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# Tribological Behavior of WS<sub>2</sub>-based Solid/Liquid Lubricating Systems Dominated by Surface Property of WS<sub>2</sub> Crystallographic Planes

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## Abstract

In this paper, the WS<sub>2</sub>-based solid/liquid systems were established successfully by combining pure WS<sub>2</sub> film with FCPSO (trifluorinated-propyl and chlorinated-phenyl with methyl terminated silicone oil) and SiCH (silahydrocarbons) space oils, and the tribological performances and mechanisms were investigated. The results showed that the tribological properties of the WS<sub>2</sub> film were improved greatly as associated with the SiCH oil, and hence this composite system exhibited a low/stable friction coefficient (<0.08) and durable wear life (>3×10<sup>6</sup> sliding cycles) both in vacuum and air environments. However, a reverse effect was obtained from the WS<sub>2</sub> film/FCPSO system. The selective adsorption of WS<sub>2</sub> crystallographic planes with the specific oil seemed to dominate the tribological performances of the composite systems. The SiCH and FCPSO oils have different affinity with the base and edge planes, respectively, as composited with the WS<sub>2</sub> film. The combination of WS<sub>2</sub> base plane with SiCH was more advantageous to form perfect lubricating and transfer films at the friction contact area, resulting in the improved friction and wear performances. This result pay a significant way for us to design the solid/liquid lubricating system based on the lamellar solid lubricants.

## 1. Introduction

Up to now, solid and liquid lubrication, as the traditional and principal technologies, are used to deal with tribological problems in the space mechanisms, whereas, each

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has specific disadvantages.<sup>1,2</sup> Novel lubrication systems with lower friction and wear are needed to meet the new frontier of space mechanisms<sup>3-5</sup>. It has been proved that combining liquid and solid lubricants on sliding tribological surfaces may be effective to reduce friction and wear, especially under the boundary lubricating condition.<sup>6-14</sup> In this field of research, the solid lubricants are mainly focused on hard materials (such as DLC, Si<sub>3</sub>N<sub>4</sub>, ZrO<sub>2</sub>, etc.), as the high hardness is beneficial for improving the load capacity of composite systems.<sup>9,13,15</sup>

Sputtered films of transition metal disulfides, typical for MoS<sub>2</sub> and WS<sub>2</sub>, have been widely used in the space technology due to the low friction coefficient in vacuum,<sup>15-21</sup> but the wear life is limited because of the porous columnar microstructure. The sputtered WS<sub>2</sub> film was characterized by a duplex-layer microstructure. The dense lower layer exhibits a basal plane orientation, while the porous upper layer predominantly has an edge plane orientation.<sup>17,18,22</sup> Due to the anisotropy of WS<sub>2</sub> crystal in the mechanical property, the base-plane oriented layer has a better load capacity, while the edge-plane oriented layer fractured easily in the process of sliding friction.<sup>23-25</sup> It was suggested that the tribological properties of the sputtered WS<sub>2</sub> film should be improved by compositing with liquid lubricants.

However, it is very notable for lamellar crystal solids like WS<sub>2</sub>, MoS<sub>2</sub> and graphite. The basal and edge planes have different surface properties.<sup>26,27</sup> The basal plane has a relatively low polarity and surface energy. On the contrary, the edge plane is polar and volatile for the existence of dangling and unsaturated bonds, along with a much higher surface energy.<sup>24</sup> Previous studies revealed that as MoS<sub>2</sub> and graphite were mixed with different solvents,<sup>28,29</sup> the difference in the surface property between the crystallographic planes can result in an interesting selective adsorption phenomenon to minimize the potential energy of these systems. Comparatively, the non-polar basal plane areas preferentially adsorbed weak polarity hydrocarbon chains especially for long methylene chains, while the polar edge sites independently adsorbed polar compounds.<sup>26,27,29-34</sup> Therefore, it is reasonable to speculate that the distribution, wettability and the bond conditions of the oils at the WS<sub>2</sub> film surface should be different as they were composited. That may lead to the different friction

and wear behavior. In the present work, two specific liquid lubricants with distinct polarity and structure, FCPSO (trifluorinated-butyl and chlorinated-phenyl with methyl terminated silicone oil) and SiCH (silahydrocarbons), both of which have been successfully used in space mechanisms and they were selected to composite with the sputtered WS<sub>2</sub> films, and the friction and wear behavior of both composite systems were deeply investigated.

## 2. Experimental detail

### 2.1. Preparation of WS<sub>2</sub>-based solid/liquid lubrication system

The two solid/liquid lubrication systems were fabricated by compositing the RF-sputtered WS<sub>2</sub> films with the FCPSO and SiCH oils respectively.

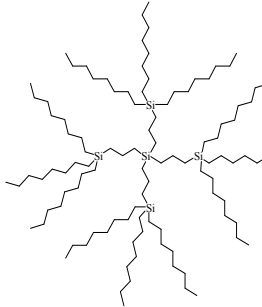
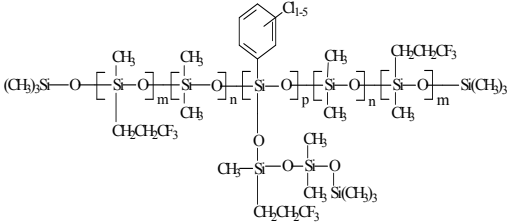
Firstly, the pure WS<sub>2</sub> films were deposited on AISI 440C steel and commercial n-type Si (100) substrates using a WS<sub>2</sub> target (80 mm in diameter, 99.9% purity) by a RF sputtering system, which were respectively used for the tribological and structural analyses. Before the deposition, the AISI 440C (Ø25 mm × 4 mm) substrates were polished to a surface roughness ( $Ra$ ) ≤ 0.03 μm and then cleaned with alcohol and acetone ultrasonically for 10 min in sequence. when the chamber vacuum was evacuated to a base pressure below  $1.0 \times 10^{-3}$  Pa, the substrate surfaces were etched by an Ar plasma for 10 min at a DC bias of -500 V to eliminate possible contaminants. Afterwards, the WS<sub>2</sub> films were sputtered under a target power density of 0.062 W·mm<sup>-2</sup>, a substrate bias voltage of -30 V and an Ar pressure of 3.0 Pa. The deposition duration was 15 min. During the deposition, the substrate was statically placed opposite to the target, and the vertical distance between the target and substrate surfaces was 60 mm.

