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Oxidation of MoS_2 by Thermal and Hyperthermal Atomic Oxygen

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ABSTRACT

The present study shows that at 1.5 eV O-atom translational energy SO_2 is generated and out gasses from a anydrous MoS_2 surface with a reactivity comparable to that of kapton. The reaction of atomic oxygen with MoS_2 has little or no translational energy barrier,i.,e., thermalally 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 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 sufuric acid. These results imply that water dumps or outgassing in low earth orbit have the potential of forming sulfuric acid covered surfaces on MoS_2 lubricants.

INTRODUCTION

At low earth orbit (LEO) altitudes of 200-1000 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, in addition to the radiation component of the environment. 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 monolayer/orbit in LEO[1] but little is known concerning 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 produce 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 exist 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 low earth orbit. 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, asses 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 sapphire substrates to a nominal thickness of 5000 Å were obtained from sources that used rf-sputter-deposition methods. Orientations of the MoS_2 crystallites in the films were random. Naturally-occurring single-crystal specimens of MoS_2 were examined to provide truly coplanar specimens. The apparatus[3] used to expose the samples to atomic oxygen consists of: 1) a laser-sustained plasma source[4,5,6] for the production of energetic (1.5 eV) oxygen atoms in an atomic beam of 10^{17} O-atoms/sec-cm^2 flux, 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[7]. 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 2 cm from the sample on a line of sight which 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 a Evanson-type discharge cavity to generate a 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 15.2 cm long, vertical section of 12 mm OD, 10 mm ID quartz tubing. After passing through the fitting (9.4 mm ID) the flow was turned 90 degrees 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 40mm 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 samples in the afterglow apparatus. Oxygen atom concentrations were verified during exposure with catalytic recombination probes[8] which 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 $(8kT/\pi m)^{1/2}$ and 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 sccm 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 with no significant radial concentration gradients was expected[8]. 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. Mg Kα (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 (AES) were collected using a scanning Auger microprobe that employed a 5 keV primary beam energy having a 1 micrometer beam diameter and 2 microampere beam current.

RESULTS

Figure 1 shows XPS spectra collected from two natural single crystal samples which were exposed to the flowing after glow apparatus for 5 min and 127 min. No high temperature treatments 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 sulphur peak at 162.2 eV is also shown and in addition another peak at 168 eV is found to have grown in as the exposure time was increased. The position of this peak is suggestive of sulfate [SO_4]. Since anhydrous $MoSO_4$ has been shown not to exist[9] and the flowing afterglow apparatus contained some moisture, it is believed that the sulphate 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.

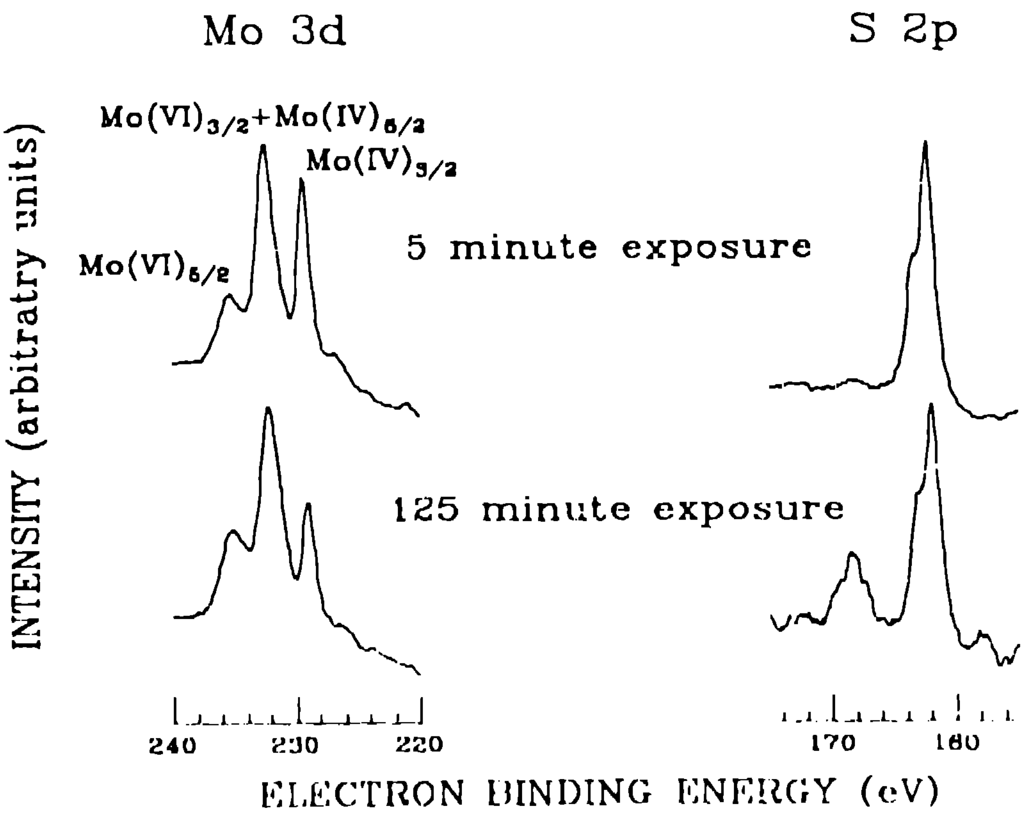

Fig. 1 XPS spectra of naturally-occurring single crystal MoS_2 before and after exposure to the thermal atomic oxygen flowing afterglow apparatus. The O atom fluences for the 5 minute and 125 minute exposures are 10^{21} and 10^{22} O atoms/cm^2 respectively

