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Improving Tribological Properties of Multialkylated Cyclopentanes under Simulated Space Environment: Two Feasible Approaches

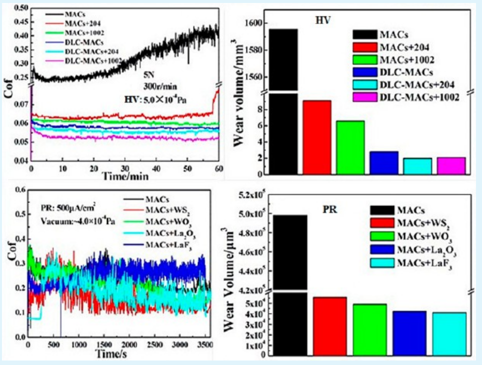
Xiaoqiang Fan,[†,‡] Liping Wang,[*,†] Wen Li,[†,‡] and Shanhong Wan[†]

[†]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P.R. China

[‡]University of Chinese Academy of Sciences, Beijing 100039, P.R. China

Supporting Information

ABSTRACT: Space mechanisms require multialkylated cyclopentanes (MACs) more lubricious, more reliable, more durable, and better adaptive to harsh space environments. In this study, two kinds of additives were added into MACs for improving the tribological properties under simulated space environments: (a) solid nanoparticles (tungsten disulfide (WS_2), tungsten trioxide (WO_3), lanthanum oxide (La_2O_3), and lanthanum trifluoride (LaF_3)) for steel/steel contacts; (b) liquid additives like zinc dialkyldithiophosphate (ZDDP) and molybdenum dialkyldithiocarbamate (MoDTC) for steel/steel and steel/diamond-like carbon (DLC) contacts. The results show that, under harsh simulated space environments, addition of the solid nanoparticles into MACs allows the wear to be reduced by up to one order magnitude, while liquid additives simultaneously reduce friction and wear by 80% and 93%, respectively. Friction mechanisms were proposed according to surface/interface analysis techniques, such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). The role of solid nanoparticles in reducing friction and wear mainly depends on their surface enhancement effect, and the liquid additives are attributed to the formation of tribochemical reaction film derived from ZDDP and MoDTC on the sliding surfaces.



KEYWORDS: *solid nanoparticles, liquid lubricants, diamond-like carbon, solid−liquid composite coatings, boundary lubrication*

1. INTRODUCTION

Liquid lubricants are frequently used in space mechanisms because they are associated with low mechanical noise, no wear in the elastohydrodynamic regime, ease of replenishment, ability to remove wear debris, and insensitivity to environmental factors.[1,2] Friction and wear behaviors of space lubricants are vital under boundary lubrication condition for reliability and longevity of space mechanisms. Multialkylated cyclopentanes (MACs), a class of synthetic hydrocarbon fluids are gaining an acceptance on actual space hardware due to the good chemical inertness, excellent viscosity properties, low volatility, low pour points and high thermal stability, which is one of the well-known liquid lubricants for space applications.[3,4] Some reports concerning the evaluation of MACs under laboratory conditions have shown that MACs possess good lubrication performance under vacuum,[5,6] whereas the same lubricity cannot be promised under more severe environmental conditions, such as high/low temperature (HT/LT), atomic oxygen (AO), ultraviolet (UV), proton (PR), and electron (EL) irradiation, absence of a gravitational field, and so on.[1,7,8] Hence, it is essential to use suitable lubricant additives to obtain the desired performance of MACs for mechanical systems under harsh conditions.

With the continuous development of various drive mechanisms over the past few decades, friction and wear of mating surfaces in relative motion have become the major roadblock to the mission requirements for mechanisms.[9−12] Especially, space vehicles with various machine elements require much higher reliability and longer durability because the breakdown of these elements can readily inflict fatal damage to the vehicles with no possibility of repair.[13,14] Accordingly, more effective control or reduction of friction and wear in moving mechanical systems is of great significance and importance for ensuring the reliability and durability. Lubricants always play a key role in ensuring the promised performance of such mechanisms.

Antiwear additives and extreme-pressure agents form a large family of additives that play an important role in reducing friction and wear during boundary lubrication by forming a protective film on the sliding surfaces. On the one hand, solid particles with various size and shape as lubricants additives have been investigated in detail, and their friction mechanisms have also been put forward.[15−20] For example, graphene and its derivatives (like carbon nanotubes and fullerene), as well as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) have been recognized as desirable solid lubricants because these materials with thin-layer structure and unique physicochemical properties can form a easy shearing protective film on friction pairs, thereby preventing the interacting surfaces from coming into direct contact and improving friction and wear.[21−25] Furthermore,

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Table 1. Physical Property Parameter of Solid Nanoparticles

sample	size (nm)	shape	density (g/cm^3)	specific surface area (m^2/g)
WS_2	80	spherical	7.50	80
WO_3	40	spherical	7.16	30
LaF_3	50	spherical	5.85	20
La_2O_3	40	spherical	6.51	30

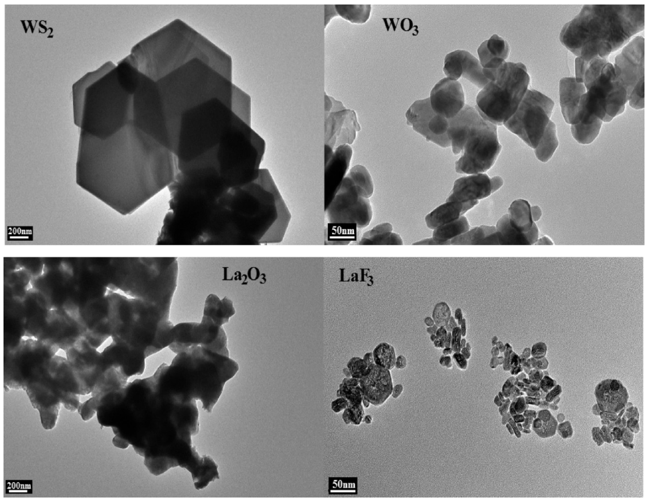

Figure 1. TEM micrographs of the solid nanoparticles including WS_2, WO_3, La_2O_3, and LaF_3.

