GROUND-BASED TRIBOLOGICAL TESTING OF THE SPUTTER-DEPOSITED MOLYBDENUM DISULFIDE FILMS IN HYPERTHERMAL ATOMIC OXYGEN EXPOSURE

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ABSTRACT

Tribological properties of the two types of sputter-deposited molybdenum disulfide (MoS_2) films (RF and RF-H samples) were evaluated under 5 eV atomic oxygen beam exposure. The experimental results using atomic oxygen-exposed RF sample indicated that a high friction force at the beginning of sliding was followed by a low friction force at the steady-state sliding. It was observed that the initial friction force of the RF sample depended on the atomic oxygen fluence. The initial friction force was observed to be 2.5 times larger than that of the steady-state friction with the atomic oxygen fluence of 2×10^{18} atoms/cm^2. Such a relationship was also observed in the case of the RF-H sample. The effect of atomic oxygen exposure on the steady-state friction was also evaluated. It was demonstrated that atomic oxygen exposure led to a high steady-state friction for both types of the sputter-deposited MoS_2 samples.

1. INTRODUCTION

The hyperthermal atomic oxygen (AO) reaction with materials used in space systems is one of the unsolved problems in the space environmental effect community. Much attention has been paid to polymer degradation due to AO attack, however little has been made clear in the last decade. As well as polymers, lubricants are one of the AO hazardous materials. A lubrication malfunction in a space system influences serious damage to the whole system. In many cases, there exists no back-up system for such tribological failure. Therefore, it should be stressed that the influence of AO exposure to the lubricants used at the exterior of the space system must be evaluated before the mission.

Molybdenum disulfide (MoS_2) is one of the widely used lubricants in space systems. Its low friction coefficient (typically 0.02-0.05) and durability in vacuum are suitable for space applications. Thin MoS_2 lubricant is usually prepared by the sputtering or the spray method. The MoS_2 films formed by these methods show a wide variety of tribological properties depending on their deposition/spray conditions.

Some research work has already been carried out to clarify the AO effect on the MoS_2 lubricants. Arita et al. reported that the degree of oxidation of MoS_2 by 5 eV AO beam depends on the crystallographic nature of MoS_2 sample [1]. At an AO fluence of 4.3×10^{20} atoms/cm^2, 72% of Mo atoms in the sputtered MoS_2 sample were oxidized, whereas only 17 % were oxidized in the case of single crystal. In contrast, Martin et al. [2] reported the experimental results using continuous 1.5 eV AO beam. They reported that the oxide layer (10-30 monolayers thick) consisted primarily of MoO_3 with less MoO_2 and the oxidation was essentially independent of crystallographic orientation of the MoS_2: single crystal and sputtered film were both oxidized similarly. Discrepancies of the experimental results are also reported in the tribological properties as well. Arita et al. observed the AO-induced high friction at the initial stage of friction and they reported it was 20-30% higher than the pristine sample. However, no significant change in wear life was reported. In contrast, Matsumoto and co workers [3] reported that the AO exposure led to an induced low friction coefficient and shorter wear life for MoS_2 sputtered film. These discrepancies may be due to the

difference in experimental conditions in each experiment such as AO beam energy, AO fluence, sample preparation and so on. Therefore, it seems to be important to clarify the experimental conditions, including AO beam characteristics, in order to simulate LEO space environment.

On the other hand, the tribological properties of MoS_2 lubricants have been carried out at the post process, so that ambient air was exposed to the AO-exposed surfaces before the tribological tests. It has not been made clear whether or not the effect of air exposure at the AO-exposed surface exists. Also since tribological tests were conducted after the exposure was finished, the effect of 5eV AO exposures on the steady-state friction have not yet been clarified. Such in-situ testing was pioneered by Wei et al., but they used a plasma asher type AO source, which may cause different chemistry on the lubricant surface [4]. Therefore, it is necessary to use well-characterized AO beam for exposure experiments to tell what is the AO-induced effect on MoS_2 in the LEO space environment.

In this study, changes in the tribological properties of the AO-exposed sputter-deposited MoS_2 films were studied. The AO reaction with the MoS_2 single crystal and the sputter-deposited MoS_2 films were also studied. X-ray photoelectron spectroscopy (XPS) data were interpreted to understand the mechanism of change in the tribological properties of the MoS_2 films.

