

The Tribological Mechanism of MoS₂ Film under Different Humidity

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Abstract Molybdenum disulfide (MoS₂) has been widely used in vacuum environment as an excellent solid lubricant. However, the application of MoS₂ is greatly limited in terrestrial atmosphere due to the sensitivity to humidity. Although the sensitivity of MoS₂ to water vapor has been widely recognized, the mechanism is not clear. To explore the tribological mechanism of MoS₂ in the presence of water vapor, a series of experiments were performed to investigate the effect of N₂ (inert gas), O₂ (active gas), air (a combination of both) and cyclic humidity change in air on the frictional response of MoS₂ to humidity. According to the results, a model that described water adsorption enhanced by active sites in MoS₂ and formed oxides, and an adsorption action change in water molecules with humidity was proposed. The model was applied to explain

the recovery and instantaneous response of friction coefficient to humidity change.

Keywords Molybdenum Disulfide · Humidity · Friction · Atmosphere · Water Adsorption

1 Introduction

Molybdenum disulfide (MoS₂) is well known as a solid lubricant due to its excellent tribological property which results from easily sheared basal plane [1]. However, its performance in vacuum and dry environment will degrade in the presence of water vapor [2]. The presence of water vapor increases not only the friction but also the wear, leading to a decrease in lifetime. Unfortunately, the assembling and storage of space equipment will expose the protected MoS₂ film to humidity and inevitably compromise the reliability and functionality of systems [3]. Therefore, a study of the interaction between H₂O and MoS₂ is necessary and important to space application.

Although the sensitivity of MoS₂ to water vapor has been widely recognized, the mechanism regarding the influence of water on the frictional response of MoS₂ is not well understood [4, 5]. The views presented to answer the question include water-induced oxidation and physical effect of water [4, 5]. In addition, some important facts and views should be taken seriously after years of research. The increased friction of MoS₂ due to the increase in humidity is weakened as a result of elevated load, speed and temperature which will influence water adsorption [6]. This fact indicates that water adsorption plays an important role in the friction of MoS₂. Holinski and Gänshemer [7] attributed the increased friction coefficient of MoS₂ to the bonding force between the hydrogen atoms of the water

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molecules and the sulfur atoms on the basal plane of MoS₂. Nonetheless, there are no dangling bonds for sulfur atoms on basal plane except those on the edge sites. Suzuki proposed that the different types of transfer films as a response to the environment were responsible for the tribological dependence of MoS₂ film [8]. In addition, Singer et al. [9] observed an increased interfacial shear strength of transfer film with increasing humidity and supposed that the interaction between MoS₂ and H₂O most likely occurred on the track surface. Though the influence of water is determined, the mechanism still needs further study. Furthermore, according to the observation that a rise of interfacial adhesion happened between MoS₂-coated tip and single-crystal MoS₂ at 50% RH, Zhao et al. assumed water could bridge two MoS₂ planes [10]. However, the reasons that water links two planes and the place at which the interaction occurs are not clear.

Meanwhile, the development of studies on water adsorption sheds light on the interaction of water and MoS₂. Hu et al. [11] observed ice-like structures of the first layers of adsorbed water on surfaces and a second phase growing at higher humidity. Foster et al. [12] observed that hydrogen bonding arrangement of adsorbed water on magnesium oxide. A description of water adsorption from hydroxylated surface to multilayer adsorption under different humidity was well summarized in Ref. [13]. Increasing humidity would bring about a growing number of hydroxy groups and an enhancement of induced interaction, which is similar to the response of MoS₂ to water. All of the results contribute to the understanding of the interaction between MoS₂ and water.

The purpose of this work is to determine the role of water vapor in the frictional behavior of MoS₂. We specially conduct the experiments in N₂ and O₂ with controlled humidity to study the effect of inert and active gases. In addition, corresponding results are compared with that in air. Based on the results, a model involving active sites enhanced water adsorption and an evolution of hydroxylated interface to multilayered water molecules adsorbed interface is proposed to explain the frictional response of MoS₂ to humidity.

2 Experimental Details

2.1 Coating Preparation

MoS₂ films were deposited by unbalanced magnetron sputtering using Teer UDP 650 system on 304 stainless steel and Si wafer. In this work, only three targets including one Ti target and two MoS₂ targets were used. After the background vacuum reached 1.33×10^{-3} Pa, substrates were cleaned by Ar⁺ ion for 15 min to remove the surface

contaminations. Then a Ti interlayer was deposited to improve the film adhesion to substrate and load capacity. Finally, two MoS₂ targets were sputtered to deposit the MoS₂ layer.

