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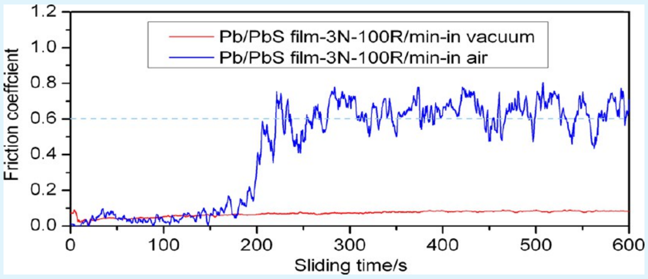
Excellent Vacuum Tribological Properties of Pb/PbS Film Deposited by Rf Magnetron Sputtering and Ion Sulfurizing

Ma Guozheng, Xu Binshi, Wang Haidou,* Chen Shuying, and Xing Zhiguo

National Key Laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, China



ABSTRACT: Soft metal Pb film of 3 μm in thickness was deposited on AISI 440C steel by RF magnetron sputtering, and then some of the Pb film samples were treated by low-temperature ion sulfurizing (LTIS) and formed Pb/PbS composite film. Tribological properties of the Pb and Pb/PbS films were tested contrastively in vacuum and air condition using a self-developed tribometer (model of MSTS-1). Scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were adopted to analyze the microstructure and chemical construction of the films and their worn surfaces. The results show that a mass of Pb was changed to PbS during the process of LTIS. In air condition, owing to the severe oxidation effect, pure Pb film showed relatively high friction coefficients (0.6), and Pb/PbS composite film also lost its friction-reduction property after sliding for a short time. In a vacuum, the average friction coefficients of Pb film were about 0.1, but the friction coefficient curve fluctuated obviously. And the Pb/PbS composite film exhibited excellent tribological properties in vacuum condition. Its friction coefficients keep stable at a low value of about 0.07 for a long time. If takes the value of friction coefficients exceeding 0.2 continuously as a criterion of lubrication failure, the sliding friction life of Pb/PbS film was as long as 3.2×10^5 r, which is 8 times of that of the Pb film. It can be concluded that the Pb/PbS film has excellent vacuum tribological properties and important foreground for applying in space solid lubrication related fields.

KEYWORDS: *RF magnetron sputtering, ion sulfurization, Pb/PbS composite film, vacuum tribological properties, solid lubrication*

INTRODUCTION

Lead sulfide (PbS) is a kind of important semiconducting material, which has a narrow band gap (0.41 eV) and large exciton Bohr radius (18 nm).[1,2] Because of its unique structure and properties, PbS is widely used in photoelectricity and temperature-sensing device, especially in sensors, detectors, and photoresistors that operating in infrared band.[3]

In normal conditions, the natural bulk and coarse-grained PbS crystallizes into rock-salt lattice with a B1 cubic structure,[4,5] its crystal planes can be cleaved along {100} orientation easily and form atomically flat surfaces.[6] According to the mechanism of solid lubrication, the crystal of PbS with low shearing strength may endow it excellent friction-reduction properties.[7] Actually, the tribological properties of PbS have already been studied by many researchers. Shuang Chen et al.[8,9] synthesized DDP-coated and oleic-acid-capped PbS nanoparticles, and added them into liquid paraffin (LP) as lubricating additives. The organic modified PbS nanoparticles can be dispersed equably in LP, and can reduce friction and wear effectively. In situ synthesis of PbS nanoparticles in lamellar liquid crystal (LLC) was also achieved by H.M.Yang et al.[10] They found PbS nanoparticles can improve the antiwear ability and extreme-pressure property of the Triton X-100/$C_{10}H_{21}OH/H_2O$ LLC system observably. A chemical reaction film composed of PbS, PbO etc. can be generated during friction, and thus reducing the friction coefficients remarkably. Zhao-Zhu Zhang et al[11] prepared PbS-filled PTFE composites and found the filling PbS particles can greatly reduce the wear of PTFE composite but also increase the friction coefficients. Luise Gudmand-Høyer et al.[12] designed a new material for automotive brake blocks, which mainly composed of PbS, Cu_2S, and Sb_2S_3, and found the lubricant PbS can modify and stabilize the friction of brake system effectively. However, until now, research on the lubricating properties of PbS is mainly about its function in fluid lubricants or composites, much less information about the direct application of PbS in the form of solid lubricating coatings/films has been available. There are various deposition methods available for PbS thin films, such as vacuum evaporation, electrodeposition, hydrothermal synthesis, and chemical bath deposition (CBD), and CBD is the most successful method to prepare PbS films.[13,14]

In the present work, a Pb/PbS composite film was prepared by RF magnetron sputtering and low-temperature ion sulfurizing (LTIS) technologies. The vacuum tribological properties of Pb/PbS film were investigated to explore its application foreground in space solid lubrication related fields.

