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TITLE LABORATORY INVESTIGATIONS OF LOW EARTH ORBIT ENVIRONMENTAL
EFFECTS ON SPACECRAFT

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SUBMITTED TO

Space 88
Engineering, Construction, and Operations in Space
Albuquerque, NM
August 29-31, 1988



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LABORATORY INVESTIGATIONS OF LOW EARTH ORBIT ENVIRONMENTAL EFFECTS ON SPACECRAFT MATERIALS

Dr. Jon B. Cross*

ABSTRACT

Operations in low earth orbit (100-500 km) must take into consideration the highly oxidative character of the environment. Partial pressures in the range of 10^{-6} - 10^{-7} torr of atomic oxygen are present which produces extensive oxidation of materials facing the direction of travel (ram direction). The ram oxidation is most severe not only because of the high flux (10^{15} O-atoms/s-cm 2) caused by the orbital velocity of the spacecraft but also because of the high collision energy of oxygen atoms with the ram surfaces (translational energy equivalent to $\approx 60,000$ K). Ground based simulation of these conditions has been accomplished using a CW laser sustained discharge source for the production of 1-5 eV beam of O-atoms with a flux of up to 10^{17} O-atoms/s-cm 2 . The reactions of atomic oxygen with kapton, Teflon, silver, and various coatings have been studied. The oxidation of kapton has an activation energy of 2.3 Kcal/mole over the temperature range of 25 C to 100 C at a beam energy of 1.5 eV and produces low molecular weight gas phase reaction products (H₂O, NO, CO₂). Teflon reacts with ≈ 0.1 - 0.2 efficiency to that of kapton at 25 C and both surfaces show a rug like texture after exposure to the O-atom beam. Angular scattering distribution measurements of O-atoms show a near cosine distribution from reactive surfaces indicating complete accommodation of the translational energy with the surface while a nonreactive surface (nickel oxide) shows specular like scattering with little accommodation (50%) of the translational energy with the surface. A technique for

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simple on orbit chemical experiments using resistance measurements coated silver strips is described.

INTRODUCTION

Long term (20 year) habitation of low earth orbit (LEO) for military and civilian use is increasing and will in all likelihood will continue to increase for the foreseeable future. The expense of operation in this arena is dominated by high launch cost thus materials with low weight and high strength are being considered as candidate construction materials. In addition to the launch cost factor these materials must exhibit other characteristics such as low coefficient of thermal expansion to withstand extensive thermal cycling over a 20-30 year lifetime. The materials best suited to satisfy these criteria are organic based carbon fiber/epoxy. These material though will encounter environmental effects which must be taken into account when assessing their performance. The LEO environment consists of oxygen atoms, nitrogen molecules and trace amounts of other neutrals such as nitrogen atoms. Figure 1 shows the concentration of O-atoms and N₂ as a function of altitude. The interaction of these species with the surfaces of orbiting structures is complicated by the high orbital velocity (8 km/is) of spacecraft. At this velocity the kinetic energy of an oxygen atom colliding perpendicular to a surface is almost 5 electron volts or a translational temperature of 60,000 K with a flux of 10¹⁵ atoms/s-cm² (1 monolayer/is) at an altitude of 330 km while the energy of N₂ is almost 9 eV. These conditions produce a 0.1 micron loss of material from those organic based surfaces exposed to the direction of travel (ram surface) (Leger).

In addition to these neutral species, there exists a low concentration of charged particles (electrons, ions-10⁴-10⁵/cm³) which provides a weak plasma environment along with a sub monolayer flux of UV and VUV photons. Figure 2 shows the vacuum ultraviolet (vuv)