Table 2. Physical Properties of Multialkylated Cyclopentanes (MACs)

lubricant	average molecular weight	kinematic viscosity (mm^2/s) 40 °C	100 °C	viscosity index	vapor pressure (Pa) at 20 °C
MACs	630	55.8	9.2	146	5.6×10^{-6}

diamond-like carbon (DLC) films, as promising carbon-based protective coatings have been studied in detail to respond to the challenge of space tribology.[26] DLC films can provide low friction and wear by minimizing abrasion, shear and adhesion due to their high mechanical strength and hardness, high thermal stability and chemical inertness, excellent tribological properties, and so forth.[27−29] On the other hand, oil additives have been studied by a number of groups and have shown remarkable friction-reducing and antiwear properties. Zinc dialkyldithiophosphate (ZDDP) and molybdenum dialkyldithiocarbamate (MoDTC), as the most successful oil-soluble lubricant additives, have been introduced over 70 years ago and are still being using in all current engine oils ever since for improving lubrication efficiency and saving energy.[30,31] Some reports have shown the remarkable performance of ZDDP as antioxidant, corrosion inhibitor, and antiwear agent and have also discussed the relevant friction mechanism.[32,33] MoDTC is still employed in engine oils to offer very low friction coefficient (~0.05) in boundary lubrication regime, which primarily depends on the formation of MoS_2-containing tribofilm on interacting surfaces.[34,35] Although no reasonably cost-effective compound has comparable antiwear and friction-reducing performance to ZDDP and MoDTC in lubricating oils, their tribological properties as MACs additives have not been systematically investigated under simulated space conditions. In addition, some researchers proposed the solid—liquid composite lubricating coatings as an ideal lubrication choice for space moving mechanical systems to reach the levels of long-term reliability and safe operation required, which can overcome the adhesion and cold-welding between interacting metal surfaces, and can minimize the cross-linking or chain scission of liquid lubricants under harsh space environment.[36−38]

In this study, the authors considered two kinds of additives: the solid nanoparticles (WS_2, WO_3, La_2O_3 and LaF_3), and the liquid additives (ZDDP and MoDTC). The tribological properties of these additives in MACs under simulated space environment were evaluated in detail, and friction mechanisms were also proposed according to surface/interface analysis techniques.

2. EXPERIMENTAL SECTION

2.1. Materials. Solid nanoparticles (WS_2, WO_3, La_2O_3 and LaF_3) were commercially obtained from Beijing DK Nano Technology Co. LTD (Beijing, China). Their physical properties are listed in Table 1. Figure 1 clearly shows their morphology with spherical and particle size of 40−80 nm. ZDDP and MoDTC were provided by Pacific United (Beijing) Petroleum Chemical Co. LTD (Beijing, China). MACs were provided by Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS, Lanzhou, China), and Table 2 highlights its physical properties. In this study, 2 wt % solid nanoparticles and 2 wt % liquid additives were added to MACs by sonication for 20 min, respectively. The deposition method of DLC is described in Supporting Information and is highlighted in refs 39 and 40.

2.2. Irradiation Procedure. The simulated space irradiation experiments were tested in ground-based simulation facilities at LICP, CAS in terms of AO, PR, and EL irradiation. For the space environment, the major atmospheric constituent in low Earth orbit (LEO) is atomic oxygen, which originates from photodissociation of O_2 in the upper atmosphere; its number density is about 8×10^7 atoms/cm^3 at 400 Km altitude, and the AO flux orbit is $10^{14} \sim 10^{15}$ atoms/cm^2 s. High-energy particulate radiation is predominantly trapped radiation-like electrons (up to several MeV) and protons (up to several hundred MeV). The effects of these types of particulate radiation on lubricants are ionization, phonon excitation, and atomic displacement, which can result in cross-linking, chain scission, or polymerization. In this paper, experimental parameters of the simulated space irradiation are listed in Table 3. The experimental atomic oxygen flux was 5.6×10^{15} atoms/cm^2 s with impingement kinetic energy of 5 eV for 120 min at the sample position. The experimental PR and EL provided the high-energy protons and electrons beam with the energy of 25 keV and the flux of 2.5×10^{14} cm^{-2} s^{-1} for 10 min.

2.3. Tribological Tests. *2.3.1. Ambient Friction Test.* The tribological performance of the lubricants under atmospheric environment were investigated using an Optimal-SRV-IV

Table 3. Experimental Parameters of Space Irradiation

irradiation	parameters	friction condition
AO	5.6×10^{15} atom/cm^2·s, 5 eV, 2 h	5 N, 300 r/min, 60 min, 4×10^{-4} Pa
PR	2.5×10^{14} cm^{-2} s^{-1}, 25 keV, 10 min	5 N, 300 r/min, 60 min, 4×10^{-4} Pa
EL	2.5×10^{14} cm^{-2} s^{-1}, 25 keV, 10 min	5 N, 300 r/min, 60 min, 4×10^{-4} Pa

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reciprocation friction tester with a ball-on-block configuration at high applied loads (100 and 200 N), room temperature (25 °C), and high temperature (200 °C) for 60 min. The upper ball (diameter of 10 mm, AISI 52100 steel, hardness 710 HV) slides reciprocally at an amplitude of 1 mm with frequency of 25 Hz against the stationary lower steel disks (AISI 52100 steel, Φ24 × 7.9 mm with hardness of about 620 HV). About 0.03 mL of lubricant was introduced to the ball−disc contact area by microsyringe and the friction coefficient was monitored continuously as a function of time by a computer connected to the Optimal-SRV-IV tester. The extreme pressure properties of the lubricants at room temperature (25 °C) and high temperature (200 °C) were also performed on the Optimal-SRV-IV reciprocation friction tester. The tests were set at a load ramp test from 50 to 1000 N stepped by 50 N and the test duration for each load was 3 min. After friction tests, the steel disks were cleaned ultrasonically several times in baths of acetone and were dried with pure nitrogen for surface analysis.

2.3.2. Friction Test at High Vacuum Conditions after Irradiation. Friction tests were performed on a self-made rotational ball-on-disk vacuum tribometer after irradiation. The fixed upper specimens were an AISI 52100 steel ball with standard 4 mm diameter, which was loaded against rotating stainless steel substrates. For space high/low temperature (170 and −120 °C) friction tests, the substrates were replaced by the steel disks (AISI 52100 steel, Φ24 × 7.9 mm with hardness of about 620 HV). All friction tests were conducted at rotational radius of 6 mm, sliding speed of 300 r/min, applied load of 5 N, and duration of 60 min under high vacuum (∼10^{-4} Pa). Each friction test was repeated three times under the same conditions in order to ensure repeatability.

2.4. Characterization and Analysis. Morphology of the solid nanoparticles were observed by FEI Tecnai F300 high-resolution transmission electron microscope (HRTEM) with an accelerating voltage of 300 kV. Fourier transform infrared (FTIR) spectra of the irradiated lubricants were recorded in the wavenumber range of 4000−500 cm^{-1} by Bruker IFS 66v/s Fourier transform infrared analysis (FTIR). The irradiated lubricants were coated homogeneously on a KBr wafer by scraper with roughness of 0.1 μm to obtain their FTIR spectra. Thermogravimetric analysis (TGA) of the lubricants before and after PR irradiation was carried out on a ZRY-2P TGA at a heating rate of 10 °C/min in flowing air.

Morphology of worn surfaces and wear volume of the substrates were measured by JEM-5600LV scanning electron microscope (SEM; JEOL, Japan) and a MicroXAM-3D surface mapping microscope profilometer, respectively. The composition of the worn surfaces was determined using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX; Oxford IE250 Energy Dispersive Spectrometer, EDS) under 20 kV accelerating voltage with 10 nA beam current, and the chemical states of the typical elements on the wear tracts were analyzed by a PHI-5702 multifunctional X-ray photoelectron spectroscopy (XPS) made by American Institute of Physics Electronics Company using Kα irradiation as the excitation source. The binding energies of the target elements were determined at a pass energy of 29.3 eV, with a resolution of about ±0.3 eV, using the binding energy of contaminated carbon (C 1s: 284.8 eV) as the reference. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) of the wear surfaces was carried out by a ION-TOF-SIMS IV instrument to understand the chemical composition, which used a Bi^+ pulsed ion beam of 30 keV energy scanning an area of 300 μm × 300 μm on the surfaces with a corresponding dose of 5.31 × 10^9 ions/cm^2.