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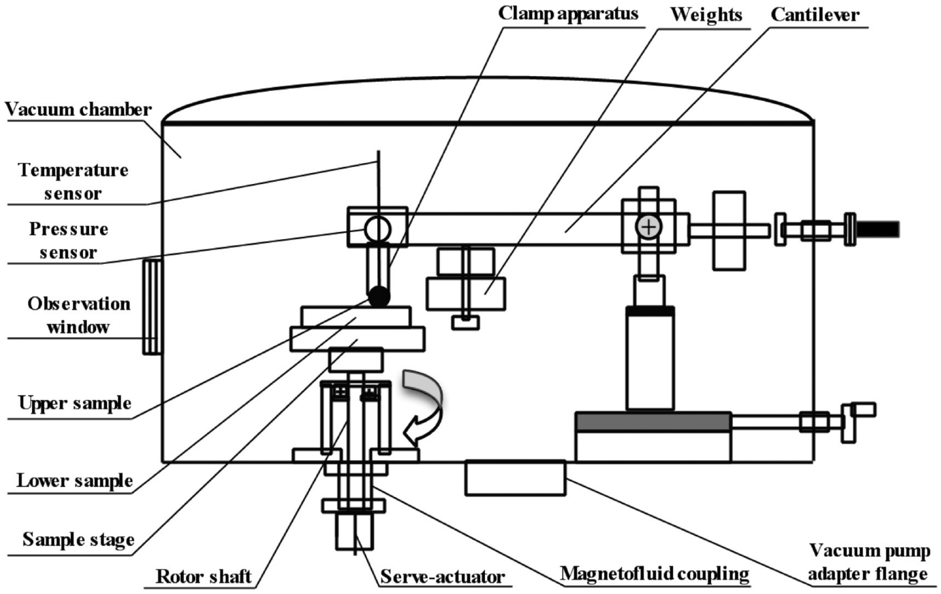


Figure 1. Schematic diagram of the MSTS-1 vacuum tribometer.

■ EXPERIMENTAL SECTION

The substrate materials for preparing films contained Q-tempered AISI 440C bearing steel and single-crystal silicon wafers (crystal orientation of 100), they were used for friction testing and microstructure characterizing, respectively.

First, a pure metal Pb film about 3 μm in thickness was deposited by RF magnetron sputtering technology. The substrates were placed 60 mm below the Pb sputtering targets (with a purity of 99.99%) and rotated with the sample holder at a speed of 5 r/min. When the base pressure was down to 5×10^{-4} Pa, introduced high-voltage and working gas Ar (99.999% purity) into the chamber to generate sputtering ion beam. Before depositing Pb film, the substrates were sputtered by Ar^+ ion beam for 15 min to remove surface oxide layer. The main processing parameters for sputtering Pb film are as follows: sputtering power of 30 W, deposition temperature of 120 °C, Ar flow of 90 sccm, and sputtering pressure of 0.2 Pa. Then some Pb film samples were treated by LTIS and formed Pb/PbS composite film. The details about the equipment and technology of LTIS can be found in refs 8. In the present work, the treat temperature and heat insulating time of the LTIS process were 230 °C and 2.5 h, respectively. After LTIS (sulfurizing) treatment, the samples were vacuum packed immediately.

The friction and wear tests were carried out in air and high vacuum (1×10^{-5} Pa) condition using a ball-on-disc vacuum tribometer (model of MSTS-1). Its schematic diagram is shown in Figure 1. In this work, the upper samples were AISI 440C steel balls with diameter of 9.525 mm, hardness of HRC58 and surface roughness of Ra0.032 μm. And the lower samples were the 440C steel discs coated with Pb or Pb/PbS composite films. First, normal load of 3 N and rotating speed of 100 r/min were fixed to investigate the variation of friction coefficients with sliding time of the two films (Pb and Pb/PbS composite films) during 600 s. Then, choosing the value of friction coefficients exceeding 0.2 in continual 5 s as a criterion of lubrication failure, the sliding friction lives of the two films were tested in condition of high vacuum, 6 N and 1000 r/min. As comparison, the original 440C steel substrate samples without films were also tested under the same condition. After wearing tests, 3D pattern of the wear scars were obtained using a laser scanning microscope (OLYMPUS), and wear loss of the samples were calculated approximately according to volume of the wear scars.

