低地球軌道環境における FEP 劣化に対する窒素分子寄与の可能性

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Possibility of N_2-induced erosion of fluoropolymer was discussed based on the ground-based experiment and flight data. Multiple composition beams with velocity of 8 km/s were formed with Ar+O_2 target gas by the laser detonation source. The energy and composition of the beam, thus formed, were analyzed by time-of-flight measurements with a quadrupole mass spectrometer. It was found that atoms in different masses, O-atom and Ar, are accelerated to similar velocities, i.e., different translational energies (4.5 eV O-atom and 9 eV Ar). This is suitable for simulating sub-low Earth orbit neutral gas environment. Erosion yields of fluoropolymer by O-atom and by Ar were evaluated individually. It was found that the erosion yields of fluoropolymer by 9 eV Ar in the ground-based experiment and those by 9 eV N_2 in LEO measured by MISSE-2 showed good agreement. In contrast, erosion yield of fluoropolymer by 5 eV O-atom in the ground-based experiment and that in the orbit were not consistent. These results strongly suggested that the erosion of fluoropolymer is due not by O-atom, but by Ar and N_2.

1. INTRODUCTION

Materials used at the exterior surface of a spacecraft encounter severe space environment which includes high vacuum, thermal cycling, ultraviolet and radiation exposures, and collision with neutral atoms. It is well known that many polymeric materials, which cover spacecraft for thermal control purposes, are eroded in space especially by the collision with atomic oxygen. After this phenomenon was discovered by early space shuttle mission, effect of O-atom collision on material erosion has been studied intensively [1]. However, effect of other neutral gas components in upper atmosphere such as N_2, Ar, O_2 and He has been ignored for the last 30 years. This is reasonable since more than 95% of the gas atoms/molecules collide with spacecraft surface is O-atom at the altitude of 400-500 km where STS and ISS are orbiting. The development of very low altitude satellites (for example GOCE by ESA or SLATS by JAXA), which are orbiting the altitude of 200 km or below, requires the knowledge of material response in the environment of simultaneous hyperthermal collisions both of O-atom and N_2.

Recent understanding of the fluorinated polymer erosion suggested that the fluorinated polymer is more sensitive to the collision energy of gas molecules even they are chemically inactive [2-5]. If N_2 collision owed a part of fluorinated polymer degradation in LEO, it would be remarkably increased with decreasing altitude because of the N_2 density increased more rapidly than that of O-atom density.

In this study, we present data/discussions regarding the fluoropolymer erosion in a neutral gas environment in sub-low Earth orbit (LEO) region. Origin of fluoropolymer degradation in space is also discussed based on the experimental results.

2. EXPERIMENTS

Figure 1 shows the laser-detonation O-atom beam source used in this study. This hyperthermal beam source has been developed at Kobe University in order to study material degradation in LEO at 400-500 km [6-8]. This type of the source is known as a Physical Sciences Inc. (PSI)-type source [9], and 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 target gas 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-

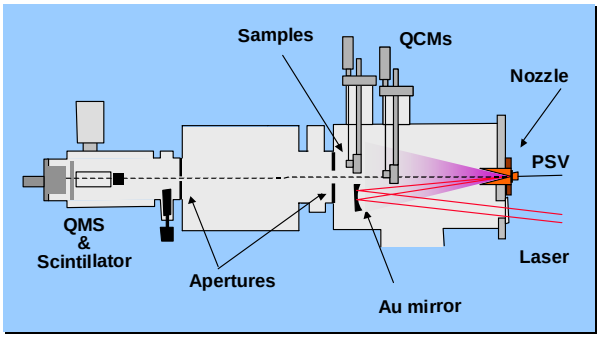

Figure 1 Laser detonation beam source used in this study. Time-of–flight mass spectrometer was used to analyse a beam.