3. RESULTS AND DISCUSSION

3.1. Physical Properties of the Lubricants Before and After Irradiation. Figure 2 shows the FTIR spectra of the lubricants with solid nanoparticles after irradiation. Compared with these FTIR spectra, it was found the appearance of some oxygen-containing functional groups including hydroxyl, carboxy, and carbonyl after AO irradiation, whose peaks are located at around 3375, 1710, and 1067 cm^{-1}, respectively. After EL and PR irradiation, all the spectra are quite similar, such as the absorption bands of C−H stretching of the alkyl chains on the MACs in the range of 2926−2850 cm^{-1} and the peaks of CH_2 scissoring vibration located at around 1465 cm^{-1},[41] and no new peaks are detected from the irradiated lubricants.

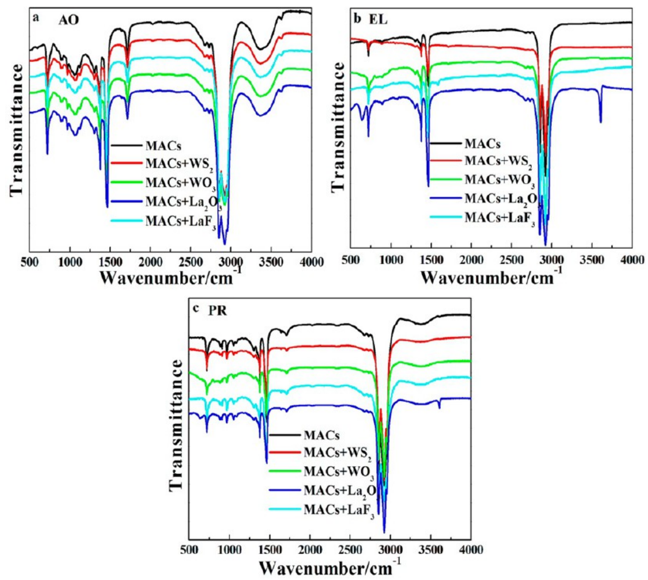

Figure 2. Fourier transform infrared analysis spectra of multialkylated cyclopentanes (MACs) with solid nanoparticles after (a) atomic oxygen (AO), (b) proton (PR), and (c) electron-beam (EL) irradiation.

TGA is a valuable and simple method in investigating the thermal stability and analyzing the presence of functional groups in materials. Figure 3 shows TGA curves of MACs with solid nanoparticles before and after PR irradiation and MACs with liquid additives before and after PR irradiation, as well as FTIR spectra of MACs with liquid additives before and after PR irradiation. Compared with TGA curves of MACs with solid nanoparticles before and after PR irradiation (panels a and b), it is observed that there is a slight decline in the beginning decomposition temperature after PR irradiation because PR irradiation caused partial destruction of MACs molecules. It is noted in Figure 3c that the liquid additives improve the thermal stability of MACs because ZDDP and MoDTC in MACs form the miscible systems and increase the decomposition temperature from 235 to 267 and 292 °C, respectively. Surprisingly, the lubricants after high-energy particles (PR) irradiation have a higher thermal stability than those before the irradiation probably because energetic particles make the atoms with relatively low binding energy in an excited and ionized state to reassemble into new molecule or be carbonized.[42−44]

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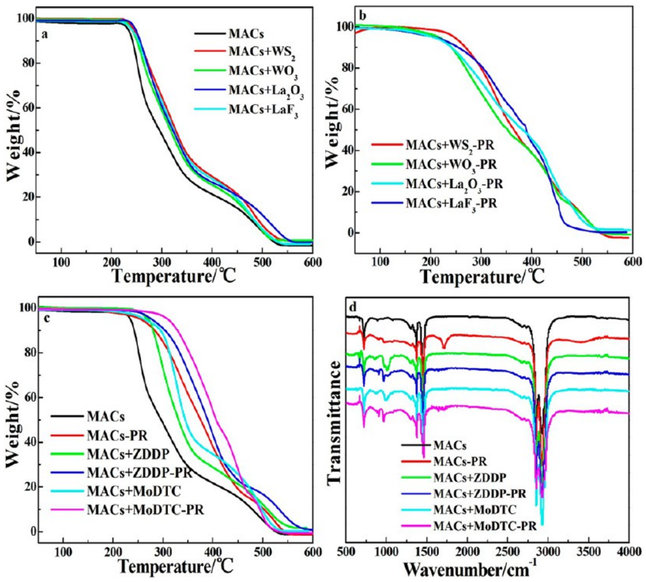

Figure 3. Thermogravimetric analysis (TGA) curves of (a) MACs with solid nanoparticles, (b) MACs with solid nanoparticles after PR irradiation and (c) MACs with liquid additives (ZDDP and MoDTC) before and after PR irradiation, as well as (d) Fourier transform infrared (FTIR) spectra of MACs with liquid additives before and after PR irradiation.

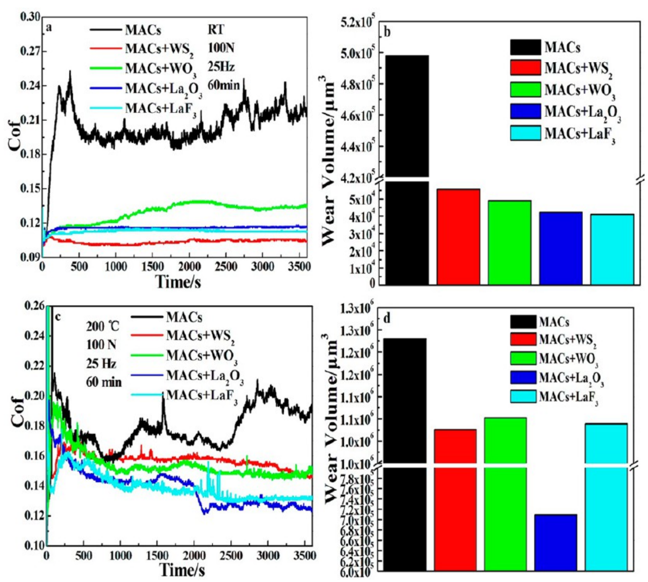

Figure 4. Friction curves (a, c) and wear volume (b, d) of MACs with solid nanoparticles at applied load of 100 N with room temperature (RT: 25 °C) and high temperature (HT: 200 °C).

