

フッ素系高分子の原子状酸素誘起エロージョンにおける非線形エネルギー依存性

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ABSTRACT

In order to study the origin of accelerated erosion phenomena of fluorinated polymers in ground-based atomic oxygen test facilities, we have studied the contribution of high-energy component in the atomic oxygen beam. The experiment was carried out with a combination of polymer-coated quartz crystal microbalance and high-speed chopper wheel in the laser-detonation atomic oxygen source. It was clearly observed that the mass-loss rates of both polyimide and fluorinated polymer strongly depend on the impact energy of atomic oxygen. However, the effect was more significant on fluorinated polymer compared with that on polyimide; i.e., translational energies higher than 6 eV provide a significant mass-loss on fluorinated polymer. This experimental finding agrees with the volatile product data and theoretical predictions. It was confirmed that the presence of high-energy component in atomic oxygen beams resulted in the increase of mass-loss rate on fluorinated polymer relative to polyimide.

1. INTRODUCTION

It has been recognized that the erosion rate of fluorinated ethylene polymer (FEP) in the ground-based atomic oxygen test using laser-detonation atomic oxygen source is much greater than that in the flight tests in low earth orbit (LEO). Because FEP has been widely used as a thermal control material for satellites in LEO, this is one of the major problems on the ground-based AO testing using the laser detonation source that is a standard for the ground-based atomic oxygen testing. The origin of this problem has been recognized due to the extreme ultraviolet (EUV) from the laser-sustained oxygen plasma in the nozzle [1].

In ICPMSE-9 (2008), we have reported the real-time mass change of fluorinated polymer during atomic oxygen exposure with/without the ultraviolet emission form laser plasma [2]. It was confirmed that the role of EUV from laser plasma on the fluorinated polymer erosion do exist, but it does not show significant synergistic effect with atomic oxygen on the accelerated erosion of FEP in a laser-detonation source. Thus, the question still remains: why FEP erosion is much faster in laser detonation source than in space?

The experimental finding, that shows the role of ultraviolet from the oxygen plasma is not a major origin, strongly suggests that the origin of this phenomenon is included in the atomic oxygen beam itself.

In order to answer this question, we studied the energy dependence of atomic oxygen reactivity with polyimide and fluorinated polymer. The role of high-energy component of the atomic oxygen, which is included in the atomic oxygen beam formed by the laser-detonation method, is discussed.

2. EXPERIMENTS AND SPECIMENS

The laser-detonation atomic oxygen beam source used in this study has been developed at Kobe University in order to study gas/surface reactions of atomic oxygen with solid materials [3-6]. This type of the source is known as a Physical Sciences Inc. (PSI)-type source [7]. Figure 1 shows a photograph of the facility. This type of beam source uses pulsed supersonic valve (PSV) and carbon dioxide laser (10.6 μm , 5-7 J/pulse). The laser light was focused on the nozzle throat with a concave Au mirror located 50 cm away from the nozzle. The PSV introduced pure oxygen gas (99.8%) into the nozzle and the laser light was focused on the gas cloud in the nozzle. The energies for the dissociation and acceleration were provided by the inverse Bremsstrahlung process. The hyperthermal beam, thus generated, was characterized by a time-of-flight (TOF) distribution measured by the quadrupole mass spectrometer with scintillation detector which are installed in the beam line. Translational energies of the species in the beam were calculated using TOF distributions with the flight length of 238 cm. This type of source can deliver intense atomic oxygen beam pulses with velocity of approximately 8 km/s.

