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## LABORATORY INVESTIGATIONS: LOW EARTH ORBIT ENVIRONMENT CHEMISTRY WITH SPACECRAFT SURFACES

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### ABSTRACT

Long-term space operations that require exposure of material to the low earth orbit (LEO) environment must take into account the effects of this highly oxidative atmosphere on material properties and the possible contamination of the spacecraft surroundings. Ground-based laboratory experiments at Los Alamos using a newly developed hyperthermal atomic oxygen (AO) source have shown that not only are hydrocarbon based materials effected but that inorganic materials such as  $\text{MoS}_2$  are also oxidized and that thin (750 Å) protective coatings such as  $\text{Al}_2\text{O}_3$  can be breached, producing oxidation of the underlying substrate material. Gas-phase reaction products, such as  $\text{SO}_2$  from oxidation of  $\text{MoS}_2$  and  $\text{CO}$  and  $\text{CO}_2$  from hydrocarbon materials, have been detected and have consequences in terms of spacecraft contamination. Energy loss through gas-surface collisions causing spacecraft drag has been measured for a few select surfaces and has been found to be highly dependent on the surface reactivity.

### INTRODUCTION

Interest in long-term (20-year) habitation of low earth orbit (LEO) for military and civilian use is increasing and will in all likelihood continue to increase for the foreseeable future. The Russian space station Mir is functional, and the United States is designing its own station--FREEDOM. Operations in LEO (200-500 km) however must take into consideration the high partial pressure ( $10^{-6}$  to  $10^{-7}$  torr) of atomic oxygen (AO) that exists at these altitudes. These partial pressures produce extensive oxidation of materials facing the direction of travel (ram direction of spacecraft). The ram oxidation is most severe not only because of the high flux ( $10^{15}$  AO/s- $\text{cm}^2$ ) but also because of the high collision energy (5 eV) of AO with the ram surfaces. Both the high flux and the high collisional energy are a result of the high orbital velocity (8 km/s) of the spacecraft. Los Alamos is performing ground-based simulations of these conditions using a continuous-wave (cw), laser-sustained discharge source for the production of a 1- to 5-eV beam of AO with a flux of up to  $1 \times 10^{17}$  AO/s- $\text{cm}^2$  ( $100 \times$  LEO flux).

### ATOMIC OXYGEN FACILITY

The AO source<sup>1-3</sup> (Fig. 1) employs a cw plasma formed by focusing a high-power  $\text{CO}_2$  laser beam to produce plasma temperatures of 15 000 to 20 000 K in a rare-gas/oxygen mixture. The cw  $\text{CO}_2$  laser (10.6  $\mu\text{m}$ ) is used to sustain the spark-initiated plasma in the mixture, which subsequently flows through a 0.3-mm-diam nozzle in an isentropic expansion producing an atomic beam of neutral species. Stagnation pressures of 2 to 8 atm are employed depending on the rare gas, i.e., 2 atm for 50%  $\text{O}_2$  in argon and 8 atm for 15%  $\text{O}_2$  in helium. The isentropic expansion acts as an atomic accelerator where collisions of the excess lighter gas (helium) with the heavier AO bring the AO velocity up to or near that of the helium.<sup>4</sup> A 2.54-cm focal-length ZnSe lens is used to focus the  $\text{CO}_2$  laser beam to a 100- $\mu\text{m}$  spot, which produces power densities of  $10^7$  W/ $\text{cm}^2$  and sustains the plasma at a roughly 50% ionized condition. The lens is moved axially to position the plasma ball in the throat of the water-cooled nozzle. We have obtained continuous operation times of >75 hours with fluences of  $>10^{22}$  AO/ $\text{cm}^2$ , roughly equal to the fluence that the U.S. Space Station will receive at 500 km over its operational lifetime (20-30 years). The source is mounted in a molecular beam apparatus (Fig. 2), where the gas mixture is skimmed after exiting the nozzle and then collimated into a neutral atomic beam of rare gas and AO. The facility consists of

