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INTERACTION OF HYPERTHERMAL ATOMS ON SURFACES IN ORBIT:
THE UNIVERSITY OF ALABAMA EXPERIMENT

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Abstract

The UAH experiment which flew on the STS-8 mission had several objectives which were mostly of a speculative nature since so little was known of the processes of interest. The experiment provided original, if limited, data on: (a) oxidation of metal surfaces, (b) reaction rates of atomic oxygen with carbon and other surfaces and the dependence of these rates on temperature, and (c) the angular distribution of 5eV atoms scattered off a solid surface. This paper provides a review of the results, with references given to fuller published accounts where these are available.

Introduction

The chemistry of reactions between species with relative kinetic energies in the range of a few eV to a few 10's of eV has only been sparsely studied, principally because of the experimental difficulties and expense of generating beams of usable flux at these energies. The region is of considerable theoretical interest since it overlaps the region of energies of chemical bonds and activation energies. Thus enhancement of reaction rates (over those at ordinary temperatures) is possible and even likely. With this in mind, in 1974 we proposed an experiment for the Long Duration Exposure Facility (LDEF) spacecraft, originally projected to fly in 1978 (Ref. 1). This mission was launched in 1984 and has not yet been recovered from orbit. The early 1980's saw an awakening of interest within NASA in the effect of hyperthermal oxygen atoms on spacecraft materials, and several exposures of materials were made and studied. In 1983 a NASA-wide materials experiment was proposed, for which UAH was invited to provide a modified version of the LDEF hardware. This composite experiment, designated EIOM-2, was flown in September of the same year, which must be one of the shortest completion times for a flight experiment of this size.

The UAH experiment included the following components:

- (a) Seven thin (optically-transmitting) metal films deposited on quartz flats. The metals used were Al, Au, Ir, Nb, Ni, Pt and W.
- (b) Samples of materials known or suspected to exhibit gross erosion or corrosion effects (C, polymers, Os, Ag). These samples were mounted on heated plates at different temperatures to allow measurement of temperature dependence of rate.
- (c) Scatterometers: a passive device of novel design in which the intensity of oxygen atoms reflected from a solid surface was measured.
- (d) In addition to the above, carbon specimens were provided to Johnson Space Center experiments designed to measure (i) synergistic effects of solar UV on reaction rates and (ii) effects of atmospheric oxygen ions on those rates.

A short description of the experimental approach and the hardware is given below for each of these components, together with a summary of the results. Orbital exposure data pertinent to the results described here is given in Table I.

TABLE I: STS-8 ATOMIC OXYGEN EXPOSURE DATA

Payload Bay Forward Facing:	t = 41.2 hrs.
Altitude:	120 nautical mi. (225 km)
Velocity:	7.8 km s ⁻¹
Mean Oxygen Atom Density (Calculated:	2.65 x 10 ⁹ cm ⁻³
Surface Impact Frequency:	2.07 x 10 ¹⁵ cm ⁻² s ⁻¹
Integral Fluence:	3.5 x 10 ²⁰ atoms cm ⁻²

Results

(a) Effects on Optical Surfaces

This investigation was directed to determining some quantitative effects on uncoated optical surfaces. Others have shown that standard optical coatings (where permissible) of metal oxides or metal fluorides are very resistant to atomic oxygen.

The surfaces studied were of two types: high-purity thin films sputtered or evaporated onto 2.54-cm diam $\lambda/20$ fused silica optical flats, and highly polished bulk samples. Films were prepared with optical densities of ~ 2.5 or less. Measurement of optical densities using a Perkin-Elmer PDS scanning microdensitometer allowed sensitive determination of any changes to these thin films produced by the exposure. By masking one-half of each sample during flight as a control it was possible to measure changes in optical density of ~ 0.01 , corresponding to a few percent change in the thickness of ~ 10 -nm thick films. (No increase in scattering was assumed, since most films became smoother; changes in reflection due to very small oxide thickness increases were

