酸素原子環境計測用材料としてのポリイミドのエロージョン特性（2）
—入射角度依存性について—

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The ground-based experimental results of the incident angle dependence on the erosion rate of polyimide under hyperthermal atomic oxygen beam exposures are reported. A hyperthermal atomic oxygen beam was generated by a laser detonation-type atomic oxygen beam source. *In-situ* mass loss measurement was made during the atomic oxygen exposure using a quartz crystal microbalance. It was observed that the erosion rate of polymers was followed cosine function with respect to the incident angle of atomic oxygen. This experimental finding clearly indicates that the reaction yield of atomic oxygen with polymers is independent of the incident angle. As for the fluence monitoring material, erosion depth or mass loss of polyimide simply reflects the effective atomic oxygen fluence which is calculated by multiplying normal flux and cosine of the incident angle.

1. Introduction

There exist many environmental factors in low Earth orbit (LEO) such as microgravity, thermal cycling, plasma, ultraviolet, radiation, neutral gas and space debris. In particular, one of the most important factors that gives serious damage to the many polymeric material is atomic oxygen, which is a dominant neutral species in LEO. Due to the difficulty to simulate atomic oxygen environment in laboratory, details of the erosion properties are still not understood deeply. Many polymeric materials are exposed to real space environment as well as simulated atomic oxygen environment to study their survivability. Since the absolute fluence of atomic oxygen in material exposure test is difficult to determine, Kapton equivalent fluence is widely accepted as a method to measure atomic oxygen fluence. In this method, the material erosion of a targeted polymer is compared with that of Kapton-H whose erosion rate is assumed to be 3.0 x 10^{-24} cm^3/atom. However, it is natural to consider that the material response with hyperthermal atomic oxygen collision depends on a material. It is thus emphasized that the erosion properties of Kapton-H (PMDA-ODA polyimide) in various exposure conditions have to be well-understood as a standard material for material erosion tests. Not only PMDA-ODA polyimide, but also polyethylene and fluorinated polymer should be studied in the same manner since ASTM-E2089, which describes standard method of atomic oxygen testing, requires the measurement of the erosion rate of these polymers as standard materials [1].

In our previous study, we have reported the temperature dependence of polyimide erosion under hyperthermal atomic oxygen beam exposure [2]. It was discovered that the erosion rate of polyimide is almost independent of temperature under 120 °C. From the slope of the Arrhenius plots, the activation energy of the mass loss reaction is calculated to be 5.7 x 10^{-4} eV for the 5.0 eV atomic oxygen beam. This activation energy is evaluated that the erosion of polyimide in hyperthermal atomic oxygen bombardment is temperature-independent below 120 °C. This unique property is due to impact energy as high as 5 eV. In contrast, Minton et al. reported that the erosion rate of polyimide increases in the temperature range higher than 120 °C [3]. These research results suggest that the material exposure test should be conducted below 120 °C in order to use the erosion yield of 3.0 x 10^{-24} cm^3/atom for Kapton-H.

On the other hand, these material erosion properties have been experimentally measured by the normal incidence of atomic oxygen. However, the incident angle of atomic oxygen in the flight tests depends on the attitude of spacecraft. Especially, the exposure time of flight experiments aboard the International Space Station are usually longer than those aboard space shuttle, and may be affected by its attitude. Also actual MLI is bombarded by atomic oxygen in various incident angles and the effect of incident angle should be taken into account for precise predictions of its erosion.

In this paper, we summarize our recent results regarding incident angle dependence of atomic oxygen-induced erosion of polyimide and some other polymeric materials from the viewpoint of space environment monitoring material.

2. Experimental details

The laser detonation atomic oxygen source was used in this experiment [4]. The atomic oxygen source is based on the laser detonation phenomenon and is originally developed by Physical Sciences Inc.

[10, 11]. This type of atomic oxygen source uses a pulsed CO_2 laser (5-7 J/pulse) and a piezoelectric pulsed supersonic valve (PSV). The laser light is focused on the nozzle throat with the concave Au mirror located 50 cm away from the nozzle. The PSV introduces pure oxygen gas into the nozzle and the laser light is focused on the oxygen gas in the nozzle. The energies for the dissociation of oxygen molecule to oxygen atom and for the acceleration are provided by the multiphoton absorption process. The atomic oxygen beam, thus generated, is characterized by a time-of-flight (TOF) distribution measured by the quadrupole mass spectrometer installed in the beam line. Translational energy of the species in the beam is calculated using TOF distributions with the flight length of 181 cm. The mean energy of the hyperthermal atomic oxygen was calculated to be 4.7 - 5.0 eV, whereas that of molecular oxygen (byproducts) was 5.0 – 6.0 eV. The atomic oxygen fraction in the beam was approximately 45 %, balance molecular oxygen (thermal and hyperthermal). The atomic oxygen flux of the beam was measured by an Ag-coated QCM. A typical atomic oxygen flux at the sample position was calculated to be 10^{13} – 10^{15} atoms/cm^2/s depending on the distance from the nozzle.

