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Formation of Microparticles from Silicone Contaminants under Simulated Space Environment

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Abstract

The mitigation of space debris is an important issue in current and future space exploration. It is much important to make clear the formation process of space debris as well as their origin for the mitigation, although it is not easy to make clear those of small sized space debris. In the present work, a formation mechanism of microparticle space debris has been proposed through experimental approaches with silicone contaminants outgassed from silicone adhesive deposited on polyimide film and irradiated by ultraviolet (UV) and atomic oxygen (AO). Observation by scanning electron microscopy showed that the silicone contaminants formed droplets with size around 20 μm on the surface of polyimide film. The droplets then solidified under the combined action of UV and AO irradiation, while polyimide film was eroded in the areas not covered by the droplets. Energy-dispersive X-ray spectroscopy showed that microparticles that formed under UV and AO irradiation mainly consisted of silicon and oxygen. The present findings could help to clarify the origin of microparticle space debris found in space.

Keyword(s): Microparticle, Space debris, Silicone contaminants, Atomic oxygen.
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1. Introduction

The impacts of space debris in various sizes on spacecraft are both apparent and substantial[1-3]. The evidence of a number of "microparticle space debris" smaller than 1 mm in diameter had been confirmed by analyzing the retrieved materials of solar panels of the Hubble Space Telescope[4], the Russian Space Station "Mir" [5], and others[6]. However, these microparticle space debris cannot be observed from the Earth, even though problems originating from such debris have been reported. The damages to spacecraft caused by such microparticle space debris were obviously serious; even microparticle space debris had reportedly degraded sensitive spacecraft surfaces and equipment, such as mirrors, optical sensors and thermal control surfaces. Moreover, such space debris from tens to hundreds of microns in size could penetrate outer spacecraft coatings and foils as well as solar cells, and every hypervelocity impact creates plasma that can result in electromagnetic interference[7]. Thus, it is important to perceive the correct abundance of space debris including microparticle space debris and the composition thereof, when designing protection for spacecraft.

The material exposure mission of the Micro-Particles Capturer (MPAC) units with the Space Environment Exposure Device (SEED) units was conducted to examine the abundance and composition of microparticle meteoroids and microparticle space debris[8]. Silica aerogel is one of the materials used in order to capture microparticle meteoroids and microparticle space debris, and analyze its composition, collision energy and direction of approach[8]. By examining the 144 pieces of retrieved silica aerogel, it was found that those pieces had captured micro-debris, secondary debris, a micrometeoroid, and a number of microparticles[9-11]. Although the characteristics of the microparticles space debris has been studied and made clear, their formation process is not clear even by chemical or physical approach. The diameter of the microparticles was ca. 10 μm. By analyzing the microparticles captured by the aerogel mounted on the MPAC units with X-ray microanalysis and Fourier transform infrared spectrophotometry, it was confirmed that all of the analyzed microparticles had Alkanes, CO, -OH, Si-CH_3, and Si-O-Si bonds, and that silicon dioxide (SiO_2) was the main component[10]. Most of space debris formations have been discussed from a step shown as follows:

1) Spacecraft after the end of their missions
2) Wreckage from explosions and collisions of spacecraft
3) Collisions of space dust with spacecraft
4) Collisions between space dust

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5) Parts disassociated from spacecraft

6) Paint fragments detached from spacecraft

On the other hand, the formation process of microparticles includes not only physical steps but also chemical ones, which is different from those proposed for general space debris formations. In the case of the microparticles captured by the aerogel mounted on the MPAC units, their formation process was explained to be much influenced by a chemical reaction between unburned propellant and aerogel by using the elimination method[10]. The aerogel mounted on the MPAC units can capture micrometer-sized meteoroids and space debris without destroying their shapes. If the microparticles would be from impacts of unburned propellant in the exhaust plume, the value of the aspect ratio (D/L defined as the absolute length or depth (L) relative to its diameter (D)) was less than 2[12]. The aspect ratios of those captured by the aerogel mounted on the MPAC units are obviously more than 2. Therefore, the different aspect ratio means that the microparticles are not formed from unburned propellant in the exhaust plume.

