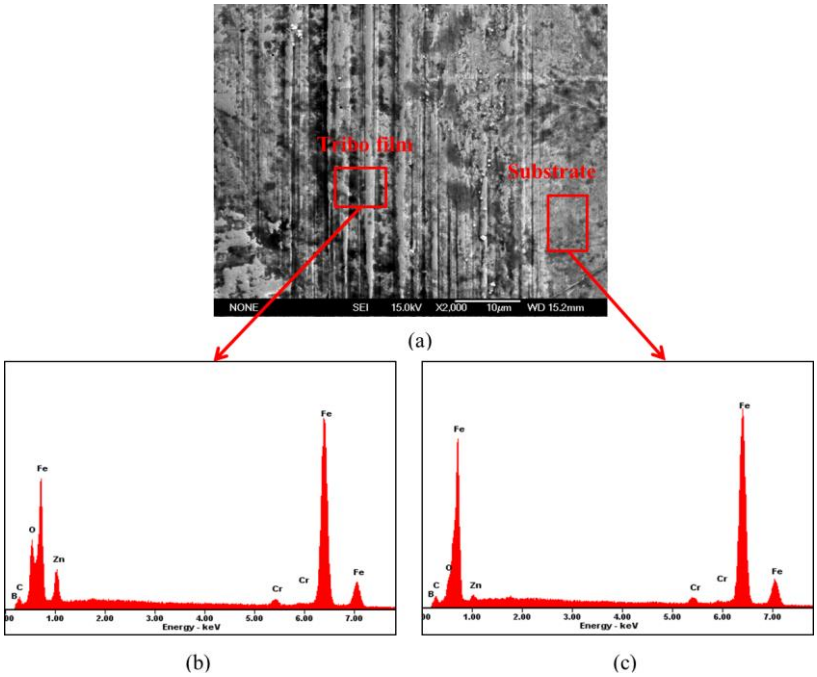

Fig. 11 SEM images and EDS patterns of worn surfaces lubricated with LP with HDTMOS-ZB UFPs: (a) worn surface morphology, (b) EDS patterns of the tribo-film, (c) EDS patterns of substrate.