2.2 Coatings Characterization

The films deposited on Si wafer were used to investigate the composition, morphology and crystal structure. The stoichiometry of MoS₂ film was analyzed by using an energy-dispersive spectrometer (EDS). The surface and cross-sectional morphologies were observed by field emission scanning electron microscopy (FESEM, Hitachi SU8020) and atomic force microscopy (AFM, CSPM 4000). The crystal structure of deposited MoS₂ film was measured by Philips X'Pert Pro X-ray diffractometer (XRD).

The tribological performance of the films deposited on 304 stainless steel were evaluated by reciprocating sliding tests, which were performed by a tribometer (CSM, Tribo-S-D-0000) with ball-on-disk configuration. The operation conditions were fixed at 5 Hz, 5 mm, 10,000 cycles, a load of 2 N and a GCr15 ball with a diameter of 4 mm (theoretical initial Hertzian contact pressure of 1.05 GPa). Commercially available pure oxygen (purity of 99.99%, active gas), nitrogen (purity of 99.95%, inert gas) from nitrogen generator and dry air (a combination of active gas and inert gas) were used. Corresponding gas was introduced into the cover of the tribometer for 10 min to drive out of the original air before tests. Then the water vapor was provided by a humidifier placed inside the shell. The relative humidity (RH) monitored by a hygrometer was fixed at 10, 30, 50 and 70%, respectively. Once the RH was stable, the test started. In particular, a tribological test with a circular change in humidity in air was designed to observe the continuous change in friction coefficient and the possibility of multilayer adsorption of water vapor.

The wear volumes were measured with an assistance of a profilometer (Alpha-Step D-100). Selected wear tracks and scars were investigated by optical microscopy and Tescan Mira3 SEM equipped with an EDS detector.

3 Results

The composition of as-deposited film was investigated by an EDS detector. The atomic percent of elements were 37.28% for Mo, 55.32% for S and 7.40% for O. The S/Mo ratio was calculated to be 1.48. The results indicated an oxygen incorporated and sulfur-deficient structure.

Figure 1a shows the SEM image of surface morphology of MoS₂ films and its 3D topography is illustrated in