The deposition of silicone contaminants occurring in spacecraft on orbit is a well-known phenomenon; the fact that silica and/or methyl silicone have been detected on most of surfaces of the retrieved Long Duration Exposure Facility (LDEF) which is one of American space material exposure satellite was reported[13]. Similar phenomena were also reported in other literatures[14,15]. Silicone contaminants pose problems relative to operating spacecraft on orbit because silicone generates silicon oxide (SiOx), which cannot be easily removed, by reacting with AO[3], which is produced from molecular oxygen with UV irradiation and especially exists in Low Earth Orbit (LEO) under ca. 600 km high[16]. Silicon dioxide (SiO_2) was actually detected on the surface of the flexible optical solar reflector mounted on the SEED units[17]. Erosion of polymeric materials by AO has been reported[3]. In our previous work[18], the ultraviolet (UV) light and atomic oxygen (AO)-irradiated silicone contaminants were evaluated through optical property measurement[19].

Although the existence of many microparticles in space has become clear, a sufficient amount of microparticles could not be collected for component analysis and evaluation because their shapes were destroyed upon colliding with spacecraft[5]. There were many microparticles whose origin was not clarified in previous works, such as not being able to identify whether the origin of detected glass residues were interplanetary dust particles or space debris. Identifying the origin of microparticles makes it possible to prevent the provision of microparticles. The present work experimentally verifies the process whereby silicone contaminants (reportedly the substances that adhere to the surface of materials exposed to space) could be origin of such microparticles under the effects of space environment.

2. Experimental

In order to simulate conditions existing in space environment, materials widely used in spacecraft have been used. A room-temperature- vulcanizing silicone adhesive No. 691 (RTV-S691) from Wacker Asahikasei Silicone Co., Ltd. was selected as the silicone outgassing source and polyimide film from 125-μm thick UPILEX-S from UBE Industries, Ltd. was selected as the substrate material, which was deposited by silicone contaminants outgassed from RTV-S691. The former is actually designed for a wide range of adhering, sealing, and protection of spacecraft and the latter was actually applied as a base film for the flexible solar array of the Space Flyer Unit and certain satellites. The conditions of UV and AO irradiation were decided to clarify the morphological impacts of UV and/or AO irradiation to polyimide film with silicone contaminants, which were widely detected on the surface of materials exposed on orbit[13-15]. The brief experimental procedures are as follows: RTV-S691, whose size was 40 mm x 40 mm x 6 mm, was cured at room temperature. And, polyimide film samples, whose size was ϕ 25 mm and t 125 μm, were cleaned with ultrasonic cleaning using ethyl alcohol and acetone. Then, the RTV-S691 as the silicone outgassing source was heated at 125 ℃ in a chamber under 10^{-3} Pa, which proceeded its deposition on the surface of polyimide film samples at 25 ℃. The depositing area

Table 1 UV and AO irradiation conditions

Experiment No.	Irradiation in series				Irradiation angle
	UV-1st (J/cm^2)	UV-2nd (J/cm^2)	AO-1st ($atoms/cm^2$)	AO-2nd ($atoms/cm^2$)	
Expt.-No.1	9×10^4	6×10^4	none	none	90°
Expt.-No.2	none	none	1.5×10^{21}	1.0×10^{21}	90°
Expt.-No.3	9×10^4	6×10^4	1.5×10^{21}	1.0×10^{21}	Both UV and AO: 90°
Expt.-No.4	9×10^4	6×10^4	1.5×10^{21}	1.0×10^{21}	UV: 90°, AO: 90° for the AO-1st, 45° and 135° for AO-2nd

Table 2 UV irradiation conditions

Item	Parameter
Light source	Type UXL-2501YA 2.5 kW Xe short-arc lamp
Irradiation wavelength, nm	250 - 500
Irradiation intensity, UV-sun*	10
UV irradiation fluence, J/ cm^2·s	0.35
UV irradiation time, days	3.0 (UV-1st) and 2.0 (UV-2nd)

