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ATOMIC OXYGEN-MoS_2 CHEMICAL INTERACTIONS

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ABSTRACT

The present study shows that, at 1.5 eV O-atom translation energy, SO_2 is generated and outgases from an anhydrous MoS_2 surface with an initial reactivity nearly 50% that of kapton. The reaction of atomic oxygen with MoS_2 has little or no translational energy barier; i.e., thermally generated atomic oxygen reacts as readily as that having 1.5 eV of translational energy. It is also shown that water, present in the flowing afterglow apparatus used to study thermal O-atom reactivity, formed sulfates on the MoS_2 surface and that the sulfate is most likely in the form of sulfuric acid. These results imply that water dumps or outgasing in low earth orbit have the potential of forming sulfuric acid covered surfaces on MoS_2 lubricants. For MoS_2 films sputter-deposited at 50-70°C, friction measurements show a high initial friction coefficient for O-atom exposed MoS_2 surfaces (up to 0.25) which drops to the normal low values after several cycles of operation in air and ultrahigh vacuum. For MoS_2 films deposited at 200°C, the friction coefficient was not affected by the O-atom exposure.

INTRODUCTION

At low earth orbit (LEO) altitudes of 100-1000 km, pressures are high (10^{-7} torr) and the residual atmosphere consists primarily of atomic oxygen [1]. Spacecraft orbital velocities at LEO altitudes result in a reactive chemical environment that is equivalent to bombardment of exposed, forward-facing surfaces with 5 eV atomic oxygen at a flux level of about 1 monolayer/second. Long-term (10-30 years) operation of spacecraft at LEO altitudes requires lubricants that can withstand the extreme chemical environment. Flight- and ground-based investigations have shown that organic-based materials erode at a rate of about 0.1 monolayers/orbit in LEO [1], but little is known about the LEO environmental interactions with solid lubricants.

Previous work [2] by the authors has shown that exposure of MoS_2 to 1.5 eV atomic oxygen in an anhydrous environment produces a degree of oxidation that is essentially independent of crystallite orientation, and the surface adsorbed reaction products are MoO_3 and MoO_2. A mixture of oxides and sulfide exists over a depth of about 90 Å, and this layer has a low diffusion rate for oxygen. It was concluded that a protective oxide layer will form on MoS_2 upon exposure to the atomic-oxygen-rich environment of LEO. It is the purpose of this investigation to determine the gas phase products of the reaction of atomic oxygen with solid MoS_2, to determine the effect of O-atom kinetic energy on the reaction rate, to assess the importance of co-deposited water on the reaction mechanism, and to measure the effect of O-atom oxidation on the tribological properties of MoS_2.

MATERIALS PREPARATION AND ATOMIC OXYGEN EXPOSURE

MoS_2 thin films deposited onto 440C stainless steel substrates (hardened to 61 HRC) to a nominal thickness of 10,000 Å were obtained from sources [3] that used rf-sputter-deposition methods. The basal planes of the MoS_2 crystallites in the films were predominantly perpendicular to the substrate surface and had the typical plate-like growth pattern. These films were used for friction coefficient measurements and were only exposed to the hypervelocity atomic beam source and not the thermal source. Naturally occurring single-crystal specimens of MoS_2 were examined to provide truly coplanar specimens. The apparatus [4] used to expose the samples to atomic oxygen consists of: 1) a laser-sustained plasma source [4-7] for the production of energetic (1.5 eV) oxygen atoms in an atomic beam having a flux of 10^{17} O-atoms/sec-cm^2, 2) a means for controlling sample temperature and position relative to the atomic beam, and 3) a means for absolute flux calibration of the O-atom beam [8]. All exposures were performed with the sample temperature at 25°C and a beam energy of 1.5 eV. Gas phase reaction products were measured using a residual gas analyzer whose ionizer was placed 20 mm from the sample on a line of sight that was 45° from the surface normal.