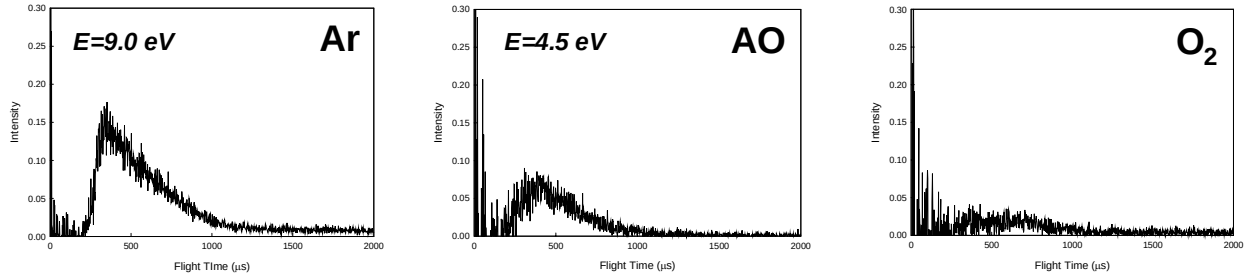

Figure 2 Time-of-flight spectra of m/z=16, 32 and 40 compositions in the beam formed by the target gas consist of 50%Ar+50%O_2. With higher energies, O_2 component becomes weak.

flight (TOF) distribution measured by the quadrupole mass spectrometer with scintillation detector which is 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. A high-speed chopper system was not used in this study [8].

Three types of mixed gases were used in this study; 50%N_2+50%O_2, 50%Ar+50%O_2, and 70%Ar+30%O_2. 100%O_2 gas was also used as a reference. Hyperthermal multiple composition beams were formed by the conditions as follows; high voltage for piezoelectric actuator: 900 V, PSV opening duration: 0.4 ms, pressure in the target gas supply line: 0.3 MPa, and laser power 5-7 J/pulse.

Material degradation was evaluated by real-time measurement of mass loss by a quartz crystal micro-balance (QCM) [10]. 5 MHz polymer-coated QCM sensors were equipped at the bottom of the rotatable mount in order to measure the flux of the beam. Samples used in this study are two types of polymers; polyimide and fluorinated polymer. A polyimide amide acid was coated on a quartz crystal and curing treatments at 150 °C for 1 hr. and 300 °C for 1 hr. were carried out in order to form the polyimide structure with a thickness of approximately 0.1-2.0 μm. In contrast, fluorinated polymer was prepared by the plasma-assisted physical vapor deposition technique developed at the Technology Research Institute of Osaka Prefecture [11]. 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 at room temperature with normal incidence.

4. RESULTS & DISCUSSION

4.1 TIME-OF-FLIGHT SPECTRA

In order to simulate the high-energy collision of N_2 in sub-LEO environment, Ar, which is monoatomic molecule, is mixed to O_2 gas on behalf of N_2. This is due to avoid the unexpected decomposition of N_2 molecules into N atoms. Figure 2 shows TOF spectra of m/z=16, 32 and 40 compositions in the beam formed by the target gas consist of 50%Ar+50%O_2. It is obvious that O_2 signal is very weak and hardly detected whereas O-atom and Ar peaks are clearly observed. The promotion of O_2 decomposition is suggested in the target gas of Ar+O_2. Promotion of the decomposition reaction in the Ar+O_2 target gas is due to the high-energy collision between O_2 and Ar. Average energies of these components are 4.5 and 9.0 eV for O-atom and Ar, respectively. This is ideal for the sub-LEO simulation from the viewpoint of collision energy.

4.2 MASS-LOSS MEASUREMENTS

Real-time mass-loss measurements of polyimide and fluoropolymer under the simultaneous exposure to O-atom and Ar beams were carried out. The experiment was performed using two QCMs, which are coated by polyimide and fluoropolymer. Spatial distribution of O-atom flux was compensated using two polyimide-coated QCMs at both positions (L- and R-positions). It was measured that O-atom flux in the R-position, where polyimide-coated QCM locates, is 1.28 times greater that that of the L-position. On the other hand, spatial distribution of Ar flux, which could not be measured by polyimide, was assumed the same of O-atom distribution.

Erosion yield (Ey) of fluoropolymer by 4.5 eV O-atom and 9 eV Ar were calculated by the following equation;

$$Ey = [S \times C] / [A \times F \times d] \qquad (1)$$

where S is the slope of frequency change (Hz/s), C is the constant for 5 MHz QCM (-2.002E-8 g/Hz), A is the area of sample (cm^2), F is the flux (atoms/cm^2) and d is the density of the material (g/cm^3). O-atom flux was measured from the erosion of polyimide with standard erosion yield of 3.0E-24 cm^3/atom with 100%O_2 target gas (translational energy of the O-atom in the calibration was 4.5 eV). In contrast, Ar flux was measured with TOF spectra intensities with a relative sensitive factor of AO, 3.76. Densities and area of the materials are 1.4 g/cm^3 and 0.28 cm^2 for polyimide and