*1UV-sun = 11.8 mW/cm^2 (integration of spectral intensity of 200-400 nm in orbit)

Table 3 AO irradiation conditions

Item	Parameter
AO average flux, atoms/cm^2·s	5.5×10^{15}
AO beam velocity, km/s	ca. 8
AO average speed, km/s	8.11
AO Irradiation time, days	3.16 (AO-1st) and 2.1 (AO-2nd)

of silicone contaminants on the polyimide film samples was 314 mm^2. The deposited-side surface of the polyimide film samples was irradiated by UV and/or AO under the irradiation conditions listed in **Table 1**. **Tables 2** and **3** list the UV and AO irradiation conditions, respectively. UV irradiated to the samples by using a high-vacuum chamber equipped with a Xe lamp[20], and AO irradiated to the samples by using the Combined Space Effects Test Facility[21] at the Tsukuba Space Center. After the irradiation tests, the cross sections of polyimide film samples with silicone contaminants were observed by field emission scanning electron microscope (FE-SEM) in order to evaluate the morphological impacts of UV and/or AO irradiation and the different angles of AO irradiation to those films.

In order to confirm the elemental distribution of polyimide films with silicone contaminants and evaluate the composition of those contaminants, the cross section of the polyimide film sample tested with Expt.-No.4 (polyimide film with silicone contaminants irradiated UV (total of 1.5×10^5 J/cm^2) and AO (total of 2.5×10^{21} atoms/cm^2 (90 ° for 60 % irradiation, 45 ° for 20 % and 135 ° for 20 % ones)) was analyzed with energy dispersive X-ray spectroscopy (EDX).