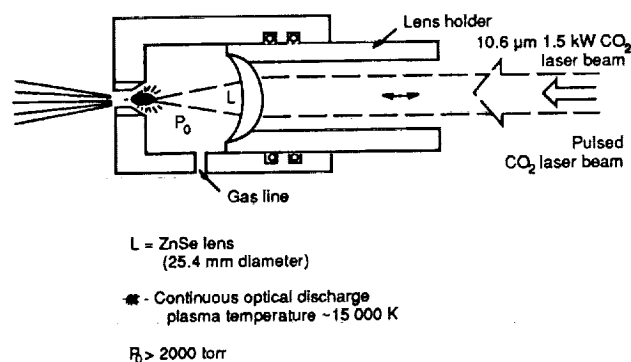


Figure 1. Laser-sustained plasma atomic oxygen beam source. Plasma is initiated by one pulse from a pulsed  $\text{CO}_2$  laser and sustained by a 1.5 kW cw  $\text{CO}_2$  laser.

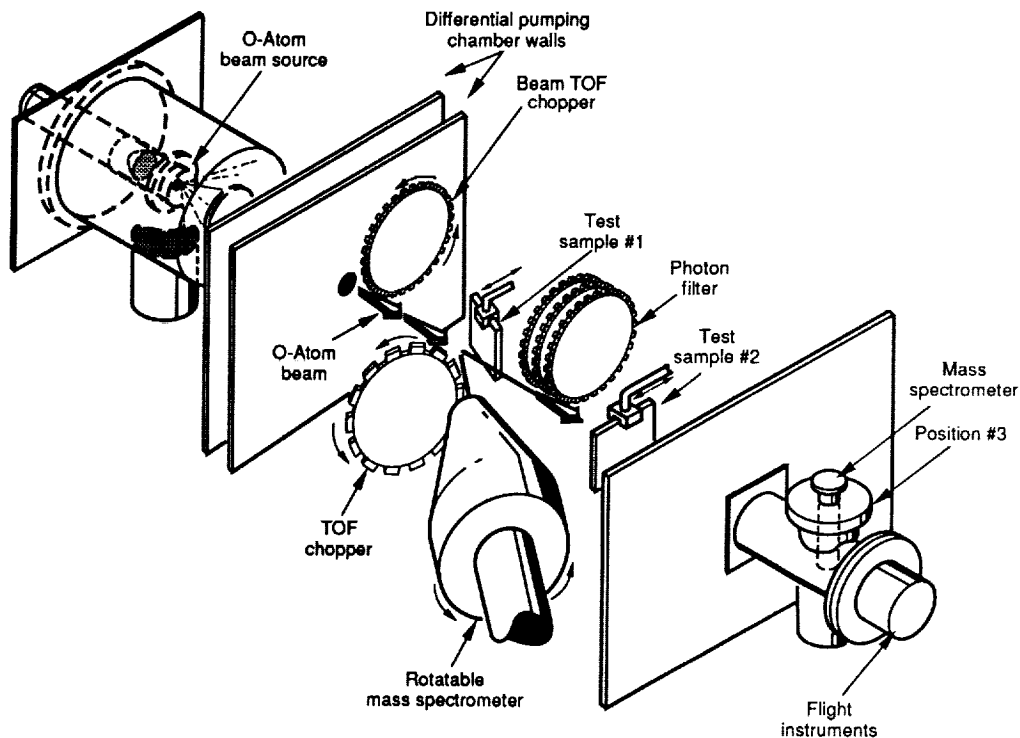


Figure 2. Primary components of the molecular beam apparatus that contains the AO source. The TOF chopper and mass spectrometer at the flight instrument position are used to obtain beam velocity distributions while the rotatable quadrupole mass filter is used to measure angular scattering distributions. The photon filter will be used to filter out plasma produced light from the AO beam to isolate the effects of photons on gas-surface reactions.