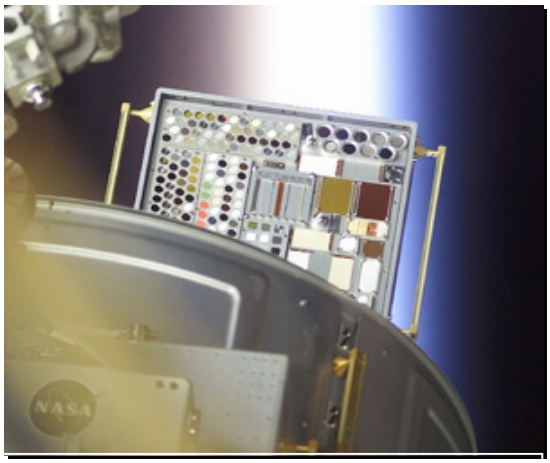

Figure 3 MISSE-2 PEC-1 pallet in orbit (upper left corner is the PEACE polymer tray).

2.1 g/cm^3 and 0.38 cm^2 for fluoropolymer. From the slope of polyimide at R-position, flux of O-atom is measured to be 7.8E+13 atoms/cm^2/s. The O-atom flux at the position-L, where the fluoropolymer QCM was located, was estimated to be 6.1E+13 atoms/cm^2/s. On the other hand, the Ar flux was estimated to be 3.8E+13 atoms/cm^2/s. By using equation (1), Ey of fluoropolymer by 9 eV Ar was calculated to be 2.8E-24 cm^3/atom, which is close to the Ey of polyimide by 4.5 eV O-atom. On the other hand, Ey of fluoropolymer by 4.5 eV O-atom is calculated to be 1.7E-24 cm^3/atom.

4.3 COMPARISION WITH MISSE-2 DATA

The Ey data measured in this study was compared with the MISSE-2 flight data. A fluorinated ethylene propylene (FEP) specimen was exposed to space environment from August 16, 2001 to July 30, 2005 by MISSE-2 PEACE polymer experiment (Figure 3). Following data on the FEP erosion was reported by de Groh; mass loss: 0.01248 g, density: 2.144 g/cm^3, exposed area 3.447 cm^2, Kapton equivalent O-atom flux: 8.43E+21 atoms/cm^2 [12]. As a result, erosion yield of FEP is calculated to be 1.9E-25 cm^3/atom. However, N_2 fluence during the exposure was not reported. Therefore, N_2 fluence was estimated by the MSIS-E90 atmospheric model in this study. The N_2 fluence during MISSE-2 exposure was calculated to be 6.1E+20 molecules/cm^2. The accuracy of this estimation was confirmed by the comparison of O-atom fluences calculated in the same condition and actually measured during the MISSE-2 mission. The O-atom fluence calculated by MSIS-E90 was 8.8E+21 atoms/cm^2, which is within the error of 5 % from the measured value in the MISSE-2 mission with Kapton-H. With this N_2 fluence, the erosion yield of FEP by N_2 was calculated to be 2.8E-24 cm^3/atom, which is the same value of the ground-based data obtained in this study described in the section 4.2 (Table 1). This result strongly suggests that the erosions of fluoropolymer and FEP are due not by the 5 eV O-atom but by the 9 eV N_2 or Ar. The consistency of erosion yields also suggests that the N_2 effect in LEO could be simulated by Ar in the ground-based simulation.

Table 1 Erosion yield of fluoropolymer calculated in this study (on ground and in orbit).

Experiment	FEP Erosion yields (cm3/atom)	
	AO	N2 or Ar
MISSE-2	1.9E-25	2.8E-24
Multiple Beam	1.7E-24	2.8E-24

5. CONCLUSIONS

Possibility of N_2-induced erosion of fluoropolymer was discussed based on the ground-based experiment and flight data. It was found that the erosion yields of fluoropolymer by 9 eV Ar in the ground-based experiment and those by 9 eV N_2 in LEO measured by MISSE-2 showed good agreement. In contrast, erosion yield of fluoropolymer by 5 eV O-atom in the ground-based experiment and that in the orbit were not consistent. These results strongly suggested that the erosion of fluoropolymer is due not by O-atom, but by Ar and N_2.

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