3.2. Tribological Properties of the Lubricants. *3.2.1. Tribological Properties under Ambient Environment.* Figure 4 presents the friction curves and wear volume of the MACs with solid nanoparticles at applied load of 100 N and the frequency of 25 Hz under room temperature (25 °C) and high temperature (200 °C), respectively. As compared with pure MACs, addition of solid nanoparticles reduces friction and wear at room and high temperature, especially at room temperature, they can reduce friction coefficient by 48% from 0.21 to 0.11, and the wear volume (~4.9 × 10^4 μm^3) can be reduced about 1 order of magnitude as a comparison with MACs (~5.0 × 10^5 μm^3). Figure 5 displays the tribological behaviors of MACs with liquid

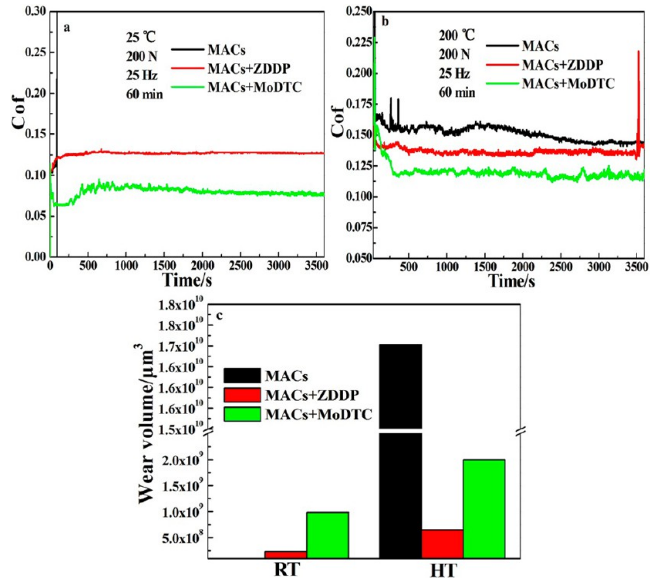

Figure 5. Friction curves (a, b) and wear volume (c) of MACs with ZDDP and MoDTC at applied load of 200 N with room temperature (25 °C) and high temperature (200 °C).

additives at applid load of 200 N and the frequency of 25 Hz under room temperature (25 °C) and high temperature (200 °C), respectively. The failure load of pure MACs at room temperature (25 °C) is 200 N, whereas MACs under high temperature (200 °C) can maintain a relatively stable friction coefficient (0.16). MoDTC provides lower friction coefficient (0.08 and 0.12 at 25 and 200 °C, respectively) than ZDDP, whereas ZDDP affords the lowest wear volume (2.38 × 10^8 μm^3 and 6.45 × 10^8 μm^3 at 25 and 200 °C, respectively) than MACs and MACs with MoDTC.

MACs can improve the tribological performance in the running-in stage and mild test conditions because they form a thin oil-film in the region of the rubbing surfaces, whereas the film could reach a limiting thickness and even damage with increase of temperature and applied load. In this case, the solid nanoparticles and liquid additives will improve the tribological behaviors through lubrication enhancement of solid nanoparticles and formation of tribo-chemical reaction film derived from ZDDP and MoDTC, respectively.[16,32] Under such harsh test conditions (high temperature and high applied loads), for example, solid nanoparticle acts as the third-body material between the surfaces for enhancing lubrication and preventing the direct contact of the mating surfaces.[17,45] Liquid additive could cause a tribo-chemical reaction and form a reaction film acting as a protective barrier that prevents the direct contact and adhesion between the sliding surfaces.[30]

Figure 6a gives the 3D topography of the worn surfaces lubricated by MACs with nanoparticles under high applied load of 100 N and high temperature (200 °C). It can be observed that the worn surfaces have small and narrow wear tracks with obvious bulges in the direction of the sliding that may be a protective film from the solid nanoparticles additives, whereas the worn surface lubricated by MACs shows deep and relatively wide wear track. Figure 6b shows the 3D topography of the worn surfaces lubricated by MACs with liquid additives under high applied load of 200 N, room temperature (25 °C), and high temperature (200 °C), respectively. The worn surfaces show remarkable difference at 25 and 200 °C in contrast to the pure MACs lubricated surface, and liquid additives significantly reduced

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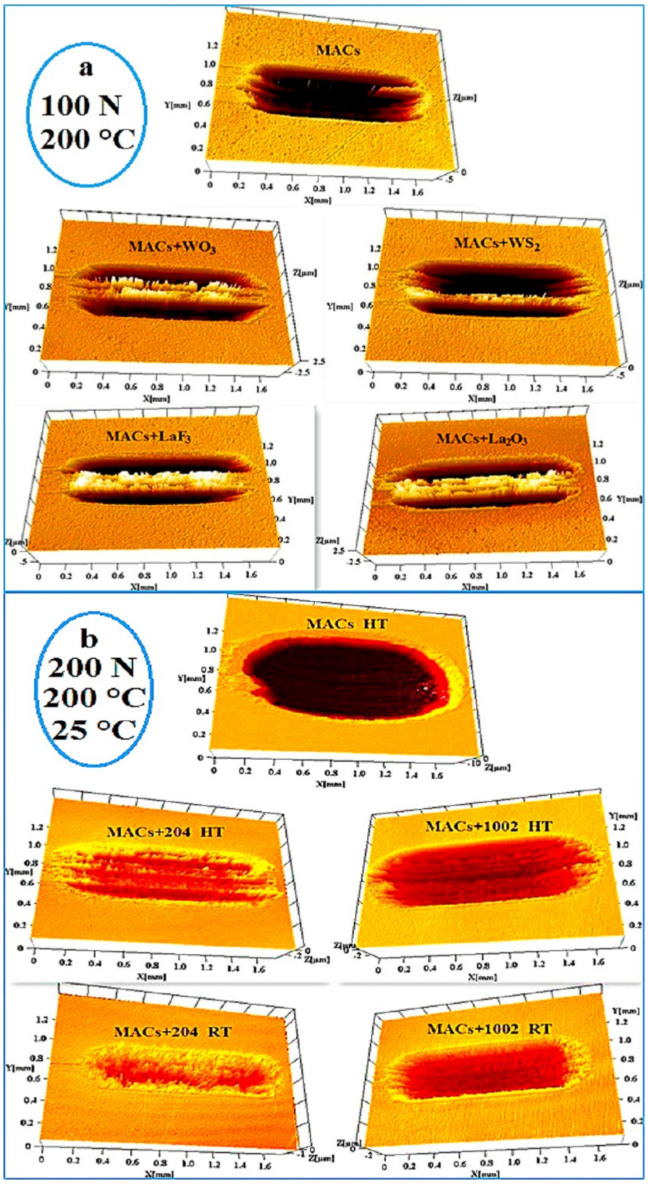

Figure 6. 3D topography of the worn surfaces (a) lubricated by MACs with nanoparticles at high temperature and that (b) lubricated by MACs with ZDDP and MoDTC at room temperature (RT: 25 °C) and high temperature (HT: 200 °C).