- the laser-sustained AO beam source,
- three stages of differential pumping between the source and three sample manipulators located 15, 55, and 120 cm from the source,
- a rotatable mass spectrometer with time-of-flight (TOF) capability for measuring scattered particle angular and velocity distributions to determine drag coefficients and gas-phase reaction products,
- a quadrupole mass spectrometer (located 120 cm in line with the source) used for beam TOF measurements and a mass spectrometer calibration chamber, and
- a photon filter used to filter out photons created in the AO source for studying the effects of vacuum ultraviolet (vuv) radiation on polymer-coating reactions.

At the sample manipulator position, 15 cm from the source, AO flux densities of  $\approx 10^{17}$  AO/s-cm<sup>2</sup> are obtained, whereas at the mass spectrometer calibration chamber position, flux densities of  $\approx 10^{15}$  AO/s-cm<sup>2</sup> are recorded. A base pressure of  $1 \times 10^{-9}$  torr, which rises to  $2 \times 10^{-6}$  torr when the AO beam is operating, is created in the sample exposure chamber. Figure 3 shows AO energy distributions obtained from TOF analysis of the AO beam. The rare-gas symbols indicate the oxygen/rare-gas composition, i.e., neon designates a mixture of 50% neon + 50% O<sub>2</sub>, whereas Ne/He designates 25% O<sub>2</sub> + 25% neon + 50% helium. For comparison, the calculated in-orbit AO energy distribution, assuming an atmospheric temperature of 1000 K, is shown. The O<sub>2</sub> dissociation for the

argon, neon, Ne/He, and helium mixtures is 85%, 87%, 96%, and an estimated 98% at stagnation pressures of 1900, 2200, 4200, and 6000 torr, respectively.

Vacuum ultraviolet intensities comparable to that of solar radiation are observed with a Ne/O<sub>2</sub> mixture, whereas Ar/O<sub>2</sub> produces vuv intensities that are a factor of 3 higher; thus, polymer materials can be investigated under the same vuv conditions that exist in orbit. However, the high transmission velocity filter can be used to eliminate photons from the AO beam for investigation of the mechanisms of vuv/AO polymer degradation.

### BEAM FLUX CALIBRATION

Samples are normally exposed to the beam at the sample manipulator 15 cm from the nozzle (position #1), and beam calibration is performed at the mass spectrometer calibration position 120 cm from the nozzle (position #3). A simple technique<sup>5</sup> has been developed to perform beam calibrations and to evaluate reaction rates of coatings and conductive materials. A thin strip of conductive material is deposited on a nonconducting and nonreactive substrate, and a resistance measurement is made as a function of time of exposure to the AO beam to determine the rate of material loss or the conversion to a nonconducting oxide. In the case of silver, the conducting metal is transformed into its nonconducting oxide, thus increasing the device's resistance, whereas carbon, if

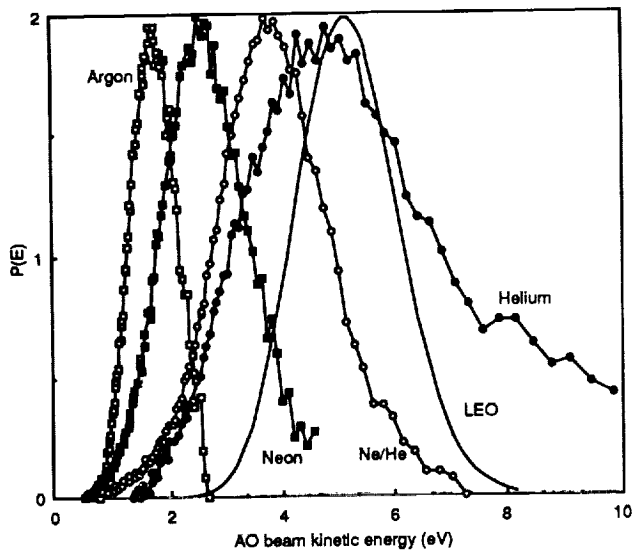


Figure 3. Atomic oxygen kinetic energy distributions. Solid line without data points is approximate orbital kinetic energy distribution of AO with surfaces facing the direction of travel (ram surface).

