

Temperature-dependent morphological evolution of HOPG graphite upon exposure to hyperthermal O(³P) atoms

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Abstract

The chemical reactivity and morphological evolution of highly-ordered pyrolytic graphite upon exposure to hyperthermal (~ 5 eV) O(³P) atoms have been investigated. The erosion rate and surface roughness exhibit a profound dependence on the temperature of the sample during the experiment. Atomic force microscopy images of eroded surfaces exposed to atomic oxygen at 298 K reveal embedded cylindrical erosion pits which span nanometer through micrometer length-scales. In contrast to this, very rough matted surfaces are observed following exposure at a surface temperature of 493 K. The erosion rate triples upon this increase in sample temperature. These data are compared to those of experiment EOIM-III, collected in low-earth orbit on-board the spacecraft Atlantis during STS-046.

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1. Introduction

Carbon-based materials, such as organic thin films, polymers, and carbon fiber reinforced composites, are commonly employed on spacecraft because of their light weight and desirable chemical and/or mechanical properties. In the harsh low-earth orbital (LEO) environment, hyperthermal collisions between spacecraft and O(³P) atoms in addition to exposure to vacuum ultraviolet (VUV) light, X-rays, and charged particles frequently produce chemical and physical changes in these materials that result in erosion and degradation of many properties [1–3]. Atomic oxygen dominates the rarefied atmosphere at ~ 200 – 700 km where a combination of the impact velocity and O atom density yields a fluence of approximately 10^{15} O atoms $\text{cm}^{-2} \text{s}^{-1}$ on the ram surfaces of spacecraft with a mean collision energy of ~ 4.5 eV [4].

An understanding of the fundamental chemical reactivity and dynamics behind hyperthermal (0.1–20 eV) collisions of gaseous species with organic surfaces is needed in order to predict the long-term behavior of current materials in LEO and to design more durable materials for use on future spacecraft. Highly-ordered pyrolytic graphite (HOPG) is a viable model surface for this kind of investigation. An HOPG surface is essentially a collection of compressed sheets of basal-plane carbon [5]. Its structure, at the atomic level, has

been well characterized by scanning tunneling microscopy (STM).

The reactivity of HOPG with O₂ and/or air has been investigated by several research groups. Upon heating the sample to temperatures greater than 800 K, O₂ reacts only at the defect sites (steps and point defects) to create single and multi-layer erosion cylinders with diameters on the order of 1–200 nm [6]. Using a Cs⁺ or Ar⁺ ion beam, defect arrays may be intentionally created [7,8] that can be used as oxidative templates toward micro- and nanostructure design [9–11]. Similar defect nucleation centers have also been created using fast beams of C₆₀⁺ buckyballs [12]. In small, well-controlled dosages of hyperthermal O(³P) (4×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$) protrusions have been reported at the very early stages of erosion [13].

The chemical reactivity of HOPG in a space environment, specifically the LEO, is apparently quite different. Ngo et al. [14] have observed a highly eroded graphite surface after exposure to the low-earth orbit chemical environment for an estimated fluence of 2.3×10^{20} atoms cm^{-2} (Fig. 1). Several “hillocks” of varying size and shape have been observed with an average RMS roughness for a $7 \mu\text{m} \times 7 \mu\text{m}$ area of ~ 85 nm. Approximately one C atom was etched for every eight impinging O atoms (or 1.1×10^{-24} cm³ per O atom). This is roughly equivalent to one atomic layer for every 10 s in LEO at an altitude of ~ 300 km.