also neglected.) In several cases the sensitivity of the method was ± 1 monolayer of surface atoms. Total film thicknesses were accurately measured by step height changes in stylus traces of the film/substrate surfaces using a Tencor Alpha-Step 200 stylus profilometer with a nominal 2- μm radius diamond stylus. Decreases in both the optical density and total film thickness were attributed to metal film removal. A decrease in optical density but an increase in total film thickness was attributed to film expansion due to formation of a non-volatile oxide of lower density than the original film. Topographic measurements were also made on a number of surfaces with an optical heterodyne instrument. These measurements provided an optical determination of surface roughnesses for comparison to stylus results as well as several correlation functions from the same measurement. A fuller account of these measurements is given in Ref. 2.

Estimates of metallic film thicknesses in exposed and unexposed areas were calculated from the optical density measurements using equations for transmission and reflection.

A summary of the results is shown in Table II. Al, Ni, Nb and Cu showed small but measurable increases in oxide thickness over that obtained by normal exposure to the atmosphere. Au, Pt and Si showed no measurable effects by these techniques. Os showed massive erosion, and Ag massive corrosion. Ir showed evidence of slight erosion.

TABLE II

Material	Nominal Thickness (nm)	Thickness of Metal Converted to Oxide (nm)	Thickness of Metal Lost (nm)
Al film	3.4	0.8	none
Au film	35.5	none	none
Ir film	32.3	none	2.5
Ni film	54.2	0.7	none
Nb film	16.8	1.3	none
Pt film	10	none	none
Os bulk	bulk	none	1100nm
Ag bulk	bulk	>100nm, variable	none
Cu bulk	bulk	~3.5	none
Si bulk	bulk	no measurable effect	

(b) Kinetic Studies on Carbon and Other Highly Erodible Surfaces

The experimental approach used was necessarily very simple as on electro-mechanical devices such as lids, shutters, etc. were available, and no intermediate measurements could be made, i.e., only a single integral effect could be measured for each sample. Samples were nominally one inch discs, with the hot-plate discs only being one quarter-inch diameter. For the case of the erodible materials discussed here, a bar-pattern of small rectangles of niobium was deposited on the surface using a photo-resist technique. The niobium was sputtered on as a uniform film ~200-nm thick. Although it oxidized, it still served to protect the underlying carbonaceous material. The bar-pattern allowed multiple measurements of the step-height to be made using the Tencor stylus profilometer. Amplitudes were checked using SEM micrographs. Half of each sample was covered at all times before and during the flight, and served as a control.

Erodible surfaces studied included single crystal graphite (basal and prismatic planes, vitreous (or glassy) carbon from various manufacturers, polymethyl methacrylate (lucite), bisallyl diglycol carbonate (CR-39, an optical plastic), and diamond.

Erosion observed by this experiment ranged from 75-nm for diamond (which appears to be particularly resistant to oxidation under these conditions), to about 10,000-nm for the poly-carbonate resin, CR-39, which was the most heavily eroded sample reported on any flight exposure.

The temperature dependence of the oxidative effects was measured by conducting the erosion measurements at three temperatures spanning about 120°C. The Arrhenius activation energy, ΔE , was estimated, assuming:

$$r = A e^{-\Delta E/RT}$$

where r is the rate of the reaction and A is a constant assumed independent of temperature T . These studies were performed for 6 materials, vitreous carbon, 2 graphites, CR-39, silver, and osmium. All activation energies were small and positive.

The conclusions from the measurements on various forms of carbon exposed in the STS-8 mission appear applicable to organic solids in general. They may be summarized as follows:

1. Measured erosion was linear with total fluence (Fig. 1).
2. No induction time was observed before onset of erosion (Fig. 1).
3. Erosion rate linear with oxygen flux (i.e., reaction probability independent of flux) measured over a small range 1.5 to 2.5 x 10^{15} atoms cm^{-2} s^{-1} .
4. Arrhenius activation energies for the reactions were measured (Fig. 2) as follows:

vitreous carbon	1200 (cal mole ⁻¹)
graphite (basal plane)	1400
CR-39	1050

5. Reaction probabilities depend on temperature as shown in (4) above. Reaction probabilities for carbons exposed at $\sim 300^{\circ}\text{K}$ ranged from .1 to .15 where reaction probability equals the number of carbon atoms lost divided by the number of incident oxygen atoms.
6. No effect was observed on the measured erosion rates (at the 5% level) which could be ascribed to the presence for absence either of solar UV or of charged oxygen species.