Quartz crystal microbalance (QCM) was applied to measure mass change of the polymer films. QCM is a device measuring a mass change of the oscillating quartz crystal, and it is proud of one of the highest mass resolution in mass-measurement technologies existed. In space engineering, QCM was used as a molecular contamination monitor during a flight mission [6]. QCM has also been used in the atomic oxygen-related researches. We have pioneered using QCM in order to measure translational energy dependence of polyimide erosion with an ion beam-type atomic oxygen source in 1994 [7, 8]. The synergistic effect with simultaneous ultraviolet exposure has been studied with this method [9-11].

In this study, spin-coated PMDA-ODA polyimide film (Semicofine SP-510, Toray) on an Au-QCM was used as a target material. A polyimide amide acid was spin-coated on a quartz crystal at 12,000 rpm for 30 s, and the curing treatment at 150 °C for 1 hour then 300 °C for 1 hour was carried out in order to form polyimide structure with a thickness of approximately 0.1 μm. Polyethylene is also spin-coated on a QCM sensor crystal. In contrast, fluorinated polymer-coated QCM was prepared by the plasma-assisted physical vapor deposition [12].

3. Results and discussion

3.1 Polyimide

Figure 1 displays the frequency shift of the QCM during atomic oxygen beam exposures at impingement angles from 0 to 90 degrees. The impingement angle was taken with respect to the surface normal. A good linear relationship between the frequency shift and exposure time, i.e., mass loss and atomic oxygen fluence, was observed at all impingement angles. The good linearity of the mass loss with fluence was also identified for larger time scale [13]. The results shown in Figure 1 were obtained at a sample temperature of 38 °C, but similar results were also observed at sample temperatures from 15 °C to 70 °C. The slope of the mass loss rate at every impingement angle was calculated by a least squares fit, and plotted against the impingement angle. The results are presented in Figure 2. It is clear that the rate of frequency shift, or erosion rate, of polyimide depends on the impingement angle and the dependence follows cosine law as indicated by the solid line in Figure 2. Note that the data point at the impingement angle of 80

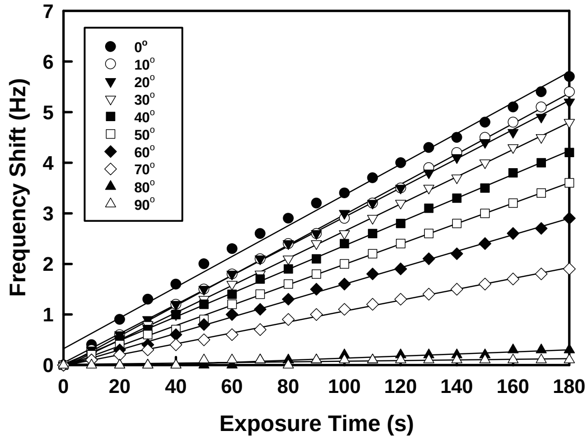

Figure 1 Frequency shift of polyimide-coated QCM during atomic oxygen exposure.

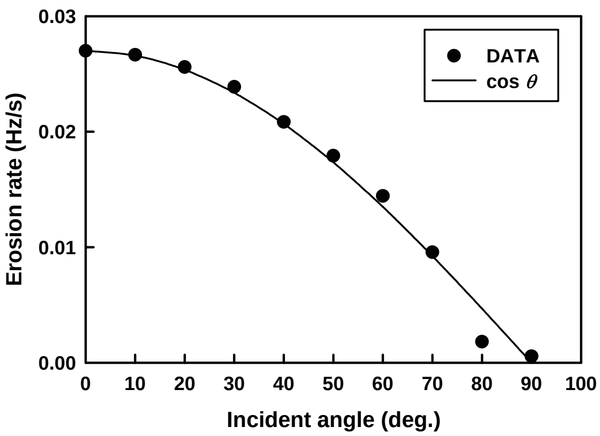

Figure 2 Incident angle dependence of atomic oxygen-induced erosion for polyimide.

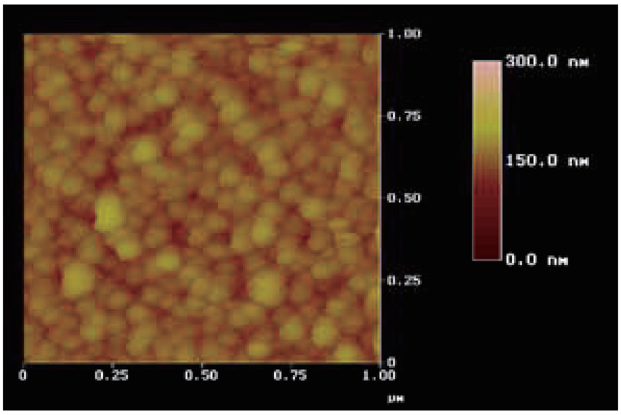

Figure 3　AFM image of polyimide after exposure to atomic oxygen.　4.6 eV, 9.6 x 10^{17} atoms/cm^2

degrees was affected by the QCM holder which blocked a part of the incoming atomic oxygen beam.