A flowing afterglow apparatus was used to perform thermal O-atom exposures. A microwave power supply operating at 2450 MHz was used with an Evanson-type discharge in a flowing argon/oxygen (90%/10%) gas mixture at a total pressure of 2 torr. The forced-air-cooled Evanson cavity was placed near the center of a 152-mm long, vertical section of 12-mm OD, 10-mm ID quartz tubing. After passing through the filling (9.4-mm ID) the flow was turned 90° before entering the materials test section of the apparatus. The materials test section was 40-mm ID (cleaned by rinsing with 20% aqueous HF before use) and the test specimens were placed in this section such that they lay on the bottom of the horizontal 40-mm tubing section with both sides exposed to the flowing gas. Oxygen atom concentrations were measured by titration with NO_2 using a titration inlet positioned at the sample position. All titrations were carried out before or after placement of the MoS_2 in the afterglow apparatus. Oxygen atom concentrations were verified during exposure with catalytic recombination probes [9] that were calibrated by NO_2 titrations. Oxygen atom flux was calculated from measured concentrations using the classical wall collision rate expression, flux=[O] v/4 where v is the average velocity $(8kT/\pi m)^{1/2}$, T is the apparatus temperature and m the atomic mass. This is the maximum flux assuming that the reaction is not diffusion limited under the low pressure conditions. The gas flow rate was 171.6 standard cubic centimeters for an average velocity in the test section of 91 cm/sec and a Reynolds number much smaller than one. Under these flow conditions, a fully developed parabolic laminar velocity profile was expected with no significant radial concentration gradients [9]. No attempt was made to purify gases or to ensure that no moisture was present in the discharge.

After exposure, samples were transported in air to various vacuum chambers for analysis. Samples were analyzed for chemical composition and oxidation state using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). XPS spectra were collected using a Leybold-Heraeus LHS-10 spectrometer equipped with a hemispherical electron energy analyzer. MgK_α (1253.6 eV) radiation was used and binding energies were corrected for possible surface charging by reference to the C 1s peak at 284.6 eV. Auger electron spectra were collected using a Physical Electronics Industries Model 590 scanning Auger microprobe that employed a 5 keV primary beam energy having a 2.7-μm beam diameter and a 2.1-μA beam current. Friction coefficients (Cf) were measured with a pin-on-disc tribometer [10] both in air and ultrahigh vacuum (UHV) before and after exposure to the atomic oxygen beam. The normal load was 0.31 N (32 kgf), and the sliding speed was 2-5 cm/sec. A new unlubricated 440C pin of radius 0.79 mm was used for each track.

RESULTS

Figure 1 shows XPS spectra collected from two natural single crystal samples that were exposed to the flowing afterglow apparatus for 5 min (2×10^{23} O-atoms/cm^2) and 127 min (5×10^{24} O-atoms/cm^2). No high temperature treatments of the samples were performed, either before or after exposure. Before exposure, single crystal samples were cleaved in air using transparent tape to expose a fresh surface immediately before insertion into the vacuum chamber. After exposure, the Mo 3d spectra show three peaks that result from the conversion of some of the Mo(IV) to Mo(VI). Three peaks are formed by the superposition of the Mo(IV) and Mo(VI) doublets; the left (higher binding energy) peak corresponds to the Mo(VI) $3d_{5/2}$ component, the central peak corresponds to a sum of Mo(VI) $3d_{3/2}$ and Mo(IV) $3d_{5/2}$ components, and the right (lower binding energy) peak corresponds to the Mo(IV) $3d_{3/2}$ component. Mo(VI) is associated with MoO_3 whereas Mo(IV) is associated with both MoO_2 and MoS_2. The sulfur peak at 162.2 eV is also shown and, in addition, another sulfur peak at 168 eV is found to have grown in as exposure time was increased. The peak at 168 eV is suggestive of sulfate [SO_4]. Since anhydrous $MoSO_4$ has been shown not to exist [11] and the flowing afterglow apparatus contained some moisture, it is believed that the sulfate peak is due to sulfuric acid formation. Sulfuric acid impregnated MoS_2 was examined by XPS (not shown) and indeed a very strong peak at 169 eV binding energy was observed.