Graphite erosion at these high kinetic rates appears to be directly related to both the hyperthermal translational

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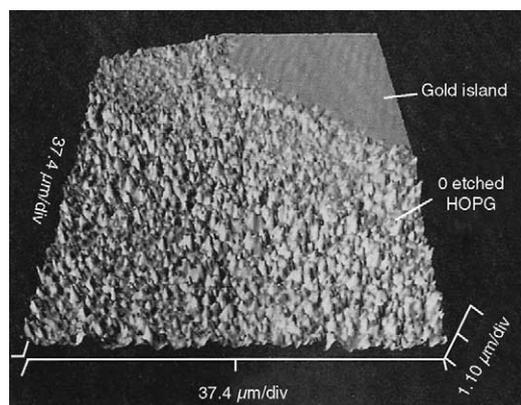


Fig. 1. HOPG exposed to 2.3×10^{20} O atoms cm^{-2} in low-earth orbit. This AFM image is reproduced from Ngo et al. [14, p. L817].

energy (5 eV) and the exposure rate of the atomic oxygen impinging upon the surface. We have undertaken a series of experiments to further explore the chemical reactivity of hyperthermal atomic $\text{O}(^3\text{P})$ with HOPG at rates commensurate with those believed to exist in LEO [15]. The detailed surface morphology has been directly imaged by atomic force microscopy (AFM) and STM. Profilometry measurements suggest that approximately one C atom is eroded for every eight incident O atoms when the sample is heated to ~ 493 K during the exposure. At this temperature, the erosion rate and surface roughness for this model study are quite consistent with the reported experiment performed in LEO. However, at lower sample temperatures (~ 300 K), a comparatively smoother surface is imaged with several embedded cylindrical erosion pits with diameters spanning nanometer through micrometer length-scales.

2. Experimental details

These experiments were performed at two locations in order to take advantage of complementary facilities and capabilities at these sites. Samples were exposed to hyperthermal $\text{O}(^3\text{P})$ atoms at Montana State University while precise AFM and STM imaging measurements and associated analyses were inducted at The University of Chicago.

A pulsed beam containing hyperthermal $\text{O}(^3\text{P})$ atoms and O_2 was directed at a HOPG surface (SPI-Materials, ZYA-Grade). Before exposure, the HOPG sample was cleaved several times using Scotch tape to yield several large terraces (micron scale) that did not contain any defects. This was confirmed by atomically-resolved STM. The beam source is based on the laser detonation source originally developed by Physical Sciences. A piezoelectric pulsed valve was employed to inject a packet of O_2 gas (10–20 bar of pressure) into a water-cooled, gold-plated copper nozzle. The dimensions, detailed design of this experimental apparatus, and beam characterization methods have all been described elsewhere [16,17]. The sample mount, whose

temperature can be controlled from 298 to 573 K, was located 40 cm from the nozzle orifice. The incident angle of the O atom beam on the samples was a few degrees from the surface normal. Samples were generally exposed for several hours at two pulses of $\text{O}(^3\text{P})$ atoms per second. On average, each pulse contained 1.75×10^{15} O atoms (mean translational energy of ~ 5 eV) and lasted for ~ 100 ms. Therefore, the estimated atomic oxygen exposure rate at this distance was $\sim 3.5 \times 10^{15}$ atoms $\text{cm}^{-2} \text{s}^{-1}$. Note that the beam diameter encompassed the entire sample mount.

An etched mesh of stainless steel was placed over the samples for the exposures. After each experiment, the mask was removed and a profilometer was used to determine the erosion yield by measuring the step height between the exposed and unexposed areas. The surface morphology of the HOPG was imaged using a Topometrix Discoverer AFM/STM system. Due to the roughness of the exposed samples, AFM rather than STM was employed most often in the analysis. All of the images contained herein are 500 dpi resolution and have been leveled using a 3-point scheme. Line scans, surface roughness, etc. have all been calculated using Topometrix software. All AFM imaging was enacted at room temperature.

3. Results and discussion

Previous studies have demonstrated that organic films react with $\text{O}(^3\text{P})$ atoms to initially yield volatile OH and H_2O , presumably through a reaction step that involves the abstraction of a hydrogen atom [18]. After continuous bombardment of $\text{O}(^3\text{P})$ atoms, a multi-step reaction mechanism is assumed where carbon-containing products such as CO and CO_2 actually carry away substantial mass from the surface, leading to erosion [15]. The chemical products and microscopic kinetics of O_2 oxidation of HOPG at elevated temperatures have also been widely investigated [19–21].