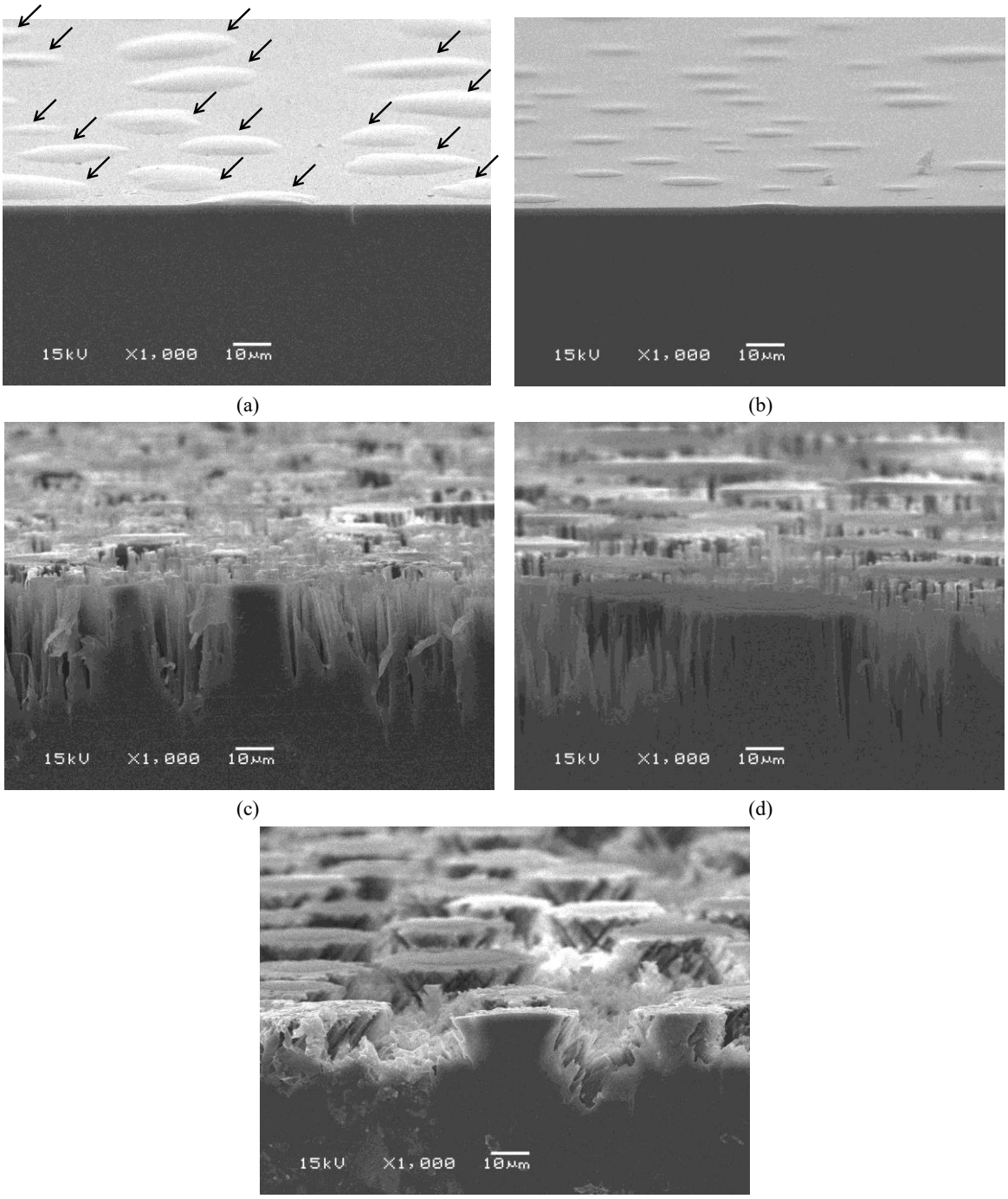
3. Results and discussion

Figure 1(a) shows SEM image of as-deposited silicone contaminants on polyimide film. As can be seen in **Fig. 1(a)** silicone contaminants formed droplets about 10-30 μm in size. **Figure 1(b)** shows the deposited silicone contaminants on polyimide film after UV irradiation. The surface of the polyimide film does not apparently change much under only UV irradiation, but changes can be observed in the sizes of silicone contaminations, which are smaller than those shown in **Fig. 1(a)**. The AO irradiation caused random etching of polyimide film, as is shown in **Fig. 1(c)**. **Figure 1(d)** shows combined effect of UV and AO. It can be seen from the Figure that there are areas of polyimide film which were etched and not by AO. Comparison with as-deposited silicone contaminant layer (**Fig. 1(a)**) makes clear that the areas of polyimide film covered with droplets of silicone contaminants were not etched, while the areas not covered by droplets were etched.

The present observation results reveal that UV affects the droplets of silicone contaminants in such a way, that the droplets become more stable to AO irradiation.

AO is known to react with spacecraft surface materials in two ways. First, AO can erode hydrocarbon materials. Secondly, silicone materials used for spacecraft are permanently fixed by oxidation with AO. The reaction between the silicone and AO generates silicon oxide (SiOx)[3]. It is conceivable that polyimide film deposited with silicone contaminants lacking a sufficient thickness to generate silicon oxide layers was eroded by AO in the present work. As a result, only the parts of polyimide film deposited with droplets of silicone contaminants were not eroded by AO as shown in **Fig. 1(c)** and **1(d)**.

The morphological changes were also verified under different angles of AO irradiation, because AO actually irradiates to spacecraft surface materials from not only one angle on orbit. The SEM images of the sample is shown in **Fig. 1(e)**. It can be seen that irradiation from various angles led to etching of polyimide film under the droplets. This means that after a certain time of irradiation to the droplets of silicone contaminants, the droplets could separate from the polyimide film and form microparticles. This is a direct verification of the morphological process of forming microparticles mainly consisting of silicone contaminants deposited on polyimide film as droplets (ca. 20 μm) shown in **Fig. 1(a)**. Under AO irradiation, the shape of droplets was changed to microparticles



(a) (b) (c) (d) (e)

Fig. 1 SEM images of cross sections of polyimide film samples tested under the irradiation conditions listed in **Table 1** afterdepositing silicone contaminants: (a) as deposited (droplets of silicone contaminants are shown with arrows), (b) Expt.-No.1, (c) Expt.-No.2, (d) Expt.-No.3 and (e) Expt.-No.4.

as observed in **Fig. 1(e)**.