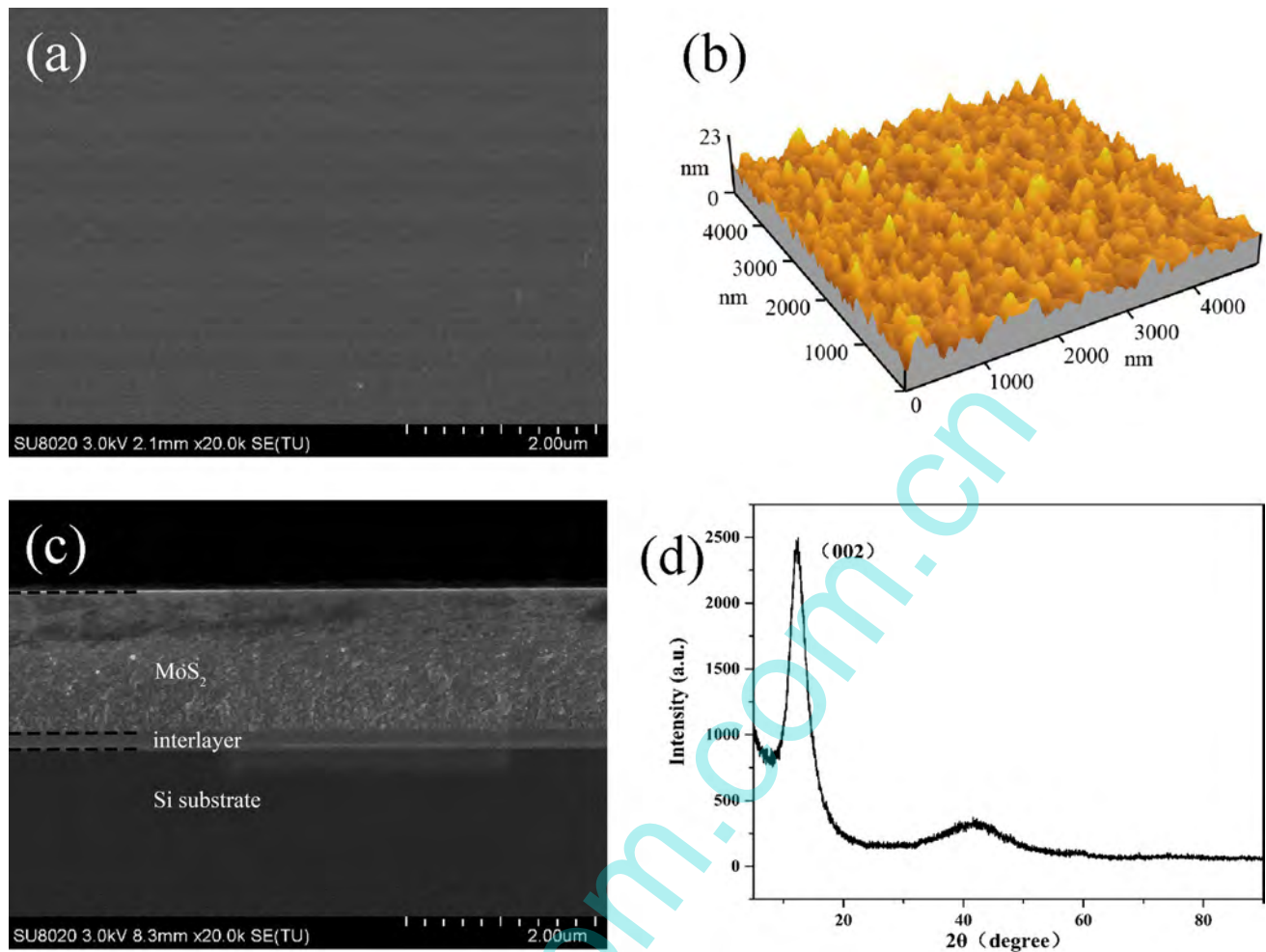


Fig. 1 **a** SEM image of surface morphology, **b** 3D topography of surface, **c** SEM image of cross section and **d** crystal structure of the MoS₂ film

Fig. 1b. The SEM picture displayed a featureless surface which was composed of densely packed particles without visible holes. The AFM image illustrated uniformly distributed hills and valleys on a surface of which the average roughness was measured to be 1.64 nm, which indicated a rather smooth surface. The cross-sectional picture is presented in Fig. 1c. Similar to the surface morphology, the cross section of MoS₂ layer consisted of dense granules. In addition, the crystal structure of the deposited film was characterized by XRD spectrum. A prominent peak located at about 12.9° suggested a prevailing (002) basal planes orientation parallel to the substrate [14]. The broad diffuse peak that extended from 30° to 50° arose from the random stacking of S–Mo–S sandwich layers [15].

Figure 2 shows the friction coefficient curve of MoS₂ films in N₂, O₂ and air atmospheres with different relative humidity, and wear rates are summarized in Fig. 2d for contrast. As shown in Fig. 2a, a lowest friction coefficient of 0.04 is obtained at 10% RH in N₂. The friction coefficient rose with increased humidity and it was about three

times higher at 70% RH than that at 10% RH. Meanwhile, a higher humidity led to a longer run-in period and a poorer stability of the friction coefficient. The friction coefficient was around 0.04 at 10% RH in O₂. As the humidity increased to 30% RH, the friction coefficient increased significantly to 0.23, followed by a fluctuation. The friction coefficient at 50% RH was similar to that at 30% RH except for a longer stable stage. When the humidity reached 70% RH, a highest friction coefficient of 0.4 was observed. In comparison, the friction coefficient was approximately 0.04, 0.13, 0.17 and 0.25 at 10, 30, 50 and 70% RH in air, respectively. Overall, the film exhibited weak dependence on atmospheres at 10% RH, as all the friction coefficients were near 0.04. It needs to be emphasized that the friction coefficient obtained in O₂ was unstable. Additional evident is provided in supplementary file (Fig. s1), which compared the friction coefficients at ≤0.1% RH. The increased humidity led to a rise of friction coefficient, and more oxygen in the atmosphere resulted in a faster increase in the friction coefficient.