2. EXPERIMENT

The specimens used in this study were single crystal and sputter-deposited MoS_2 Films. The single crystal MoS_2 specimens are naturally produced crystals, whereas the sputtered films are prepared by the radio frequency (RF) sputtering technique at the National Aerospace Laboratory (NAL), Japan. Sputtering conditions of the RF sputtered specimens are listed in Table 1 [3]. Two types of RF sputter-deposited MoS_2 samples were prepared; i.e., RF and RF-H samples. These two samples were sputtered in the same sputtering condition except for the substrate temperature. The RF sample was sputter-deposited at 60 °C, in contrast the RF-H was done at 160 °C. The samples prepared by the same procedure have also been aboard STS-85 (ESEM program) and correlated with the ground-based experiment reported here.

Table 1. The sputtering condition of the MoS_2 film

Sputtering gas	Argon
Pressure	6.5 Pa
Sputtering power	220 W
Substrate Temperature	60 ºC for RF sample, 160 ºC for RF-H sample
Thickness	1 μm
Substrates	SUS440C

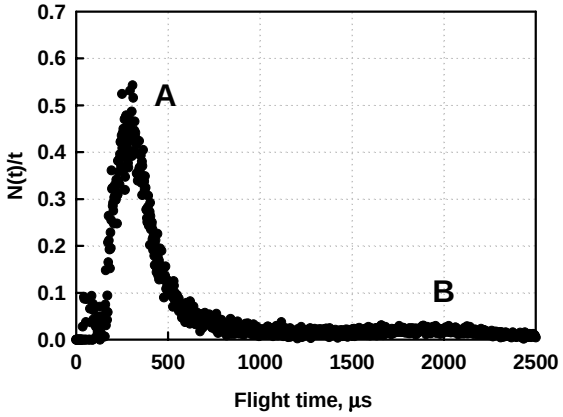


Figure. 1 Typical TOF distribution of the AO beam obtained in this facility. Average energy of the hyperthermal AO component (labeled "A") is 4.5eV.

The AO source used in this study was based upon the laser-induced detonation phenomenon and originally developed by the Physical Sciences Incorporation (PSI) [5]. The AO source is attached to the AO testing facility developed in our laboratory [6]. The AO beam is always monitored by the time-of-flight (TOF) measurement system consisting of a quadrupole mass spectrometer (QMS) and a multi channel scalar. Typical m/q=16 TOF spectrum is shown in Figure 1. The time-zero in Figure 1 corresponds to the laser firing. In this spectrum, the peak at around 300 μs comes from the hyperthermal AO component of the beam. The m/q = 16 signal also includes the signal originated from molecular oxygen (MO) that cracked to O^+ in the ionizer. This cracking component is located at 2000 μs (labeled "B") in Figure 1. This contribution was subtracted from the original data for further data processing. We used the relationship of the translational energy distribution $P(E) \propto t^2 N(t)$ to calculate the translational energy. The mean energy of the hyperthermal AO was calculated to be 4.5 eV. The AO fraction in the beam was approximately 45 %, balance MO. The AO flux of the beam was measured by an Ag-coated quartz crystal microbalance (QCM) with an accommodation coefficient of 1.0. A typical AO flux at the sample position for XPS measurements (134 cm away from the nozzle throat) was 2.6×10^{13} AO/cm^2/s, and that at tribological test position (47 cm from the nozzle) was 2.3×10^{14} AO/cm^2/s. The tribological testing of the specimen was carried out in the AO source chamber (Figure 2). The UHV-friction tester used in this study was especially designed for this facility. This UHV-friction tester is based upon the conventional pin-on-disk layout. The testing conditions are summarized

in Table 2. The sample surfaces before and after exposure to AO beam were characterized by XPS.

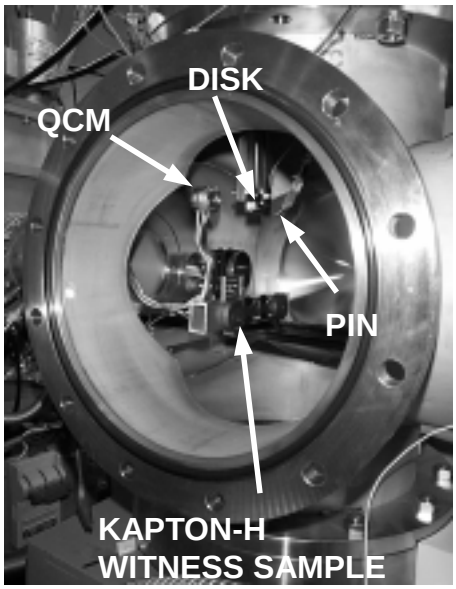


Figure 2. Experimental setup for the in-situ tribological tests during AO exposure. A concave mirror, a quartz crystal microbalance, Kapton-H samples (held by magnets) and the UHV-friction tester (from the top flange) are obvious.