The Navo NanoSEM 450 type field emission scanning electron microscope (FESEM) equipped with energy dispersion spectrum (EDS, OXFORD Feature Max) was employed to characterize surface morphologies and composition of the two films. A TTR III type X-ray diffraction (XRD) was adopted to examine the phase constituents of the films. After sliding friction tests, the wear scars on the lower sample disks and upper sample balls were roundly analyzed by SEM, EDS, XRD, and X-ray photoelectron spectroscope (XPS).

■ RESULTS AND DISCUSSION

Microstructure Characterization of the Films. Figure 2 shows SEM images of the as-prepared and sulfurized Pb films.

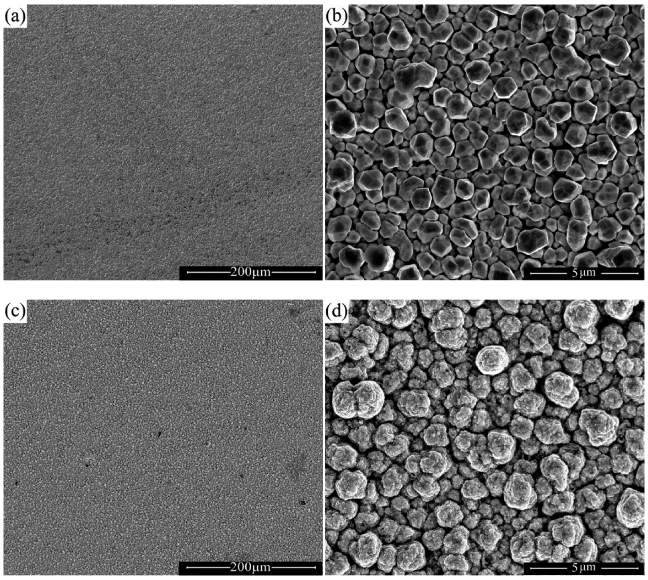
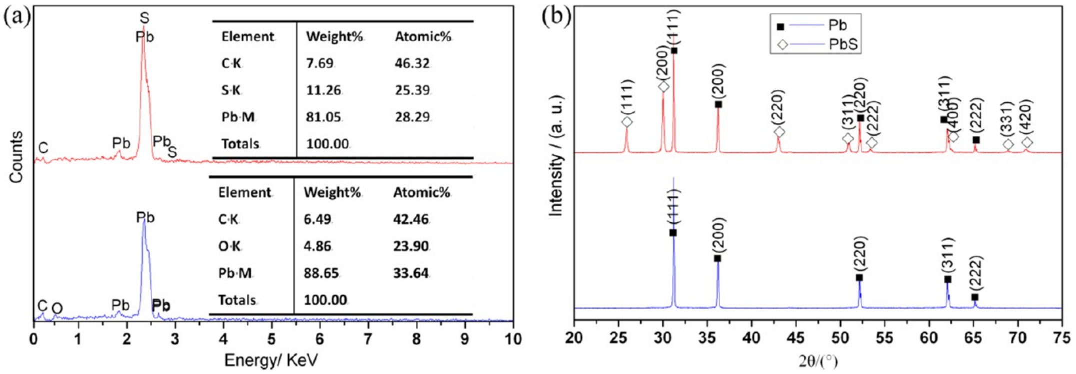


Figure 2. SEM imagies of the (a, b) original and (c, d) sulfurized Pb films.

It can be found that both of the two films composed of many fine particles. However, they are obviously different in microcosmic structure units. The original Pb film is heaped by regular polyhedron particles (particle size ranged from several hundred nm to 2 μm), and the particles with clear geometrical profile are self-existent with each other. In contrast with the original Pb film, the minimum structure units of the sulfurized Pb film are spherical nanoparticles, but most of them



Element	Weight%	Atomic%
C K	7.69	46.32
S K	11.26	25.39
Pb M	81.05	28.29
Totals	100.00	

Element	Weight%	Atomic%
C K	6.49	42.46
O K	4.86	23.90
Pb M	88.65	33.64
Totals	100.00	

Figure 3. (a) EDS spectra and (b) XRD pattern of the original and sulfurized Pb film.