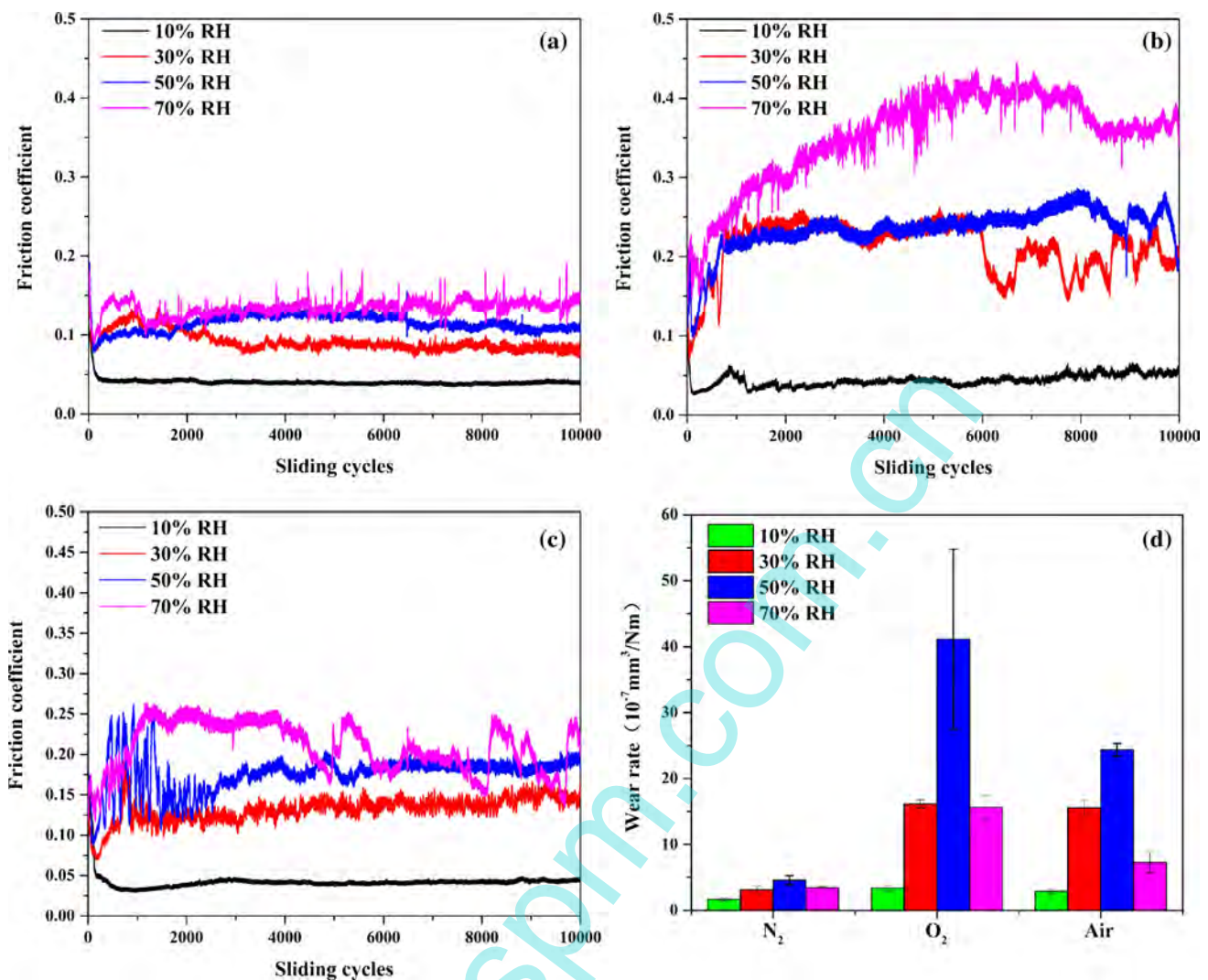


Fig. 2 Friction coefficients of MoS₂ film at different RH in **a** N₂, **b** O₂, **c** air and **d** wear rates collected by groups in above atmospheres

The wear rates are sorted by groups in Fig. 2d and exhibit a same trend in all atmospheres. The wear rates increased monotonically with humidity from 10 to 50% RH. Further increased humidity resulted in a significant drop in wear rates. Likewise, more oxygen in the atmosphere led to a faster increase in the wear rate.

The wear tracks generated in air were selected to investigate the details that how humidity influences the tribological performance. As shown in Fig. 3a, a large amount of tribofilm was attached to the wear track and trapped in the grooves to repair the wear damage at 10% RH. Nonetheless, a part of fine wear debris was ejected from the sliding path and distributed along the wear track. The widths of wears tracks measured by a profilometer are provided in supplementary file (Table s1). The wear debris left in the wear track was less and those distributed along the wear track greatly became more at 30% RH. The finer ones were on the inside, and the bigger ones were on the

outside. When it came to 50% RH, the wear track became broader and more grooves were clearly seen with a lack of wear debris covering them. Though it was not shown in the picture, the expelled wear debris became more. At 70% RH, the wear track was broad and smooth without much wear debris in it. Similarly, there was plenty of wear debris left out of the wear track.