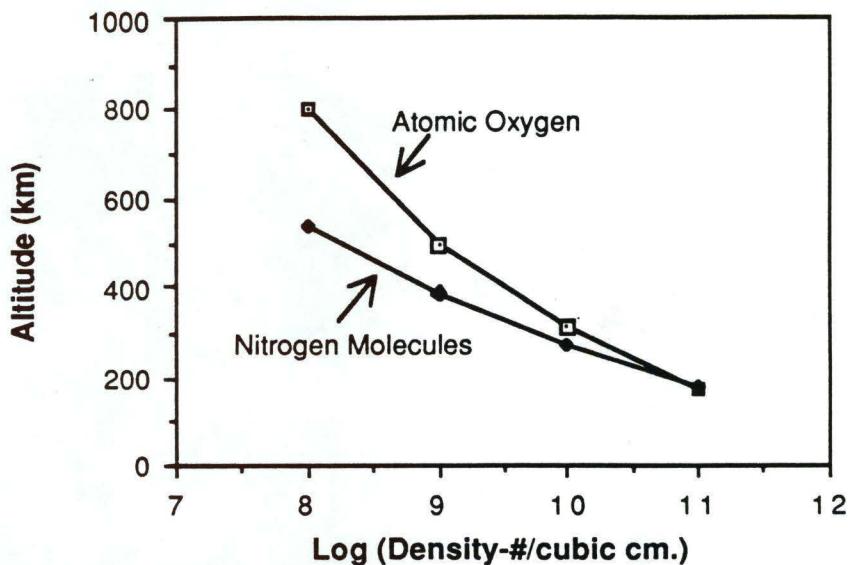


Figure 1. Atmospheric composition as a function of altitude

spectral distribution produced by the sun (Detwiler). Though most of the power (heat) resides in the visible and infrared region of the spectra, the vuv photons are energetic and intense enough to cause photodissociation of organic polymers which then allows further reactions with atomic oxygen (AO).

Meteoroid impact is another environmental factor which has been little studied but which is believed will be a major factor in design considerations for long life space structures (Leger).

LABORATORY INVESTIGATIONS

Because space shuttle flight durations have been limited to 7 days or less, very little experience has been gained in long term (>1 year) operation in LEO. Initial NASA shuttle experiments though have shown that oxygen atom chemical effects are of great importance in estimating design life of organic-based fiber-epoxy space station construction material and a number of investigations are now underway in ground based laboratories to determine "fixes" for this problem (Leger, Visentine, Santos-Mason). The Los Alamos investigations into these

areas are centered around the use of 1) an intense high velocity oxygen atom source (Cross, Cremers and Cross, et al) for the simulation of the spacecraft-energetic oxygen LEO environment which is shown in Fig. 3

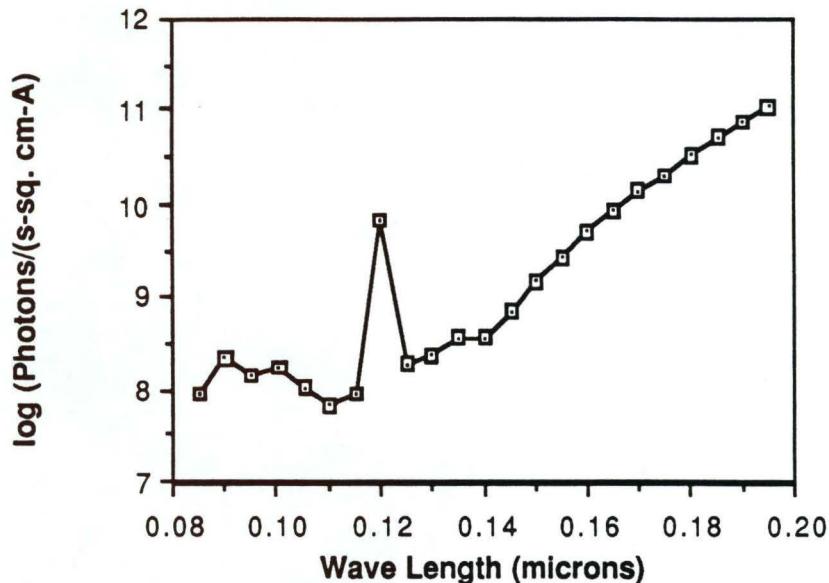


Figure 2. Solar Vacuum Ultraviolet Spectrum

and 2) molecular beam-surface diagnostics (Cross, et al-1987) (Fig. 4) for detecting the effects of the energetic oxygen atoms on surfaces of current and proposed spacecraft materials.