In order to change the collision energy of atomic oxygen, a high-speed chopper system was installed. This high-speed chopper system was originally installed in order to block the ultraviolet from oxygen plasma [8]. The collision energy of atomic oxygen could be adjusted with this chopper wheel by blocking a part of the atomic oxygen beam. Figure 2 shows the block diagram and the photograph of the chopper

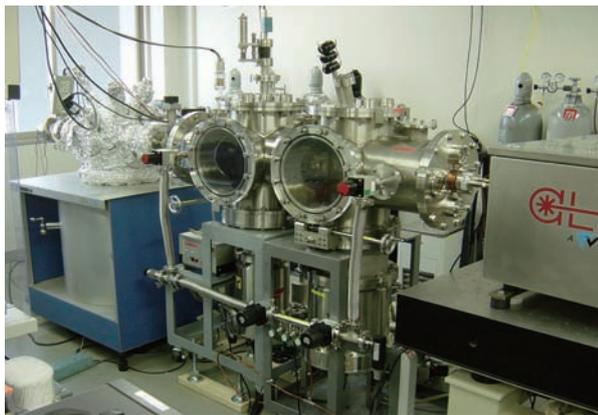


Figure 1 Photograph of the atomic oxygen beam facility used in this study. Two 1500 L/s turbo molecular pumps are used to maintain the vacuum.

system. Blocking of a part of the beam was made by changing the system delay.

A 5 MHz Ag-coated QCM sensor was equipped at the bottom of the rotatable mount in order to measure the flux of atomic oxygen [9]. Typical atomic oxygen flux after slicing by the chopper wheel was measured to be $0.7\text{--}2.0 \times 10^{13}$ atoms/cm²/s at the sample position.

Samples used in this study are two types of polymers; polyimide and fluorinated polymer. A polyimide amide acid was spin-coated on a quartz crystal at 12,000 rpm for 30 s, and curing treatments at 150 °C for 1 hr. and 300 °C for 1 hr. were carried out in order to form the spin-coated polyimide structure with a thickness of approximately 0.1 μm. The spin-coated polyimide film, thus formed, and Kapton-H film has the same repeating unit of polymer (PMDA-ODA polyimide). In contrast, fluorinated polymer was prepared by the plasma-assisted physical vapor deposition technique developed at the Technology Research Institute of Osaka Prefecture [10]. Change in mass of the films was detected from the frequency shift of quartz crystal microbalance (QCM) on which the films were coated. The resonant frequency of QCM was recorded in every 10 seconds with the frequency resolution of 0.1 Hz. All beam exposure experiments were carried out with the sample temperature at 38 °C with normal incidence.

3. EXPERIMENTAL RESULTS

Time-of-Flight (TOF) spectra and average collision energy of atomic oxygen beam sliced by the chopper wheel are shown in Figure 3. Figure 3 (a) and 3 (b) show the TOF distributions in which a slow- and fast-part of the beam pulse was partially blocked by chopper wheel, respectively. It is clearly observed that the atomic oxygen beam pulse, overall average energy of 5.5 eV and full width at half maximum (FWHM) of

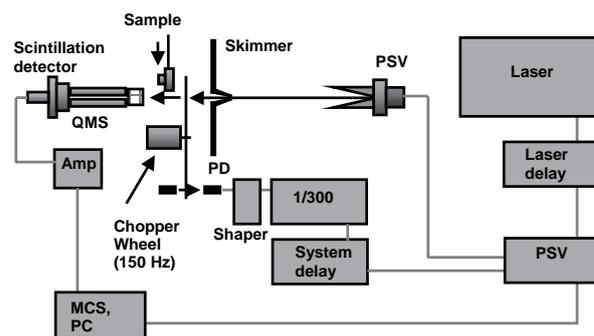
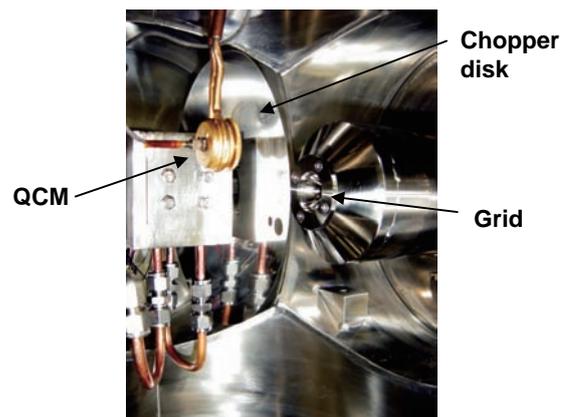


Figure 2 Photograph of the chopper wheel inside the laser detonation atomic oxygen beam source (upper panel) and the system diagram (lower panel). The chopper was operated at 9,000 rpm under the pressure of 4×10^{-7} Torr.