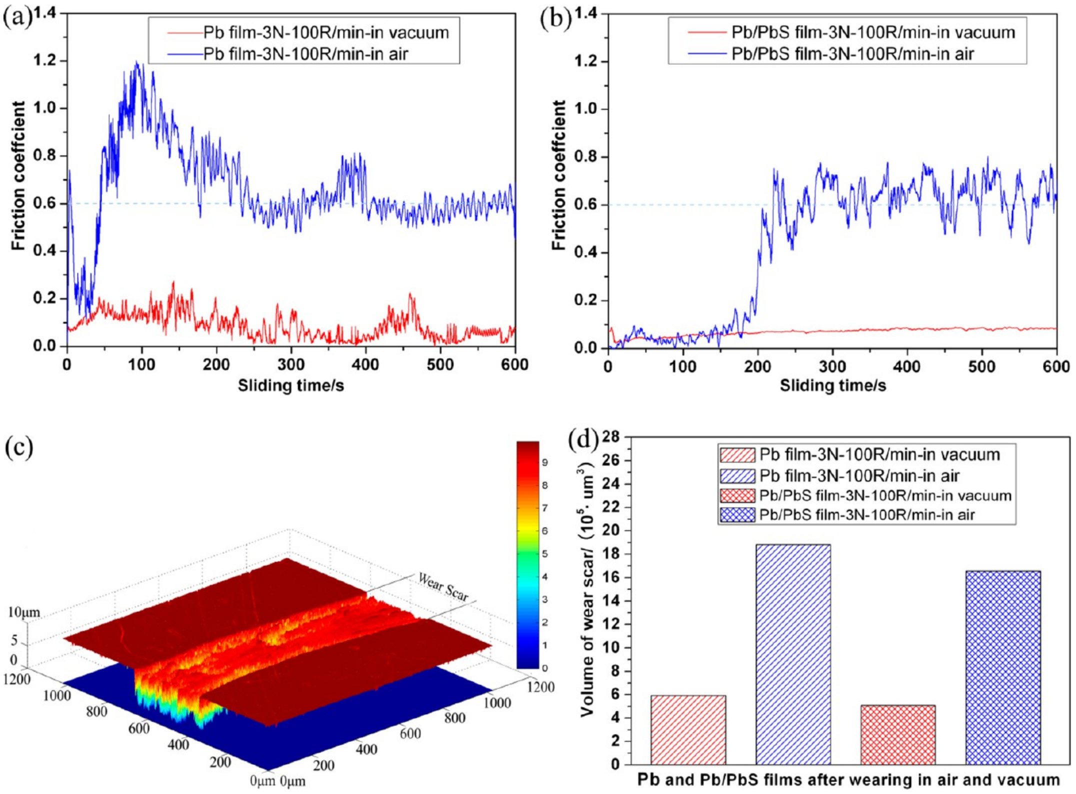


Figure 4. Comparison of tribological properties of the Pb and Pb/PbS composite films.

agglomerate with each other and form cauliflower-shape coarse grains. The change in microstructure of the Pb film after sulfurizing mainly resulted from etching effect of the ion beam and formation of the PbS nanoparticles during LTIS process.

Figure 3a shows the EDS analysis results of the original and sulfurized Pb films (p.s. The influence of carbon element can be ignored because EDS device is insensitive to light element.). It can be seen that the original Pb film is mainly made up of Pb and O elements. After sulfurizing, the peak of O element disappeared, while the content of S element increased remarkably. This is because the surface oxide layer on the Pb film was removed by ion bombardment, and the sulfide film may have a stronger oxidation-resistant property.[15]

As shown in Figure 3b, it can be seen from the phase structure analysis of the original and sulfurized Pb films that, both of the two films have high crystallinity. The original Pb film presented pure polycrystalline Pb, and the sulfurized film is mainly composed of crystal Pb and PbS. Previous study[16] had indicated that, when the supersaturation of S^{2-} in a system is low, the theoretic growth habit of PbS crystal is fcc structure. Actually, the diffraction peaks of PbS in the sulfurized Pb film are completely accordant with the standard spectrum (JCPDS 5−0592) of fcc PbS. The crystal structure of fcc PbS are symmetrical, it can be cleaved completely in various orientation and has very low shearing strength.[6]

Tribological Properties of Pb/PbS Composite Film. As is known to all, the soft metal Pb also has good lubricating properties. To examine whether or not the LTIS (sulfurizing) treatment induces damage to the friction-reduction property of Pb film, we tested tribological properties of the Pb film and Pb/PbS composite film in air and vacuum condition comparatively. Figure 4 shows the friction and wear properties of the two films.