Banks and co-workers reported that the impingement angle dependence of the erosion of FEP Teflon in the LDEF flight experiment followed $\cos^{1.5}\theta$ law rather than a cosine law [14]. An analysis of the flight data of Kapton-H and Mylar aboard STS-8 concluded that the impingement angle dependence followed $\cos^{1.5}\theta$ law [15]. However, their conclusions were based either on a small number of data points obtained by the flight experiments or on the large uncertainty of the data which spoils the accuracy of the analysis. Furthermore, no physical explanation was provided for the $\cos^{1.5}\theta$ dependence.

The cosine law of the impingement angle dependence observed in this experiment was physically explained as follows: the effective flux of atomic oxygen at the sample surface decreases with increasing impingement angle; the effective flux of atomic oxygen is in proportion to the cosine of the impingement angle. The fact that the impingement angle dependence of the erosion rate follows a cosine law clearly indicates that the erosion rate is proportional to the effective flux of atomic oxygen; i. e., the reaction yield of oxygen atom with polyimide is independent of the impingement angle. Figure 3 shows the atomic force microscope image of the polyimide film that was exposed to atomic oxygen with a fluence of 8.8 x 10^{17} atom/cm^2. Note that all experimental data shown in Figures 1 and 2 were obtained using the same sample, so that the atomic oxygen fluence at the sample surface reached 10^{18} atoms/cm^2, including pre-exposure of 6 x 10^{17} atoms/cm^2, when mass loss data were taken. Although, the atomic oxygen fluence in this study is relatively small compared with many in-flight experiments, the surface of the polyimide was already roughened due to the atomic oxygen attack. The peak-to-valley height of the surface was larger than 10 nm which is approximately 100 times larger than the size of a carbon atom. Therefore, on the microscopic scale, the impingement angle of oxygen atoms incident to the polyimide surface is widely distributed due to the presence of microscale roughness even though the macroscopic impingement angle is fixed. Therefore, the microscopic roughness at the polyimide surface erase the impingement angle dependence of atomic oxygen reactivity and the macroscopic erosion phenomena of polyimide simply reflects the effective fluence of atomic oxygen which follows cosine law with the macroscopic impingement angle.

3.2 Other polymers

The same experiments were carried out using polyethylene and fluorinated polymer-coated QCM. Figures 4 and 5 show the incident angle-dependence of erosion rate for polyethylene and fluorinated polymer. It is clearly indicated that the erosion rates for both materials follow cosine function. From the

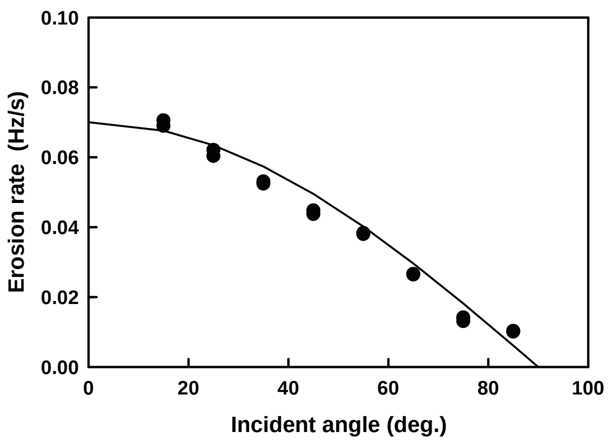

Figure 4　Incident angle dependence for polyethylene.

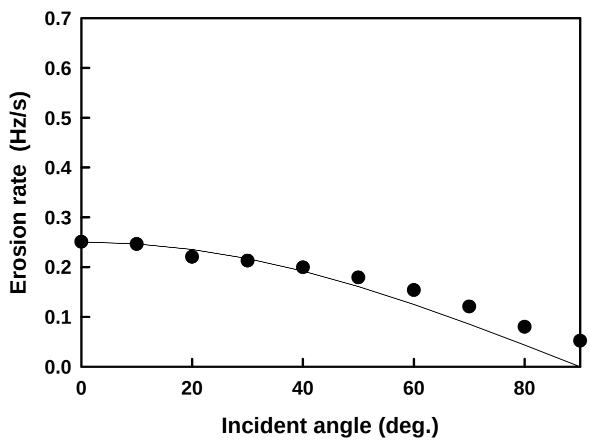

Figure 5　Incident angle dependence for fluorinated polymer.

experimental results shown in Figure 4 and 5, it is concluded that the cosine rule is applicable for material gasification reaction by hyperthermal atomic oxygen in many polymeric materials.