Secondly, the SiCH and FCPSO were coated on the pre-deposited film surfaces by a spin coating method, respectively. The WS<sub>2</sub>-based solid/liquid lubrication system was composed of an upper oil layer with a thickness about 20 μm and an under WS<sub>2</sub> layer with a thickness about 3 μm. The thickness of oil film was evaluated as following: Firstly, the mass ( $m_1$ ) of the disk was measured by analytical

balance with accuracy of one over ten-thousand, then we used a manual microinjector to add several drops of oil to the middle of the WS<sub>2</sub> film surface. Secondly, the oil was spread by spinning the disk for 30 min with a rotational speed of 1000 rev/min. In this process, a part of oil would be thrown away from the disk for centrifugation. After the spinning, the excess oil on the edge of disk was removed by wiping with a silk cloth. And then, the mass ( $m_2$ ) was weighed again. Therefore, the pure mass of the oil spread on the surface of WS<sub>2</sub> film was  $m$  ( $m=m_2-m_1$ ). And the volume of the oil was calculated by the formula:  $v=m/\rho$  (where  $v$  is the volume,  $m$  the mass, and  $\rho$  the density of oil). It was approximately thought that the oil film was evenly spread out in the film surface, then the thickness of oil film could be evaluated:  $h=v/s$  (where  $h$  is the thickness,  $v$  the volume, and  $s$  is the bottom area of disk).

Then, the WS<sub>2</sub>-based solid/liquid composited lubrication systems were successfully formed for follow-up tests. The SiCH and FCPSO oils were synthesized by the State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, suitable for space applications due to the extremely low volatility, high viscosity index, wide running temperature, low pour point and excellent lubrication property,<sup>35-37</sup> and their typical properties are listed in Table 1.

**Table 1** Typical properties of SiCH and FCPSO oils

	SiCH	FCPSO
Average molecular weight	872	9000
Molecular structure		
Viscosity at 40°C/mm <sup>2</sup> ·s <sup>-1</sup>	97	109
Viscosity at 100°C/mm <sup>2</sup> ·s <sup>-1</sup>	17.0	34.0
Viscosity index	194	350

Density at 20°C/kg·m <sup>-3</sup>	842.5	1113.0
Vapor pressure at 20°C/Pa	2.7×10 <sup>-7</sup>	3.1×10 <sup>-9</sup>

## 2.2. Friction and wear tests

The friction and wear tests for the composited systems were carried out by a ball-on-disk tribometer in vacuum (lower than 5.0×10<sup>-3</sup> Pa) and atmospheric environment (30% RH, 20±5 °C). The tribological properties of the pure WS<sub>2</sub> film and oils were also tested for comparison. The upper specimens were the cleaned AISI 440C steel balls (HRC~60, Ra~0.10 μm) of 8 mm in diameter, loaded against rotating discs with a normal load of 3 N. The rotational speed was 1000 rev/min for all tests, corresponding to a linear speed of 0.52 m/s. Each friction test was repeated three times under the same conditions. After the friction tests, the wear track profiles were analyzed by a non-contact 3D surface profiler (AD Corporation, Massachusetts, USA), and then the wear rates ( $W$ ) were calculated by the formula:

$$W = \frac{V}{F \cdot L}$$

where  $V$  is the wear volume,  $F$  the normal load, and  $L$  the total friction distance.

The theoretical minimum film thickness ( $h_{min}$ ) and its ratio with roughness ( $\lambda$ ) were calculated using Eq. (1) and Eq. (2). The calculated  $\lambda$  parameter was 0.263 for WS<sub>2</sub>/SiCH and 0.403 for WS<sub>2</sub>/FCPSO which state that the lubrication regime for the two lubrication systems were boundary lubrication ( $\lambda < 1$ ). The surface roughness of WS<sub>2</sub> film deposited on disk  $Ra$  was about 0.5 μm measured by 3D surface profiler. The load of 3 N resulted in an initial average Hertzian contact stress ( $P_0$ ) about 0.25 GPa and theoretical contact radius ( $\alpha$ ) about 0.75×10<sup>-4</sup> m calculated by Eq. (3) and Eq. (4).

$$\frac{h_{min}}{R'} = 3.63 \left( \frac{U\eta_0}{E^*R'} \right)^{0.68} (\alpha E^*)^{0.49} \left( \frac{w}{E^*R'^2} \right)^{-0.073} (1 - e^{-0.68k}) \dots (1)$$

$$\lambda = \frac{h_{min}}{\sqrt{\sigma_1^2 + \sigma_2^2}} \dots (2)$$

$$P_0 = \left( \frac{6WE^*}{\pi^3 R'^2} \right)^{1/3} \dots (3)$$

$$\alpha = \left( \frac{3WR'}{4E^*} \right)^{1/3} \dots(4)$$

where  $R'$  is the reduced radius of curvature,  $U$  is the entraining surface velocity,  $W$  is the normal load,  $E^*$  is the reduced Young's modulus,  $\eta_0$  is the dynamic viscosity,  $\alpha$  is the pressure–viscosity coefficient,  $\sigma_1$  is the surface roughness of ball and  $\sigma_2$  is the surface roughness of lower disk.