A number of projects are being pursued at Los Alamos which we hope will eventually lead to the development of improved materials and coatings having long term (20-30 year) performance life time when exposed to the LEO environment. The Los Alamos LEO atomic oxygen program is aimed at 1) screening various proposed space station construction materials, coatings, and lubricants for their resistance to atomic oxygen, 2) determining fundamental mechanisms of interaction between the laboratory simulated LEO environment and space station surfaces, and 3) supporting various on orbit experiments. The on orbit experiments are designed to more accurately determine the existing O-atom number density in orbit, to assess its reactivity toward a wide range of materials, and to assess the accuracy of ground based LEO environment simulation methods.

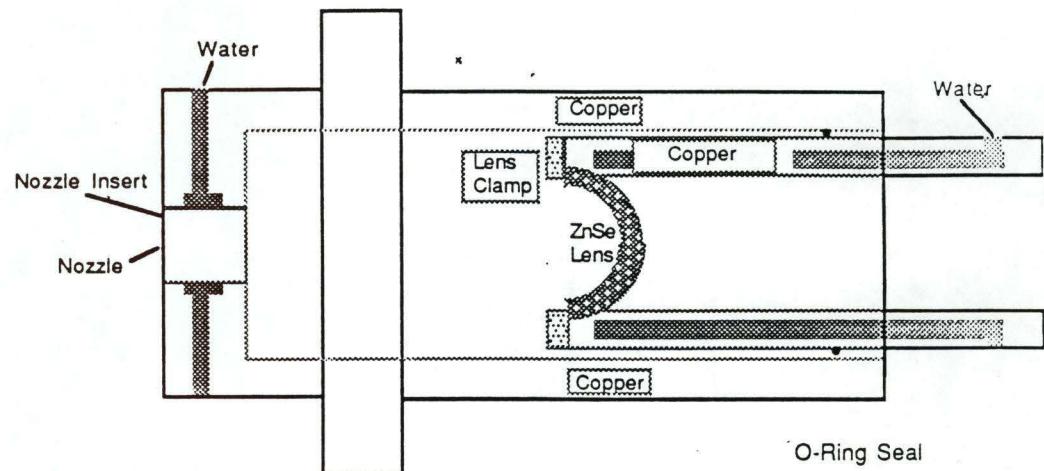


Figure 3. Atomic Oxygen Source: Employs laser sustained plasma to obtain high kinetic energy O-atoms.