In addition, many microparticles much smaller than the droplets mentioned above were found by detailed observation of the parts eroded by AO as shown in **Fig. 2**. The existence of these smaller microparticles suggests that there is another morphological process of forming smaller microparticles different from that of forming larger microparticles.

To confirm the elemental distributions of the polyimide film and silicone contaminants, the cross section of polyimide film sample tested with Expt.-No.4, irradiated by both UV and AO,

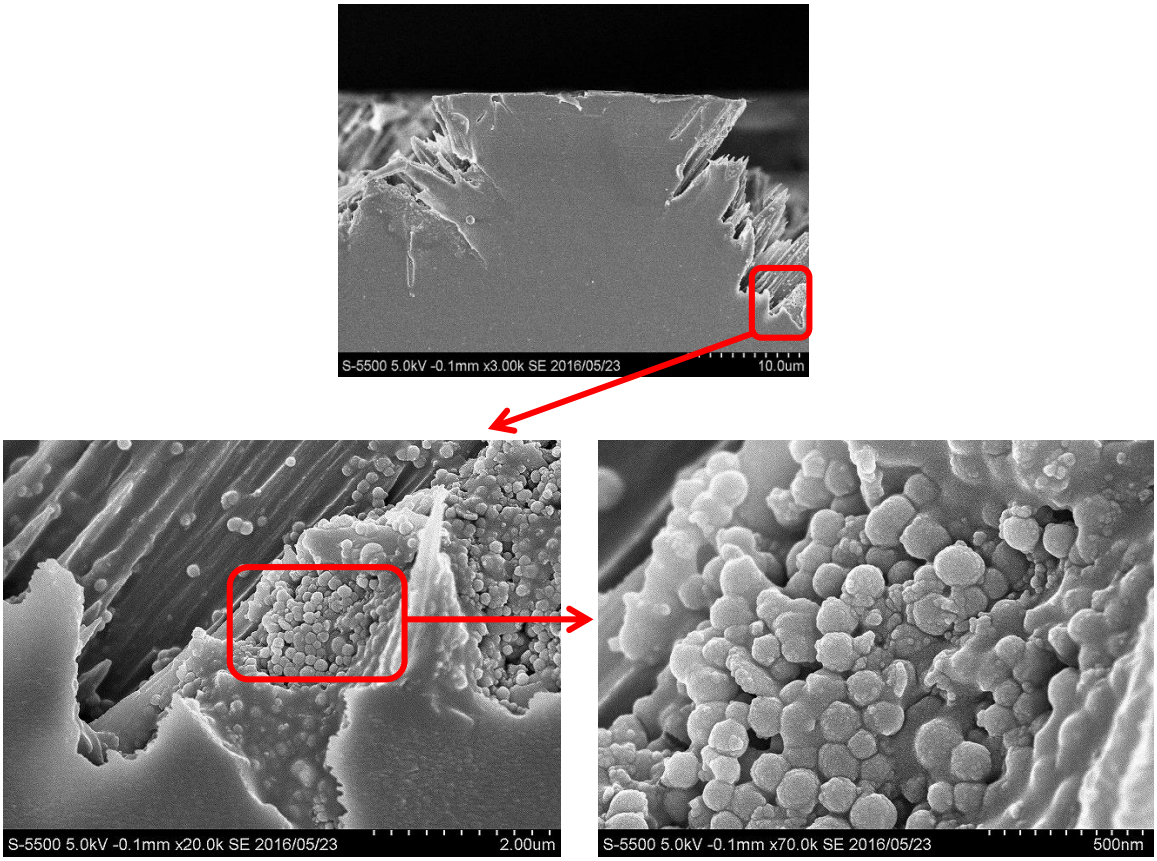


Fig. 2 SEM images of cross sections in three magnifications for the polyimide film with smaller microparticles shown in **Fig. 1(e)**.

was analyzed using energy dispersive X-ray spectroscopy (EDX). **Figure 3** shows the elemental distribution obtained by EDX.