An AFM image ($15 \mu\text{m} \times 15 \mu\text{m}$) of a freshly cleaved sample of HOPG is illustrated in Fig. 2A. This ZYA-Grade graphite has terraces on the scale of microns without any steps or point defects. Upon the introduction of hyperthermal atomic $\text{O}(^3\text{P})$ using the methods described herein, a grossly etched surface is observed. An AFM image ($15 \mu\text{m} \times 15 \mu\text{m}$) taken after HOPG was exposed to 1.8×10^{20} O atoms cm^{-2} at 298 K is shown in Fig. 2B. The surface normal for this sample was oriented 3.3° from the incident direction of the atomic oxygen beam during the experiment. The erosion depth of $1.08 \mu\text{m}$ corresponds to an erosion rate of one C atom for every 22 incident O atoms. The average RMS surface roughness for a $7 \mu\text{m} \times 7 \mu\text{m}$ cross-section is 8 nm.

The cylindrical nature of these pits is quite consistent with recently reported experiments involving the oxidation of graphite by O_2 [6]. The origin of these pits is presumed to be reactive nucleation occurring at point defects or atomic steps within or between the basal planes of HOPG. The diameter of the largest pit imaged in Fig. 2B is $1.85 \mu\text{m}$

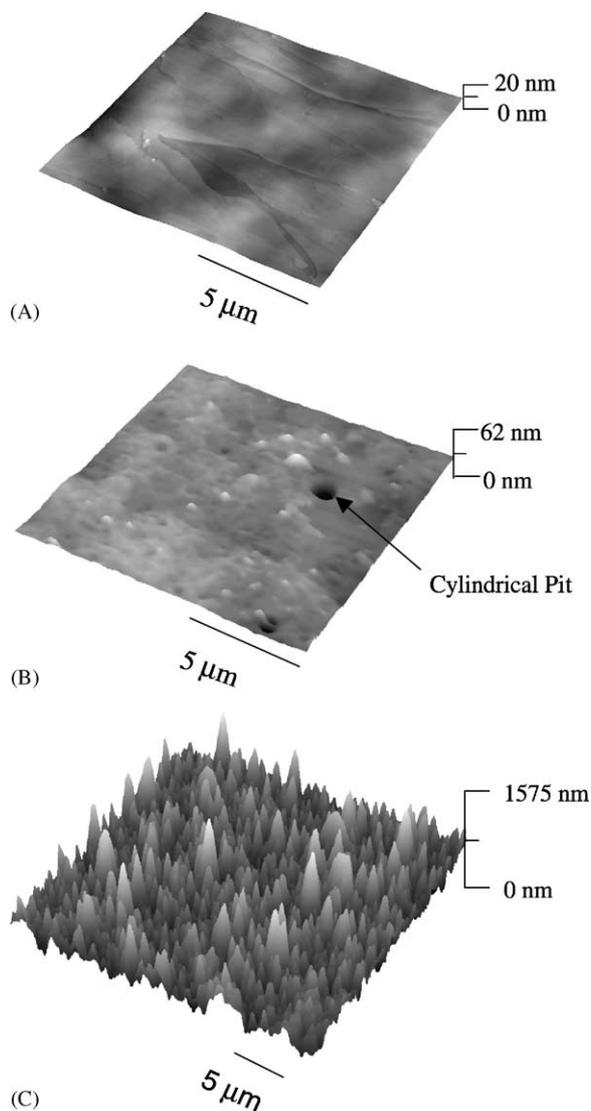


Fig. 2. (A) AFM image ($15\ \mu\text{m} \times 15\ \mu\text{m}$) of freshly cleaved HOPG (ZYA-Grade). (B) AFM image ($15\ \mu\text{m} \times 15\ \mu\text{m}$) of HOPG exposed to 1.8×10^{20} atoms cm^{-2} $\text{O}(^3\text{P})$ using the described experimental apparatus. The sample temperature during exposure was 300 K. An arrow designates a cylindrical pit with diameter $1.85\ \mu\text{m}$ and depth of 38.1 nm. (C) AFM image ($37.4\ \mu\text{m} \times 37.4\ \mu\text{m}$) of HOPG exposed to 2.0×10^{20} O atoms cm^{-2} using the described experimental apparatus. The sample temperature was 493 K during the hyperthermal $\text{O}(^3\text{P})$ exposure. All of the images were collected at ambient temperature.

with depth 38.1 nm. Throughout this sample, the cylinder diameter ranges from several nanometers to a few microns while the depths are most often a few to tens of nanometers.