### 2.3. Characterization

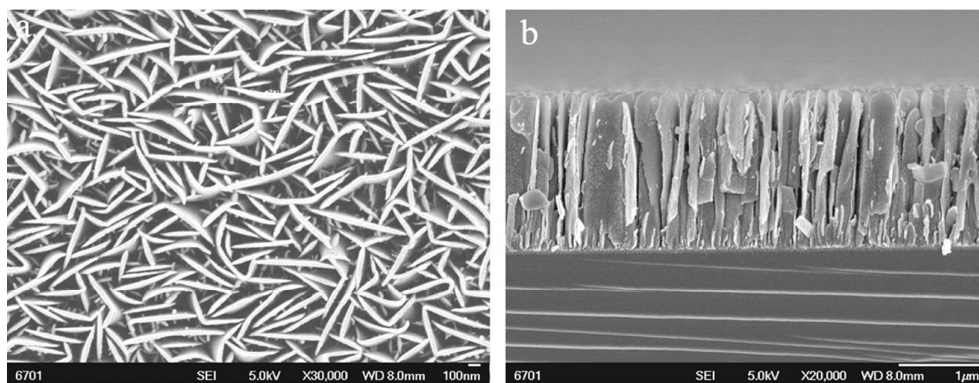
The morphology of  $WS_2$  film was observed by a JSM-6701F field emission scanning electron microscopy (FESEM). After the friction tests, the structure of oils was analyzed by the IFS 66v/s Fourier transformation infrared spectroscopy (FTIR). The morphology and composition of the worn surfaces were examined by the JMS-5600L JEOL scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). Before the characterization, the steel balls were ultrasonically cleaned for 5 minutes in proper solvents. The wear debris for the composited systems after the vacuum friction tests were collected and rinsed, and then examined by the JEM-1200EX/S transmission electron microscopy (TEM).

## 3. Results and discussion

### 3.1. Structure of sputtered pure $WS_2$ film

The structure of studied  $WS_2$  film has been investigated systematically and reported in elsewhere.<sup>17, 18, 25</sup> It can be characterized by a duplex layer structure, common for the sputtered  $MoS_2$  film,<sup>22, 38</sup> and the typical surface and cross-sectional FESEM micrographs were shown in Fig. 1. The lower was a dense and coherent layer (about 100 nm) near the interface of film and substrate, where the crystallites were normally characterized by a basal plane oriented growth. The upper was a loose columnar platelet layer with a predominantly edge plane oriented growth. This structure was a zone 2 morphology based on the Thornton's structure zone model.<sup>39</sup>

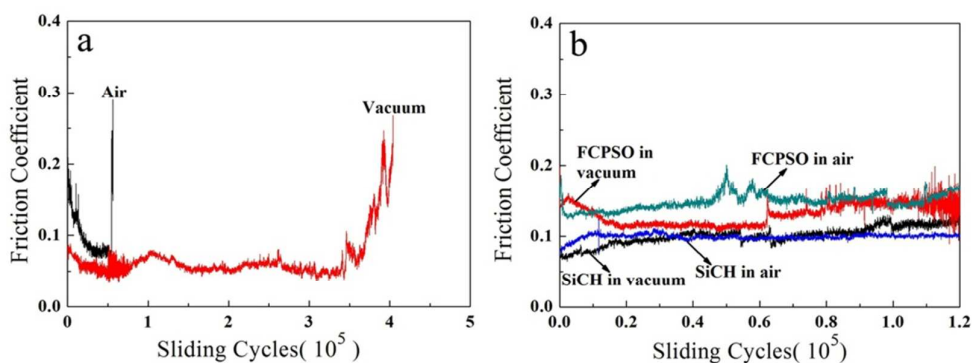




**Fig. 1** FESEM micrographs of RF-sputtered WS<sub>2</sub> film: a. surface and b. cross-section

### 3.2. Friction and wear performances

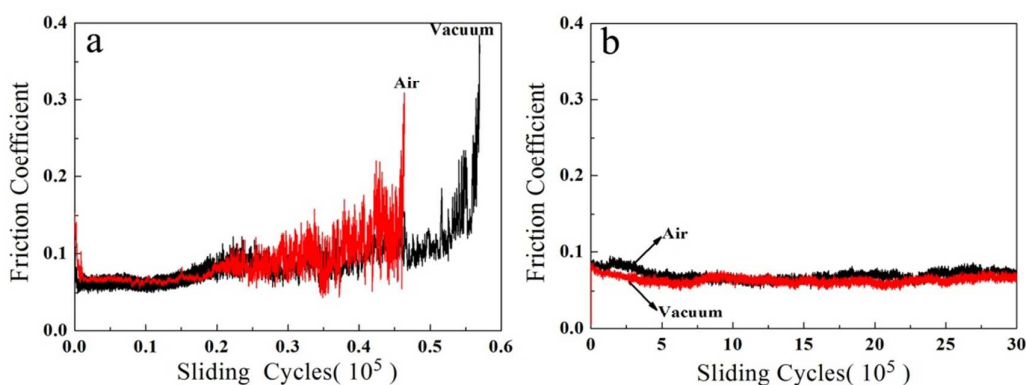
Fig. 2a shows the typical friction curves of the pure WS<sub>2</sub> films under air and vacuum conditions. The wear life was defined as the sliding cycles before the friction coefficient exceeding the value of 0.25. Clearly, for the WS<sub>2</sub> film the tribological properties were better in vacuum than in air. In vacuum, the friction coefficient was low and stable, and the wear life was much longer. The mean friction coefficient and wear life were 0.09 and  $\sim 4.1 \times 10^5$  r in vacuum, and 0.12 and  $\sim 0.56 \times 10^5$  r in air. The deterioration of the tribological properties mainly resulted from the oxidation process of O<sub>2</sub> or H<sub>2</sub>O in ambient for the existence of unsaturated or dangling bonds at the WS<sub>2</sub> edge planes.<sup>22</sup> The lubricating properties of both FCPSO and SiCH oils for the steel/steel test pair were investigated comparatively and the typical friction curves of  $1.2 \times 10^5$  cycles were shown in Fig. 2b. The mean friction coefficients in vacuum and air conditions were  $\sim 0.13$  and 0.15 for FCPSO, and both  $\sim 0.10$  for SiCH, respectively.