The silver and osmium data has not been fully analyzed, but it is clear that the apparent activation energy of the rate-controlling step in both the osmium-loss process and for the production of bulk silver oxide under these conditions is positive.

(c) Atom Scattering at Orbital Velocities

When an atom or molecule strikes a surface a number of processes may take place. Some of these are:

1. Accommodation of momentum and energy.
2. Chemical reaction with a surface atom or adsorbed molecule.
3. Recombination, dissociation or excitation of projectile species.
4. Sputtering.

Measurements of the spacial and energy distribution of scattered species provides a probe of the interaction potential existing between the projectile and target species. Understanding of the processes taking place during such an interaction requires some knowledge of this potential.

While the UAH experiment was passive and very simple, it has provided a unique measurement of the angular distribution of oxygen atoms scattered from a polished carbon surface in orbit. It was not capable of measuring the velocity or energy profile of scattered species. The apparatus has been described elsewhere (Ref. 3), and the data has been used to estimate satellite lift and drag parameters (Ref. 4).

The scatterometer, shown in Figure 3, consisted of an aluminum enclosure, a polished vitreous carbon disc mounted so that the stream of fast atoms passing through the entry slit impinged on its center at 55° . Detection of reflected atoms was accomplished by a silvered strip of clear CR-39 plastic mounted in the can like the x-ray film in a diffraction camera.

Silver absorbs oxygen atoms with efficiency $\sim 100\%$ and is converted to clear oxide. Increase in optical transmission measured with a scanning optical densitometer yields reflected 0 intensity as a function of angle.

The resultant angular distribution of 5eV O atoms is shown in Figure 4. Such a distribution is described as wide lobular with a maximum intensity in the reflection hemisphere 15° from the surface normal.

A calculation of the mass balance for atomic O showed that the silver converted to oxide accounted for at least 80% of atoms incident on the carbon (after deducting those which reacted with carbon).

Conclusions, discussed more fully in Ref. 3, are that the incident atoms are almost, but not quite, fully accommodated at the carbon surface, and that recombination efficiency (to form O₂ molecules is low (<20%). We intend to pursue further studies of scattering in this energy regime both in space and in simulation facilities on the ground.

References

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Acknowledgements

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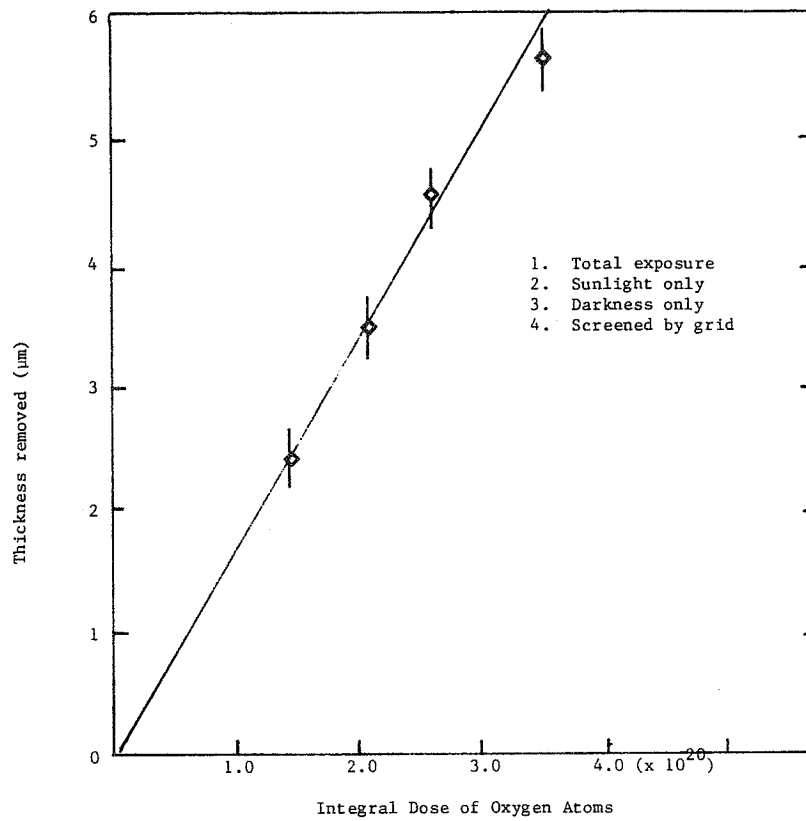