Figure 4 shows the optical micrographs of the ball surfaces after tribological tests in respective air humidity, which presents differences in morphologies of wear scars and transfer levels. The wear scar formed at 10% RH was characterized by a compact, discrete transfer film of which the major part was on the sides of the contact area. Moreover, no obvious wear was found in the contact area and little wear debris scattered around the contact zone. At 30% RH, the center of the wear scar was covered by a thin transfer film. The transferred layers around the contact zone were mainly dense, but the edges were undergoing

Fig. 3 Wear tracks of MoS₂ film at a RH of **a** 10%, **b** 30%, **c** 50% and **d** 70% in air

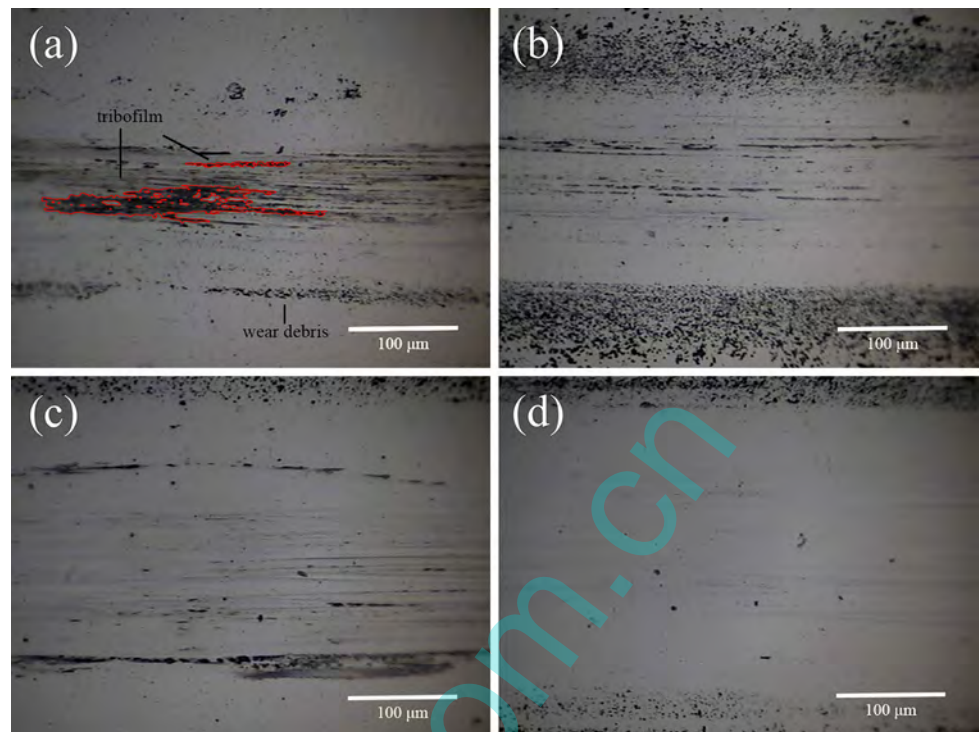
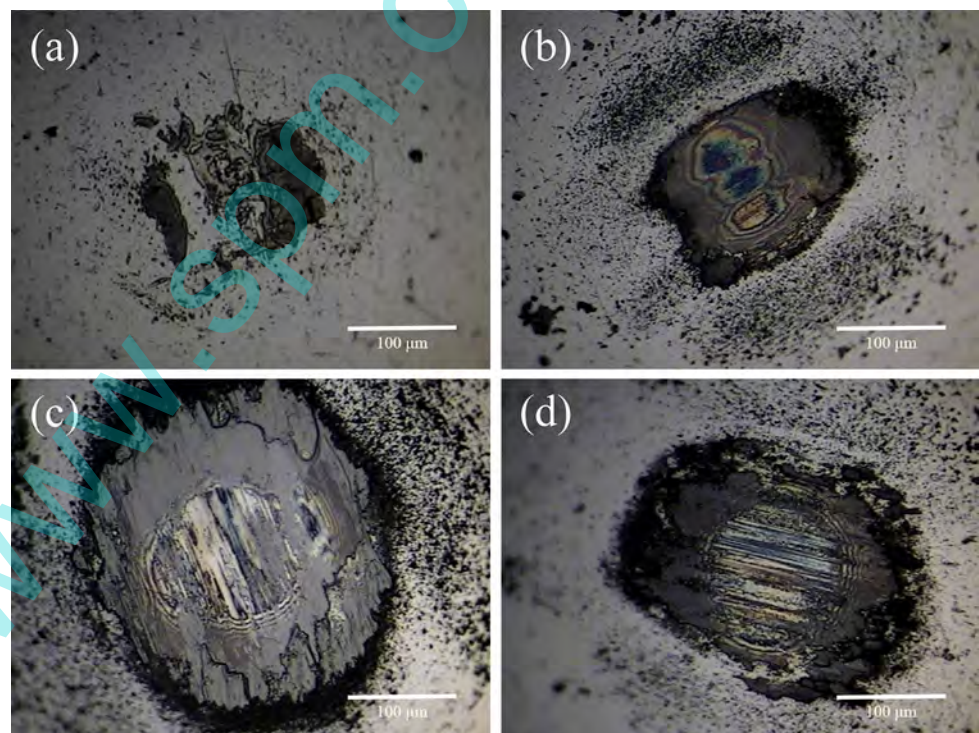