deposited in place of the silver, forms volatile oxides, which alter the film's cross-sectional area. The time history of a 250-Å-thick bare silver film, when exposed to the AO beam (2.5 eV) at position #3, is shown in Fig. 4 and represents an oxidation rate of roughly 1.7 monolayers/s or a beam flux of approximately  $2 \times 10^{15}$  AO/s-cm<sup>2</sup>. In addition, the reactivity of coating<sup>6</sup> can be determined by measuring the time required to burn through a known thickness of the coating. The burn-through is detected by the subsequent oxidation of the silver.

## RESULTS

### Surface Temperature/Beam Energy Effects

Investigations were performed to determine the relative importance of surface temperature (activation energy) and beam translational energy on the reaction rate of AO with sputter-deposited graphite. Figure 4 shows a typical data set, where a silver strip is used to obtain a beam flux calibration at position #3, and then a sputter-deposited graphite strip is exposed at position #1. The 250-Å bare silver strip required over 100 s before the silver began to react. This effect is caused by the burning off of a hydrocarbon overlayer, which was produced in the device fabrication. A large number of bare silver actinometers have been exposed, and in all cases, the lag or burn-off time correlates with the silver oxidation rate or the AO flux.

Figure 5 shows the reaction efficiency variation of the sputter-deposited graphite with AO over the kinetic energy range of 1.5 to 3 eV at a surface temperature of 35°C. The data represent a 10% to 30% change in reaction efficiency between 1.5 and 3 eV. Similar investigations with varying surface temperatures at a constant beam energy show an activation energy of 800 cal/mole for graphite oxidation, which agrees with shuttle-based flight experiments.<sup>7</sup> These results indicate that graphite-based materials are affected primarily by high kinetic

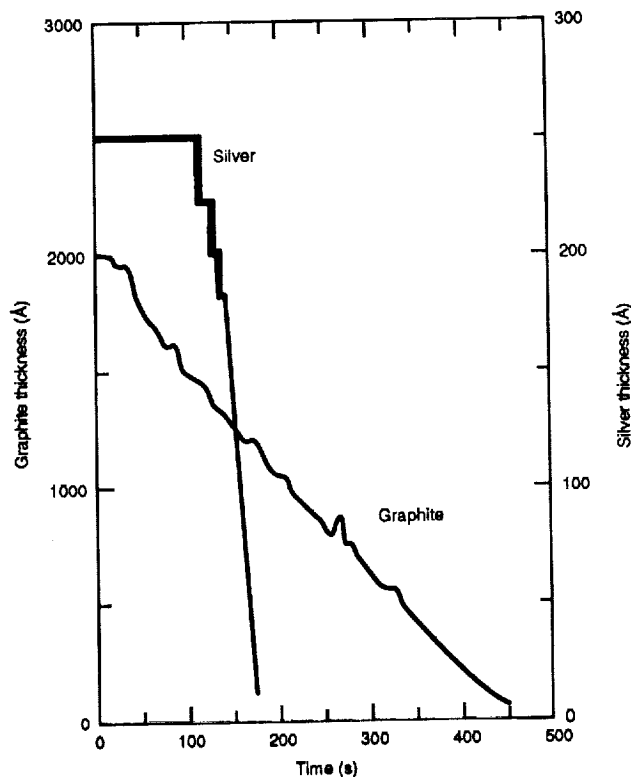


Figure 4. Reaction rates of 250 Å silver film at position #3 and 2000 Å sputter deposited graphite at position #1.