The surface morphology of HOPG exposed to hyperthermal atomic $\text{O}(^3\text{P})$ has a marked dependence on sample temperature. A three-dimensional $37.4\ \mu\text{m} \times 37.4\ \mu\text{m}$ AFM image of a HOPG sample after exposure to $\sim 2 \times 10^{20}$ O atoms cm^{-2} is shown in Fig. 2C. This sample has been oriented 3.3° from normal incidence of the atomic beam and heated to 493 K during the exposure. The erosion depth measured by profilometry is $2.95\ \mu\text{m}$, which corre-

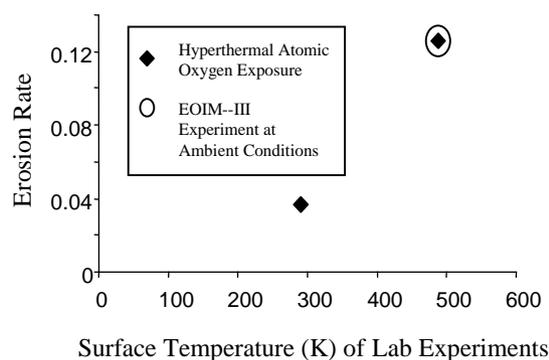


Fig. 3. Comparison of HOPG erosion rates at sample temperatures of 300 and 493 K with the EOIM-III experiment. The oval represents the HOPG erosion rate as reported from EOIM-III. The erosion rate is determined from the calculated number of carbon atoms eroded per incident oxygen atom [14].

sponds to an etching rate of approximately one C atom for every eight incident O atoms. The RMS roughness for a $7\ \mu\text{m} \times 7\ \mu\text{m}$ cross-section of this image is 93 nm. Instead of a comparatively smooth surface with several embedded cylindrical erosion pits, towers or “hillocks” are imaged in the eroded area. The peaks and valleys between the towers are most often on the order of hundreds of nanometers.

These two experiments, where HOPG has been exposed to laboratory-generated hyperthermal $\text{O}(^3\text{P})$, can be directly compared with that of graphite exposed to the LEO environment on the EOIM-III space flight experiment [14,22]. An AFM image, $37.4\ \mu\text{m} \times 37.4\ \mu\text{m}$, has been reproduced from published results (Fig. 1). In this case, the sample was exposed to 2.3×10^{20} O atoms cm^{-2} at an exposure rate of $\sim 1.6 \times 10^{15}$ atoms $\text{cm}^{-2} \text{s}^{-1}$ (very similar to the model experiment described herein). The reported erosion rate is one C for every eight incident O atoms, while the average RMS surface roughness for a $7\ \mu\text{m} \times 7\ \mu\text{m}$ cross-section is 85 nm.