**Fig. 2** Friction curves: a. pure  $WS_2$  film in vacuum and air, b. liquid lubricants under steel/steel contacts in vacuum and air

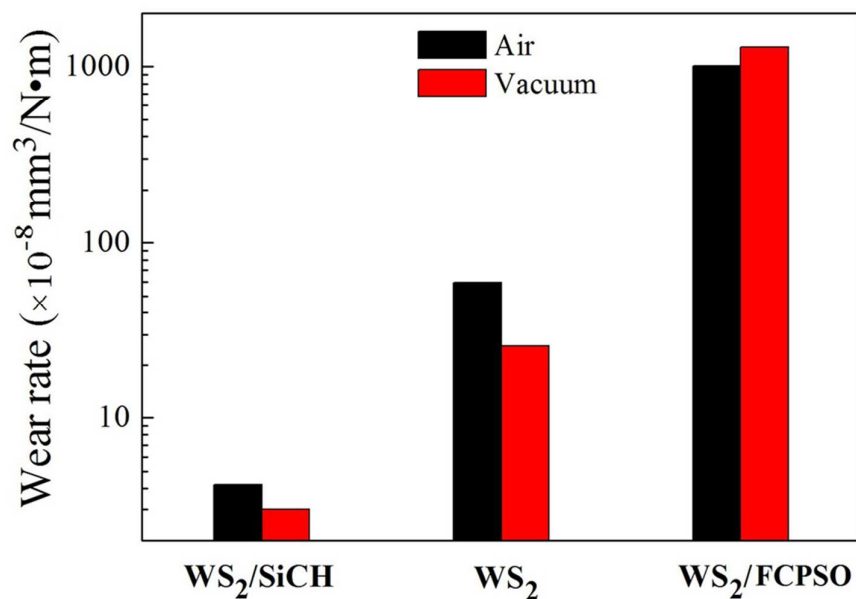
Fig. 3 shows the typical friction curves of the  $WS_2/FCPSO$  and  $WS_2/SiCH$  lubrication systems in vacuum and air. For the  $WS_2/FCPSO$  lubrication system (see in Fig. 3a), both in air and vacuum, the friction coefficients were relatively stable only in the beginning stage, and then became fluctuant and high until the lubrication failures after the sliding cycles of  $0.46 \times 10^5$  and  $0.57 \times 10^5$  in air and vacuum, respectively. For the  $WS_2/SiCH$  lubrication system (see in Fig. 3b), the friction coefficient was as low as 0.06 and kept stable either in vacuum or air even as the sliding had been lasted up to  $30 \times 10^5$  cycles, which was obviously superior to the former.



**Fig. 3** Friction curves of solid/liquid lubrication systems in vacuum and air: a.  $WS_2/FCPSO$ ; b.  $WS_2/SiCH$

The wear rates of the  $WS_2$  film,  $WS_2/FCPSO$  and  $WS_2/SiCH$  lubrication systems were shown in Fig. 4. In comparison, the  $WS_2/SiCH$  lubrication system exhibited a very well wear resistance both in vacuum (the wear rate was about  $3.0 \times 10^{-8} \text{ mm}^3/\text{Nm}$ ) and air (about  $4.2 \times 10^{-8} \text{ mm}^3/\text{Nm}$ ). However,  $WS_2/FCPSO$  lubrication system exhibited a poor wear resistance both in vacuum (the wear rate was about  $1286.6 \times 10^{-8} \text{ mm}^3/\text{Nm}$ ) and air (about  $1009.3 \times 10^{-8} \text{ mm}^3/\text{Nm}$ ). The wear rates in both vacuum and air increased in the following order:  $WS_2/SiCH < WS_2 < WS_2/FCPSO$ . In summary, to combine the  $WS_2$  film with only suitable oil can generate a synergistic lubrication effect and result in the improved tribological property. Therefore, it was noticed that the selection of oils should be careful, because the opposite action could be obtained from the different composite systems, such as  $WS_2/SiCH$  and  $WS_2/FCPSO$ . For

different lubrication conditions, the friction and wear results were summarized in Table 2 and Fig. 4.



**Fig. 4** Wear rates of the solid/liquid lubrication systems and pure WS<sub>2</sub> film

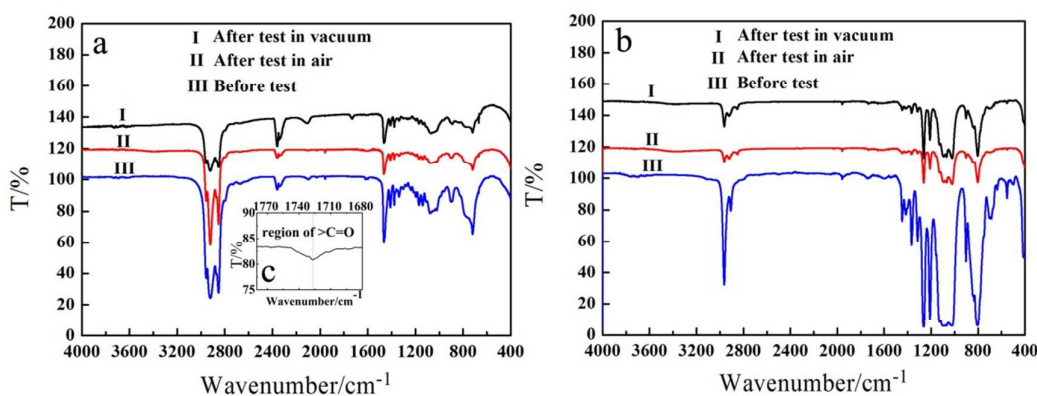
**Table 2.** Mean friction coefficient of the oils, WS<sub>2</sub> film and their composite systems in vacuum and air environments

	FCPSO (Steel/Steel)	SiCH (Steel/Steel)	WS <sub>2</sub>	WS <sub>2</sub> /FCPSO	WS <sub>2</sub> /SiCH
Vacuum	0.13	0.10	0.09	0.09	0.06
Air	0.15	0.10	0.12	0.09	0.07

### 3.3. Friction and wear mechanism

Fig. 5 gives the analysis results of the FTIR spectra of SiCH and FCPSO before and after friction tests. The oils for FTIR analysis after the friction tests were collected from the wear track surfaces of composite systems. There were no obvious structure changes for FCPSO after the friction tests in both vacuum and air as well for SiCH in air. Only for SiCH in vacuum, it was found that a new characteristic peak of C=O at  $1726 \text{ cm}^{-1}$  appeared after the tribotest, suggesting that an oxidative polymerization process might be generated under this condition.<sup>40</sup> The more specific scanning of this new peak from  $1780 \text{ cm}^{-1}$  to  $1680 \text{ cm}^{-1}$  was showed as an inset in Fig. 5c. However,

the carbonyl was not detected even after the sliding of  $20 \times 10^5$  cycles in vacuum for SiCH. Therefore, it can be concluded that this structure change of SiCH in vacuum was not mainly responsible for the vacuum friction and wear behavior of the  $WS_2/SiCH$  system. No oxidative polymerization detected for SiCH after test in air condition seems to be the reason that the nascent steel surfaces were absent under high oxygen atmosphere, which could afford a key catalysis action for this process.<sup>40</sup>

