表面帯電時における原子状酸素誘起高分子エロージョン
Atomic Oxygen-induced Erosion of Polymers under Surface Charging

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Key words: atomic oxygen, charging, low earth orbit, synergy, erosion, polyimide, polysulfone

Abstract: Effect of surface charging on the atomic oxygen-induced erosion of polyimide was investigated. Polyimide sample was spin-coated on the quartz crystal microbalance (QCM), and mass loss of the film was directly measured from the resonant frequency shift of QCM during atomic oxygen exposure. The experiment was carried out using the specially designed QCM, which allowed a sample bias voltage up to 1500 V during resonant frequency measurements. From the experimental results, we confirmed that the erosion rates of polyimide at ±1500 V were almost identical to that at grounded. It was, thus, concluded that the polyimide erosion by atomic oxygen is hardly affected by surface charging. Similar conclusion was also obtained with polysulfone. This conclusion was inconsistent with that reported by King et al. Discrepancy of the experimental results would be due to the surface ionization yield of reaction products under surface charging.

1. INTRODUCTION

Pyromelliticdianhydride-oxydianiline (PMDA-ODA) polyimide (Kapton-H, DuPont) has been used as a reference material for atomic oxygen fluence measurement both in flight and in ground-based experiments. In order to maintain the accuracy of atomic oxygen fluence measurement in exposure tests, erosion properties of PMDA-ODA polyimide in various synergistic exposure conditions have to be fully understood. We have investigated the effect of ambient air exposure [1], temperature [2], incident angle [3], and ultraviolet exposure [4] on the atomic oxygen-induced erosion rate of PMDA-ODA polyimide. Following results were obtained from a series of experiments shown above; (1) The amount of oxygen adsorbed during atomic oxygen exposure would be higher than that analyzed after ambient air exposure, (2) Due to high impact energy of atomic oxygen, the activation energy of gasification reaction of polyimide is in the order of 10^{-4} eV and temperature dependence of erosion is not appeared below 100 °C, (3) Erosion rate of polyimide follows cosine function with respect to incident angle of atomic oxygen which suggests reaction yield of atomic oxygen is independent of the incident angle, and (4) Simultaneous 172 nm ultraviolet exposure promote erosion of polyimide up to 400 % depending on the relative intensity of ultraviolet. Conclusions of synergistic testing listed above showed that polyimide erosion is influenced by the environmental factors beside atomic oxygen in low Earth orbit.

On the other hand, spacecraft charging has been recognized as a serious problem on electronic systems aboard spacecraft. It sometimes seriously damages spacecraft system due to discharge. However, effect of charging on material erosion has not been studied intensively. The only literature was the effect of electron beam irradiation in the atomic oxygen erosion of polysulfone that was reported by King and Wilson [5]. They found that electron beam irradiation or bias voltages applied to the back plate of polysulfone increased the signal of reactive products; CO and CO_2. They examined only for polysulfone. If surface charging also influenced the erosion rate of polyimide, surface charging phenomenon during flight or ground-based test needs to be considered to provide an accurate fluence measurement of atomic oxygen.

In this study, we examined the effect of surface charging on the atomic oxygen-induced erosion of polyimide. A quartz crystal microbalance (QCM) technique, which was established to study synergistic effect of atomic oxygen and ultraviolet on polymer erosion [1-4], was used to measure the erosion rate of polyimide under biased or electron beam exposed conditions. Effect of bias potential and electron beam exposure on the atomic oxygen-induced mass loss phenomenon of polyimide witness sample was analyzed and discussed.

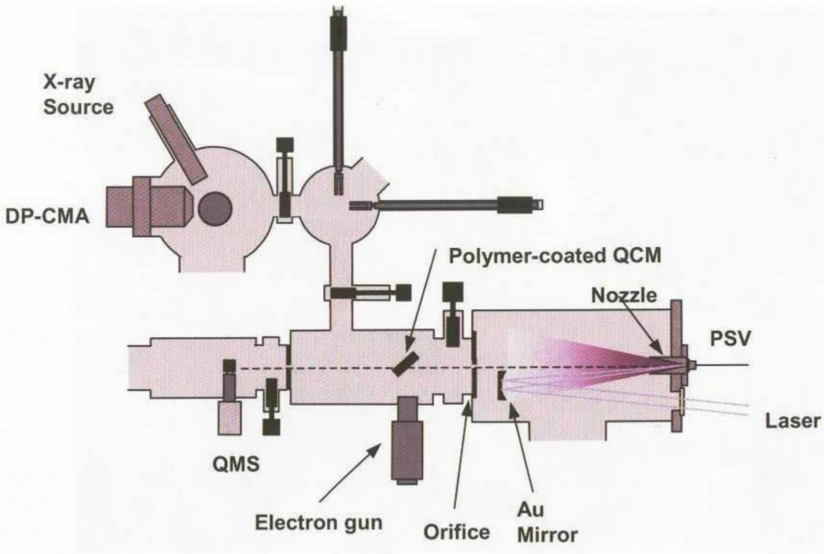

Figure 1. Atomic oxygen beam facility used in this study. Laser detonation atomic oxygen source and high-energy electron gun are equipped.