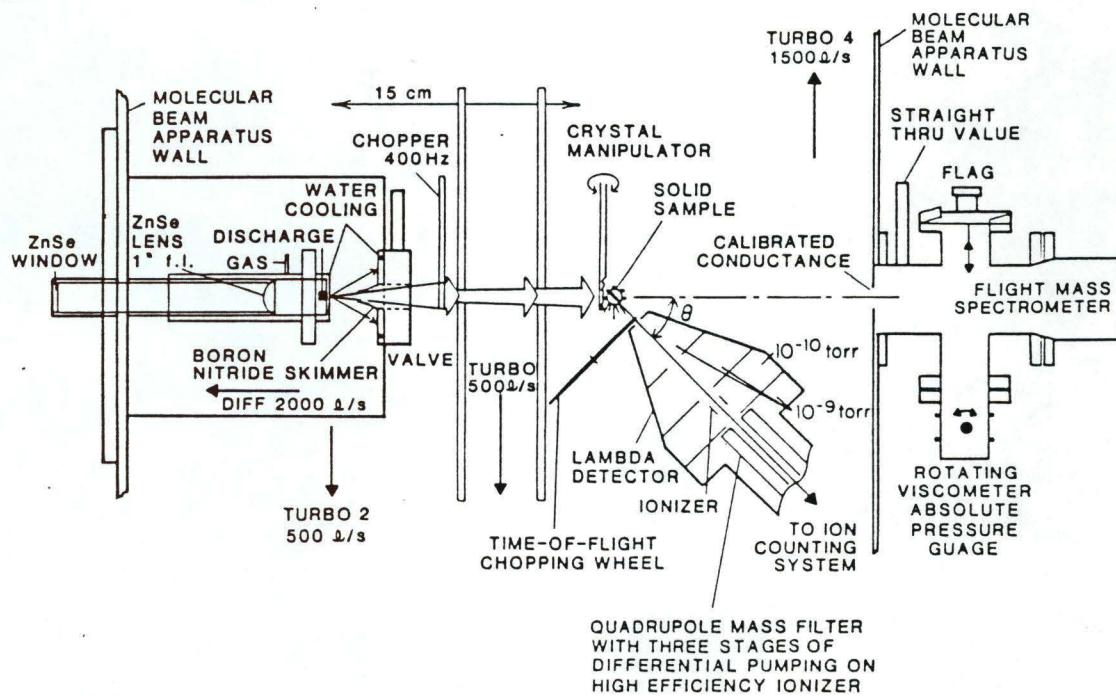


Figure 4. Los Alamos Molecular Beam Dynamics Apparatus.

SCREENING PROGRAM

The screening portion of our program points up some of the problems associated with materials interaction with the environment. Figure 5 shows a scanning electron microscope (SEM) photograph of kapton exposed for 14 hours to our O-atom beam operating at 1.5 eV with an intensity of 1×10^{16} O-atoms/s-cm². From measurement of the amount of surface recession produced under these conditions, a reaction efficiency of $2-4 \times 10^{-24}$ cm³/atom is obtained in good agreement with flight data (Leger, Visentine, Santos-Mason). Our preliminary data for graphite indicates a reaction efficiency 1/3 that of kapton. If carbon fiber/epoxy tubes react as graphite does, then a 1/8" thick tube wall facing the direction of travel (ram direction) would be eroded away in 10 years when a flux of 1×10^{15} O-atoms/s-cm² (200-300 km) was impinging on the wall. Failure due to uneven forces on the structure could occur though at a much earlier time. Figure 6 shows the volatile