In our previous work for 1.5 eV atomic oxygen exposure [2], the relative amounts of MoO_3 and MoO_2 were estimated by assuming that all of the detectable sulfur is in the form of MoS_2, that Mo(IV) is exclusively associated with either MoS_2 or MoO_2, and that analysis of the S 1s peak area relative to the Mo(IV) 3d peak area permits determination of the relative amounts of MoS_2, MoO_2 and MoO_3. Using these assumptions, it was found that exposure of single-crystal MoS_2 to the 1.5 eV oxygen beam resulted in conversion of 45% of the near-surface molybdenum into MoO_3 and 15% into MoO_2. Only slightly less oxide was formed in the coplanar, single crystal case (basal planes parallel to the surface) compared to the sputter-deposited MoS_2 film (basal planes predominantly perpendicular to the surface), indicating that crystallographic orientation is relatively unimportant in the oxidation process. In the present work (thermal O-atom exposure) it is unclear how to account for the SO_4 component in obtaining percentage conversion into molybdenum oxides. However, the Mo 3d peak shapes and absolute intensities compared to our previous work [2], indicate that to within factors of 2-4 the extent of oxide formation in the thermal exposure case is the same as in 1.5-eV atomic oxygen exposure experiments.

Figure 2 shows the gas-phase products formed when a flux of 1-2 monolayer/sec of atomic oxygen at a kinetic energy of 1.5 eV bombards a 25°C surface of natural single-crystal MoS_2. With the sample of MoS_2 removed from the oxygen atom beam, no mass 64 (SO_2) was observed. After insertion of the sample into the beam, an induction period of ~500 sec is observed before SO_2 (mass 64) begins to degas from the sample surface. An induction period has been observed for a variety of materials exposed to the atomic oxygen beam, and it is presumed that during the induction period hydrocarbon overlayers are burned off, exposing the underlying material. After an additional ~400 sec, a 90-Å protective oxide layer is formed, which stops the emission of SO_2. Roughly 4% of the atomic oxygen reacted forming MoO_3, MoO_2 and SO_2. This compares to a 10% reactivity of kapton to atomic oxygen. Mass 48 (SO) was subsequently monitored while exposing a different portion of the sample to the beam, and the evolution of SO is found to have approximately the same time history as SO_2, indicating that the SO most likely comes from the dissociative ionization cracking of SO_2

in the ion source of the residual gas analyzer rather than a direct gas-phase reaction product.

Figure 3 shows the friction coefficients of a MoS_2 film deposited at 50-70°C (AT) as a function of the number of cycles, i.e. the number of times that the pin traverses each part of the wear track. Two measurements were made before exposure to the oxygen atom beam: in air and in UHV. The UHV environment produced a friction coefficient of 0.03 ± 0.01 which is typical for these films, while the air environment gave a friction coefficient two times higher (0.06 ± 0.01) due to oxidation at the stylus tip. In contrast, after exposure to the O-atom beam both the UHV and air measurements gave very high friction coefficients (0.25 in air and 0.17 in UHV) initially, where upon the high friction gave way to the usually low friction coefficients which were measured before the O-atom exposure. Fewer cycles were required in UHV than in air to achieve the values obtained for the unexposed films. For MoS_2 films deposited at 200°C (HT), a significant difference is observed; the O-atom exposure did not affect the friction coefficients in air or UHV. This difference is attributed to the MoS_2 crystallite size, because previous measurements [2] suggest that both films would be oxidized approximately the same by the O-atom exposure.