3. XPS AND QMS ANALYSES

In the Mo3d spectrum of the control surface of MoS_2 (0001), we saw two XPS peaks from MoS_2 at 229.3 and 232.2 eV (not shown). These two peaks are due to spin-orbital splitting of Mo3d orbit of Mo (IV) atoms in the MoS_2 structure. An additional XPS peak at 235.3 eV was obvious in the XPS spectrum of the AO-exposed MoS_2 (0001). Also, the peak at 232.2 eV became higher than that at 229.3 eV. These spectral changes were explained by the oxidation of Mo. Namely, Mo (IV) was converted to Mo (VI), which showed a chemical shift of +3.5 eV, by means of the formation of MoO_3 [7]. From the peak deconvolution of these spectra, we found that 52 % of Mo was oxidized to MoO_3 by the AO exposure at 6.7 x 10^{17} atoms/cm^2. Surface composition of the AO-exposed MoS_2 (0001) examined by the XPS is summarized in Table 2. From Table 2, the loss of S (60 to 18 %) and

Table 2. Sliding conditions of the tribological testing

Pin	Ti-6Al-4V (r=2mm)
Disk	Single crystal or Sputtered MoS_2 (RF, RF-H)
Load	2 N
Sampling frequency	20 Hz
Track length	8 mm

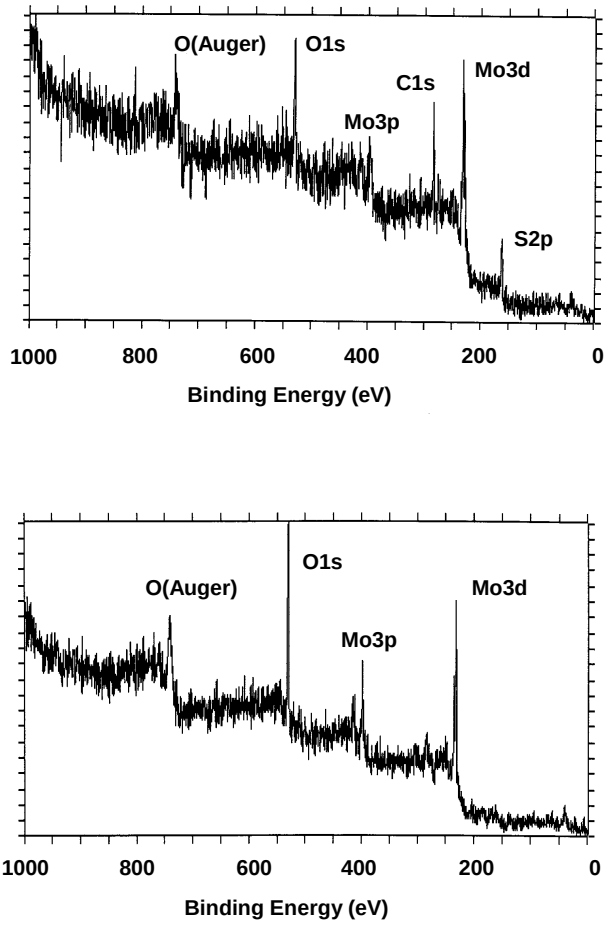


Figure 3. XPS survey spectra of the unexposed RF sample (upper panel) and AO-exposed sample (lower panel). AO fluence is 3.1 x 10^{18} atoms/cm^2). Loss of sulfur and carbon, and increase of oxygen are remarkable.

increase of O (4 to 54 %) are remarkable. However, the amount of Mo does not change significantly (36 to 28 %). After the sliding, recovery of the amount of S was clearly detected in the wear track (18 to 26 %).

The atomic concentration of the AO-exposed MoS_2 (0001) surface was also examined by Auger electron spectroscopy (AES). The results of AES analysis did not agree with the XPS data shown in Table 3, i.e., only 3% of oxygen was detected in the 10,000 AO shots sample. Similar results were observed, not only in the other MoS_2 specimens, but also in the AO/HOPG system [8]. Since the high-energy primary electron beam of AES may cause electron stimulated desorption of the weakly bonded gaseous atoms/molecules on the surface, we believe XPS data is trustworthy even though it is affected by exposure to ambient air.