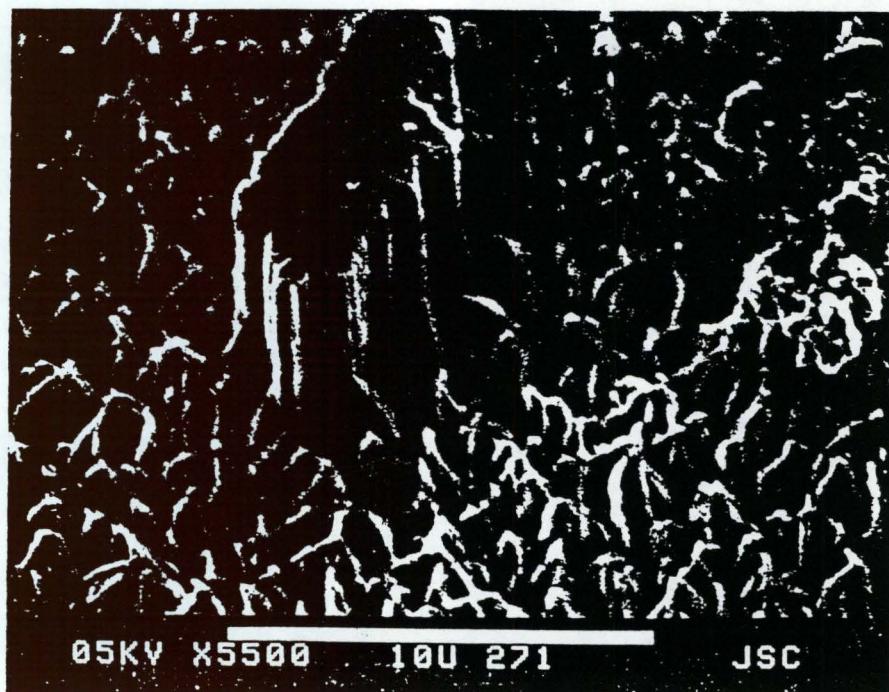


Figure 5. SEM Photograph of Kapton Exposed to AO Beam

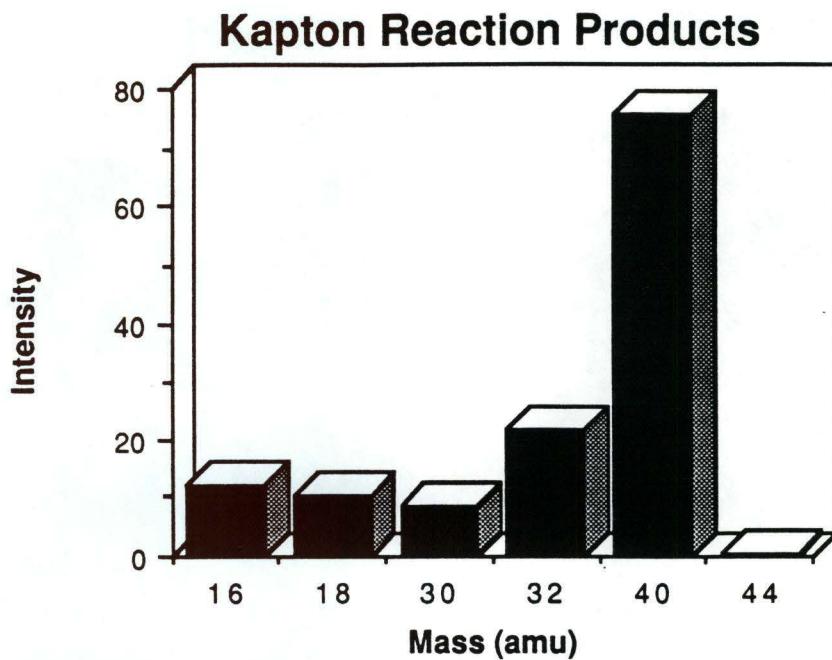


Figure 6. Identity of reaction products produced by the interaction of 1 eV oxygen atoms with kapton at 25 C. Intensity is in arbitrary units. CO was not measured because of the large background at mass 28.

reaction products emitted from the kapton surface under our exposure conditions. Reaction products produced by the interaction of high velocity O-atoms with kapton have been shown to consist of low molecular weight gases such as CO, CO₂, and NO with no species of molecular weight greater than 44 (Fig. 4) appearing in the gas phase. A cosine angular scattering distribution is produced under these conditions. At a O-atom beam energy of 1.5 eV an activation energy of 2.3 Kcal/mole was observed over the temperature range of 25 C to 100 C. The presence of gas phase reaction products must be taken into account in a global simulation of structures in LEO. This very simple calculation points up the problem of using organic based materials for long life structures in LEO.

Light weight flexible oxygen resistant coatings will be needed to protect organic materials exposed to the LEO environment. Teflon (DuPont) has been suggested as a possible materials

coating. It has good oxidation resistance in many chemical processing applications but is susceptible to degradation by UV radiation. Figure 7 shows a SEM photograph of Teflon after 72 hours of exposure to our AO beam. The



Figure 7. SEM Photograph of Teflon surface after exposure to O-atom beam.

reaction efficiency calculated under these conditions is 0.1 that of kapton. Preliminary indications are that our AO source produces no more VUV radiation than would be present in orbit so that the reactivity in orbit would not be much greater than that which we measure in our laboratory. Using silver film oxidation as the means of detecting oxygen permeation through the coating (Cross, Lan, and Smith), experiments are being performed to measure the permeation rate as a function of temperature, porosity, UV flux, and material type. It is anticipated that this work will lead to a sufficiently good fundamental understanding of the reaction and permeation processes that space station coating design guidelines can be formulated.