Fig. 4 Wear scars of MoS₂ film at a RH of **a** 10%, **b** 30%, **c** 50% and **d** 70% in air



some transformation which was indicated by loose and black wear debris. The wear debris distributed along the sliding direction became more than that at 10% RH. The contact area at 50% RH became larger, where a worn surface of the counter ball with residual patchy transfer

film was observed. Moreover, more transferred MoS₂ layers and wear debris piled around the contact region. The contact area at 70% RH was almost same with that at 50% RH, and the transfer film was heavily damaged with an obvious steel wear at the contact center.

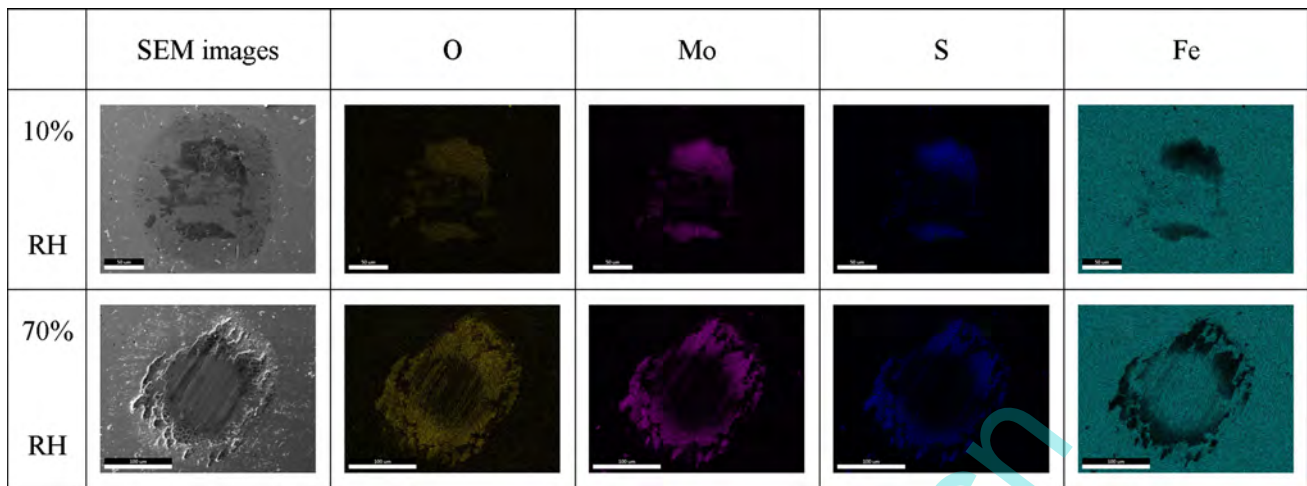


Fig. 5 SEM images of wear scars of MoS₂ film formed at 10 and 70% RH in air with EDS analysis

EDS was applied to investigate the elemental differences of the wear scars formed at 10 and 70% RH. Figure 5 shows that the transfer films mainly consist of three elements including O, Mo and S besides Fe which is the composition of the counter ball. Though tested at 10% RH, oxygen was clearly observed and the distribution of O, Mo and S almost overlapped. In contrast, the signals were stronger at 70% RH, which was supported by the heavier colors. Though the differences in the Mo and S signals within the contact zone at 10 and 70% RH were negligible, the contact zone at 70% RH was mainly covered by an oxide layer, which indicated an increase in the number of oxides. A published work of ours showed the oxides contained MoO₃ [16]. The EDS information of wear scars formed in N₂ and O₂ is provided in supplementary file (Table s2), which showed more oxides were formed in O₂ at same humidity.