Figure 1. Vitreous Carbon Dosimeter, STS-8 Exposure

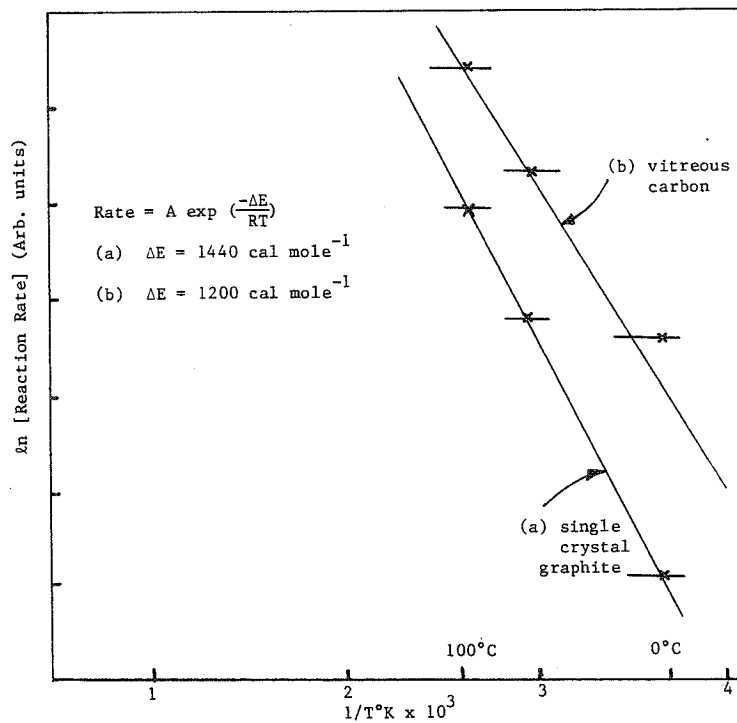


Figure 2. Arrhenius Plots for Carbon Oxidation by 5eV Oxygen Atoms (STS-8 data)