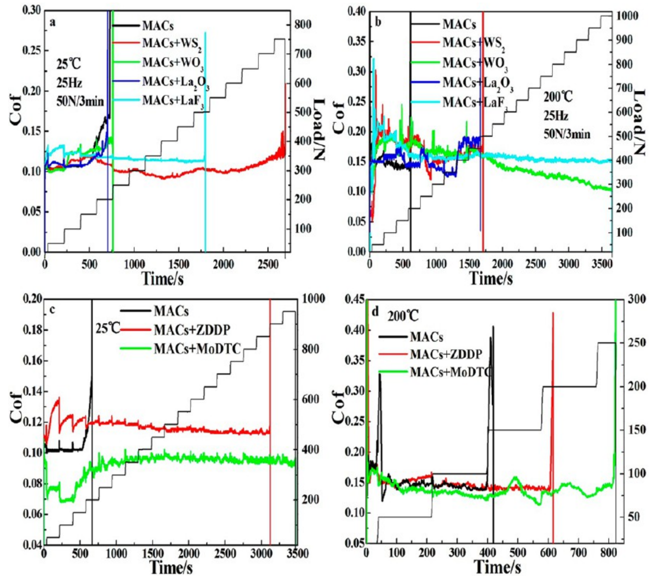

Figure 7. Extreme pressure properties of MACs with solid nanoparticles (a) at room temperature (25 °C) and (b) high temperature (200 °C), and those of MACs with ZDDP and MoDTC (c) at 25 °C and (d) at 200 °C.

the width and depth of worn tracks. Figure S1 in Supporting Information presents SEM images with 3D topography of the worn surfaces lubricated by MACs with nanoparticles at room temperature. It can be inferred that the nanoparticles deposit on the sliding surfaces and compensate for the loss, known as mending effect, and the roughness of the worn surfaces is improved by the nanoparticles, known as polishing effect.[45] Figure S2 in Supporting Information shows SEM images of the sliding surfaces lubricated by MACs with liquid additives under room and high temperature conditions. It can be observed that the worn surfaces lubricated by the liquid additives are smaller and smoother than that of MACs. These results indicate that the solid nanoparticles and liquid additives can improve the friction reducing and antiwear behaviors of MACs under room and high temperature.

Figure 7 displays the extreme pressure properties of the lubricants at the frequency of 25 Hz under room temperature (25 °C) and high temperature (200 °C). At room temperature, pure MACs fails at 200 N, whereas addition of WS_2 and LaF_3 enhances the load carrying capacity of MACs up to 750 and 500 N, respectively (Figure 7a). When the temperature is 200 °C, the improvement in load-carrying ability is more distinct. For example, WO_3 and LaF_3 always remain stable and low friction coefficient at applied load up to 1000 N (Figure 7b), which is attributed to the high thermal stability of solid nanoparticles and the formation of a nanoparticle-containing protective film on the sliding surfaces.[16−18] ZDDP and MoDTC additives can provide higher load carrying capacities than solid nanoparticles at room temperature. Figure 7c indicates that the load-carrying capacities of MACs with ZDDP and MoDTC are increased to 850 N and over 1000 N, respectively. However, the load carrying capacity of liquid additives at high temperature is not as good as that at room temperature (Figure 7d) because these two liquid additives could have resulted in thermal decomposition at a temperature over 160 °C and high applied load.[30] Therefore, the solid nanoparticles have good extreme pressure properties at high temperature, whereas the liquid additives are just the opposite.

3.2.2. Tribological Properties under High Vacuum Conditions. Figure 8 shows the space tribological properties of MACs with the solid nanoparticles after irradiation (AO, PR, and EL) at rotational radius of 6 mm, sliding speed of 300 r/min, applied load of 5 N under high vacuum. It can be seen that the friction curves of pure MACs and MACs with the nanoparticles nearly overlap, whereas the wear volume of MACs with the nanoparticles is significantly lower than that of pure MACs. This result illustrates that addition of the solid nanoparticles into MACs did not reduce the friction at applied loads of 5 N, whereas they significantly reduced the wear loss because the nanoparticles made a protective film through depositing and adsorbing on the sliding surface, which mend wear and protect the mating surfaces.

Figure 9 gives the friction curves and wear volume of MACs with liquid additives for the contacts of steel/DLC and steel/steel under simulated space environment. The friction coefficient (~0.06) and wear volume (~8×10^8 μm^3) of MACs with liquid additives reduce about 80% and 3 orders of magnitude than those

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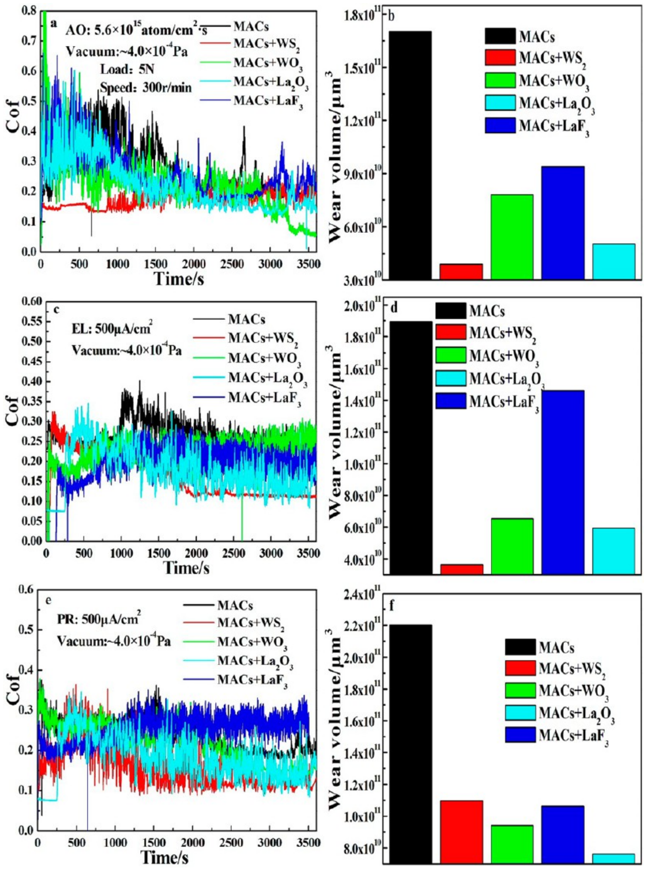

Figure 8. Friction curves and wear volume of MACs with the solid nanoparticles after stimulated space irradiation: (a, b) AO, (c, d) EL, and (e, f) PR.

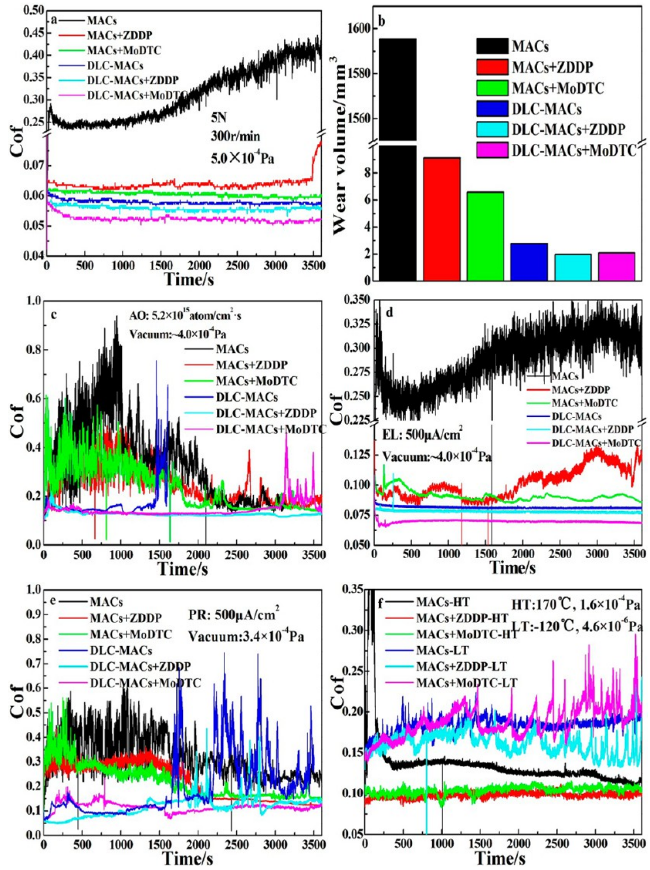

Figure 9. Friction curves (a) and wear volume (b) of MACs with ZDDP and MoDTC additives under high vacuum, their friction curves for the contact of Steel/Steel and Steel/DLC under simulated space environment: (c) under AO, (d) under EL, (e) under PR, and (f) under high/low temperature with high vacuum.