MECHANISMS

The LEO environment is highly nonequilibrium in nature, i.e., the local gas temperature is ≈ 1000 K while the collision temperature with ram surfaces is $\approx 60,000$ K and the surface temperature can be anywhere between 10 K for surfaces viewing deep space and 1000 K for surfaces of heat rejecters. This situation requires a sound knowledge of the *mechanisms* of gas-surface interactions in order to design long lived structures to operate in this chemical environment. For example, what is the most important variable in controlling the rate of surface oxidation-surface temperature or O-atom kinetic energy? Do O-atoms strike the surface directly using their kinetic energy to break surface bonds and causing oxidation or do they give up their energy to the surface through inelastic encounters and equilibrate to the surface temperature and then react? If the translational energy is not as important as surface temperature then cooling the ram surfaces would reduce the oxidation rate by orders of magnitude. This is just one example of the types of basic research mechanistic problems which must be solved in order to obtain the most efficient design for long lived structures. Measurements have been made of angular and recoil energy distributions of both atomic oxygen and reaction products scattered from various types of surfaces. Figure 8 shows the angular scattering distributions of atomic oxygen from nonreactive oxide and acrylic surfaces. Nonreactive metal oxide layers such as nickel oxide and stainless steel (#32 surface finish) produce specular like scattering (both parallel and perpendicular momentum components are equally conserved) with approximately 50% energy transfer to the surface when the angle of incidence (angle from surface normal) is large. Reactive surfaces such as acrylic produce complete accommodation of atomic oxygen and reaction products which results in a near cosine angular distribution for both of them. This type of information provides the basis for modeling of LEO environmental interaction with spacecraft and the consequences to the spacecraft from the interactions. For example specularly scattered unreacted atomic oxygen can strike and react with other surfaces which would normally be shielded from ram oxygen attack.

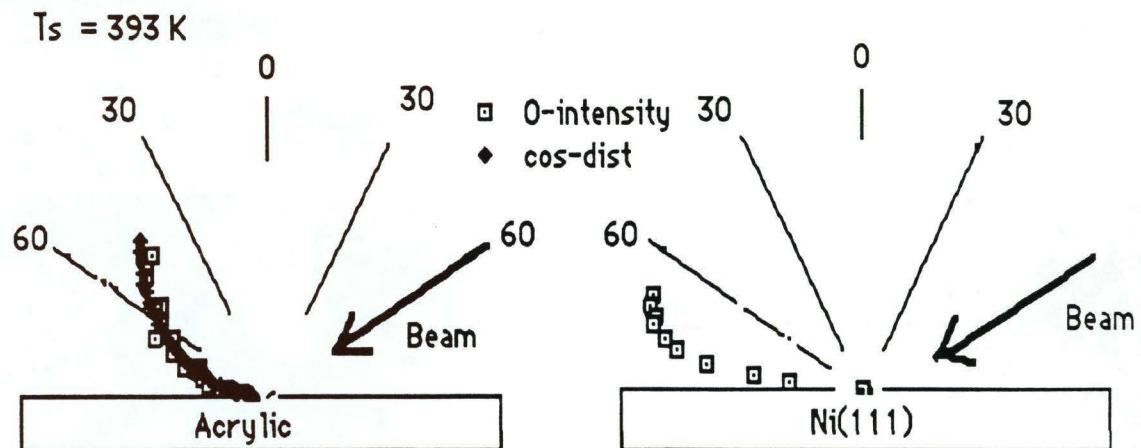


Figure 8. Angular distributions of O-atom scattering from a reactive surface (acrylic) and nonreactive surface (nickel oxide).

High vapor pressure reaction products leaving one surface may condense on other surfaces such as windows and have an adverse effect on some function of the craft. Atomic oxygen reactions with materials may also affect the basic strength or survivability of the over all system. All of these possibilities can be predicted and modeled before the spacecraft is ever flown *if* the reactive and nonreactive scattering cross sections and mechanisms are known.

Laboratory observations at Los Alamos of LWIR and visible chemiluminescence have been made which indicated that high molecular weight (100 amu) organic compounds will react with a very high probability (reaction cross section \approx 20 angstroms 2) when introduced into the LEO environment. These fluorescing chemical reaction products may interfere with optical observations from LEO platforms or may provide a convenient optical signature with which to track and identify platforms.