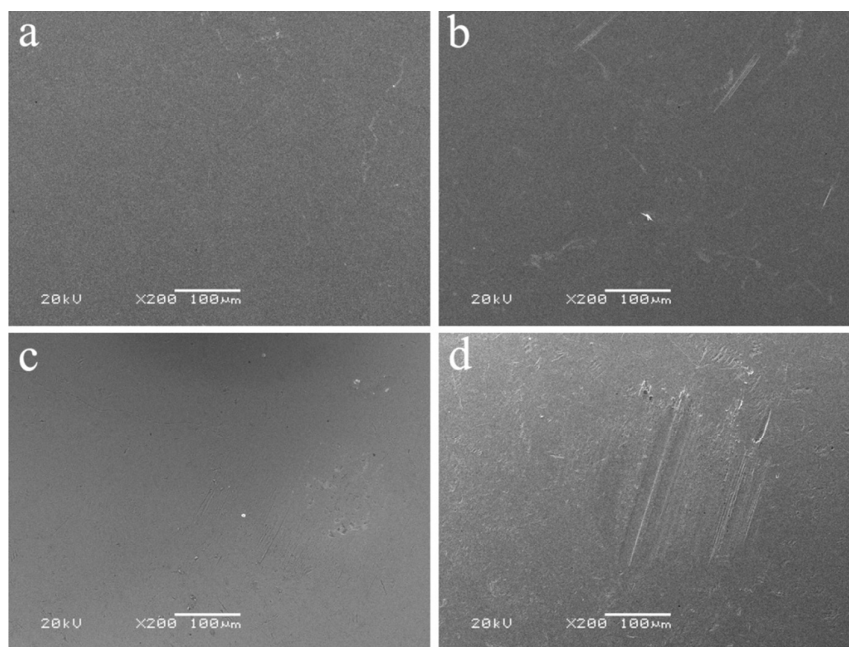


**Fig. 5** The FIRT spectra of liquid lubricants before and after the tribotests: a. SiCH, b. FCPSO, c. specific scanning of SiCH after test in vacuum

During the friction process, the FCPSO oil might produce many Si-containing or O-containing species with the strong polarity under the repeated shearing of the loaded pressure, which should have preferential affinity with the edge sites of the  $WS_2$  film. However, there are many long hydrocarbon chains in the structure of SiCH molecules, such as octyl or decyl groups, which would be preferentially adsorbed with the basal plane of  $WS_2$  film. In the beginning of friction process, the upper  $WS_2$  columnar platelets were cracked under the shearing action,<sup>16</sup> and then a plenty of  $WS_2$  fragmentation would be mixed with the liquid lubricant to form an upper lubrication layer. In this stage, the mixed layer seems to mainly afford the effective lubrication. That's why the relatively low and stable friction coefficients were shown up in the initial stage for the two systems. The duplex lubricating layers, composed of the upper mixed layer and lower thin  $WS_2$  denser layer, were firstly established.

As the sliding continued, the selective adsorption could occur when the oil sufficiently contacted with the  $WS_2$  fragmentation. Obviously, the oil layer would

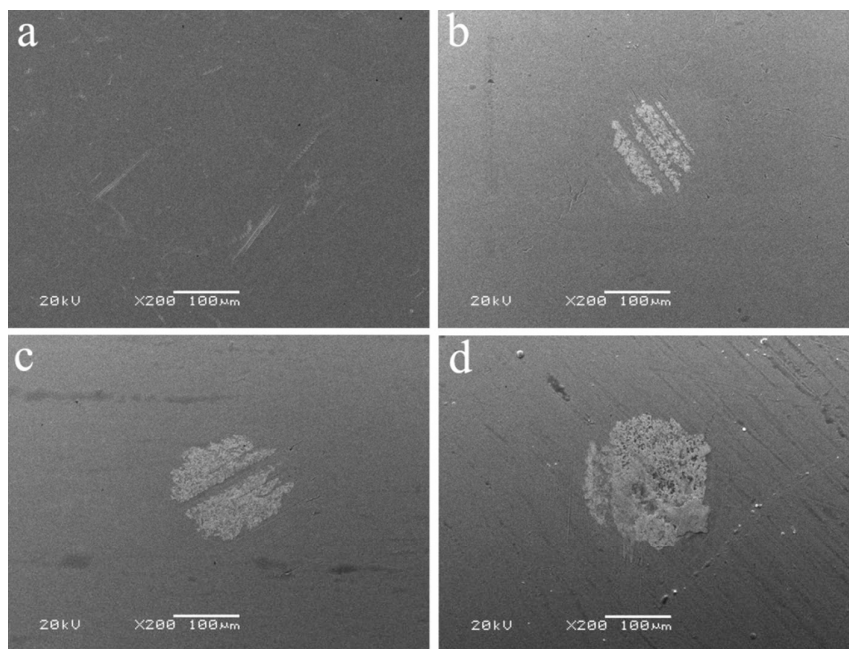
firstly occupy the surface of the counterpart ball due to its low surface energy. Thus, the transferring action of  $WS_2$  film to counterpart ball may be sensitive to the selective adsorption. In order to confirm this surmise, the friction tests with different sliding cycles were implemented, and then the morphology and chemical composition of the wear tracks and wear scars on the counterpart ball were analyzed in detail. Figs. 6 and 7 as well as Table. 3 and 4 show the SEM images and EDS results of the wear scars on the steel balls for the  $WS_2$ /FCPSO and  $WS_2$ /SiCH systems after different vacuum sliding cycles, respectively. For  $WS_2$ /FCPSO system (Fig. 6 and Table. 3), no obvious wear scar were observed by SEM and element weight percent ( wt % ) of W and S were detected from the steel ball surface after  $0.1 \times 10^5$  cycles, indicating that the oil may play an important role in the relative low and stable friction in the beginning sliding stage. Afterwards, the W and S elements were detectable from the friction contact areas on the steel ball surfaces and the contents increased with the sliding cycles, but still limited (the highest sum of W and S contents  $\leq 4$  at.%). Therefore, the effective transfer film of  $WS_2$  was not observed even after the lubrication failed, except for some scratches were observed from the wear scars. However, for the  $WS_2$ /SiCH system, the morphology and composition of the wear scars was quite distinct from that of  $WS_2$ /FCPSO. The wear scar was smooth and the signal of W and S elements were not detected by EDS analysis until the sliding cycles higher than  $0.5 \times 10^5$  cycles, indicating that the sliding cycles of SiCH were longer than that of FCPSO when the lubrication was mainly provided by the oil composited with the  $WS_2$  films. Afterwards, the transfer film was observed clearly and became more and more continuous and dense as the sliding cycles increased (Fig. 7b, 7c and 7d), accompanied by a relatively high and gradually increased contents of W and S elements. These results indicated that the composited oils had an important influence on the transferring of  $WS_2$  film to the counterpart surface. In comparison, to composite with the SiCH oil was conducive to the formation of a continuous and dense transfer film on the counterpart surface. Correspondingly, better tribological performances were obtained from the  $WS_2$  film-SiCH composite system.



