

REACTION OF HIGH VELOCITY ATOMIC OXYGEN WITH GRAPHITE

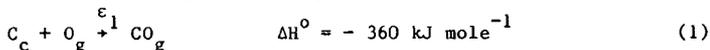
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Atmospheric bombardment of a spacecraft in low Earth orbit (LEO) presents a regime of gas-surface chemistry which has been the subject of very little laboratory investigation. The predominant atmospheric species in LEO (200-800 km) is ground state, neutral atomic oxygen (1). Although the ambient temperature is not extremely high ($\sim 10^3$ K), the 8 km sec^{-1} orbital velocity of the spacecraft causes oxygen atoms to strike the satellite's surfaces with an average collision energy of $5 \times 10^2 \text{ kJ mole}^{-1}$ ($\sim 5 \text{ eV}$). At the altitude at which the space shuttle operates ($\sim 240 \text{ km}$) the flux of atomic oxygen striking surfaces normal to the craft's velocity vector is of the order of $8 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$. (1) The phenomenology of oxygen atom-surface interactions at such a collision energy is completely unstudied in the laboratory. The lack of experimentation in this area owes not to any assumption that such chemistry is fundamentally uninteresting, but rather reflects the difficulties inherent in reproducing in the laboratory the 8 km sec^{-1} impact velocity.

The details of oxygen atom surface interactions at orbital velocity are of particular interest for the prediction of the integrated effects of long-term exposure of materials to the LEO atmosphere. The unique opportunity which the shuttle orbiter provides to recover a variety of materials from LEO has highlighted the need for such an understanding. Organic polymers, including polyimides, polyesters, and polyurethanes, have been observed to erode at significant rates (2). A silver surface 2100\AA thick was completely oxidized (3). Osmium and graphite surfaces exposed to the atmosphere were completely removed (3,4).

The reaction of atomic oxygen with graphite:



is well known and so initially one does not find the removal of graphite surfaces by atmospheric oxygen to be particularly surprising (5). The rate at which graphite was removed was, however, quite unexpected. On the third shuttle flight (STS-3), a graphite surface estimated to be 10^{-4} in. thick was completely removed. The total time of direct exposure of the surface to the atmosphere was approximately 9 hours. If reaction 1 were responsible for the removal of the graphite, then it must have been occurring with a probability in excess of 0.8 per oxygen atom collision.

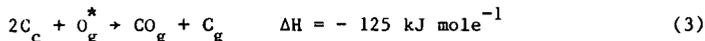
Reference 5 reports that the variation with surface temperature of the probability of reaction 1, ϵ_1 , for the case of oxygen atoms impacting at thermal velocities is given by:

$$\epsilon_1 = 0.63 e^{-1160/T} \quad (2)$$

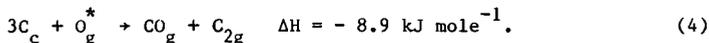
The temperature of the graphite exposed on STS-3 is expected not to exceed 420K , a temperature at which the Arrhenius expression given above predicts a value of ϵ_1 of 0.04. Even though the estimate of reaction probability on orbit is based on data which are somewhat less precise than might be desirable, the difference between prediction and observation is substantial.

Such a discrepancy in predicted and observed reaction probabilities indicates the possibility that the high translational energy of oxygen atoms striking graphite surfaces on orbit results in the enhancement of the probability that an oxygen atom removes a carbon atom on impact (as compared to the thermal oxidation of graphite by

O atoms). It is instructive to note that if one includes the translational energy of the atomic oxygen in one's accounting, channels for the removal of carbon atoms in addition to reaction 1 are at least thermodynamically allowed. Two of these reactions are:



and



Thus the oxidation of graphite was selected as the initial subject for investigation in a new facility constructed specifically for the study of high energy oxygen atom surface chemistry. In addition to providing further insight into a gas-surface interaction of great fundamental and practical interest, such experimentation serves as the prototype for the investigation of the oxidation of spacecraft materials by high energy atomic oxygen.

Figure 1 shows a schematic representation of the beam apparatus designed for the investigation of high energy oxygen atom surface chemistry. The vacuum system is comprised of four chambers. The first three are stainless steel boxes, 18 in. cubed, sealed with Buna-N "O-Rings". The first is pumped by an un baffled 16 in. oil diffusion pump (Varian VHS-400). Each of the second and third chambers is pumped by a 10 in. oil diffusion pump (Consolidated Vacuum Corp.), topped with a liquid nitrogen cooled trap (Mt. Vernon Research Corp.), and an electro-pneumatically operated, viton-sealed gate valve (Vacuum Research Manufacturing Corp.). The fourth chamber uses crushed metal seals and is pumped by a high-speed turbomolecular pump (Balzers TPU 510).

The oxygen atom beam source (described below) is housed in chamber 1. The source is recessed into chamber 1 in order to minimize the distance from source to target thereby delivering the maximum available beam flux to the target. A Beam Dynamics Inc. model 2 nickel skimmer, 0.90 mm orifice diameter, connects chambers 1 and 2. Chambers 2 and 3 act as buffers to aid in the reduction of pressure between the source and the target. A beam chopper and beam flag which aid in the characterization of the beam are mounted in chamber 2. The second chamber also provides space for installation of a low resolution slotted disk velocity filter, which may be used when it is desirable to prevent light from the beam source from falling upon the target.

The solid target is contained in the fourth chamber, which is recessed into the third chamber to minimize source to target distance. A quadrupole mass spectrometer (Extranuclear Laboratories) is provided for characterization of the atomic beam and also for identification of the volatile products of bombardment of the target.