Graphical plots that demonstrate the sample temperature dependence of the erosion rate and surface roughness are illustrated in Figs. 3 and 4, respectively. An oval designates the reported data points for the EOIM-III experiment,

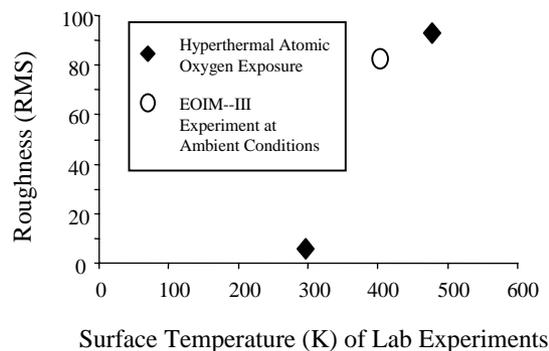


Fig. 4. Comparison of HOPG surface roughness (RMS) at sample temperatures of 300 and 493 K with the EOIM-III experiment. The oval represents the surface roughness of the eroded area for the EOIM-III experiment. These plotted data were analyzed for an image size of $7\ \mu\text{m} \times 7\ \mu\text{m}$ [14].

assuming the HOPG samples were placed on one of the ambient trays at a presumed temperature of ~ 300 K. (The actual temperature of the sample may have been somewhat higher due to the presence of a heated sample tray on this flight.) The reported erosion rate for the EOIM-III experiment is essentially identical to the terrestrial hyperthermal $O(^3P)$ exposure where the sample was heated to 493 K (Fig. 3). Comparison of the surface roughness and overall morphology of the model terrestrial experiments with the LEO exposure reveals that sample heating clearly produces a better overall agreement (Fig. 4).

The qualitative differences between the HOPG exposed to hyperthermal atomic $O(^3P)$ at 300 and 493 K have several implications for the fundamental chemical reactivity of high-energy atomic oxygen with HOPG. Specifically, the distinct changes in the surface morphology (cylindrical pits vs. towering hillocks) and erosion rate demonstrate a dramatic shift in $O(^3P)$ reactivity with respect to sample temperature. Presumably, at some critical temperature, the basal plane of HOPG becomes equally reactive or at least more susceptible to reaction by high-energy atomic oxygen atoms as compared to the defect structures that dominate the reactivity at lower temperatures. Additional experiments are currently underway to further probe the microscopic chemical dynamics of this thermally activated process.

These data also suggest that there may be additional factors operating in the LEO experiment that yield an erosion rate and surface morphology comparable to HOPG exposed exclusively to hyperthermal $O(^3P)$ and O_2 at 493 K. Perhaps there are synergistic effects between the VUV (120–200 nm) light from the sun, X-ray radiation, and/or other hyperthermal atomic species that mechanistically change or at least enhance the chemistry between the 5 eV atomic oxygen and HOPG at 300 K. These synergistic effects are currently being incorporated into our model terrestrial experiments in order to determine the role of each potential player in the complex, but quite interesting, low-earth orbit reaction environment.

4. Summary and conclusions

The erosion and degradation of HOPG upon exposure to 5 eV atomic $O(^3P)$ have been explored in a laboratory setting. Profilometry measurements between the etched and unetched areas reveal a marked kinetic dependence for a sample temperature range of 300–493 K. AFM imaging has been employed to examine the surface topography. Samples exposed to hyperthermal $O(^3P)$ at 300 K are found to be relatively smooth but to contain embedded cylindrical erosion pits which span nanometer through micrometer length-scales. In contrast to this behavior, very rough matted surfaces are observed following exposure at a surface temperature of 493 K which may be described as consisting of numerous “hillocks” that are hundreds of nanometers in height. These results have been directly compared to previ-

ous experiments in LEO [14] and other model experiments [13]. Expanded experiments are currently underway in our laboratories to determine how atomistic chemical kinetic processes evolve as a function of temperature and O atom fluence, most notably including reactivity changes at perfect and defect-containing regions of the interface. The role of VUV and/or X-ray irradiation on the chemical dynamics will also be investigated. Such elementary chemical processes are responsible for the temperature-dependent evolution in graphite morphology that have been observed for samples irradiated with 5 eV atomic $O(^3P)$ and the mechanistic steps which play a key role in the degradation of materials in the low-earth orbit chemical environment.

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