Carbon (C), which is contained in the chemical structure of polyimide film, was confirmed as being evenly distributed throughout the sample. Oxygen (O) was particularly distributed in the parts eroded by AO, which suggests that AO caused oxidation at the parts. Silicon (Si) was particularly distributed on the surface of the sample and in the parts of the sample eroded by AO. This fact indicated two things: first, the parts of polyimide film deposited with droplets of silicone contaminants were not eroded by AO; and second, the eroded silicone contaminants, which are thought to form smaller microparticles, remained at the parts of the sample eroded by AO.

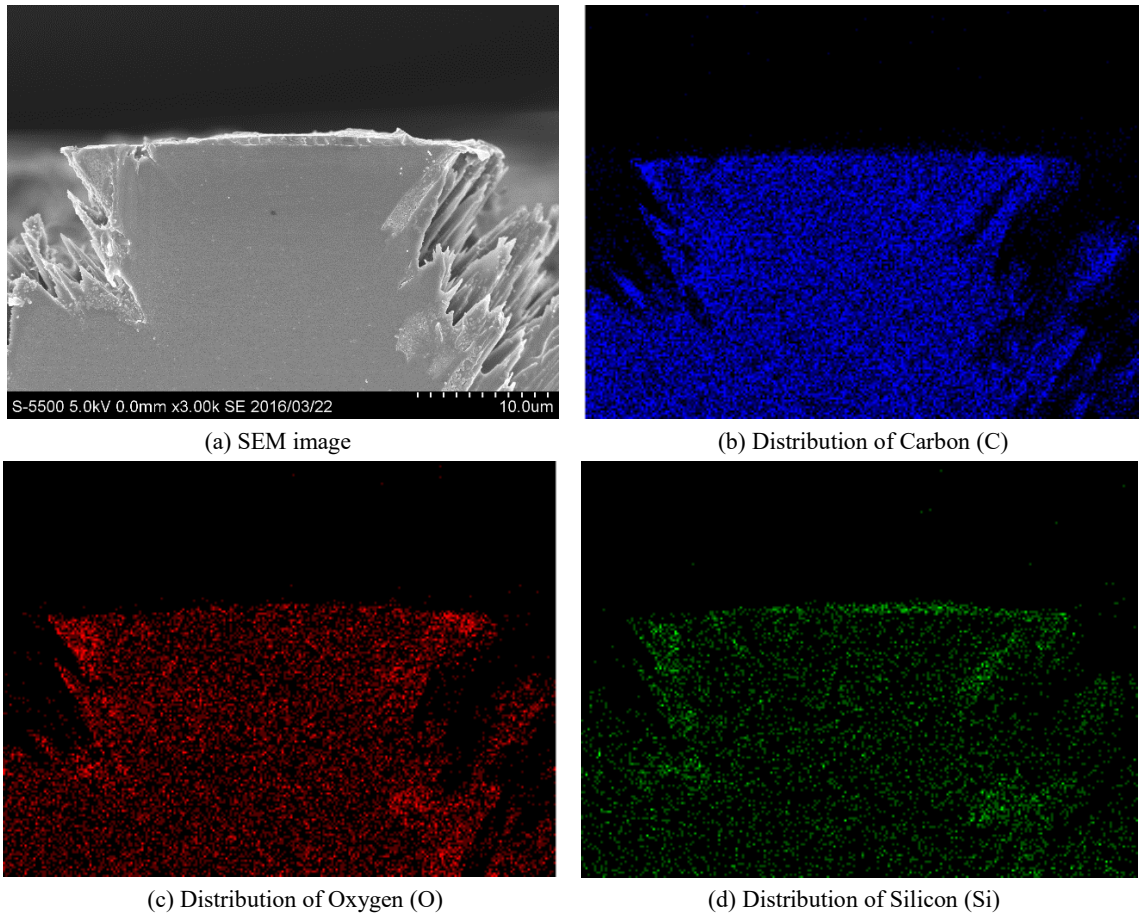
For evaluating the composition of silicone contaminants on the surface of the polyimide film sample tested with Expt.-No.4 (polyimide film irradiated by UV (total of 1.5×10^5 J/cm^2) and AO (total of 2.5×10^{21} atoms/cm^2 (90 ° for 60 % irradiation, 45 ° for 20 % and 135 ° for 20 % ones))) and the smaller microparticles on the parts of the polyimide film sample eroded by AO, the elements of the silicone contaminants and the smaller microparticles were analyzed with EDX. **Figure 4** shows the analysis point (the silicone contaminants on the polyimide film sample tested with Expt.-No.4) by SEM image and the analysis spectrum of that point. The analysis spectrum of the smaller microparticles (the part of the polyimide film sample eroded by AO) showed an analysis spectrum similar to that of the silicone contaminants. The result indicates the existence of a similar substance, which contains Si, O and C, in the silicone contaminants on the polyimide film sample tested with Expt.-No.4 and smaller microparticles.