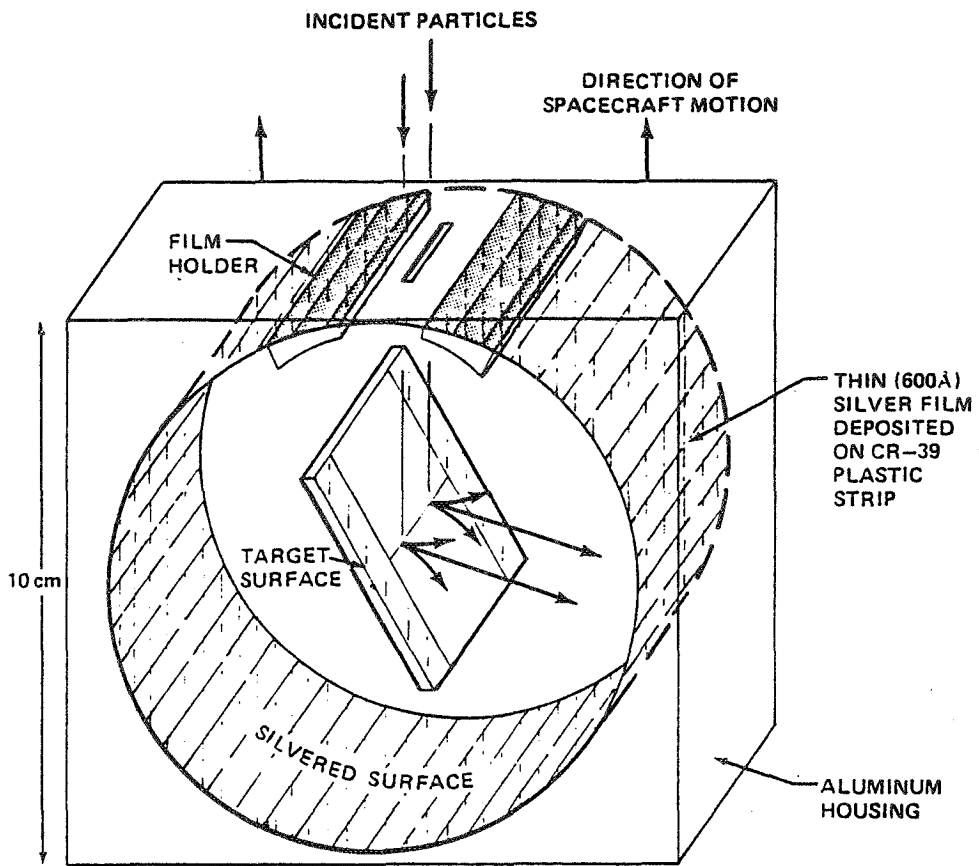


FIGURE 3. THE OXYGEN ATOM REFLECTOMETER FLOWN ON SHUTTLE STS-8 AND THE LONG DURATION EXPOSURE FACILITY

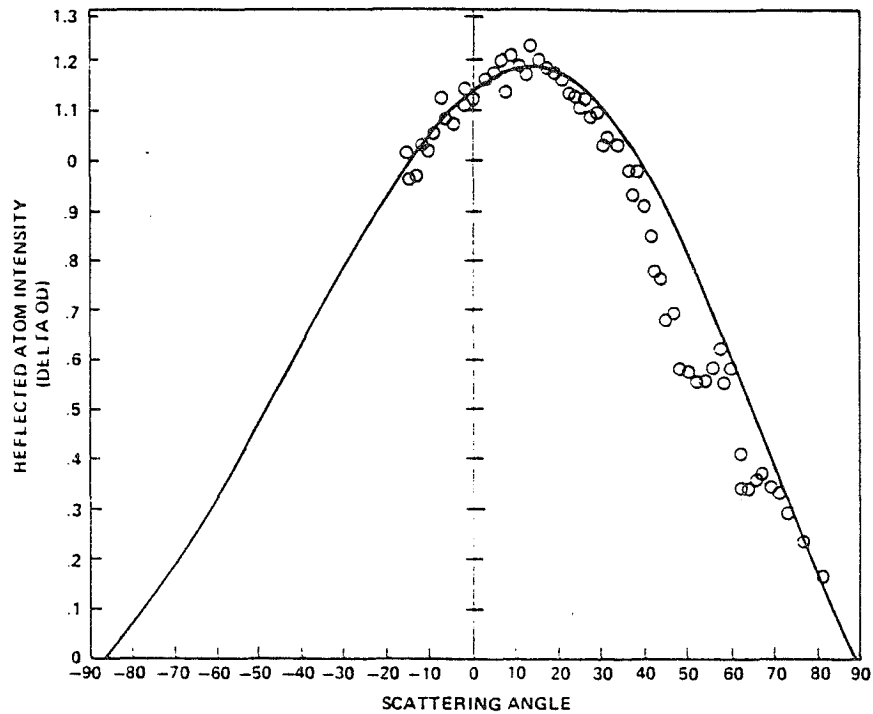


FIGURE 4. FIT USING NOCILLA MODEL TO THE OUTSIDE ENVELOPE OF THE FLIGHT DATA. DISCREPANCIES ASSUMED DUE TO ABSORPTION ARTIFACTS IN THE SILVER FILM θ_c (NOCILLA) = 40° ; $S_r = 0.2$