Reaction of Atomic Oxygen with Vitreous Carbon: Laboratory and STS-5 Data Comparisons

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Introduction

A SPACECRAFT in low-Earth orbit (LEO), 200-700 km, experiences bombardment by the ambient atmosphere, the predominant species of which is neutral atomic oxygen.[1] Although the ambient gas temperature is only on the order of 1000 K, the 8 km-s^{-1} velocity of the spacecraft causes the oxygen atoms to strike satellite surfaces with a relative kinetic energy of 500 kJ-mole^{-1} (5 eV). At Shuttle altitudes the O atom density is approximately 10^9 cm^{-3} which corresponds to a flux of approximately 10^{15} cm^{-2}-s^{-1}. These conditions present a regime of gas-surface chemistry which has been the subject of very little experimental investigation because of the difficulties inherent in reproducing them in the laboratory.

A variety of materials exposed to the LEO environment on the Shuttle Orbiter have been observed to undergo erosion which has been ascribed to the action of atomic oxygen. These include organic polymers,[2-5] organic paints,[4,6] carbon, and osmium.[7] An experiment entitled Evaluation of Oxygen Interaction with Materials (EOIM) was flown on the STS-5 mission to investigate these effects.[3] One of the samples included in a temperature-uncontrolled area of this experiment was a disk of polished vitreous (or glassy) carbon. The area of the disk exposed to the LEO atmosphere was roughened and material had been removed.[8]

This Note reports the result of an experiment in which a polished disk of vitreous carbon, identical to that flown on STS-5, was exposed to bombardment by suprathermal (1 eV) atomic oxygen under high vacuum conditions. A quantitative agreement between the erosion rates inferred from orbital exposure and laboratory simulation was observed.

Experimental

The apparatus used to perform this laboratory measurement consists of a three-chamber, differentially pumped (oil diffusion pumps) vacuum system (see Fig. 1). The oxygen atom beam source is attached to the first chamber, which provides differential pumping for the source. The second chamber contained the sample to be bombarded, which was temperature controlled at 299 K and surrounded by a liquid-nitrogen-cooled shroud to inhibit contamination. The third chamber contained a quadrupole mass spectrometer used to measure beam composition. During the sample exposure, the pressures in chambers 1, 2, and 3 were approximately 5×10^{-4}, 5×10^{-6}, and 3×10^{-7} Torr, respectively. The primary residual gas in the first and second chambers was helium.

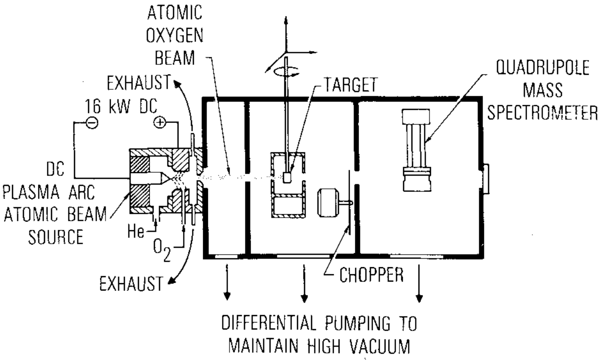

Fig. 1 High-energy oxygen atom surface chemistry apparatus.

The oxygen atom source has been described elsewhere[9] and is similar to another source reported in the literature.[10] A dc arc, dissipating approximately 16 kW, heats a flowing stream of helium at atmospheric pressure. A small quantity of O_2 (~2% of the total gas flow) is injected into the flow downstream of the arc, where it is thermally dissociated into oxygen atoms by the hot helium. A small portion of the hot gas mixture expands into the vacuum system producing a suprathermal beam.

For this measurement the ratio of atomic to molecular oxygen ranged from 0.6-0.8 as measured by the mass spectrometer periodically throughout the course of the sample exposure.[11] The flux of atomic oxygen incident on the sample was in the range 5-7×10^{15} cm^{-2}-s^{-1}. The absolute value of the flux is subject to a systematic error assigned to be ±50% due to uncertainty in the mass spectrometer calibration.[9] The velocity of impact was 3.5 km-s^{-1} which corresponds to an impact energy of approximately 1 eV. The total exposure time was 5 h producing a fluence of atomic oxygen, F_0, on the target of $1.04 \pm 0.52 \times 10^{20}$ cm^{-2}.

The atomic beam was collimated to subtend a roughly circular spot of 7 mm diameter on the target. The extent of erosion was ascertained by measuring the surface profile of the sample at the exposure edge with a stylus profilometer (Sloan Dektak FLM or Tencor Alpha-Step 200).

Results and Discussion

The exposed area of the sample was visibly roughened in a manner similar to the flight sample.[8] The etching process also revealed macroscopic irregularities in the material not observable on the original polished surface. Examination of the sample by optical and electron microscopy qualitatively supported these visual observations.