As the pure Pb film wearing in air, the initial friction coefficients were relatively high; the friction coefficient curve then falls to a short (duration of 30 s) valley (about 0.2); and then it increased quickly and reached the peak value of 1.2 when sliding for 90 s; finally, the friction coefficient curve stabilized at about 0.6. The change regularity of the friction coefficient curve was mainly correlated with oxidizing of the lubricant (Pb). Surface layer of the pure Pb film was ineluctable to be oxidized when it was exposed to air, so its initiating friction coefficients were high. Then, the hard oxide layer was removed by sliding quickly, and the friction coefficients decreased accordingly. With the going on of sliding and increasing of friction temperature, the fresh metal surface would be oxidized and formed hard oxide particles again, and so the friction coefficients increased quickly. In the end, a recurrent state of "oxidation—softening—materials removal" was formed in the contact zone of Pb film, and the friction coefficient curve tended to be stable gradually. The friction coefficients of Pb film wearing in vacuum were very low (about 0.1 in stable period), though the friction coefficient curve still showed a fluctuation obviously.

It is different from pure Pb film in that the initiating friction coefficients of Pb/PbS composite film wearing in air were relatively low. The friction coefficient curve was kept below 0.1 in the first 200 s, and then it increased rapidly and fluctuated acutely. Finally, the value of friction coefficients also stabilized at about 0.6. Referring to the composition and phase analysis results (shown in Figure 3), oxygen and oxides in the Pb/PbS film were hardly detected. The two solid lubricants in the film, PbS and Pb, can provide good antifriction action. But the unreacted Pb in the Pb/PbS film would be oxidized continuously after the surface thin film was worn out, and the friction coefficients increased correspondingly. The Pb/PbS composite film showed excellent friction-reduction properties in vacuum; its friction coefficients were low (about 0.07) and stable during the entire testing time.

It can be seen from panels a and b in Figure 4 that, the friction coefficients of the two films wearing in vacuum were much lower than those in air. But in the same vacuum condition, the friction coefficient curve of Pb film fluctuated observably, whereas that of Pb/PbS composite film was low and stable.

Figure 4c shows the 3D pattern of the typical wear scars corresponding to Pb/PbS film after wearing in vacuum. And then, wear loss of the two films were calculated approximately according to volume of the wear scars, as shown in Figure 4d. It implied that wear rates of the samples were well accordant with the friction coefficient curves. Wear losses of the two films were remarkably affected by atmospheric pressure. Whether for Pb film or Pb/PbS film, the wear loss in vacuum was about 1/3 of that in air condition. The wear loss of Pb/PbS film was always less than that of Pb film tested in the same condition.

Figure 5 shows SEM morphologies of the above-mentioned worn surfaces. As shown in Figure 5a, the substrate sample (440C steel) suffered severe wearing damage, large-scale plastic deformation, and material removal; meanwhile, a lot of material accumulated at local area. The worn surface of Pb film after wearing in vacuum was relatively smooth. Because Pb has a good ability for plastic flow, the soft metal Pb in the contact zone was transferred to two sides of the wear tracks. The wear scar of the Pb/PbS film after wearing in vacuum was similar to that of the pure Pb film: lots of soft materials were transferred away from the wear track and left a clean worn surface. However, the worn surface of Pb/PbS film in air condition was relatively rough. There were not only some wide and deep grooves but also lots of debris on the wear scar. The severe wearing damage of Pb/PbS film in air condition may result from oxidization and the relevant increase in brittleness of the surface layer.

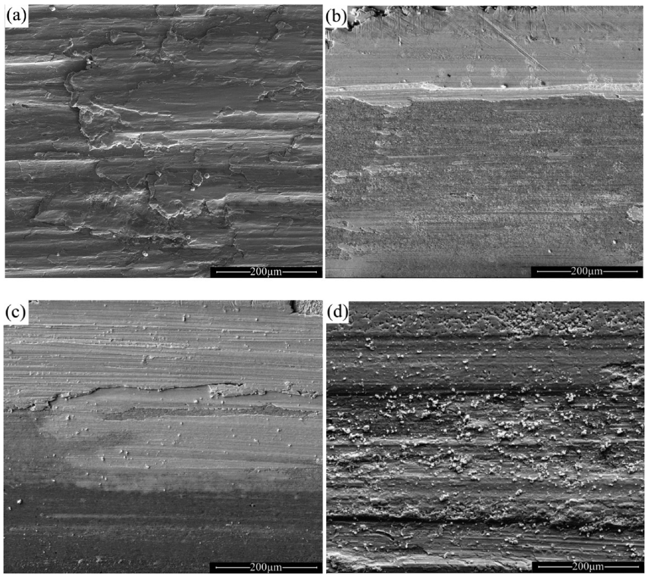


Figure 5. Morphologies of the worn surfaces: (a) substrate, in vacuum; (b) Pb film, in vacuum; (c) Pb/PbS film, in vacuum; (d) Pb/PbS film, in air.