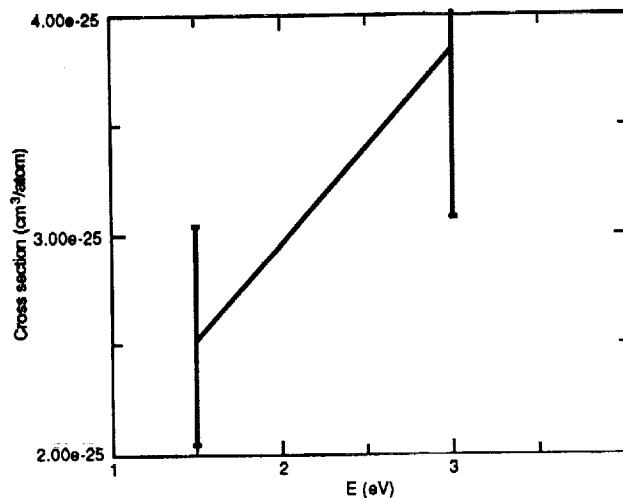


Figure 5. Translational energy dependence of sputter deposited graphite with AO at a surface temperature of 35 °C.

AO but that high-temperature surfaces will suffer additional degradation in LEO because of the thermal energy component of the reaction.

### Beam Surface Scattering

AO angular scattering distributions from reactive and nonreactive materials were measured at a beam kinetic energy of 1.5 eV using the rotatable mass spectrometer (Fig. 2). These

distributions indicate that the reactive surface produces complete accommodation of the AO and that the AO leaves the surface in a cosine distribution, having forgotten its initial velocity vector (Fig. 6). The nonreactive surface, however, produces specular-like scattering, with the AO remembering its initial velocity vector as it leaves. Separate TOF experiments<sup>1</sup> (not shown here) indicate that approximately 50% of the initial energy is lost to the nonreactive surface, whereas the reactive surface showed complete accommodation. The polyethylene gas-phase products were H<sub>2</sub>O, CO, and CO<sub>2</sub>, all of which showed accommodation to the material surface temperature (393 K). These results have important implications for long-term operation of spacecraft in the LEO environment in terms of spacecraft drag and contamination. Nonreactive surfaces reduce spacecraft drag more than reactive ones and simultaneously act as mirrors for AO, possibly creating higher than normal AO fluxes on nonram surfaces that are shielded from direct AO attack. The H<sub>2</sub>O, CO<sub>2</sub>, and CO reaction products are emitted in a cosine distribution from surfaces and may contaminate other parts of the craft. Information on detailed angular/velocity scattering distributions and reaction product identity will allow complete computer simulation of spacecraft interaction with the LEO environment. Predictions can then be made on long-term drag, contamination, and materials degradation, all of which determine the spacecraft operational lifetime.

### Tribology Investigations

In our first study,<sup>8</sup> the oxidation properties of various crystalline forms of MoS<sub>2</sub> were investigated to determine possible tribological implications for lubricating films used on spacecraft in LEO. The following conclusions were drawn from that work:

- Exposure of MoS<sub>2</sub> to energetic (1.5 eV) AO under anhydrous conditions results predominantly in the formation of MoO<sub>3</sub> in the near-surface region with lesser amounts of MoO<sub>2</sub> (Fig. 7).
- The oxide layer is roughly 10-30 monolayers in thickness and consists of a mixture of the oxides with MoS<sub>2</sub>.
- The extent of oxidation is essentially independent of crystallographic orientation of the MoS<sub>2</sub>.
- Diffusion of oxygen atoms through the oxide layer is very slow.

The reaction independence from crystallographic orientation is not surprising since exposure to AO bypasses the dissociative adsorption step in O<sub>2</sub> oxidation whose rate is highly dependent upon surface defects and crystallographic orientation.