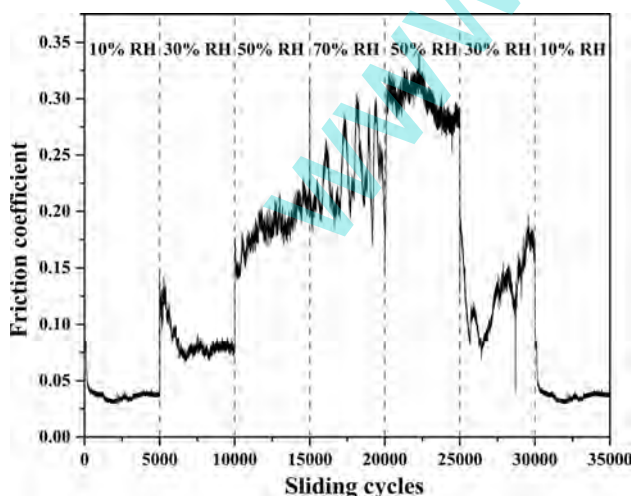


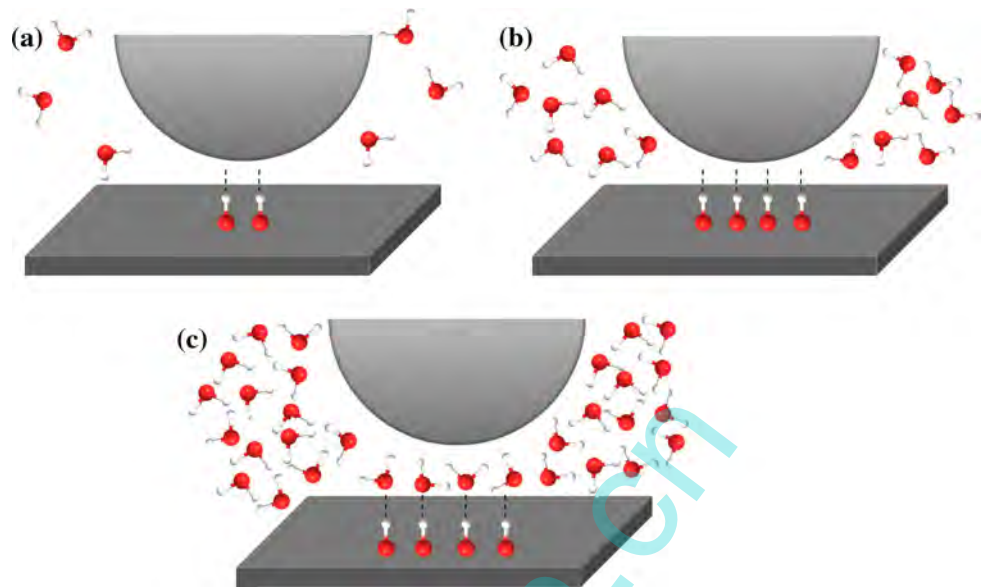
Fig. 6 Friction coefficient versus sliding cycles of MoS₂ coating under cyclic humidity condition

Considering the possibility of multilayer adsorption of water vapor, a test with varied humidity was performed. Figure 6 shows the result that was conducted in a cyclic mode on the same wear track, first at 10% RH in air, then elevated humid air (the humidity was increased by 20% RH every time until 70% RH and the dwell time was about 5 min) and finally back to initial humidity in an opposite way. At the first 10% RH, the friction coefficient reached a stable level around 0.04 after a short run-in period. The run-in period was prolonged and the stable friction coefficient was about 0.07 at the first 30% RH. As the humidity increased from 30 to 70% RH, the friction coefficient continued to increase and fluctuated drastically between 0.20 and 0.30. More interestingly, the change in the friction coefficient with the following decreased humidity was beyond the expectation of traditional view that the friction coefficient decreased as the humidity was reduced, indicating a different mechanism was happening. When the humidity returned to 30% RH, the friction coefficient decreased quickly and rose to 0.15 at the end. Finally, the friction coefficient recovered regardless of its tribological history as the humidity was back to 10% RH, which indicated the interaction between tribological interfaces was reversible.