AES measurements were taken of MoS_2 films before and after O-atom exposure. The S_{152}/Mo_{186} peak height ratio decreased from 7.7 to 4.8 for AT films and from 6.7 to 4.4 for HT films due to O-atom exposure, which correlates with the oxidation process of MoS_2 discussed previously. Based on the AES measurements the extent of the oxidation is similar for AT and HT films, though the crystallite size is larger and the surface area of edge sites is smaller for the HT film AES measurements were also taken of wear tracks formed in air before and after O-atom exposure. The S_{152}/Mo_{186} peak height ratios were essentially the same after 600 cycles, indicating that the oxidized material had been lost as debris and sliding was occurring on unoxidized bulk-like MoS_2 at the end of a 600 cycle test. AES measurements taken of wear tracks in situ in UHV cannot be used to determine the thickness of the oxidized layer because of unknown factors like transfer films and loss of debris. However, these measurements indicate the number of wear cycles necessary to remove the oxidized material producing bulk-like MoS_2 in wear tracks. For the HT film in UHV the S_{152}/Mo_{186} peak height ratio was 4.8 after 2 cycles, increasing to 6.1 by 10 cycles. The S_{152}/Mo_{186} peak height ratio for the AT film in UHV was 6.4 after 10 cycles. As shown in Figure 3 for the AT film in UHV, by 10 cycles the friction coefficient of the exposed film was the same as that for the unexposed film. We suggest, therefore, that rubbing in UHV requires less than 10 cycles to remove the oxidized material from wear tracks. Based on the friction coefficient curve in Figure 3 for air testing, approximately 20 cycles are required before the oxidized material has been removed from the wear track.

CONCLUSIONS

In our previous study [2] the oxidation properties of various crystalline forms of MoS_2 were investigated under conditions that simulate the LEO environment to determine possible tribological implications for lubricating films used on spacecraft. The following conclusions were drawn from that work: 1) exposure of MoS_2 to energetic (1.5 eV) atomic oxygen under anhydrous conditions results predominantly in the formation of MoO_3 in the near-surface region with lesser amounts of MoO_2; 2) the oxide layer is roughly 10-30 monolayers in thickness and consists of a mixture of the oxides with MoS_2; 3) the extent of oxidation is essentially independent of crystallographic orientation of the MoS_2; and 4) diffusion of oxygen atoms through the oxide layer is very slow. The absence of a crystallographic orientation dependence during oxidation is not surprising, since no dissociative step occurs for atomic oxygen exposure. Therefore, there is no barrier to adsorption and subsequent reaction of atomic oxygen. Exposure to atomic oxygen instead of molecular oxygen bypasses the dissociative adsorption step and the reactivity will be relatively independent of material crystallinity, in agreement with the results of that study.

The present study shows that SO_2 is generated and outgases from the surface with an initial reactivity 50% that of kapton. The reaction of atomic oxygen with MoS_2 has little or no translational energy barrier, i.e. thermally generated atomic oxygen reacts as readily as that having 1.5 eV of translational energy. It has also been shown that water present in the flowing afterglow apparatus formed sulfates on the MoS_2 surface and that the sulfate is most likely in the form of sulfuric acid. These results imply that water dumps or outgasing in LEO have the potential to form sulfuric-acid-covered surfaces on MoS_2 lubricants. A 1-μm thick sputter deposited MoS_2 film which was exposed to the hyperthermal O-atom beam gave a very high initial friction coefficient in air (0.25) due to oxide formation on the surface. The friction dropped very quickly (within 10 cycles in UHV and within 20 cycles in air) as the < 100 Å oxidized film was worn away exposing fresh MoS_2 material. The friction measurements indicate that a high initial starting tangential force would be required after O-atom exposure of MoS_2 films with the force dropping to its normal low value after ~10 cycles of operation. A continuous flux of atomic oxygen striking the MoS_2 surface would result in a much higher value of the average friction which would depend upon the speed per cycle and absolute value of the O-atom flux.

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FIGURE CAPTIONS

Figure 1. XPS spectra of naturally occurring single crystal MoS_2 after exposure to the thermal atomic oxygen flowing afterglow apparatus. The O-atom fluences for the 5-minute and 125-minute exposures are 2×10^{25} and 5×10^{26} O-atoms/mm^2, respectively.

Figure 2. Gas-phase reaction products from the reaction of hyperthermal O-atoms with MoS_2. O-atom beam is turned on at zero time. The mass 64 and mass 48 evolution traces are from different experiments at different locations on the sample. Mass 48 (SO) comes from the dissociative ionization of SO_2.

Figure 3. Friction coefficient (Cf) as a function of the number of wear cycles before and after exposure to the hyperthermal atomic oxygen beam. The measurements were taken both in air and in ultrahigh vacuum for a sputter deposition temperature of 50-70°C.