The next study<sup>9</sup> showed that SO<sub>2</sub> is generated and outgases from the MoS<sub>2</sub> surface (Fig. 8) with a reactivity comparable to that of kapton, and the reaction of AO with MoS<sub>2</sub> has little or no translational energy barrier, i.e., thermally generated AO reacts as readily (within factors of 2-4) as that having 1.5 eV of translational energy. It was discovered that if water is present, sulfates are formed on the MoS<sub>2</sub> 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

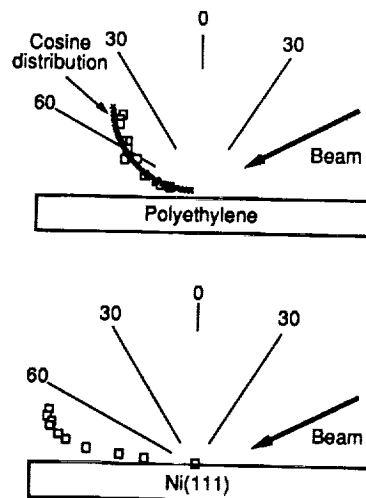


Figure 6. Angular scattering distributions of AO from a reactive surface (cosine) and a nonreactive surface of nickel oxide (specular like).

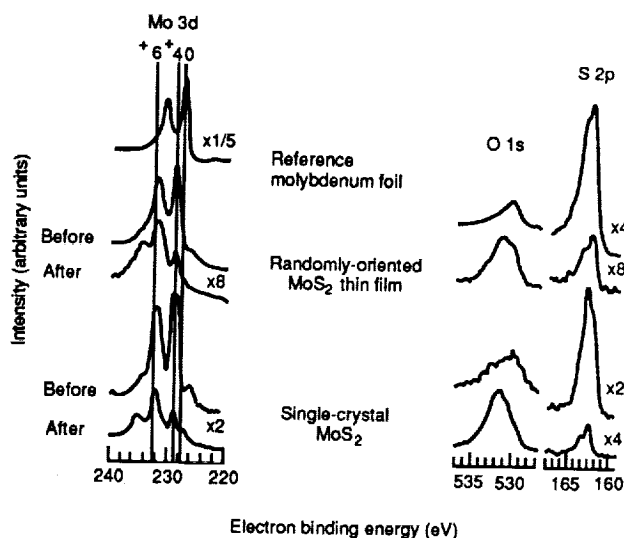


Figure 7. X-Ray photoelectron spectra of reference molybdenum foil, randomly oriented MoS<sub>2</sub> thin film, and single-crystal MoS<sub>2</sub>. Note the presence of Mo<sup>6+</sup> state indicating MoO<sub>3</sub> formation.

potential to form sulfuric-acid-covered surfaces on MoS<sub>2</sub> lubricants.

Friction studies were undertaken, and it was found that a 1-micron-thick sputter-deposited MoS<sub>2</sub> film that was exposed to the hyperthermal AO beam produced a very high (0.2) friction coefficient because of oxide formation on the surface. The friction dropped very quickly as the 100 Å oxide film was worn away exposing fresh MoS<sub>2</sub> material (friction coefficient = 0.05). The friction measurements indicate that a high initial starting force would be required after MoS<sub>2</sub> exposure to AO with the force dropping to its normal low value after several cycles of operation. A continuous flux of AO striking the MoS<sub>2</sub> surface would result in a higher average value of the friction depending upon the speed per cycle and absolute value of the AO flux.

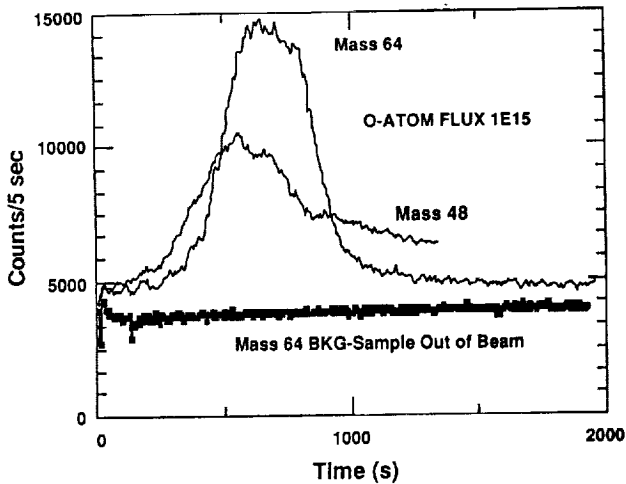


Figure 8. The mass spectrometric signal showing the outgassing rate of  $SO_2$  and  $SO$  from a  $MoS_2$  surface exposed to the indicated AO flux.