To compare the endurance of the two films in vacuum environment, we tested the sliding friction lives of the two films in a condition of "high vacuum-6 N-1000 r/min". It can be found from Figure 6 that if the value of the friction coefficients exceeds 0.2 for a continual 5 s as a criterion of lubrication failure, the sliding friction life of the Pb film was about 4×10^4 cycles, whereas that of Pb/PbS film was as long as 3.2×10^5 cycles.

On the basis of the above results and analysis, it can be concluded that both of the two films have very short lubricating lives in air condition. In vacuum conditions, both of the two films exhibited much superior tribological properties, but the endurance of the Pb/PbS composite film in vacuum is about 8 times that of the pure Pb film.

Mechanism of the Excellent Tribological Properties of Pb/PbS Film in Vacuum. With the purpose to well-understand the internal mechanisms of the excellent tribological properties of Pb/PbS film in vacuum, the counterpart balls after wearing tests in air and vacuum condition were characterized contrastively.

Figure 7 shows the SEM morphologies of worn scars on the balls after testing in air and vacuum condition. After wearing in vacuum, the contact area on the ball was coated by transfer film tightly. Some parallel grooves resulted from relative sliding of the friction couple can be observed on the transfer film. The content of Pb and S elements was very high, and that of Fe and Cr elements was relatively low. Apparently, the transfer film can avoid direct contact between substrates effectively. The sliding just occurred between the lubricating film and transfer film, and thus showing very low friction coefficients when wearing in vacuum.

After wearing in air, some area of the ball was also covered by transfer film, but the central area of the worn scar had been scratched. Lots of debris distributed on the rough worn surface randomly. The content of Pb and S elements decreased observably, whereas that of Fe and Cr elements increased

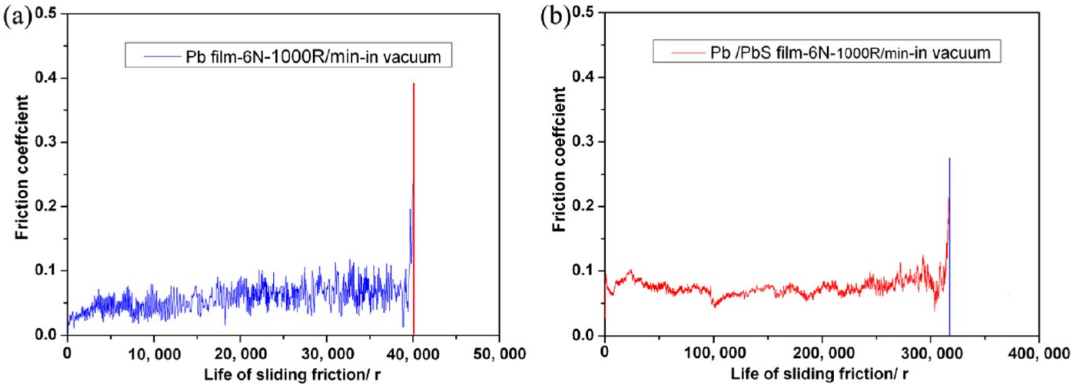


Figure 6. Comparison of effectual life of the (a) Pb and (b) Pb/PbS composite films.