2. EXPERIMENTAL DETAILS

2.1 Atomic oxygen beam source

The atomic oxygen source used in this study was a laser detonation atomic oxygen source. This type of source was developed by Physical Sciences Incorporation [6]. Detail of the source used in this study was described elsewhere [7]. The PSI-type atomic oxygen source was attached to the space environment simulation facility at Kobe University (Figure 1). The translational energy of atomic oxygen beam was monitored by the time-of-flight (TOF) measurement system consisting of a quadrupole mass spectrometer (QMS) and a multichannel scalar. Mean translational energy of the atomic oxygen was calculated to be 5.0 eV, which corresponds to the orbital velocity of spacecraft.

The atomic oxygen flux in a beam was measured by an Ag-coated QCM with an accommodation coefficient of 0.62 [8]. The principle of measurement is explained in following section. Since the reaction of atomic oxygen with Ag is a non-linear phenomenon, only the initial reaction, which gave a linear mass gain, was used to calculate atomic oxygen flux [9].

2.2 Erosion measurement

Erosion rate of polyimide film was measured from the resonant frequency of QCM, which was coated by a polyimide film. Resonance frequency of QCM is expressed in the formula;

$$\Delta f = -f_0^2 \, \Delta W / NA\rho \qquad (1)$$

where, N is the frequency constant, A is the electrode area, ρ is the density of quartz, and f_0 is the resonant frequency. Since N, A, ρ, f_0 are known factors, one can calculate the mass change (ΔW) of the sensor crystal from the frequency shift (Δf) of the QCM. Resonant frequency was measured in every 10 seconds with accuracy of 0.1 Hz. For a 5 MHz AT-cut QCM sensor crystal used in this study, frequency resolution of 0.1 Hz corresponds to mass resolution of 2 ng. The QCM system used in study was modified in order to apply bias voltages to the front surface of a sensor crystal. Since a conventional QCM surface was grounded to avoid ion-sputtering effect during plasma-enhanced chemical vapor deposition (PECVD) processes, an electrically isolated manifold was used to float the QCM from the grounded vacuum chamber. Bias voltage up to 1500 V was superimposed to the driving voltage of QCM sensor crystal (DC 8V) and the QCM holder. However, the computer interface of the QCM driver was maintained to be grounded. This electric isolation was achieved by a specially designed circuit.

Formation of PMDA-ODA polyimide film on a QCM sensor crystal was achieved by the process

Figure 2. Photograph of the experimental setup for the e-beam experiment. A high-energy electron gun is installed at the top flange of the reaction chamber. QCM was temporally attached to the source chamber in order to measure atomic oxygen flux.

below. Precursor of PMDA-ODA polyimide (Semicofine SP-510, Toray) was spin-coated on a QCM sensor crystal and rotated with 12,000 rpm, 10 seconds. Two-stage cure treatment (150 °C, 1 hour followed by 300 °C, 1 hour) in N_2 atmosphere was carried out to create PMDA-ODA structure. The PMDA-ODA film, thus formed, has a thickness of approximately 0.1 μm, and X-ray photoelectron spectrum of the film was similar to that of commercially available polyimide (Kapton-H). Polysulfone film was also spin-coated with a solution involving polysulfone pellet (Mw=63,000) and N, N-dimethylformamide as solvent. The spin-coated solution containing polysulfone was dried in air at 70 °C, 1 hour.

3. RESULTS

3.1 Synergistic effect with electron beam

Figure 2 shows the experimental setup for the experiment on the effect of simultaneous electron beam. Electron beam (acceleration voltage: 7 kV, filament current: 2.2 A) irradiated the sample during atomic oxygen exposure. Experimental results on polyimide are shown in Figure 3. Open circle indicates the resonant frequency of polyimide-coated QCM under atomic oxygen exposure alone, open triangle and solid circle are those under simultaneous atomic oxygen and electron beam exposures. Open triangles are the data when sample was grounded, whereas solid circles are for floating cases. The experimental data in Figure 3 are somewhat noisy, however, it is clear that no significant change in the slop of the lines is obvious. The slopes of the lines calculated by a least square fit are listed in Table 1. As listed in Table 1, the slopes of the resonant frequency in three exposure conditions are distributed within an error of 3 %. Since electron beam exposure alone did not affect the mass of the polyimide (Figure 4), it was concluded from a series of experiments that simultaneous electron beam exposure hardly affects the mass loss phenomenon of polyimide due to atomic oxygen-induced erosion. The same experiments were carried out with polysulfone, and similar results were obtained.