4. Conclusions

The ground-based experimental results of incident angle dependence on the erosion rate of polyimide under hyperthermal atomic oxygen beam exposures are reported. The *in-situ* mass loss measurement was made during the atomic oxygen exposure by using a quartz crystal microbalance. It was observed that the erosion rate of polymers was followed cosine function with respect to incident angle of atomic oxygen. This experimental finding clearly indicates that the reaction yield of atomic oxygen with polymers is independent of the incident angle.

As for the fluence monitoring material, erosion depth or mass loss of polyimide simply reflects the effective atomic oxygen fluence which is calculated by multiplying normal flux by cosine of the incident angle. It is thus concluded that the Kapton equivalent fluence can be calculated by taking into account the cosine rule for the incident angle even if the Kapton witness sample is exposed to atomic oxygen in angled incidence conditions.

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References

[1] Designation: E2089-00, The American Society for Testing of Materials, 2000.

[2] Yokota, K., Tagawa, M., Ohmae, N., Temperature dependence in erosion rates of polyimide under hyperthermal atomic oxygen exposures, *Journal of Spacecraft and Rockets*, Vol.40, No1, 143-144, 2003.

[3] Buczala, D. M. and Minton, T. K., Erosion of kapton H by Hyperthermal Atomic Oxygen: dependence on O-Atom Fluence and Surface Temperature, Protection of Materials and Structure from Space Environment, Kleiman J. Ed., Springer, Dordrecht, 317-330, 2006.

[4] Tagawa, M., Yokota, K., Ohmae, N., and Kinoshita, H., Volume Diffusion of Atomic Oxygen in α-SiO_2 Protective Coating, *High Performance Polymers*, Vol.12, No.1, 53-63, 2000.

[5] Caledonia, G. E., Krech, R. H., Green, B. D., A high flux source of energetic oxygen atoms for material degradation studies, *AIAA Journal*, Vol.25, 59, 1987.

[6] Hall, D. F., Flight Measurement of Molecular Contaminant Environment, *Proceedings of 6th International Symposium on Materials in a Space Environment*, Noordwijk, November 1994, ESA SP-368, pp.27-33.

[7] Tagawa, M., Matsushita, M., Umeno, M., Ohmae, N., Laboratory studies of atomic oxygen reactions on spin-coated polyimide films, *Proceedings of the 6th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, ESA SP-368, 189-194, 1994.

[8] Tagawa, M., Matsushita, M., Suetomi, T., Umeno, M., Ohmae, N., A consideration of synergetic testing condition of atomic oxygen and solar radiation on materials, *Collection of Abstracts, Methodologies for Simulation of Space environment*, 15, 1996.

[9] Tagawa, M., Suetomi, T., Kinoshita, H., Umeno, M., Ohmae, N., Surface reaction of a low flux atomic oxygen beam with a spin-coated polyimide film: Synergetic effect of atomic oxygen and ultraviolet light, *Transactions of the Japan Society for Aeronautics and Space Sciences*, Vol.42, No.135, 40-45, 1999.

[10] Yokota, K., Tagawa, M., Ohmae, N., Impingement angle dependence of erosion rate of polyimide in atomic oxygen exposures, *Journal of Spacecraft and Rockets*, Vol.39, No.1, 155-156, 2002.

[11] Tagawa, M., Yokota, K., Ohmae, N., and Kinoshita H., Effect of ambient air exposure on the atomic oxygen-exposed Kapton films, *Journal of Spacecraft and Rockets*, Vol.39, No.3, 447-451, 2002.

[12] Okamoto, A., Matsunaga, T., Proceeding of the 45th Annual Meeting of the Vacuum Society of Japan 72, 2004. (in Japanese)

[13] Kinoshita, H., Yokota, K., Tagawa, M., and Ohmae, N., "The Degradation of Polyimide Films due to Hyperthermal Atomic Oxygen Exposures: In-situ Mass Loss Measurement and Effect of Air Exposure," Kleiman, J. and Werling, E. Eds, *Proceedings of 8th International Symposium on Materials in a Space Environment*, 581-588, 2000.

[14] Banks, B. A., Dever J. A., Gebauer, L., and Hill, C. M., "Atomic Oxygen Interactions with FEP Teflon and Silicones on LDEF," *LDEF-69 months in space*, NASA CP-3134, 801-815, 1991.

[15] Visentine, J. T., Leger, L. J., Kuminecz J. F., and Spiker, I. K., "STS-8 Atomic Oxygen Effects Experiment," AIAA Paper 85-0415, Jan. 1985.