In our previous work[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 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 the above assumptions, it was found that exposure of single crystal MoS2 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 compared to the randomly-oriented film, indicating that crystallographic orientation is relatively unimportant in the oxidation process. In the present work 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 that 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 monolayers/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)

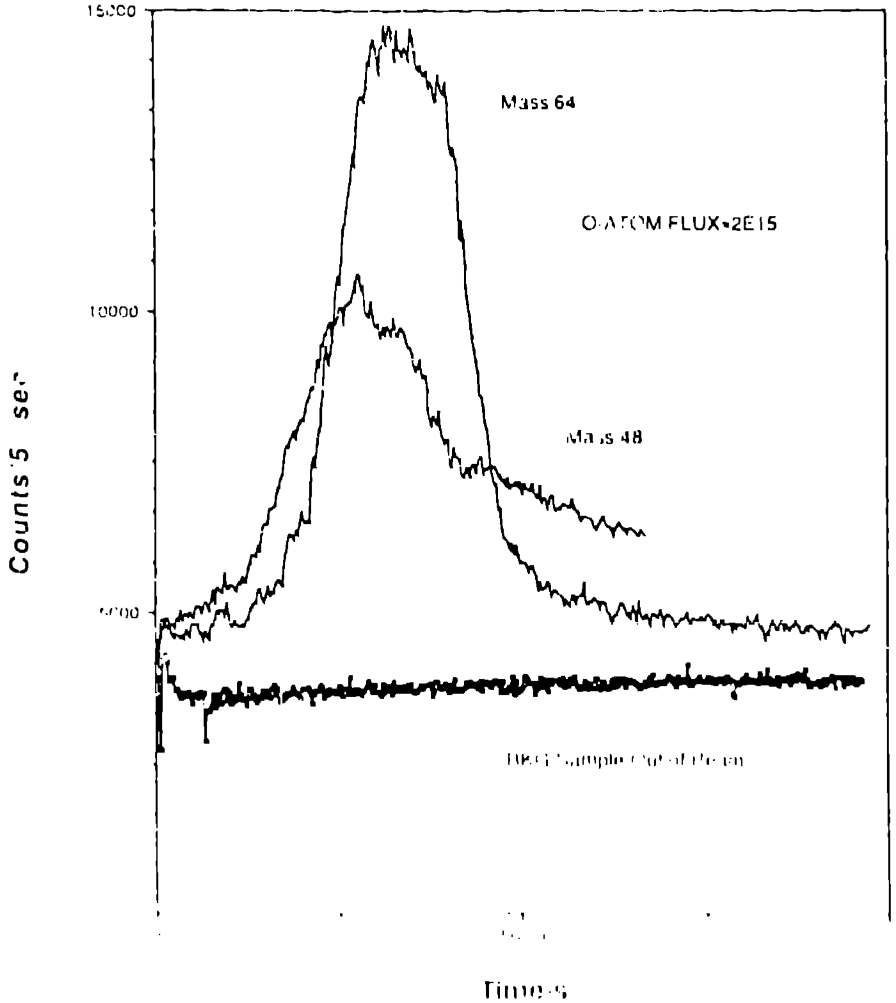

Fig 2 Gas phase reaction products from the reaction of hyperthermal O atoms with MoS_2. O atom beam is turned on at zero time. Mass 48 [SO] comes from the dissociative ionization of SO_2

begins to degas from the sample surface. During the induction period hydrocarbon overlayers are burned off exposing the underlying MoS_2 surface. In a period of roughly 400 seconds a 90Å 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 roughly 10% reactivity of kapton to atomic oxygen. Mass 48 (SO) was monitored after exposing a different portion of the sample to the beam and is found to have approximately the same time history as SO_2 indicting 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.

CONCLUSIONS

In our previous study[2] the oxidation properties of various crystalline forms of MoS_2 were investigated under conditions that simulate the low earth orbit environment to determine possible tribological implications for lubricating films used on spacecraft. The following conclusions were drawn from this 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. This is not surprising since 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 out gasses from the surface with a reactivity comparable to that of kapton. The reaction of atomic oxygen with MoS_2 has little or no translational energy barrier, i.,e . thermalally 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 sufuric acid. These results imply that water dumps or outgassing in low earth orbit have the potential to form sulfuric acid covered surfaces on MoS_2 lubricants.

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REFERENCES

1. L. Leger, J. Visentine, B. Santos-Mason, 18th International SAMPE Technical Conference 18, October 7-9, 1986, Seattle, WA.
2. J.B. Cross, J.A. Martin, and L.E. Pope; Proceedings of the Materials Research Society 1988 Fall Meeting, Boston, MA.
3. J.B. Cross, L.H. Spangler, M.A. Hoffbauer, and F.A. Archuleta, 18th International SAMPE Technical Conference, October 7-9, 1986, Seattle, WA.

4. J.B. Cross and D.A. Cremers, Nucl. Instr. Methods B13, 658 (1986).
5. J.B. Cross, D.A. Cremers, L.H. Spangler, M.A. Hoffbauer, F.A. Archuleta, Proceedings of the 15th International Symposium on Rarefied Gas Dynamics 1, June 16-20, 1986, Grado, Italy.
6. J.B. Cross and N.C. Blais, Proceedings of the 16th International Symposium on Rarefied Gas Dynamics, July 11-15, 1988, Pasadena, CA (in press).
7. J.B. Cross, E.H. Lan, C.A. Smith, 33rd International SAMPE Symposium & Exhibition, March 7-10, 1988, Anaheim, CA.
8. F. Kaufman, Prog. React. Kinet. 1, pp1-39, 1961.
9. S.S. Pollack, Inorg. Chem., 26, pp 1825, 1987.