4 Discussion

Perfect MoS₂ is inactive to water for a lack of dangling bonds [17]. However, sputtering process inevitably introduces defects such as oxygen substitution, random orientation and vacancies [16]. In addition, edge sites and vacancies have the potential use of water dissociation [18, 19]. So these defects will enhance water adsorption and dissociation as active sites. Moreover, MoO₃, a product

Fig. 7 Interaction of contacting interface at **a** low humidity, **b** middle humidity and **c** high humidity



of friction process, will promote the chemisorption of water [20]. Thus, a simplified model shown in Fig. 7 is proposed to describe the tribological behavior of MoS₂ in the presence of different humidity.

Interfacial friction is a dynamic phenomenon in which develops toward a balance of exposed intrinsic active sites, formed oxides, the adsorption and desorption of water as a result of sliding. At low humidity, water molecules are adsorbed on the active sites and dissociate into hydroxy groups which exhibit a strong interaction with the counterball (Fig. 7a). At this stage, the active sites are excess compared with adsorbed water. The friction coefficient is largely dependent on the number of adsorbed water, which is eventually determined by environmental humidity. A higher humidity leads to more water molecules adsorbed on the surface and dissociated into hydroxy groups, so the attraction from hydrogen bonds become stronger (Fig. 7b). If the test is carried out in an active atmosphere, the formed oxides will increase the adsorption capacity of water, which will further increase the friction coefficient. However, the excess humidity will result in multilayer adsorption (Fig. 7c). This will weaken the hydrogen bonds interaction between MoS₂ film and the counterball.

Based on this model, the adsorbed water on surface at 10% RH is deficient to occupy the active sites, so the friction coefficients in N₂, O₂ and air are approximate despite of friction fluctuation resulting from oxides. The friction coefficient is mainly determined by the shear strength of MoS₂ layers, which is the case presented in Fig. 2. The adsorbed water gradually increases with increased humidity, so the friction coefficient at 30% RH is higher than that at 10% RH in all atmosphere. Considering the oxygen content in different atmospheres, the amount of formed oxides is different. The content of oxides in oxygen

is more than that in nitrogen. Plenty of oxides will substantially increase the amount of adsorbed water, leading to a stronger interaction between the film and the counterpart. This is consistent with the result that the increase in friction coefficient is slightest in N₂, followed by in air, in O₂ next (Fig. 2). The increase in humidity to 50% RH is a similar condition. According to the EDS results in Fig. 5, the content of oxides in the contact zone at 70% RH is higher than that at 10% RH, so it needs more time to achieve a balance between water adsorption and desorption. Meanwhile, if there are oxides in the contacting interface, the adsorption of water will be enhanced and the friction coefficient will become unstable. Therefore, the run-in period becomes much longer at 70% RH and the friction coefficient fluctuates drastically in O₂ and air. The decreased wear rate at highest humidity results from multilayer adsorption. Though the friction coefficient is highest due to a large quantity of adsorbed water, the interaction between the upper multilayered adsorbed water and the atom of the counterpart becomes weaker. Hence, the wear rate of MoS₂ film decreases at sufficiently high humidity. As indicated in Fig. 6, when the oxides were comparable, the decrease in humidity from 70 to 50% RH led to a desorption of upper adsorbed water and a direct interaction between hydrogen bonds and the counterpart, so an increased friction coefficient was observed.

5 Conclusions

We have investigated the influence of humidity on the tribological performance of MoS₂ film. The film was composed of densely packed particles and showed (002) basal plane preferential orientation. The friction

coefficients rose with increased humidity in all three kinds of atmosphere. The wear rates increased with the increased humidity in the range of 10–50% RH, and further increasing the humidity resulted in a decrease in wear rates. More oxygen in the atmosphere led to a faster increase in the friction coefficient and wear rate. Water molecules dissociated into hydroxy groups on the surface active sites at low humidity. Increasing humidity led to a growth of hydroxy groups, which resulted in a stronger interaction of friction pairs and higher friction coefficient. In active atmosphere, more oxides were formed. This provided additional active sites for water adsorption and further increased the friction coefficient. Multilayer adsorption happened at higher humidity, accompanied with a reduced interaction and friction coefficient.

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