**Fig. 6** Typical SEM micrographs of the steel ball in vacuum for WS<sub>2</sub>/FCPSO system after different sliding cycles: a, for  $0.1 \times 10^5$  cycles; b for  $0.2 \times 10^5$  cycles; c for  $0.3 \times 10^5$  cycles; d for  $0.57 \times 10^5$  cycles

**Table 3.** Comparisons of the element weight percent ( wt % ) of the wear scar from EDS analysis for WS<sub>2</sub>/FCPSO system in vacuum after different sliding cycles

cycles ( $\times 10^5$ )	S ( wt % )	W ( wt % )	Fe ( wt % )	Cr ( wt % )
0.10	0.00	0.00	98.33	1.67
0.20	0.00	1.04	97.28	1.68
0.300	0.32	2.98	76.81	19.89
0.57	0.24	3.67	94.41	3.68



**Fig. 7** Typical SEM micrographs of the steel ball in vacuum for WS<sub>2</sub>/ SiCH system after different sliding cycles: a for 0.5×10<sup>5</sup> cycles; b for 5×10<sup>5</sup> cycles; c for 15×10<sup>5</sup> cycles; d for 30×10<sup>5</sup> cycles

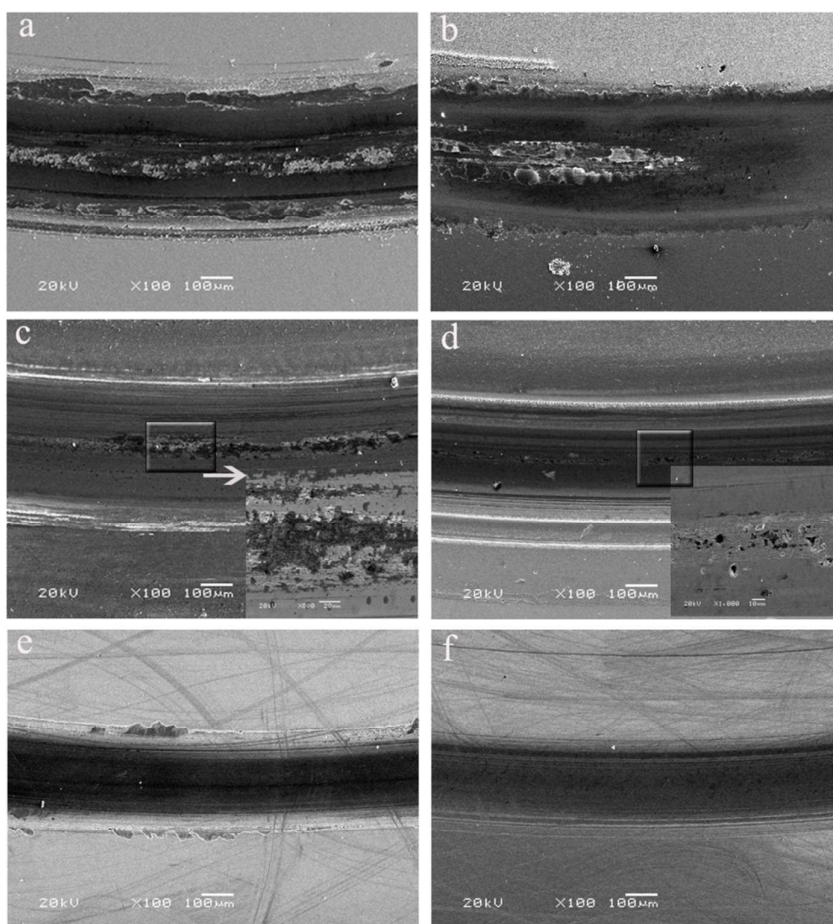
**Table 4.** Comparisons of the element weight percent ( wt % ) from EDS analysis of the wear scar for WS<sub>2</sub>/SiCH system in vacuum after different sliding cycles

cycles (×10 <sup>5</sup> )	S ( wt % )	W ( wt % )	Fe ( wt % )	Cr ( wt % )
0.5	0.00	0.00	97.98	2.02
5.0	0.85	13.66	83.78	1.71
15.0	0.74	35.34	49.84	14.07
30.0	1.49	66.68	28.40	3.43

To further elucidate the friction and wear mechanism, the SEM and 3D images of the wear tracks after the friction tests were investigated in detail as shown in Figs. 8 and 9. It could be seen that a great deal of bulky fragmentation wear debris accumulated along the edges and inside of wear track for pure WS<sub>2</sub> film ( Fig. 8a-b and Fig. 9a-b), suggesting that the films underwent the adhesive wear as well as severe plastic deformation.<sup>18</sup> The bulky fragmentation wear debris, generated from the section of collapsed columns or fibers after sliding, was due to the porous microstructure.<sup>22</sup> Fig. 8e and 8f show that wear tracks for WS<sub>2</sub>/SiCH system were relatively smooth and narrow. The calculated theoretical Hertzian diameter was about