ON ORBIT EXPERIMENTS

Because of the high cost and low availability of orbital exposure time, a great deal of effort has been expended over the years to develop sources which simulate the LEO environment. None of the presently

available sources though can totally simulate the LEO environment (charged particles, VUV, neutrals) so there is a very real need for some form of on orbit investigations to determine those LEO environmental factors which are most important in limiting the operational life time of orbiting structures. At the present time the sophistication of such experiments is limited by payload and power capacity of satellites, so very simple experiments must be devised to probe the important aspects of the environment. We are developing some very simple chemical systems which will be capable of directly measuring the absolute time rate of change of O-atom flux on spacecraft,i.e., devices than are capable of measuring absolute (5-10% accuracy) number densities. Silver is oxidized quite rapidly (near collision frequency) by atomic oxygen (hardly at all be O₂) and can be used to detect the end point of oxidation of over coatings (Cross,Lan and Smith). A thin silver strip is deposited onto an insulator so that its resistance can be measured. The assembly is coated with a material of interest and exposed to either the LEO environment or a simulator environment. After the coating is burned away the silver oxidizes forming a nonconductor. By measuring the resistance of the device as a function of time and knowing the coating thickness a reaction rate can be obtained. A bare silver strip is also included on the device in order to determine a relative measure the ambient O-atom flux. If the sticking coefficient of atomic oxygen were known as a function of the silver oxide depth, the data would give an absolute value of the flux. Work is in progress to determine the sticking coefficient. Figure 9 shows a drawing of the silver O-atom actinometer with one strip coated. Figure 10 shows the oxidation rate of 250 angstroms of silver when exposed to our beam and Figure 11 shows the rate of Teflon oxidation as a function of beam fluence.

Other reactive systems may be used to obtain the ambient O-atom flux,i.e., graphite could be put in place of silver and the rate of surface recession measured. The absolute reaction cross section would be

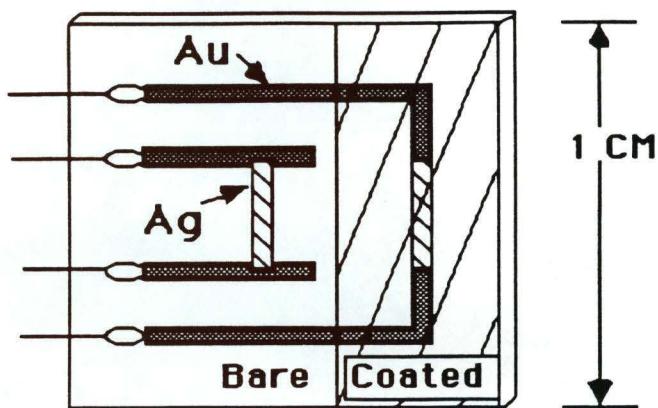


Figure 9. Silver actinometer used to detect the end point of coating oxidation. The bare silver strip is used to monitor the flux of atomic oxygen.

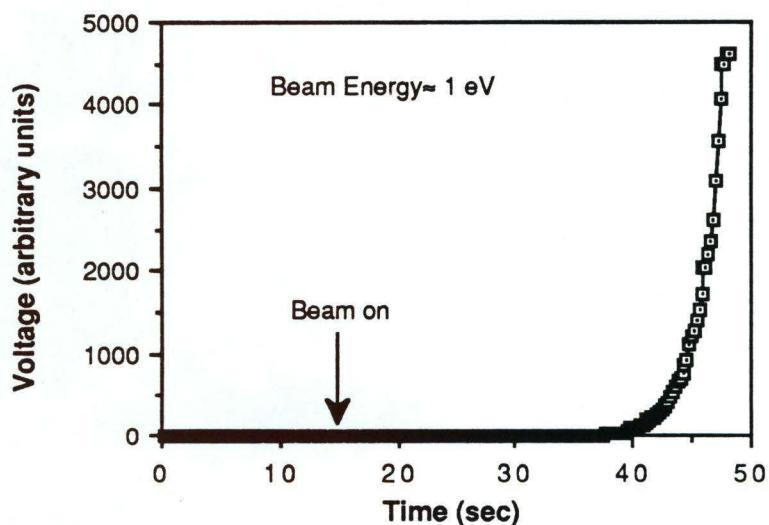


Figure 10. The voltage drop across the bare silver actinometer is plotted as a function of time. Note the roughly 25-s delay from the time the beam was turned on to the time the silver began to oxidize. This time delay is believed to be due to hydrocarbon contamination on the silver.