### Protective Coatings

Because protective coatings will be needed to impede the degradation of specialized materials for solar arrays, solar concentrators, and mirrors, etc., a series of studies on the durability of thin inorganic coatings has been undertaken. Thin films (250 Å) of silver were overcoated with sputter-deposited  $Al_2O_3$  (750-Å thickness) on rough (1-micron rms roughness) alumina and also on smooth single crystal sapphire substrates. Resistance measurements were taken on the coated silver as a function of substrate temperature while being exposed to the AO beam. The reaction rates measured on the coated silver on the rough alumina substrate were not reproducible presumably because of the inability to uniformly coat over the high roughness of the substrate. The reaction rates measured on the smooth sapphire substrates though showed a much greater reproducibility than those measured on the alumina. Figures 9 and 10 show some typical data obtained using the sapphire substrate. Figure 9 shows the results of heating the  $Al_2O_3$ -coated silver strip during exposure to a 3-eV neutral argon beam having a flux of  $\approx 10^{17}$  Ar/s- $cm^2$ . The resistance changes correlate with the substrate temperature, indicating that the silver is not oxidized by reaction with the substrate or coating but rather that the resistance is only changing because of the temperature coefficient of resistance. Note that the absolute resistance change is only on the order of 0.5 ohms. Figure 10 on the other hand shows the results of heating the coated silver during exposure to a 1.5-eV AO beam having a flux of  $\approx 10^{17}$  AO/s- $cm^2$ . The resistance change does not correlate with small temperature variations, and the absolute resistance change is on the order of 3 K ohms, indicating that the presence of hyperthermal AO causes severe degradation of coated silver. Figure 11 summarizes the temperature variation of the coated silver reaction rate, i.e., the activation energy is  $\approx 5$  kcal/mole. This activation energy is an order of magnitude lower than the diffusion-limited activation energy for high-temperature  $O_2$  interaction with  $Al_2O_3$ . Further experiments are under way to understand the degradation mechanism, i.e., whether there are microscopic flaws in the film that

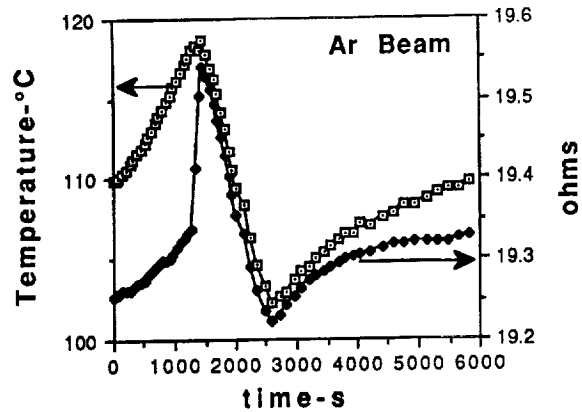


Figure 9. Results of heating the  $Al_2O_3$ -coated silver strip during exposure to a 3-eV neutral argon beam.

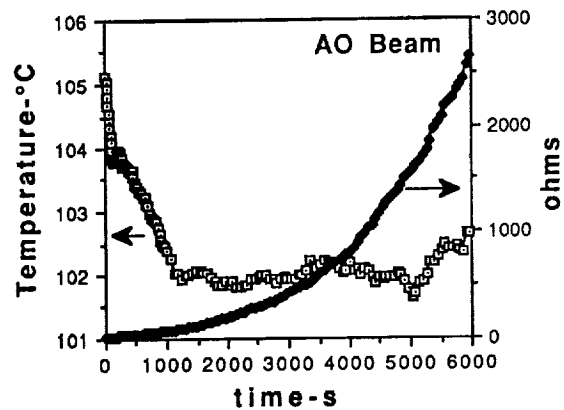


Figure 10. Results of heating the coated silver during exposure to a 1.5-eV AO beam.