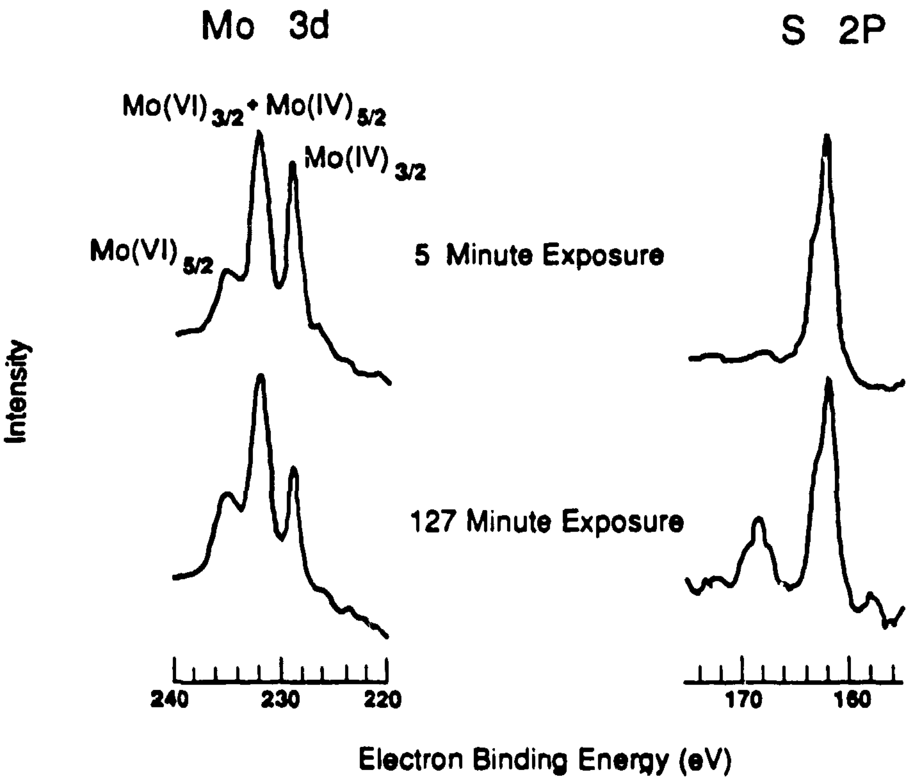

Fig. 1

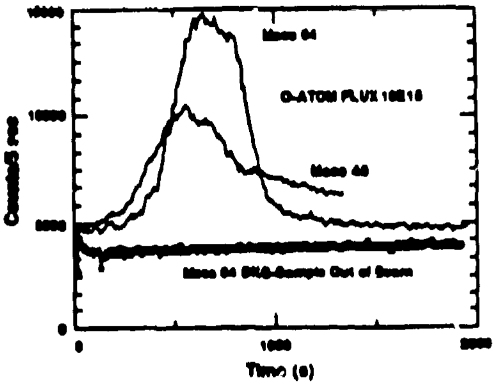

Fig. 2

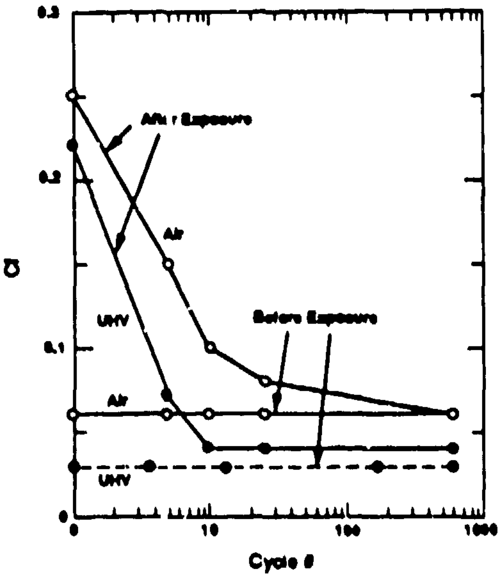

Fig. 3