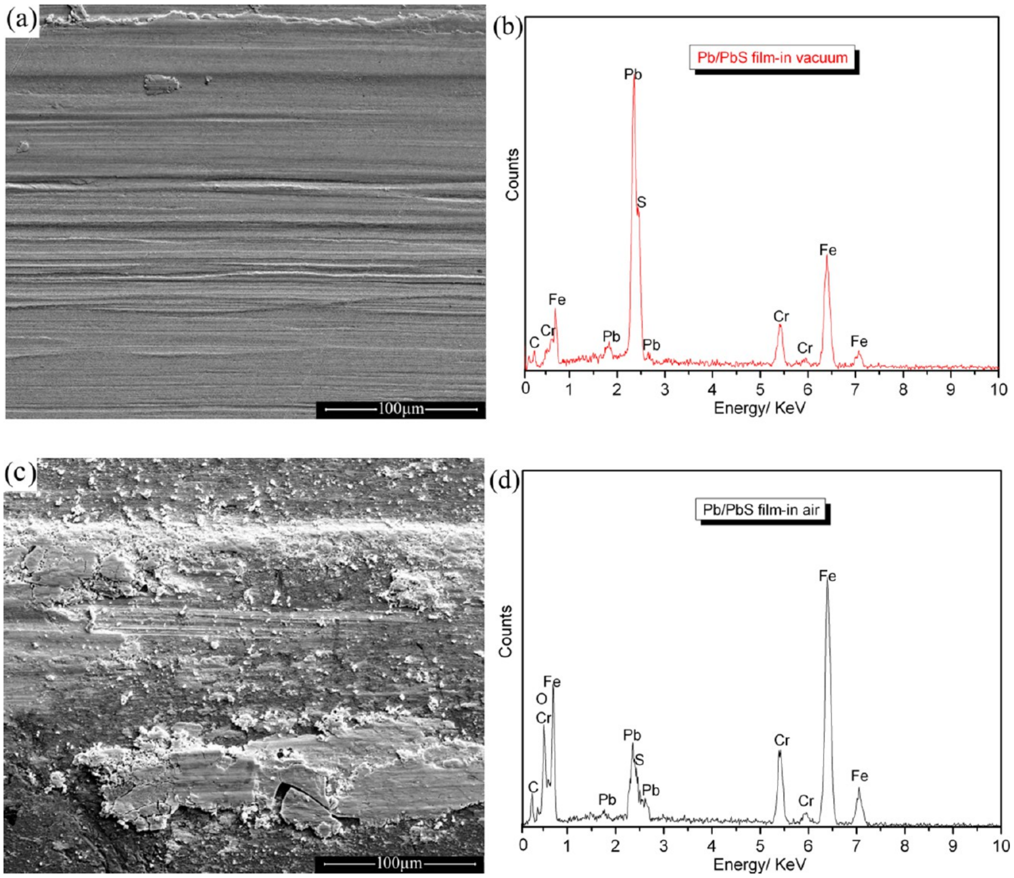


Figure 7. SEM images and composition of worn scars of the balls after sliding with Pb/PbS film: (a, b) in vacuum, (c, d) in air.

evidently. And it is worth noting that a high peak corresponding to O element appeared on the EDS spectrum. It can be concluded that the Pb/PbS composite film had been oxidized after wearing in air, and so its plastic deformation and adhesion properties were decreased accordingly. With the progressing of sliding in air condition, the content of S element decreased and O element increased on the frictional interface, the lubricating properties of Pb/PbS film degraded sharply, and so the friction coefficients increased rapidly after sliding for some cycles (as shown in Figure 4b).

As shown in Figure 8, the valence states of Pb and Fe elements on the counterpart balls after sliding with Pb/PbS composite film in vacuum and air were analyzed by XPS. After wearing in vacuum, the Fe element mainly existed in the form of elemental iron (electron binding energy is about 706.3 eV) and a little of Fe_3O_4. And there is also a peak corresponding to FeS, which may be generated from the reaction of sulfur in the transfer film with iron in the contact area. It is well-known that FeS with close-packed hexagonal structure is also a good lubricant, so the friction coefficients can keep low and stable under the coaction of Pb, PbS, and FeS. After wearing in air condition, the Fe element on the counterpart balls mainly existed in the form of several oxides and elemental iron, and the content of oxides was very high. All of this showed that serious oxidation occurred on the friction interface.

After wearing in vacuum, Pb element of the transfer film still existed in form of elemental lead and PbS. Comparatively, after wearing in air, the content of residual PbS and Pb was very low, and the Pb element mainly existed in form of oxides (Pb_3O_4, PbO_2, and PbO). Though PbO has excellent lubricating