As a result of EDX analysis in the present work, the microparticles shown above were confirmed as being the target microparticles. As shown in **Figs 3** and **4**, the microparticles that mainly consist of Si and O are formed on the surface of polymer materials deposited with silicone contaminants in the space environment (containing AO).

The results of the present work suggest that microparticles that mainly consist of Si and O are formed on the surface of polymer materials deposited with silicone contaminants in the

space environment (containing AO). In other words, the microparticles that mainly consist of Si and O could originate from the silicone contaminants stemming from silicone materials used on spacecraft. The conceivable details of the forming process of the microparticles from silicone contaminants are indicated in 1) to 4) below. **Figure 5** shows conceptual diagrams of the formation process of the microparticles.

1) Silicone contaminants are deposited on the surface of polymer film.



(a) SEM image (b) Distribution of Carbon (C)

(c) Distribution of Oxygen (O) (d) Distribution of Silicon (Si)

Fig. 3 Elemental distribution of the cross section of polyimide film sample tested with Expt.-No.4 by EDX.

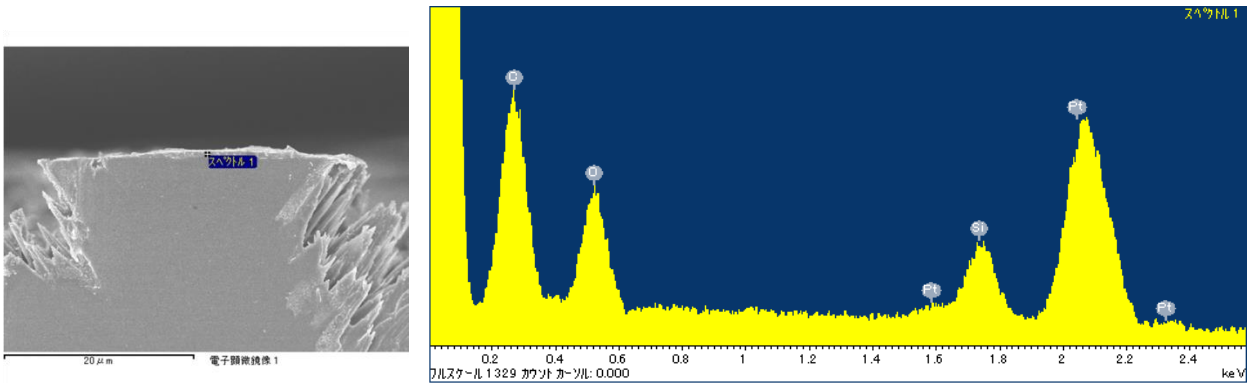


Fig. 4 Elemental analysis of the silicone contaminants on polyimide film sample tested with Expt.-No.4 (SEM image showing the analysis point).

2) Chemical bonds of silicone contaminants are changed by space environment (e.g. UV and AO).
3) Polymer film is eroded by AO except the parts of polymer films deposited with droplets of silicone contaminants.
4) Polymer film under the droplets of silicone contaminants is eroded by AO irradiation not from the right angle, and microparticles, which can be called microparticle space debris in the space environment, are formed. In addition, a part of silicone contaminants, which deposit on the polymer film not as droplets, leave form polymer film and the other stay on the parts of polymer film eroded by AO. The silicone contaminants become bigger as in a snowball effect by the energy of AO irradiation, and accordingly smaller microparticles are formed.