3.2 Synergistic effect with bias voltage

Bias voltages from 0 to 1500 V (positive and negative) were applied to polyimide-coated QCM, and the influence on atomic oxygen-induced mass loss phenomenon was examined. Measurements were carried out during the increasing and decreasing phases of bias voltages and the results were averaged. Figure 5 shows the frequency shift of polyimide-coated QCM during atomic oxygen exposures with bias voltages from 0 to 1500 V. Figures 5 (a) and 5 (b) indicate the results for negative and positive bias,

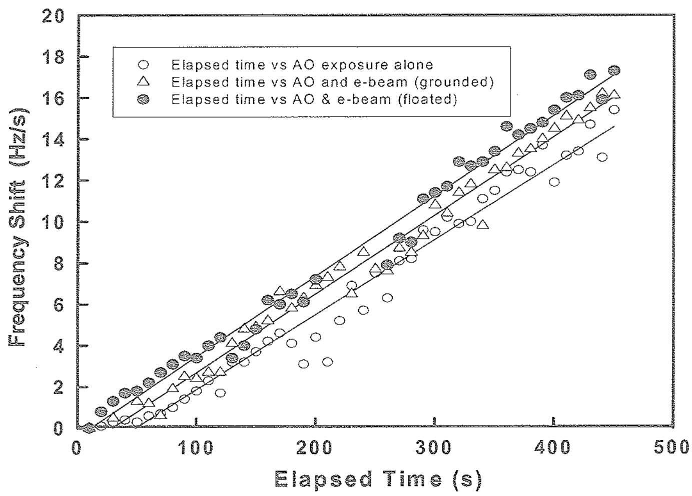

Figure 3. Frequency shift of the polyimide-coated QCM under simultaneous exposure of atomic oxygen and 7 kV electron beam.

respectively. It was clear that no significant effect of bias voltages on atomic oxygen-induced erosion was observed. We have also examined the polysulfone in the same experiment, however significant effect was not observed. From the QCM experiments reported herein, we confirmed that the bias voltage does not affect the reaction yield of atomic oxygen with polyimide. This experimental finding provided a conclusion that effect of charging on polyimide is not necessary to consider when polyimide is used as a witness sample for atomic oxygen fluence monitor.

4. DISCUSSION

The effect of electron beam irradiation and bias voltage on atomic oxygen-induced erosion of polysulfone was reported by King and Wilson [5]. They used a laser detonation atomic oxygen beam, which is the same type of atomic oxygen source used in this study, and detected the reactive products of CO and CO_2 by quadrupole mass spectrometer (QMS) during the experiment. They reported that no significant effect of electron beam irradiation when spin-coated polysulfone sample was grounded, in contrast, significant increase in CO and CO_2 signals were detected when the sample was electrically floated. Since similar effect was observed when sample was simply biased, they concluded that the increases in CO and CO_2 production yields are due to surface charging. Actually they indicated that CO_2 signal increased when bias voltage was applied to the back plate of the film.

Table 1. Slope of the frequency shift of QCM under various exposure conditions of atomic oxygen and electron beam.

Experimental conditions	Slope (Hz/s)
Atomic oxygen exposure alone	3.7×10^{-2}
Atomic oxygen plus e-beam (grounded)	3.8×10^{-2}
Atomic oxygen plus e-beam (floated)	3.8×10^{-2}

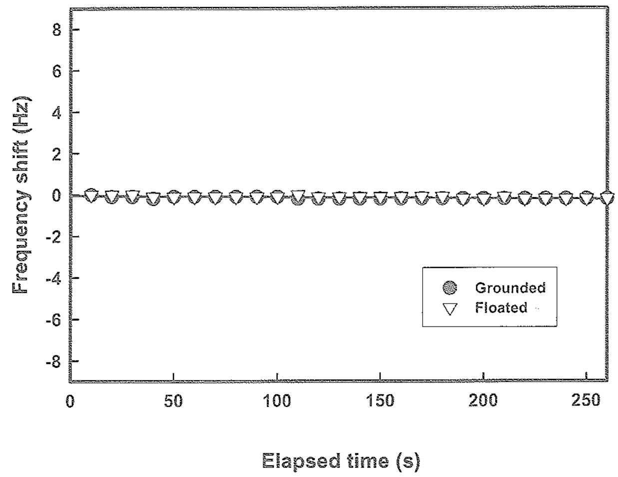

Figure 4. Frequency shift of the polyimide-coated QCM under electron beam exposure. Note that atomic oxygen beam is turned off. No erosion is detected both for grounded and floated samples.