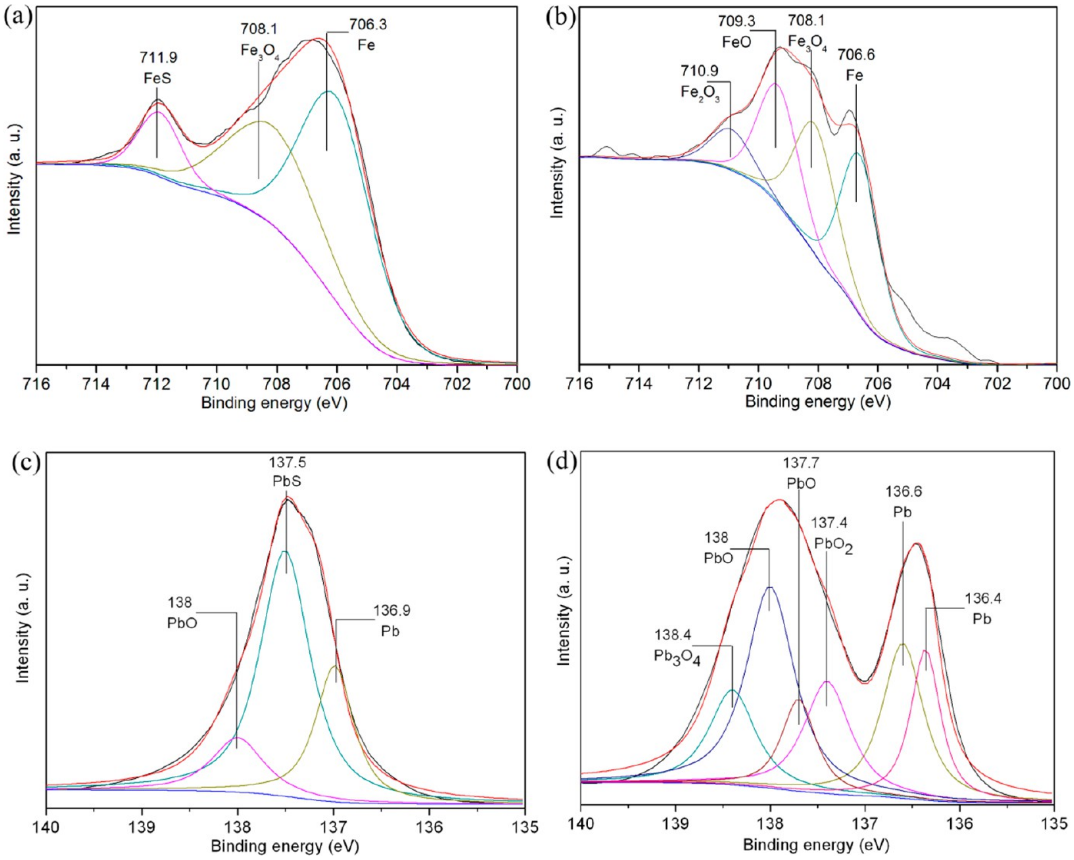


Figure 8. Valence states of Fe and Pb elements in worn scars after wearing in air and vacuum: (a) XPS Fe2p spectra, in vacuum; (b) XPS Fe2p spectra, in air; (c) XPS Pb4f spectra, in vacuum; (d) XPS Pb4f spectra, in air.

properties at high temperature (above 400 °C),[17] its lubricity is very poor at room temperature. In the present test condition, the friction-reduction properties of Pb/PbS composite film were damaged badly by oxidation.

On the basis of the above discussion, it can be concluded that the Pb/PbS composite film will be oxidized severely and form a mass of hard oxides when wearing in air. Consequently, the adhering and lubricating properties of the film decreased. Hence, the tribological properties of Pb/PbS film will be destroyed by oxidation obviously after wearing in air. In vacuum condition, oxygen is very rarefied and the friction temperature is relatively high. The soft Pb/PbS film can form continuous and compact transfer film onto the counterpart ball quickly. And a new lubricant (FeS) can be generated during wearing to achieve synergy lubrication by multiple lubricants. So the Pb/PbS composite film showed outstanding tribological properties in vacuum condition.

■ CONCLUSIONS

First, using RF magnetron sputtering technology prepared a Pb film with uniform and compact microstructure. And then a Pb/PbS composite film was obtained by the succeeding treatment of low-temperature ion sulfurizing.

When wearing in air, both of the pure Pb film and Pb/PbS film were severely oxidized and lost their friction-reduction properties gradually. In vacuum condition, Pb/PbS composite film exhibited outstanding tribological properties, the friction coefficients in stable period were about 0.07. If the value of friction coefficients exceeds 0.2 continually as a criterion of lubrication failure, the sliding friction life of Pb/PbS film was as long as 3.2×10^5 r in vacuum, which is 8 times of that of the pure Pb film. The wear loss of Pb/PbS film after wearing in vacuum was about 1/3 of that in air condition.

The excellent tribological properties of Pb/PbS composite film in vacuum can be mainly attributed to the following aspects: the soft Pb/PbS film can form continuous and compact transfer film onto the counterpart ball quickly; the crystal structure of PbS is absolutely symmetrical and can be cleaved along {100} planes completely; the active sulfur can react with iron in the contact area of frictional mates to generate FeS, and so achieving synergy lubrication of multicomponent.

The Pb/PbS composite film with excellent tribological properties in vacuum condition is promising to be used in space solid lubrication and other related fields.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wanghaidou@aliyun.com.

Author Contributions

Authors Xu Binshi, Wang Haidou, Chen Shuying, and Xing Zhiguo contributed equally to this work.

Notes

The authors declare no competing financial interest.

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