The XPS measurements were also carried out with the sputter-deposited MoS_2 surfaces. Even at the similar AO fluence (2×10^{18} atoms/cm^2), the sputter-deposited MoS_2 surfaces showed complete oxidation of Mo (Mo (IV) : Mo (VI) = 0 : 100) [7] and significant loss of S (13 %) as indicated in Table 4. This would be explained by the characteristics of the sputter-deposited MoS_2:

(1) high diffusion rate of AO into the MoS_2 film,

(2) dangling bonds of Mo and of S existing in the film.

These are mainly due to the imperfection and the orientation of the crystals, and would strongly depends on the deposition conditions.

Table 3. Atomic composition of the MoS_2 (0001) surfaces analyzed by XPS

Specimen	Mo	S	O
Control	36	60	4
10,000 AO shots[1)]	28	18	54
10,000 AO shots[2)]	24	26	50

AO fluences: [1)]6.7×10^{17}AO/cm^2, out of the wear truck, [2)]6.7×10^{17}AO/cm^2 in the wear truck after friction

Table 4. Atomic composition of the sputtered MoS_2 surfaces (RF film) analyzed by XPS

Specimen	Mo	S	O
Control	26	25	49
10,000 AO shots[1)]	26	13	61
10,000 AO shots[2)]	22	21	57
Flight sample[3)]	16	11	73

AO fluences: [1)]6.7×10^{17} AO/cm^2, out of the wear truck, [2)]6.7×10^{17}AO/cm^2 in the wear truck after friction, [3)]$4.4\text{-}15.0 \times 10^{19}$ AO/cm^2, ESEM program (STS-85), Si contamination was obvious.

Volatile species formed on the MoS_2 (0001) surfaces during AO exposure were detected by the QMS installed in the reaction chamber [7]. It became clear that the major volatile product in the AO/MoS_2 system was SO (m/q=48), but it was observable only in the beginning of the reaction. Namely, the SO signal became weaker with increasing AO fluence. This result implies that AO reacts with the surface region of MoS_2, and further reaction with MoS_2 bulk is limited due to its low diffusion rate. This also shows good agreement with the depth profile of oxygen on the AO-exposed MoS_2 measured by AES or SIMS [3].

4. TRIBOLOGICAL PROPERTIES

Tribological properties of the sputter-deposited MoS_2 films were examined with the UHV friction tester attached in the AO source chamber (see Figure 2). In our previous results [7], it has been indicated that the high friction coefficient at the initial stage of sliding, which was reported in the literature [1], is due mainly to the resistance to movement of the pin due to the wear track formation. In order to eliminate the effect of wear track formation, AO exposure in this study was carried out on the MoS_2 surface where a wear track already exists. Namely, the first sliding test was done before AO exposure, and then the wear track was submitted to AO beam exposure and sliding tests followed after the AO exposure. During a series of tests, the load of the pin was not released so that the misalignment of the pin/wear track in the sliding tests was negligible. The specimen surface was kept in vacuum at least 10^{-6} Torr during the tests.

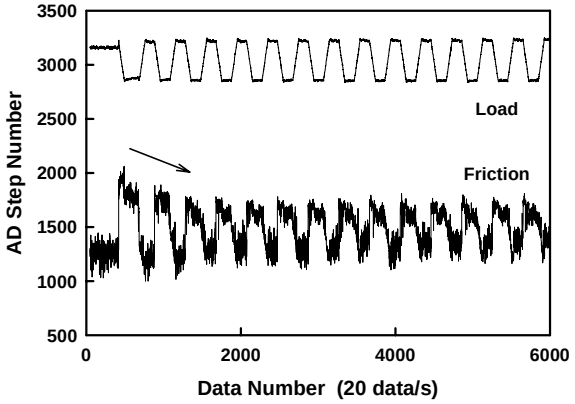


Figure 4 Load and friction force traces measured on the AO-exposed sputter-deposited MoS_2 film (RF sample, AO fluence is 2×10^{17} atoms/cm^2). Increase of the friction force at the beginning of the sliding action ($F_{initial}$) is clearly observed.