of pure MACs (0.3 and 1.596×10^{11} μm^3) for steel/steel contact under vacuum condition, respectively. Surprisingly, ZDDP and MoDTC provide the lowest friction and wear for steel/DLC contact than those for steel/steel contact under vacuum (Figure 9a,b). After AO and PR irradiation, the friction coefficients of MACs with the liquid additives reduce 50% for the contact of steel/DLC than those for the contact of steel/steel. In particular, DLC films with liquid additives present low and stable friction in the running-in stage (Figure 9c,e), and the lubricants after EL irradiation provide the excellent friction-reducing behavior for the contact of steel/DLC (Figure 9d). Electrons bombard the surface of MACs, and the kinetic energy and negative charge of the incident electrons can make the molecules of the lubricant in excited and ionized state, which strengthens the interactions between the lubricant and the substrate surface and significantly improves the tribological performance; high-energy protons with positive charge could further result in bond-breakage and cross-linking reactions of lubricant, thereby affect friction reduction. DLC is compelling because it significantly improves the friction reduction and wear resistance properties under boundary lubrication, especially addition of the liquid additives into MACs. The solid−liquid composite coatings consisted of MACs, liquid additives, and DLC films provide the lowest and most stable friction curves. Observing Figure 9f, the liquid additives give very stable and low friction coefficient (0.1) for the contact steel/steel under high temperature (170 °C) and vacuum condition (1.6×10^{-4} Pa), whereas their friction curves at low temperature (−120 °C) with high vacuum (4.6×10^{-6} Pa) are unstable because the viscosity and fluidity of MACs affect the tribology of the system. In such low temperature and high vacuum, the viscosity of MACs have been changed, which leads to poor fluidity and affects the renewal of the oil film, thereby affecting the lubrication performance of the system. When the lubrication system was heated above 160 °C, the thermal decomposition of the liquid additives occurred and generated actively intermediate products which can deposit or absorb on the worn surface and form the tribofilm including sulfide and phosphates.[30] In addition, DLC allows a more effective lubrication in the presence of the ZDDP and MoDTC through the formation of so-called "ZDDP and MoDTC tribofilm" on DLC films,[46] which provide remarkable friction reducing and antiwear properties through preventing direct contact and adhesion and cold-welding of the counterparts under harsh space conditions.[39,47]

3.3. Analysis of Friction Mechanism. Knowledge of the worn surface and understanding the substrate interaction with additives is of fundamental importance. Of primary interest in the worn surface is its composition. Figure S3 in Supporting Information presents the elemental distribution on the wear surfaces to obtain a deeper insight into the effect of the nanoparticles on the tribological performance. It is observed that the sliding surfaces make a protective film including W, S, La, and F elements from the additives as well as Fe from metal substrates, which could provide higher load-carrying ability and more effective separation of the sliding surfaces, and drastically

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improve the friction-reducing and antiwear performance. XPS spectra of O 1s, Fe 2p, La 3d, F 1s, W 4f, and S 2p on the wear tracks lubricated by MACs with nanoparticles at room temperature are shown in Figure 10 to further confirm the chemical state of these typical elements. The wide O 1s peak appearing at around 531.0 eV indicates that the worn surfaces have oxidation products. To further determine the type of generating products, XPS spectra of Fe 2p and La 3d were detected at 710.8 and 835.1 eV, respectively, making sure that Fe_2O_3 and La_2O_3 appear on the worn surfaces.[48] For the worn surface lubricated by MACs with LaF_3, the weak La 3d peak locates at 839.3 eV and the F 1s peak appears at 685.1 eV. Combined with the XPS spectrum of Fe 2p (located at 711.3 eV), it can be sure that LaF_3 nanoparticle occurred chemical reaction with Fe to form FeF_2 and LaOF during friction process because the binding energies of La 3d (836.7 eV) and F 1s (684.3 eV) in LaF_3 move toward higher values.[49,50] Two W 4f peaks on the track lubricated by MACs with WS_2 were detected at 32.8 and 35.1 eV, and the S 2p peak was detected at 162.4 eV, which is attributed to the presence of WS_2 on the worn surface.[51] For the track lubricated by MACs with WO_3, the W 4f peaks at 34.9 and 37.0 eV could be assigned to WO_3.[52] According to the XPS spectra of these typical elements, the formation of the lubricating protective film including FeF_2, La_2O_3, WS_2 and WO_3 on the worn surfaces can be confirmed. XPS analysis results confirm that the solid nanoparticles were piled up along the friction direction on the worn surface, which significantly improve the tribological performance.

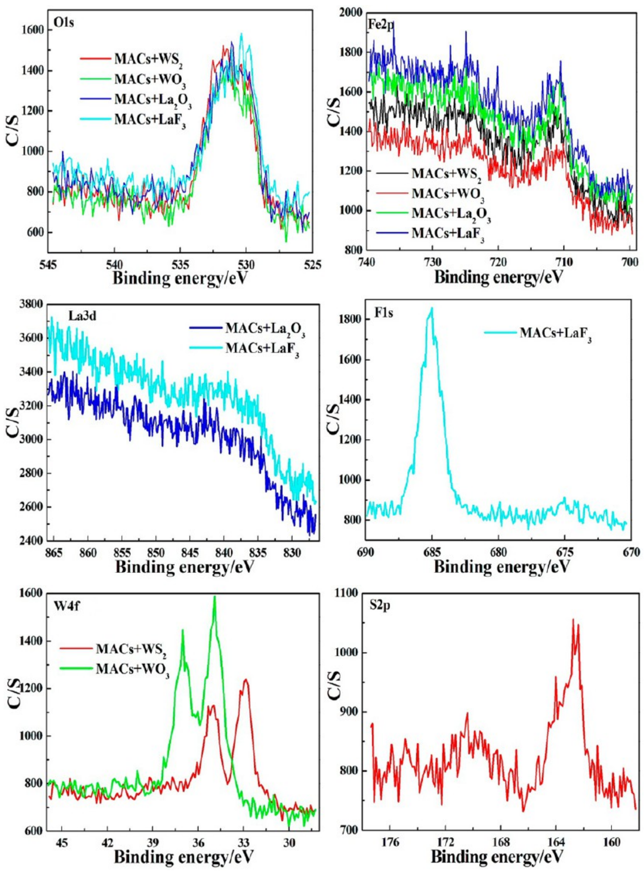

Figure 10. X-ray photoelectron spectra of the elements (O 1s, Fe 2p, La 3d, F 1s, W 4f, and S 2p) on the worn surfaces under lubrication by MACs with nanoparticles.