The production of a beam of neutral atomic oxygen of sufficient velocity and intensity for this program requires advances in the state-of-the-art of beam source technology. Indeed, one major reason for the scarcity of experimental data on atomic oxygen-surface interactions at high energies (~ 5 eV) is the difficulty in building a reliable, fast, high-intensity O atom beam source. Figure 2 shows the source constructed here to achieve such a beam. The source is a modified, commercially available plasma torch. The modifications include attachments for a water-cooled nozzle, through which the atomic beam expands into the vacuum system, and exhaust channels to dispose of excess torch gas. The torch operates in the non-transferred mode, i.e., the electric arc is confined within the torch. A plasma is formed in

* O* indicates translational excitation of 480 kJ mole⁻¹.

helium by a dc arc. A small amount of O_2 (~ 2% of the total gas flow) is injected downstream of the arc into the gas flow, where it is thermally dissociated into oxygen atoms by the hot helium. The high temperature and the isentropic expansion provide for the oxygen atom velocity, which results in a supersonic beam. A similar source has been reported by Air Force Geophysics Laboratories (6).

The arc source has been tested with pure He, He/ O_2 mixtures, He/Ar/ O_2 mixtures, and Ar/ O_2 mixtures as a function of torch power. Tests with O_2 indicate that oxidation of electrodes does not take place even at high torch current levels. He, Ar, O_2 , and O atom beams have been detected using the mass spectrometer. Conversion of molecular oxygen into atoms is determined from relative mass peak signals (measured by the quadrupole mass spectrometer), I_O/I_{O_2} , by the formula of Miller and Patch (7).

$$y = \frac{N_O}{N_{O_2}} = P \left(\frac{\sigma_{O_2}}{\sigma_O} \right) \left(\frac{1}{\eta} \frac{I_O}{I_{O_2}} - 1 \right) \quad (6)$$

where N_O/N_{O_2} is the inferred number density ratio of O to O_2 , P is the probability of dissociative ionization, σ_O/σ_{O_2} is the ratio of electron impact ionization cross sections, I_O/I_{O_2} is the ratio of mass spectrometer signals of O and O_2 with the torch on, and η is the I_O/I_{O_2} ratio with the torch off. The per cent dissociation is given by:

$$\%D = 100 y / (y + 2).$$

As one can see from figure 3, the per cent dissociation of O_2 into O ranges from ~ 30 to 48% for a 2.55% O_2 in Ar mixture, to ~ 15 to ~ 19% for various O_2 in He/Ar mixtures. These per cent dissociation translate into source temperatures of 3000-3200°K for O_2 in Ar, and 2700-2850°K for O_2 in He/Ar mixtures. Although not shown, tests made using pure He also show a lower dissociation. The greater efficacy of argon in dissociating O_2 probably owes to increased energy deposition in Ar, which flows more slowly through the torch (0.63 STP $\&$ sec⁻¹ Ar, 2.1 STP $\&$ sec⁻¹ He).

Results will be reported of measurements of the rate of volatilization of graphite by high velocity atomic oxygen in order to determine if the apparent enhancement of this rate on orbit is real. Mass spectral measurement of the products of high velocity O atom bombardment of carbon will be described as well.

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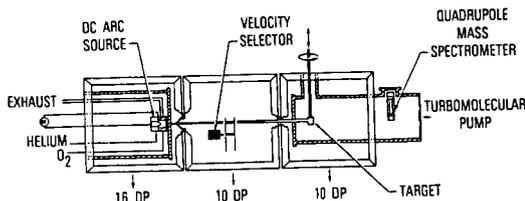


Figure 1. High energy oxygen atom surface chemistry apparatus.

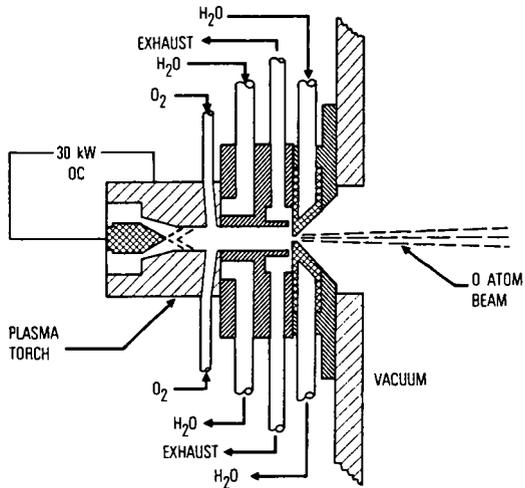


Figure 2. DC plasma arc atomic beam source.

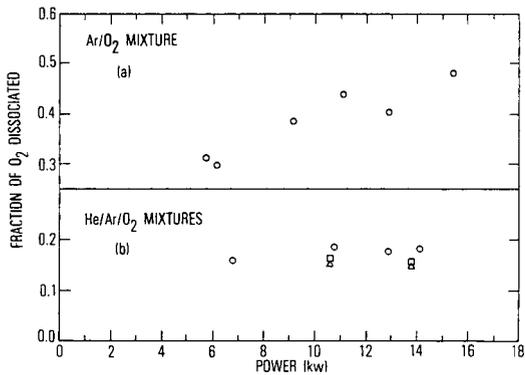


Figure 3.

Dissociation efficiency for O₂ in gas mixtures as a function of arc source power consumption: (a) 2.55% O₂ in Ar, (b) (O) 2.2% O₂, 5.9% Ar, 91.9% He; (e) 1.5% Ar, 92.6% He; and (Δ) 2.9% O₂, 5.9% Ar, 91.2% He.