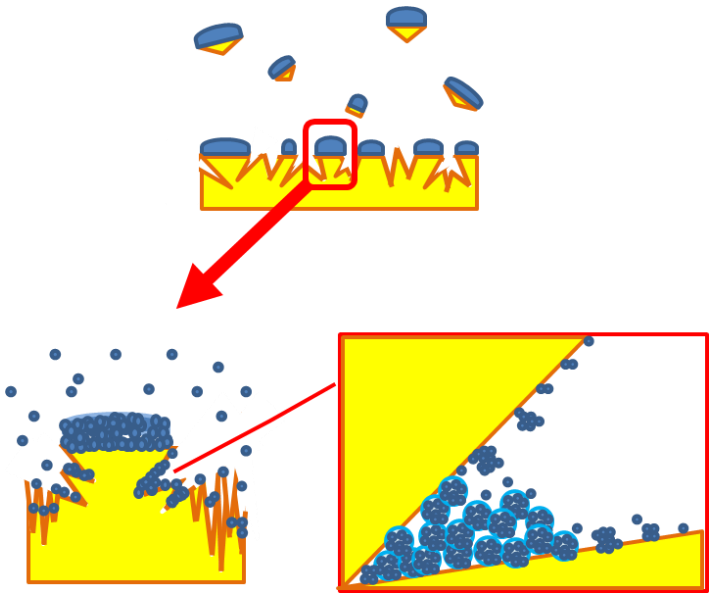
Silicone adhesives and sealants are designed for a wide range of bonding, sealing and protection of spacecraft, therefore the phenomenon of forming microparticles may occur on the surface of many polymer films that are eroded by AO[1,19] and the phenomenon of forming smaller microparticles may also occur on the surface of many types of space materials of spacecraft that are operated on orbit where AO and silicone contaminants exists.

The fact that microparticles could be formed by silicone contaminants with AO irradiation in the present work suggests that there is a high possibility that silicone contaminants are the origin of the microparticles captured by the aerogel mounted on the MPAC units, because there were AO and silicone contaminants on the ISS orbit[8] where the MPAC units had been exposed.

1) Deposition of silicone contaminants on the surface of polymer film.

2) Chemical bonds of silicone contaminants are changed by space environment.

3) Polymer film is eroded by AO.



4) Polymer film under droplets of silicone contaminants is eroded by AO irradiation, and microparticles are formed. In addition, a part of silicone contaminants, which deposit on the polymer film not as droplets, leave form polymer film and the other stay in the parts of polymer film eroded by AO. The silicone contaminants become smaller microparticles by AO irradiation.

Fig. 5 Conceptual diagrams of the formation process of microparticles.

4. Conclusions

The present work showed that microparticles consisting of Si and O can be formed from silicone contaminants outgassed from silicone adhesive and deposited on polyimide film under the effects of UV and AO irradiation. The formation process of microparticles includes the deposition of silicone contaminants as droplets on polyimide film, solidification of the droplets under UV and AO irradiation, and erosion of the areas of polyimide film not covered by the droplets with AO. It is considered that this process can take place not only in the simulated space environment but also on the surface of spacecraft in the LEO environment as well. Previously, the author had observed microparticles consisting mainly of SiO_2, which were captured by retrieved silica aerogel mounted on the MPAC units[10]. The results of the present work show the possibility that the origin of those SiO_2 microparticles could be in silicone contaminants, which transformed into microparticles through the new process proposed in this paper.

The new formation processes of microparticle space debris are thought to be phenomena that occur on the surface of many spacecraft that use silicone adhesives and which are operated under the existence of AO. New methods of protecting against the collision of microparticle space debris and reducing microparticle space debris will be developed by formulating the new formation processes of microparticle space debris as clarified in the present work.

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