Figure S4 in Supporting Information gives EDX spectra with elemental composition of the worn surfaces under lubrication by the liquid additives at room and high temperature. It is confirmed that Zn, Mo, S, and P elements from the additives appear on the sliding surfaces. Figure 11 shows the XPS spectra of Fe 2p, O 1s, Mo 3d, S 2p, P 2p, and N 1s on the wear tracks lubricated by MACs with liquid additives at room temperature. Fe 2p peaks locate at between 710.8 and 712.3 eV, which may be attributed to iron compounds. The wide O 1s peaks appear at around 531.0 eV due to oxidation products.[53] The Mo 3d and S 2p peaks with very low intensity were detected at 232.6 and 169.2 eV, respectively, which suggests that molybdenum oxide and sulfates could be generated during friction, whereas MoS_2 with a Mo 3d binding energy of 229.0 eV has not been detected.[54] XPS spectra of other elements like P and N did not detect the corresponding characteristic peaks, and this may be because they have been eliminated during the cleaning procedure of the substrates.

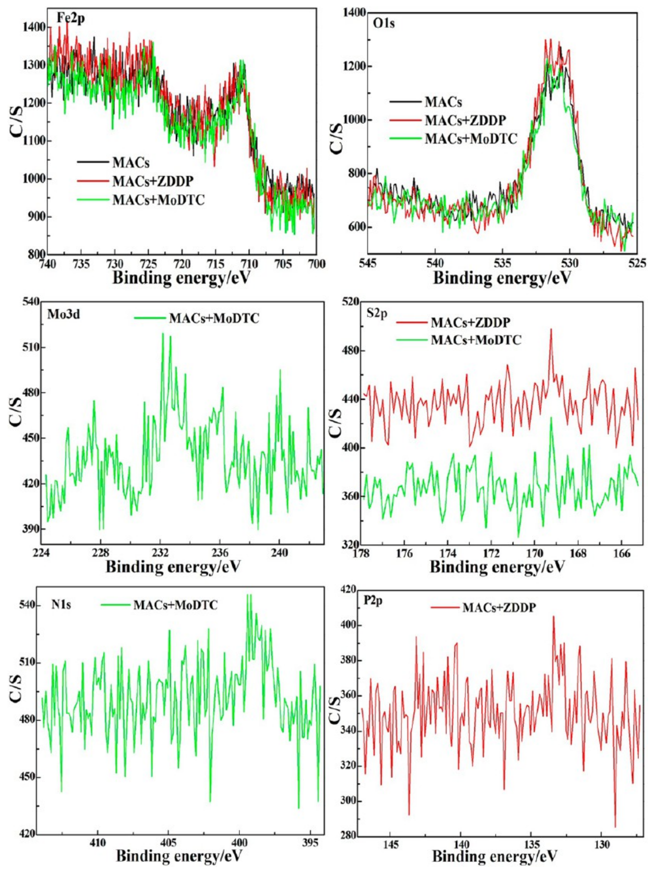

Figure 11. X-ray photoelectron spectra of the elements (Fe 2p, O 1s, Mo 3d, S 2p, N 1s, and P 2p) on the worn surfaces lubricated by ZDDP and MoDTC additives at room temperature.

In order to further understand the friction mechanism of the liquid additives, we used TOF-SIMS analysis because its sensitivity for a range of species is better than XPS.[55] Figure 12 gives the positive and negative ions TOF-SIMS spectra of the worn surfaces lubricated by MACs with ZDDP and MoDTC additives at room temperature, and Figure 13 gives TOF-SIMS spectra at high temperature. A variety of $C_xH_y^+$ ions coming from alkyl chains of MACs or the liquid additives have been identified in positive ions spectra of Figure 12 and 13, suggesting that some alkyl chains of the lubricant and additives have decomposed into shorter chains during friction. Positive ions including high

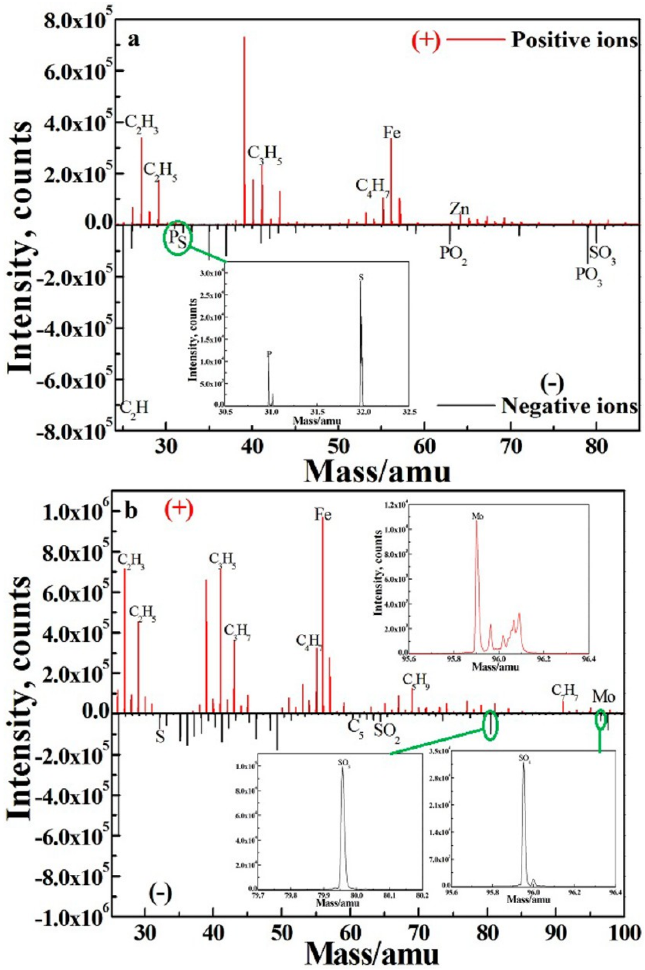

Figure 12. TOF-SIMS spectra of positive and negative ions derived from (a) ZDDP tribofilm and (b) MoDTC tribofilm on the worn surfaces at room temperature (25 °C).

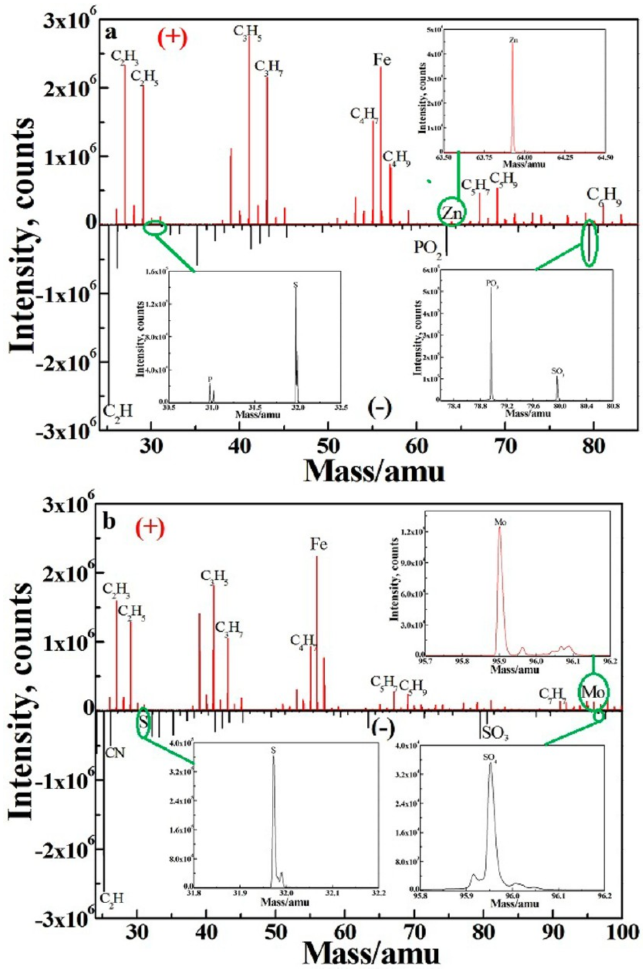

Figure 13. TOF-SIMS spectra of positive and negative ions derived from (a) ZDDP and (b) MoDTC tribofilm on the worn surfaces at high temperature (200 °C).