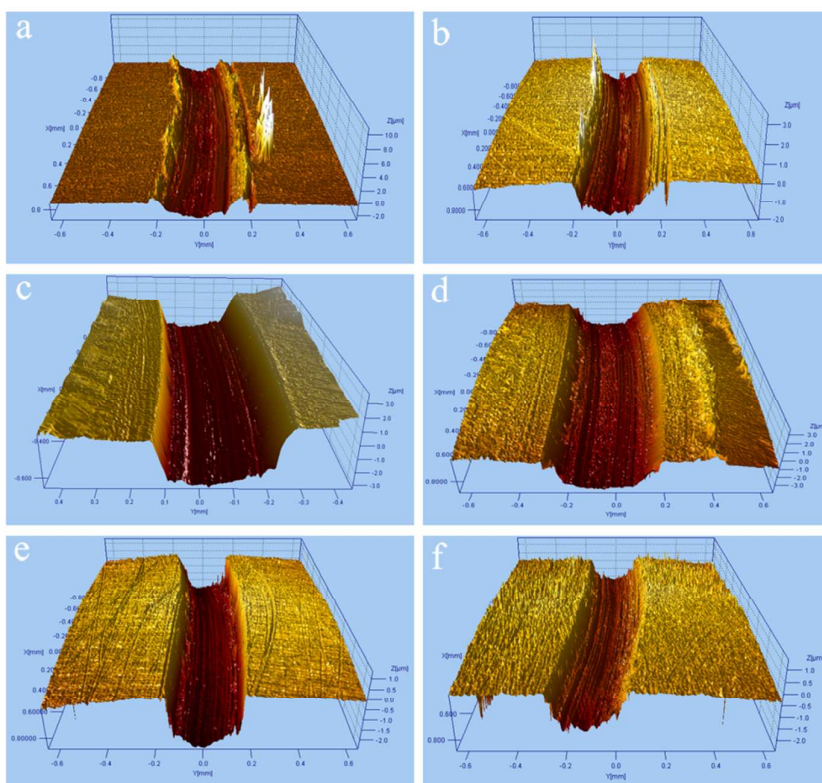
150  $\mu\text{m}$ . In Fig. 8, the wear track widths of  $\text{WS}_2/\text{SiCH}$  system (220  $\mu\text{m}$  in vacuum and 210  $\mu\text{m}$  in air) were closer to the theoretical Hertzian diameter than those of  $\text{WS}_2/\text{FCPSO}$  system (350  $\mu\text{m}$  in vacuum and 310  $\mu\text{m}$  in air). In comparison, it can be seen the wear tracks for the  $\text{WS}_2/\text{FCPSO}$  system were wide and deep from Fig. 8c and 8d. Moreover, a ribbon-like pitting wear trace was observed in the middle of wear tracks both in vacuum and air conditions in Fig. 8g and 8h, indicating that the films in these regions were peeled off. The XPS analysis result of the wear track surface in vacuum for  $\text{WS}_2/\text{FCPSO}$  could further support the lower denser film was scratched, thus leading to the exposing of steel substrate. F1s peak at the binding energy of 685.2 eV (Fig. 10) was in agreement with metal fluoride,<sup>41</sup> generating from the tribochemical reaction by FCPSO and the substrate surface metal atoms during the sliding process. Finally, the pitting phenomenon appeared, corresponding to the shorter wear life and higher friction coefficient for  $\text{WS}_2/\text{FCPSO}$  lubrication system.



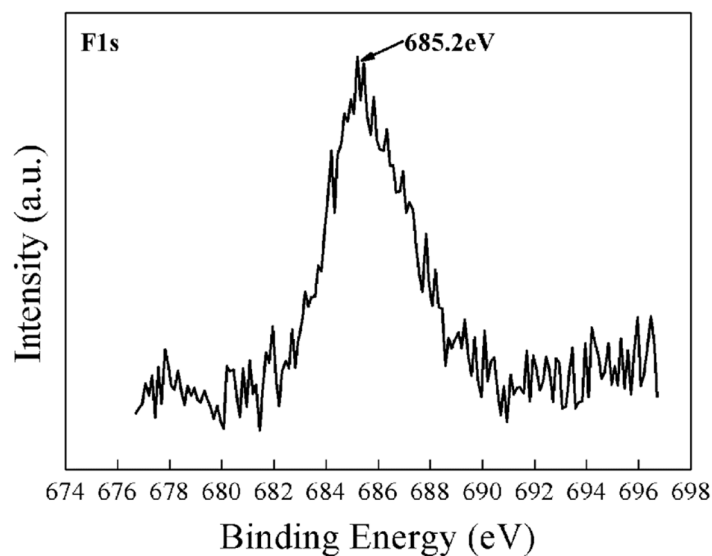
**Fig. 8** SEM micrographs of the worn surfaces: a.  $\text{WS}_2$ , c.  $\text{WS}_2/\text{FCPSO}$ , and e.



WS<sub>2</sub>/SiCH in vacuum; b. WS<sub>2</sub>, d. WS<sub>2</sub>/FCPSO, and f. WS<sub>2</sub>/SiCH in air; g. magnification of the marked area in c, h. magnification of the marked area in d

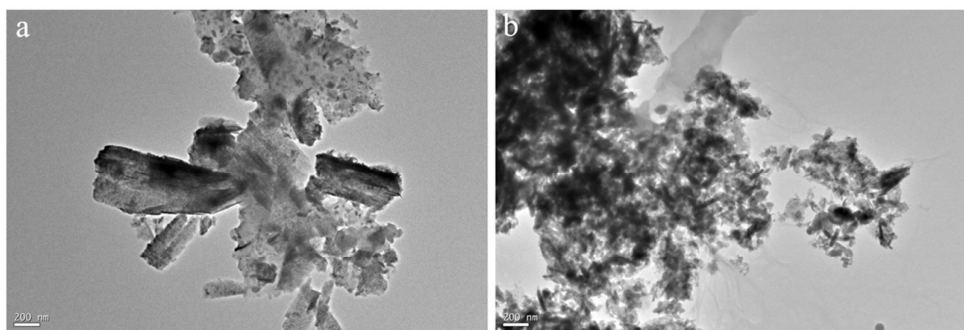


**Fig. 9** 3D non-contact surface profiler images of the wear tracks: a. WS<sub>2</sub>, c. WS<sub>2</sub>/FCPSO, e. WS<sub>2</sub>/SiCH in vacuum; b. WS<sub>2</sub>, d. WS<sub>2</sub>/FCPSO, f. WS<sub>2</sub>/SiCH in air