5.2 eV, is sliced by the chopper wheel operating 150 Hz. The average energy of the sliced beam is adjustable from 1.3 eV to 8.8 eV by changing the system delay. The polyimide and fluorinated polymer-coated QCMs were installed in the beam line and the change in resonance frequency of QCM was recorded during the exposure to the sliced atomic oxygen beam.

The frequency shift of the polyimide-coated QCM, which is proportional to the mass-loss of the film, is negative when low-energy atomic oxygen beam was irradiated ($E_{\text{coll}} < 4$ eV). Such mass-increase phenomenon was observed only for the beginning of exposure and it was concluded that the initial surface oxidization reaction, which includes oxygen atom accommodation at the polyimide surface, was the origin of this unexpected results [11]. In contrast, it is clearly observed that the frequency shift of polyimide-coated QCM increased with increasing the collision energy of atomic oxygen beam ($E_{\text{coll}} > 5$ eV). On the other hand, frequency shift of the fluorinated polymer-coated QCM becomes significant with high-energy atomic oxygen beam ($E_{\text{coll}} > 6$ eV). It is also indicated that the rate of frequency shift of the

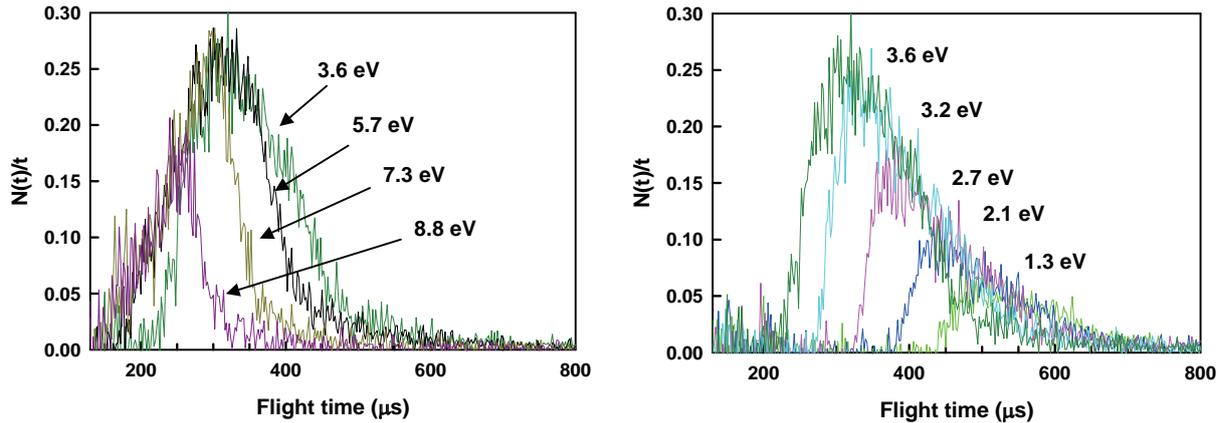


Figure 3 Time-of-flight spectra of atomic oxygen beam ($m/e=16$) sliced by the high-speed chopper wheel. For better view of the each TOF spectrum, left and right panels show the TOF spectra in which slow-part and fast-part of the beam pulses are blocked by the chopper wheel. The same TOF spectrum ($E_{coll}=3.6$ eV) is shown in both panels for comparison purpose.

fluorinated polymer at high-energy atomic oxygen collision is greater than that of polyimide.