intensity Fe, low intensity Zn, and Mo have been detected in positive ions spectra. For the negative-ions TOF-SIMS spectra, several characteristic peaks have been indexed and been identified as sulfide (S), sulfates (SO, SO_2 and SO_3), and phosphates (PO_2 and PO_3) that derive from anionic moiety. Comparative analysis of the TOF-SIMS spectra reveals that tribochemical reaction can readily occur under high temperature according to the intensity of the negative and positive ions on the worn surfaces. Figure 14 shows the chemical images using the TOF-SIMS analysis from a selected area of the worn surfaces (300 μm × 300 μm) lubricated by MACs with liquid additives at room temperature, and the chemical images at high temperature are shown in Figure S5 of Supporting Information. Contents of the positive and negative ions in the chemical images are expressed as a comparison, a brighter area means higher concentration of the detected ion. The chemical images present a good correlation between positive and negative ions products on the worn surfaces. These TOF-SIMS spectra and chemical images suggest that the negative ions derived from anionic moiety can react with metal elements and generate a tribochemcial reaction film on the sliding surface for improving the tribological properties.

Taking into account XPS surface analysis of the worn surfaces lubricated by MACs with nanoparticles, we propose that good tribological properties of the solid nanoparticles are attributed to the surface enhancement effect because they can readily adsorb and stack on the sliding surfaces to mend wear and play a protective role. According to TOF-SIMS results, we conclude that such excellent tribological behaviors of ZDDP and MoDTC for the contacts of steel/steel and steel/DLC mainly depend on the formation of so-called ZDDP and MoDTC tribofilm composed of sulfide, sulfates, and phosphates. Therefore, the adsorption film of solid nanoparticles and tribochemical reaction film of liquid additives as the third body can prevent the mating surfaces from straight asperity contact, thereby enhancing load-carrying capacity as well as improving friction and wear behaviors.

4. CONCLUSIONS

Intensive efforts have been made to improve the tribological performance of MACs under ambient and simulated space environment and to understand the relevant friction mechanism. Combined with the results of friction experiments and the analysis of worn tracks by SEM-EDX, XPS and TOF-SIMS, the conclusions can be drawn as following:

(a) Solid nanoparticles exhibit good friction reduction and wear resistance behaviors as well as high load -carrying capacity under different testing conditions including room/high temperature, space irradiation, and vacuum. Especially, the wear resistance is more significant, mainly depending on the surface enhancement effect of the nanoparticles through

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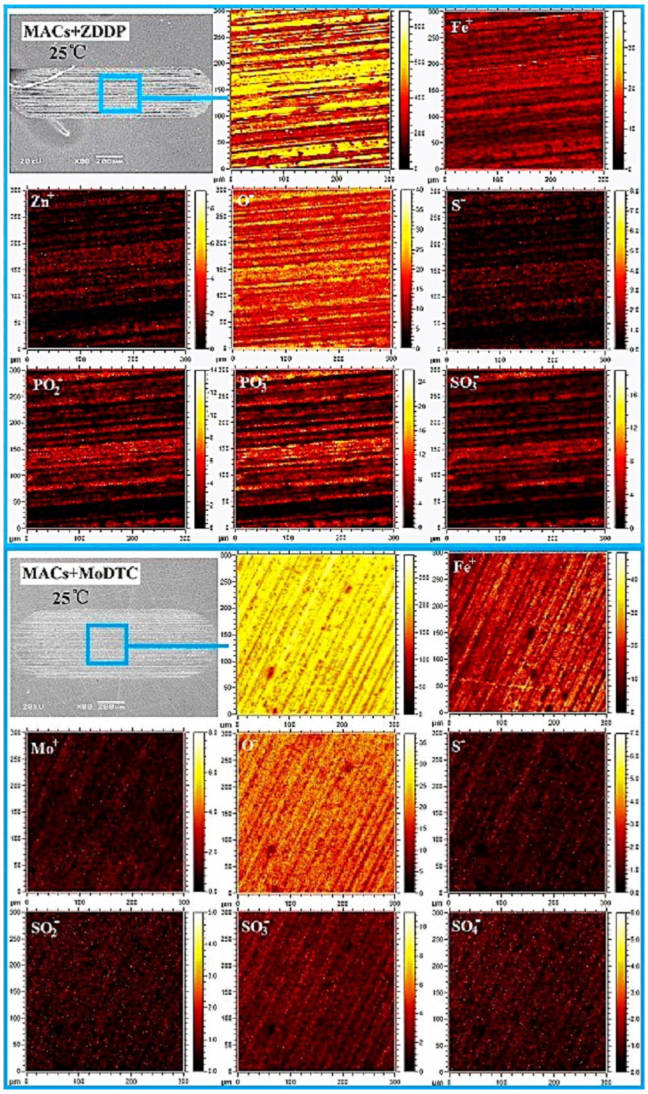

Figure 14. SEM images and 2D TOF-SIMS images of positive and negative ions from a selected area of the ZDDP and MoDTC tribofilm (300 μm × 300 μm) at room temperature (25 °C).

depositing and adsorbing on the sliding surface, thereby mending wear and protecting the mating surfaces.

(b) Liquid additives significantly improve the tribological performance of MACs under ambient and simulated space environment like EL irradiation, high temperature, and vacuum. Compared with solid nanoparticles, liquid additives have better friction-reducing and antiwear properties for the contact of steel/steel at low applied loads under simulated space environment.

(c) Boundary lubrication performance of DLC film can be greatly improved using MACs with ZDDP and MoDTC additives under the simulated space environment, especially in the running-in stage. Hence the synergistic effect of solid−liquid lubrication system will be a favorable choice for space tribology.

(d) The excellent tribological properties of the liquid additives are attributed to the formation of a tribofilm including sulfide, sulfates, and phosphates on the sliding surfaces, which provides more effective separation of the counterparts to reduce friction and wear.

■ ASSOCIATED CONTENT

Supporting Information

SEM images, elemental distributions, EDX spectra, and chemical images of the worn and sliding surfaces. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03088.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lpwang@licp.cas.cn. Tel:+86-0931-4968080.

Notes

The authors declare no competing financial interest.

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