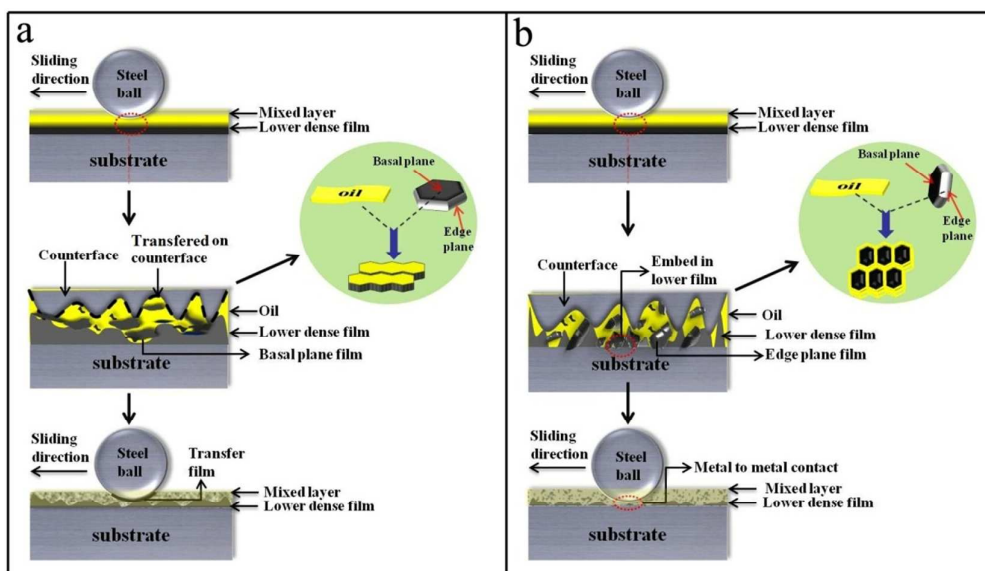


**Fig. 10** XPS F 1s spectrum from the wear track surface of WS<sub>2</sub>/FCPSO system in vacuum

Based on the results discussed above, the friction and wear mechanism of the WS<sub>2</sub>-based composite systems could be proposed. Apparently, the selective adsorption of WS<sub>2</sub> crystallographic planes on FCPSO and SiCH was the focus which governs the friction and wear mechanism. The results of TEM morphology images of wear debris can give the explanation on the mechanism from another perspective. It is clear from the Fig. 11a that the plate-like WS<sub>2</sub> thin nanosheets were observed after 30×10<sup>5</sup> cycles friction testing in vacuum for WS<sub>2</sub>/SiCH system. In comparison, a plenty of clavate-like debris with low aspect ratio was founded for WS<sub>2</sub>/FCPSO system after friction testing from Fig. 11b. This result was in well agreement with the previous studies that basal plane crystals of graphite as well MoS<sub>2</sub> always present a relatively higher aspect ratio than edge site crystals.<sup>28, 29, 42</sup> Additionally, the basal planes adsorbed with oil would have easy access to the rubbing metal surface and interact with it by the basal plane sulphur atoms, decreasing the metal surface energy and increasing the load carrying capacity of steel.<sup>27</sup> Therefore, the plate-like WS<sub>2</sub> debris should have higher proportion possessing the basal orientation. Plate-like WS<sub>2</sub> debris were very likely to lie flat with the worn metal surfaces to effectively prevent the metal to metal direct contacting and even repair them, generating a favorable tendency to form complete lubricating film on the rubbing surface for WS<sub>2</sub>/SiCH system. Whereas, for WS<sub>2</sub>/FCPSO system, the relatively hard edge plane WS<sub>2</sub> debris adsorbed with FCPSO were more likely to embed in the lower film and even the rubbing metal surfaces to scratch them.<sup>23, 27</sup> Thus, the chances of direct contacting of metal to metal increased highly, resulting in the abrasion became more pronounced. Of course, the formation of transfer films for composite systems were also strongly affected by the special adsorption. Because the complete lubricating film on the rubbing surface and high aspect ratio WS<sub>2</sub> films was more beneficial to transfer on counterface. The schematic diagram of the possible friction and wear mechanisms were showed in Fig. 12.



**Fig. 11** Typical TEM pictures of worn debris after the vacuum friction test: a,  $\text{WS}_2/\text{SiCH}$  system; b,  $\text{WS}_2/\text{FCPSO}$  system



**Fig. 12** Schematic diagram for explaining the possible friction and wear mechanisms: a,  $\text{WS}_2/\text{SiCH}$  system; b,  $\text{WS}_2/\text{FCPSO}$  system

Thus, the solid/liquid lubrication technology can unite the advantages of solid and liquid lubricants to arise synergistic effect if it is properly used. For lamellar solid lubricants, the property of selective adsorption should be a significant factor to consider for their solid/liquid lubrication in future.

#### 4. Conclusion

Two solid/liquid systems were successfully established by combining pure  $\text{WS}_2$  films with FCPSO and SiCH, separately. The results revealed that the tribological

performances of the composite systems were dominated by the selective adsorption of WS<sub>2</sub> crystallographic planes to special oils. The SiCH oil with more structure of hydrocarbon chains and weak polarity preferentially adsorbed with the basal plane of WS<sub>2</sub> films to form perfect lubricating and transfer films, resulting in a synergistic lubricating effect which brought about significant improvement in the tribological properties. However, the WS<sub>2</sub>/FCPSO system did not generate the synergistic lubricating effect due to the polarity of FCPSO oil as well as the absent of hydrocarbon chains in the molecular structure. Over all, the property of selective adsorption should be a key factor to consider to the lamellar lubricant based solid/liquid lubrication system.

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