The flux of atomic oxygen beam changes with chopper timing, e.g., energy. The mass-loss rate was divided by the relative area of TOF spectrum and flux compensated mass-loss rate, which corresponds to relative reaction efficiency (R_E) of atomic oxygen, was calculated. The results are shown in Figure 4 (a) and 4 (b). It is clearly indicated that the relative reaction efficiency, thus calculated, almost linearly increases with collision energy for polyimide. However, the reaction efficiency of atomic oxygen with fluorinated polymer is very small at collision energies lower than 5 eV and the threshold collision energy of 6 eV is clearly observed. The collision energy dependence on reaction efficiency with fluorinated polymer is much more

drastic so that the relative erosion of fluorinated polymer compared with polyimide is enhanced if high-energy component ($E_{coll} > 6$ eV) is included in the atomic oxygen beam. This is a usual case for atomic oxygen beam generated by the laser-detonation method. It is thus concluded that the accelerated erosion of fluorinated polymer in the ground-based experiment is mainly due to the contribution of high-energy component of atomic oxygen beam.

4. COMPARISON WITH THEORETICAL STUDIES

Troya and Schatz have performed direct-dynamics classical trajectory calculations of collisions of

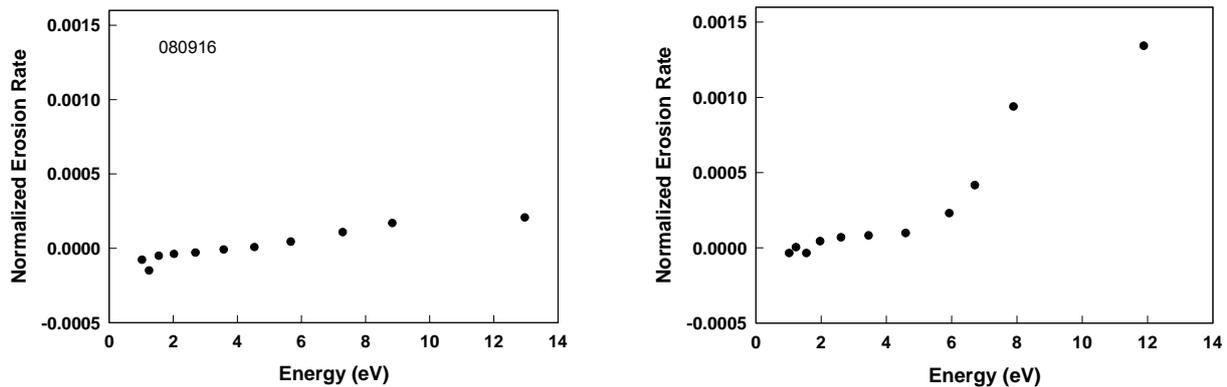


Figure 4 Normalized erosion rate of polyimide (left) and fluorinated polymer (right) as a function of collision energy of atomic oxygen. Difference in atomic oxygen fluxes in the sliced beam was compensated with dividing by the area of TOF spectrum of the each beam.

hyperthermal ($E_{\text{coll}} = 4.5 - 6$ eV) ground state atomic oxygen ($\text{O}(^3\text{P})$) with hydrocarbon (CH_4 and C_2H_6) and perfluorinated hydrocarbon (CF_4 and C_2F_6) molecules [12]. Their computational results also suggested that F-elimination is more important than F-abstraction (which is negligible), but the cross-sections for F-elimination are also very small. The C-C bond breakage cross-sections in the $\text{O}(^3\text{P}) + \text{C}_2\text{F}_6$ reaction is larger than the F-elimination cross-section. This is opposite to that of hydrocarbons. They calculated that the cross-section ratio of [F-elimination]/[C-C bond breakage] is 0.12 and 0.24 at $E_{\text{coll}} = 5.5$ and 6.0 eV, respectively. This is due to the fact that C-C bond in C_2F_6 is 0.4 eV weaker than C_2H_6 by the very electronegative fluorine atoms. The excitation function (cross-section vs. E_{coll}) for C-C bond breakage in $\text{O}(^3\text{P}) + \text{C}_2\text{F}_6$ reaction showed more E_{coll} dependence than in $\text{O}(^3\text{P}) + \text{C}_2\text{H}_6$ reaction in the $4.5 < E_{\text{coll}} < 6.0$ eV region. This is a good agreement with our results shown here. However, cross-section of direct C-C breakage in C_2F_6 is smaller than that in C_2H_6 . This is disagreement with the results obtained here.