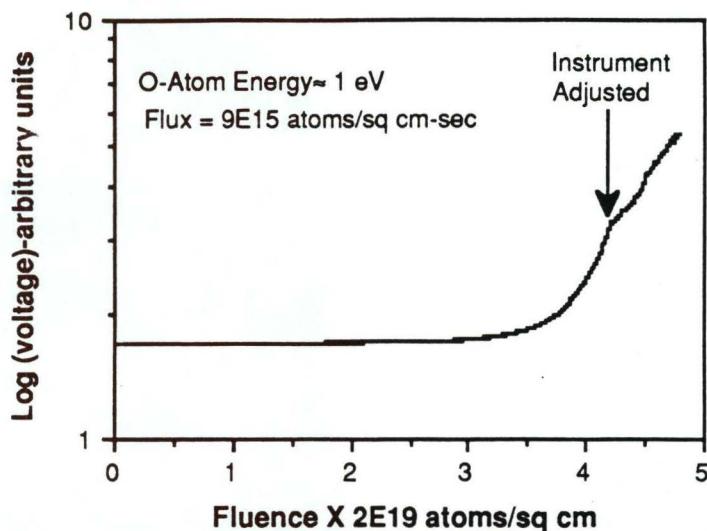


Figure 11. Log plot of resistance versus O-atom fluence for Teflon (800 Å) covered O-atom actinometer shows silver oxide formation after a fluence of about 6×10^{19} atoms/cm². Teflon was held at 25°C and positioned perpendicular to the O-atom beam axis.

needed though to determine an absolute flux. This type of simple resistance measurement is easy to implement for flight but is restricted to the measurement of atomic oxygen only. Los Alamos is also involved in orbital flight mass spectrometry (Hunton, Trzcinski, Cross, Visentine) measurements of the LEO environment in which a mass spectrometer will be calibrated in our ground based facility and flown on the shuttle to for measurement of all ambient species.

CONCLUSION

Our work at Los Alamos has shown, in agreement with shuttle data, that there is indeed a major problem in using organic based material for construction on long lived (20-30 year) structures in LEO (100-600 km). Roughly 10% of the atomic oxygen striking a ram organic surface reacts to form volatile products thus reducing the material thickness. At a 100 km to 200 km altitude this amounts to almost 0.1 microns per orbit. The

oxidation of kapton has been shown to have an activation energy of 2.3 Kcal/mole at a beam energy of 1.5 eV indicating that nonreactively scattered atomic oxygen will react more efficiently with hot surfaces than cold ones on spacecraft structures. Therefore coatings will be required for protection and some of the present candidates such as Teflon are themselves susceptible to attack especially in the presence of VUV radiation from the sun. Metal oxide coatings such as SiO_2 or Al_2O_3 will probably be resistant to AO attack but may be susceptible to microcracking and micrometeor damage in which case AO can attack the underlying substrate.

We have shown the need for additional on orbit experiments and have suggested some simple experimental techniques which can be used to relate ground based data to orbital data. We have also indicated the need to understand the underlying reaction mechanisms on various surfaces in order to implement design measures to minimize the AO problem.

ACKNOWLEDGEMENTS

We wish to acknowledge many interesting and informative discussions with Dr. Luber Leger, James T. Visentine, and Dr. Steve Koontz of NASA/Johnson Space Center. We wish to thank Dr. Steve Koontz for SEM and profilometer analysis of the kapton and Teflon samples. We wish also to acknowledge funding for this work from NASA/Johnson Space Center, McDonnel Douglas Corporation, Air Force Geophysics Laboratory, and SDIO.

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September 23, 1987

Dr. Stewart W. Johnson
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Dear Dr. Johnson,

Enclosed you will find a rough draft of a paper entitled "LABORATORY INVESTIGATIONS OF LOW EARTH ORBIT ENVIRONMENTAL EFFECTS ON SPACECRAFT MATERIALS" which I am submitting to SPACE 88 conference. I understand that this summary is in rough draft form and itself will not be published. The final camera ready copy will arrive by April 15.

Sincerely,

Dr. Jon B. Cross