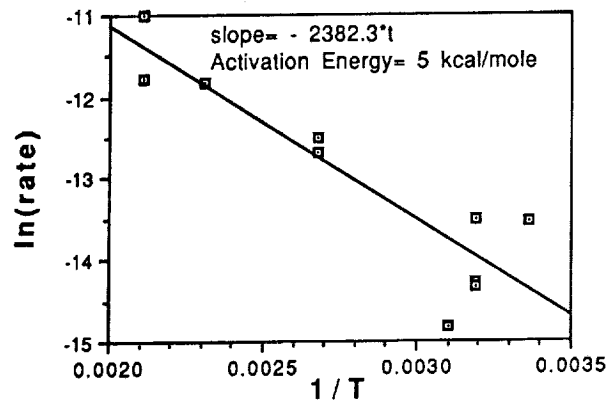


Figure 11. Summary of temperature variation of the coated silver reaction rate.

allow AO to diffuse along grain boundaries and dislocations to the silver or whether high translational energy AO produces enhanced bulk diffusion in  $Al_2O_3$ , etc. Nevertheless, these initial experiments have shed light on the difficulty of producing protective coatings that will withstand long-term exposure to this highly unusual environment.

#### Accelerated Testing

Spacecraft operating in LEO for extended periods of time (20 years) will experience total fluences of  $10^{22}$  to  $10^{23}$  AO/cm<sup>2</sup> (Ref. 10). Materials certification studies are needed to ensure reliable operation of a spacecraft over its operational lifetime and thus will require exposure of selected materials to the same total fluence that the craft will experience but in less than real time. These studies can be performed with the laser-sustained AO plasma source because of the ability to obtain a total fluence of  $3.6 \times 10^{22}$  AO/cm<sup>2</sup> at the 1-5 eV energy level in 100 hours of operation. In addition to the ability to perform such exposures, an understanding of the surface reaction mechanisms is needed to interpret the results. For example, the increased AO flux needed for accelerated testing may provide a mechanism for enhanced AO recombination on surfaces before reaction with the surface can occur, thus giving a lower materials reaction probability than actually occurs in orbit. The mechanistic studies needed to interpret accelerated testing data are now under way.

#### Orbital Flight Experiments

The LEO simulation performance requires comparison of ground-based results to the results produced by the actual LEO environment in order to have complete confidence in the simulation fidelity. We are participating in two flight experiments which will provide data that can be directly correlated to our ground-based results. We provided upwards of 50 conductive strip<sup>5</sup> samples that have been placed on a small satellite for exposure to the in-orbit LEO environment. Real-time monitoring will be performed through telemetry of the conductive strip resistances as a function of exposure time. Similar experiments with identical samples will be performed using the AO plasma source and will be compared to the flight results. This comparison will provide a good test of simulation fidelity. In addition, we are participating in a Shuttle-based experiment that is being run from NASA/Johnson Space Center (EOIM-3) in which a mass spectrometer will take measurements of the LEO ambient AO flux as well as observe the gas-phase reaction products produced by the LEO AO interaction with various samples. The flight mass spectrometer (AFGL) is being calibrated in our beam facility in order to fully compare the in-orbit data with our simulation results.

#### CONCLUSION

The design of reliable, long-term low earth orbit in space operations, automation, and robotic systems will require a broad knowledge base in "chemistry under extreme conditions." The few examples detailed in this paper reinforce the idea that the chemistry under LEO conditions is very different from that experienced under geosynchronous orbit or deep-space environments and that equipment designed for those conditions will, in general, need to be modified or protected for use in LEO.

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