Nine separate measurements of the depth of erosion d at various locations around the edge of the exposed area were performed. These measurements showed that 283 ± 73 nm of material were removed. Figure 2 shows one of the profilometer traces. The depth of erosion is equal to the height of the sharp step which occurs at $\Delta x \approx 700$ μm. The apparent steep rise of the profilometer trace from 0 to 500 μm and steep fall from 1200 to 2000 μm are manifestations of the sample curvature. The trace shown in Fig. 2 was plotted with the constraint that the beginning and end points of the profilometer scan be assigned to be level. This method of plotting and the fact that the units of the Δt and Δx axis differ by a factor of 10^3 accentuate the curvature of the sample. (Note that a height of 800 nm for a chord of length 2 mm implies that the local radius of curvature of the sample is ~0.6 m.)

The erosion is ascribed to the action of atomic oxygen. Other measurements performed in this laboratory have shown that ultraviolet light and helium, also present in the beam, have a negligible effect on carbon.[9] The rate of removal of carbon by molecular oxygen in the beam can be considered reasonably insignificant[12] at the surface temperature of 299 K.

The probability P that an oxygen atom striking the solid will remove a carbon atom (regardless of its final state of aggregation) can be calculated from

$$P = d\rho / M_c F_0 \qquad (1)$$

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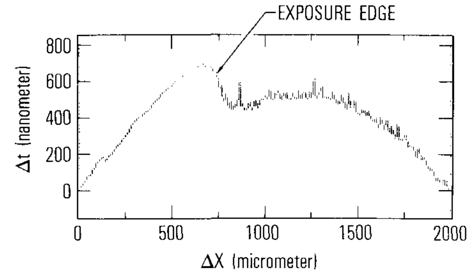

Fig. 2 Surface profilometer trace of the edge of the area of the sample exposed to oxygen atom bombardment.

Table 1 Reaction probability of atomic oxygen with carbon

Source	Type of carbon	$P \times 100$ carbon atoms/O atom	T, K
Present work	Vitreous	2.1 ± 1.2	299
STS-5[9]	Vitreous	2.3 ± 0.7	?
Park[12]	Graphitic	1.3	299
		0.6	250
		2.3	350

where ρ is the material's density[13] of 1.5386 g-cm^{-3}, M_c the mass of a carbon atom, and F_0 and d have been defined previously. The value of P, taking into account the uncertainties in d and F_0, calculated for the measurement reported here, is $2.1 \pm 1.2 \times 10^{-2}$.

The vitreous carbon sample included in the STS-5 EOIM experiment exhibited an rms loss of 0.30 μm of material as measured by laser interferometry.[8] Using the most recently updated oxygen fluence value[3] of $9.93 \pm 2.94 \times 10^{19}$ cm^{-2} one calculates a value of $2.3 \pm 0.7 \times 10^{-2}$ for P.

The agreement between the laboratory and flight measurements of the erosion rate of vitreous carbon by atomic oxygen is quite good in comparison to the uncertainties in the two measurements. (See Table 1.) The agreement is particularly good when one considers that the temperature of the laboratory sample was controlled to 299 K during its exposure, but the temperature of the flight sample was neither controlled nor monitored. The sample tray containing the carbon disk on the STS-5 EOIM experiment was located between two film arrays heated to 394 and 338 K during the majority of the sample exposure. During other portions of the flight the sample was exposed to direct sunlight.[3] Thus, it is not unreasonable to expect that the temperature of the flight sample varied substantially throughout the course of the mission. The reaction of atomic oxygen with carbon exhibits an activation energy[9,12] (with respect to the carbon surface temperature) of approximately 10 kJ-mole^{-1}. Thus, for a ±50 K variation about room temperature, one might expect the reaction rate to vary by about a factor of 4.

Park has obtained the expression

$$P = 0.63e^{-1160/T} \qquad (2)$$

from a compilation of a number of experimental measurements of the rate of oxidation of graphitic materials by atomic oxygen at thermal impact velocities.[12] For a surface temperature T of 299 K, Eq. (2) predicts a value of 1.3×10^{-2} for P. Considering the fact that Park's expression is used to approximate reaction rates for graphite, not vitreous carbon, from room temperature to 4000 K, the predicted value is in good agreement with the results of the two measurements presented here.

Conclusions

The measurement reported here represents the first laboratory confirmation that a material erosion rate observed in the STS-5 EOIM experiment can be reproduced by a controlled exposure of the material to atomic oxygen under single collision conditions. Park's summary equation, the laboratory measurement reported here, and the STS-5 EOIM result represent measurements of the probability of the reaction of atomic oxygen with carbon over a range of O atom, impact energies from 0.03-5 eV. The agreement in reaction probabilities from these three sources indicates that there is no great, if any, dependence of the rate of this reaction on the translational energy with which the oxygen strikes the carbon surface. This is consistent with other measurements performed in this laboratory.[9]

Continuing work in this laboratory is directed toward measurements of the rate of erosion of organic polymers by suprathermal atomic oxygen for which the agreement between *thermal* rates reported in the literature and rates inferred from orbital exposure is not particularly good.[3,14]

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