Troya and co-workers also reported the classical-trajectory study of the dynamics of hyperthermal (5-12 eV) collisions between $\text{Ar} + \text{C}_2\text{F}_6$ and $\text{Ar} + \text{C}_2\text{H}_6$ systems [13]. They found that the C_2F_6 is more susceptible to collision-induced dissociation (CID) than C_2H_6 due to the lower frequencies in heavier species. Three to six times energies can be transferred to C_2F_6 than C_2H_6 from incoming atoms. Their computational results suggested the role of CID in the C-C breakage reaction of fluorinated polymers. Atomic oxygen beam used in this study always contains undecomposed molecular oxygen. Not only the high-energy component of the atomic oxygen included in the beam, but also molecular oxygen will have certain role for CID on C-C bond breakage. This suspicion arises also from the O_2 flux-compensated relative reaction efficiency on fluorinated polymer indicates obviously exponential dependence with O_2 energy (Not shown).

It is, thus, concluded that two possible reactions channels are proposed for the accelerated erosion of fluorinated polymer in ground-based atomic oxygen test: direct C-C bond breakage by high-energy component of atomic oxygen and CID process by high-energy component of atomic oxygen and by molecular oxygen in the beam.

5. REAL LEO ENVIRONMENT

The atomic oxygen collision is characterized by the space experiment aboard STS-46 (EOIM-3) [14]. In space, the average collision energy of AO is reported to 5.6 eV with full width at half maximum (FWHM) about 1.7 eV. On the other hand, in our study, the

average collision energy of atomic oxygen is also approximately 5.5 eV, however its FWHM is as large as 5.2 eV. It is clear that the FWHM in the ground experiment is much greater than that in LEO. Two possible mechanisms for accelerated erosion are both energy-sensitive, it is essential to simulate the energy spectrum, energy spread as well as average energy, in ground-based experiments.

In conclusion, fluorinated polymer exhibits much stronger dependence on collision energy, thus, high-energy component of AO beam, if exists, promoted the direct or CID-associated C-C breakage reaction. The difference in reaction mechanism and collision energy dependence on polyimide and fluorinated polymer causes the accelerated erosion of fluorinated polymer in the ground-based atomic oxygen simulation.

6. CONCLUSIONS

In order to study the origin of accelerated erosion of fluorinated polymers in ground-based atomic oxygen test facilities, contribution of high-energy component in the atomic oxygen beam was studied. The experiment was carried out with a combination of polymer-coated QCM and high-speed chopper wheel in the laser-detonation atomic oxygen source. It was clearly observed that the mass-loss rates of both polyimide and fluorinated polymer strongly depend on the impact energy of atomic oxygen. However, the effect was more significant on fluorinated polymer compared with that on polyimide; i.e., translational energies higher than 6 eV provide a significant mass-loss on fluorinated polymer. This experimental finding agrees with the volatile product data and theoretical predictions. It was confirmed that the presence of high-energy component in atomic oxygen beams resulted in the increase of mass-loss rate on fluorinated polymer relative to polyimide. The results of this work suggested the importance of the control of translational energy on the quantitative results of ground-based atomic oxygen simulations not only for the accelerated erosion of FEP, but also for the validity of Kapton equivalent fluence.

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