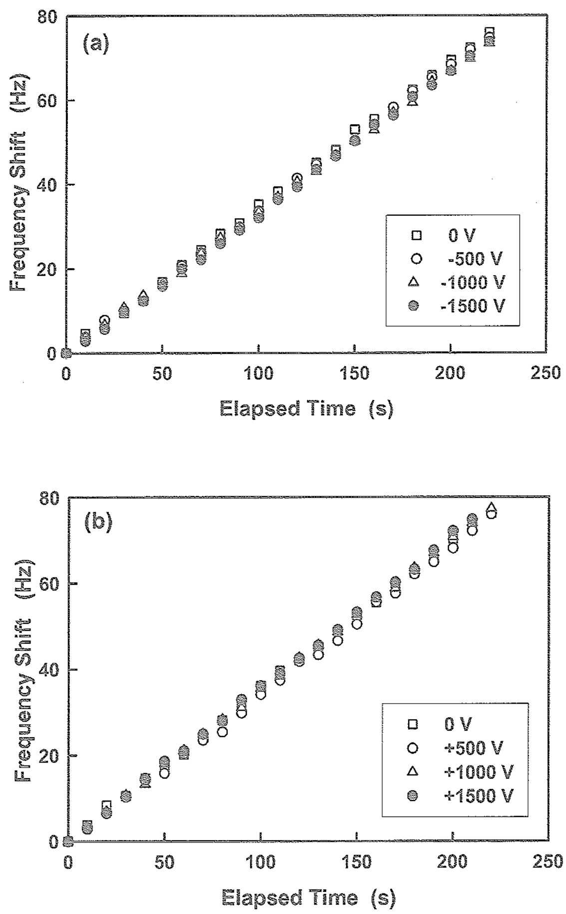

Figure 5. Frequency shift of the polyimide-coated QCM under atomic oxygen beam exposure with bias voltages of 0 to 1500 VDC. (a): Negative bias, and (b): Positive bias. Bias voltage of 0 V means that the sample was grounded.

However, the experimental results obtained in this study were inconsistent with King's report; i.e., mass loss phenomenon was affected neither by electron beam irradiation nor by application of bias voltages up to 1500 V (positive and negative). The origin of this discrepancy would be explained by a surface ionization phenomenon. In the King's experiment, they detected CO and CO_2 ions. These ions are ionized in the electron bombardment ionizer at the QMS. Ionization cross section of molecules in the electron bombardment ionizer has not been evaluated, but usually low (maybe 10^{-4} or even lower). On the other hand, ions originally containing in the beam is detected with a probability of almost 1. King's analysis, which CO and CO_2 production yields become greater with bias voltage, is based on the assumption that the amount of ions in the beam is unchanged by the application of bias voltages. One of the mechanisms that explain two inconsistent experimental results simultaneously is the effect of bias voltages to the surface ionization cross section. Namely, if the fraction of ions in the reactive products (CO and CO_2) becomes greater when bias voltage is applied, the experimental results reported by King and in this study can be explained, simultaneously. This is because the detection probability of ion is much higher than that of molecule with QMS. Measuring of the surface ionization cross section under application of bias voltages will verify the proposed mechanism herein.

5. CONCLUSION

Effect of charging on the atomic oxygen-induced erosion of polyimide was investigated. Polyimide sample was spin-coated on the quartz crystal microbalance (QCM), and mass loss of the film was directly measured from the resonant frequency shift of QCM during atomic oxygen exposure. From the experimental results, we confirmed that the erosion rate of polyimide at 1500 V was almost identical to that at grounded. It was, thus, concluded that the polyimide erosion by atomic oxygen is hardly affected by surface charging. It was confirmed that the effect of surface charging does not need to consider in atomic oxygen fluence measurements using Kapton witness sample. Similar conclusion was also obtained with polysulfone. This conclusion for polysulfone was inconsistent with that reported by King et al. The discrepancy would be explained by the change in surface ionization cross section of the reaction products under charging.

ACKNOWLEDGMENTS

A part of this work was supported by the grant-in-aid of scientific research contract No. 14350511 and 15560686 from the Ministry of Education, Culture, Sports, Science and Technology, Japan; Kawanishi memorial Shinmaywa Education Foundation. The authors are grateful to Mr. S. Seikyu for his help with experiments.

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