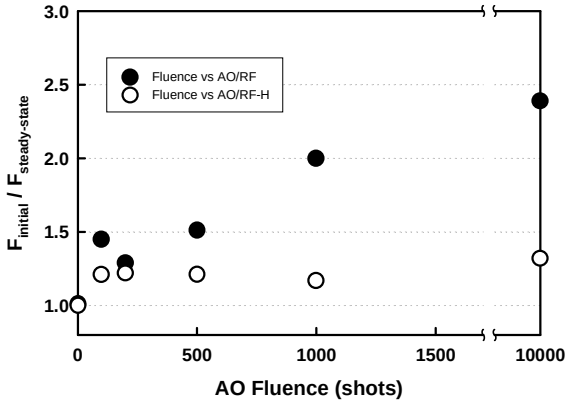
The tests were carried out with the sputter-deposited MoS_2 samples (RF and RF-H). Typical load and friction force traces are indicated in Figure 4. Analysis of these force traces were done along with the protocol written here.

(1) Since hysteresis of the friction force due to the change in direction of motion exists in this system, the law data from strain gauges can not be treated as friction forces directly. This is because the arm, to which the pin is attached, is bent by the applied normal load.

(2) Therefore, the output of friction forces during the sliding in both direction was recorded.

(3) The friction force in the forward sliding direction was subtracted from that in the backward direction. The obtained result was divided by two. The friction force thus measured was divided by the average

normal load, and friction coefficients were calculated.



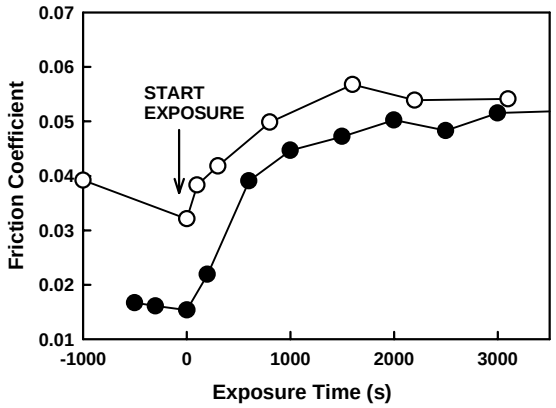
This procedure provided the friction coefficient of 0.02 for unexposed RF film, and 0.04 for unexposed RF-H

Figure 5 Increase of initial friction force compared with a steady state friction. In this graph, AO flux is 1 x 10^{14} AO/cm^2/shot. Solid and open circles indicate the results of RF and RF-H samples, respectively.

sample, respectively. These friction coefficients are consistent with those reported by the Matsumoto et al., using a conventional pin-on-disk type friction tester [3].

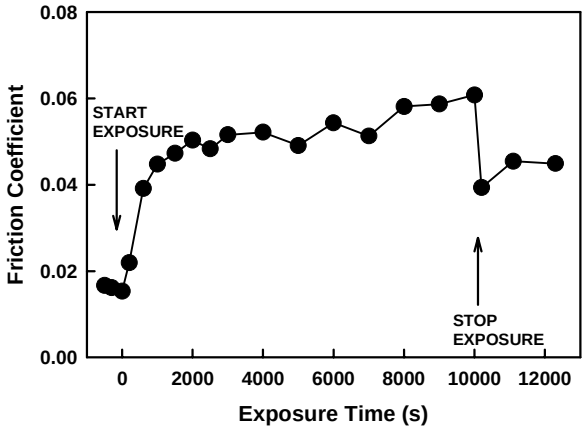
The ratio of the initial friction force ($F_{initial}$) and the steady-state friction force ($F_{steady-state}$, when measured after 10-20 cycles of sliding) was calculated both for RF and RF-H samples. The AO fluence dependence in this ratio is shown in Figure 5. Figure 5 clearly shows that the initial friction force of the RF sample increases with the AO exposure at fluences higher than 100 AO shots (2 x 10^{16} atoms/cm^2). The $F_{initial}$ reached 2.5 times larger than the $F_{steady-state}$ at the AO fluence of 10,000 AO shots (2 x 10^{18} atoms/cm^2). In contrast, F_{inital} did not show remarkable increase in the case of the RF-H sample ($F_{initial}/F_{steady-state}$ = 1.3). Also, it has been confirmed previously that the thermal MO component in the beam does not cause any influence on the friction force [7]. The XPS spectrum of the AO-exposed sputter-deposited MoS_2 film (AO fluence of 2 x 10^{18} atoms/cm^2) showed complete oxidation of Mo and loss of S (see Section 3). It is, therefore, concluded that severe oxidation of the lubricant surface and loss of S result in initial high friction. The origin of difference in these two samples will be discussed in a later paragraph. As is observed in Figure 4, the initial high friction coefficient returns to the original value in sliding cycles. The XPS data show the amount of S and Mo (IV) in the wear track increased with lubrication, and this led to the recovery of the tribological property.

Change in the steady-state friction force due to 5 eV AO beam exposures was also evaluated in this study. Figure



6 shows the friction coefficient of the RF and of the RF-H samples at the beginning of AO beam exposure. The AO beam exposure was carried out in the fluence of 3.0 x 10^{14} AO/cm^{2}s at 1 Hz operation. *Figure 6 Change in friction coefficient of the sputter-deposited MoS_2 samples due to the AO beam exposure. Solid and open circles represent the data of RF and RF-H samples. AO flux is 3.0 x 10^{14} AO/cm^2/s.*

The time-zero in the abscissa corresponds to the moment of starting AO beam exposure. The solid and open circles represent the friction coefficients of the RF and the RF-H samples, respectively. Each point was based on the calculations using nearly 4,000 data points. It is clearly indicated that the friction coefficient before AO beam exposure (negative abscissa) is as low as 0.015-0.02 for the RF sample and 0.03-0.04 for the RF-H sample. Again, these values agree with the data reported by Matsumoto with the other friction tester [3].



After starting the AO beam exposures, both samples indicated high friction coefficients of up to 0.06 at 3,000 AO *Figure 7 Change in friction coefficient of the sputter-deposited MoS_2 samples due to the AO beam exposure. AO flux is 3.0 x 10^{14} AO/cm^2/s. A correlation between AO beam exposure and the friction coefficient is clearly obvious.*

shots (AO fluence of 9.0 x 10^{17} AO/cm^2). There is no significant difference in the friction coefficients of the RF and RF-H samples being AO-exposed. It is also obvious that it took 2,000 shots to reach the saturated value of the friction coefficient. Since AO flux of this experiment was in the order of 10^{14} AO/cm^2/s, which corresponds to at the altitude of 400 km (one tenth of ordinary flight tests flown by the space shuttle, e.g., ESEM), it should be stressed that the sputter-deposited MoS_2 reveals a high steady-state friction even at such a low AO flux in the space environment.

From the experimental data shown in Figure 6, the low $F_{initial}/F_{steady\text{-}state}$ ratio of the RF-H sample (see Figure 5) is interpreted as follows. The $F_{steady\text{-}state}$ in Figure 5 reflects the friction coefficient of the unexposed samples because of the abrasion of the oxidized layer. The friction coefficient of the unexposed RF-H is twice as high as that of the RF sample as shown in Figure 6. In contrast, the friction coefficients of the RF and the RF-H under the AO beam exposure show very similar value. Therefore, it was concluded that the low $F_{initial}/F_{steady\text{-}state}$ ratio of the RF-H was mainly due to the high friction coefficient in the unexposed condition. From this discussion, it is considered that the effect of 5 eV AO beam exposure on the RF and RF-H samples is essentially similar for both materials.

The effect of the pause of the AO beam exposure was demonstrated in Figure 7. As indicated in Figure 7, the AO-induced high friction coefficient decreased when exposure was stopped. The recovery of the friction coefficient is not a hundred percent, but we saw the correlation between the AO beam exposure and the friction coefficient.

5. CONCLUSIONS

We have studied the change in the tribological properties of sputter-deposited MoS_2 films under 5 eV AO beam exposure. A combination of the PSI type high flux AO source and the UHV-friction tester attached to the source chamber is a powerful tool for evaluating the effect of AO exposure to the lubrication materials. The tribological testing performed in this study clearly showed that the effect of AO exposure on the sputter-deposited MoS_2 film was notable. It was demonstrated that the sputter-deposited MoS_2 film exposed to 5 eV AO beam with fluences higher than 2 x 10^{16} atoms/cm^2 increased the initial friction force, reaching 2.5 times higher than the normal value. It was also shown that the steady-state friction was affected by the AO exposure even in an AO flux as low as 10^{14} AO/cm^2/s. These experimental results suggest that the lubrication system operative in the LEO environment may evidence high friction in all operations due to the AO-induced oxidation.

6. ACKNOWLEDGMENTS

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