Surface Oxidation of the Silicon Carbide Ceramics during Space Environment Exposure up to 3.8 Year

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Abstract

Surface oxidation of the hot-pressed and reaction-sintered silicon carbide ceramics specimens after 0.86 year, 2.4 year and 3.8 year space exposure was evaluated using mainly secondary ion mass spectrometry and X-ray photoelectron spectroscopy. The oxygen content of both space-exposed silicon carbide specimen’s surface where was not covered by a fixture jig increased markedly compared with those of blank, AO-irradiated specimens’ surface and the covered part of the space-exposed specimens’ surface. Oxidized layer thickness of the space-exposed specimens after 0.86 year, 2.4 year and 3.8 year exposure was about 10 nm, 50 nm and 90 nm, respectively. The surface oxidized layer was consisted of mostly pure SiO\textsubscript{2} and a thin intermediate layer or a mixed layer was existed. Surface roughness of both the space-exposed specimens after 3.8 year and the AO-irradiated specimens after irradiation of corresponding three years on the orbital increased compared with the blank specimens, 2.4 year space-exposed and one year AO-irradiated specimens. The oxidation may caused mainly by the collision of atomic oxygen but other effects should be considered.

1. Introduction

In the field of space exploration, ceramic materials are necessary for heat shields and electric insulators of space shuttles and satellites. At the low earth orbit (LEO, altitude \~1000 km), neutral gas, various kinds of radiations such as high energy particles (solar flare proton), ultraviolet-ray, and electron beam are existed. The LEO satellites are normally designed with a service life of generally five years, although this mainly depends on the flight altitude. Therefore, investigation of changes in properties of materials due to long exposure in space is very important to proceed the challenges in space, but these researches were limited up to date. Property change in organic material was mainly noted\textsuperscript{1-3), but investigation of ceramic was scarcely reported. Whereas a few investigations have already been carried out by the European Space Agency (ESA) and National Aeronautics and Space Administration (NASA, USA)\textsuperscript{4-5), more experiments have to be carried out for more reliable data to clarify the effects of the space exposure on material properties. Organic materials are used for components of the external walls of space vehicles, e.g. coatings (silicone etc.) and debris bumpers (Kevlar fiber), and ceramic materials are mainly used for inside the space vehicles, except for the solar battery panel. Whereas recently, silicon carbide was selected as a main mirror of infrared-ray astronomical satellite “ASTRO-F”, due to superior characteristics of silicon carbide such as high specific strength, high Young Modulus, low thermal expansion coefficient and excellent chemical stability.

In 2001, space exposure tests of two kinds of silicon carbides ceramics fabricated by hot-pressing and reaction-sintering method have started at the SM/SEED (Service Module / Space Environment Exposure Device) of Russian service module of the ISS (International Space Station) with the exposure plan up to 3.8 year. The first to third sets of specimens were retrieved after 0.86 year, 2.4 year and 3.8 year exposure was about 10 nm, 50 nm and 90 nm, respectively. The surface oxidized layer was consisted of mostly pure SiO\textsubscript{2} and a thin intermediate layer or a mixed layer was existed. Surface roughness of both the space-exposed specimens after 3.8 year and the AO-irradiated specimens after irradiation of corresponding three years on the orbital increased compared with the blank specimens, 2.4 year space-exposed and one year AO-irradiated specimens. The oxidation may caused mainly by the collision of atomic oxygen but other effects should be considered.

2. Experimental Procedures

In the SM/SEED exposure program, five kinds of ceramic specimens have been simultaneously tested: hot-pressed silicon carbide (HP-SiC, Hitachi Ltd. SC-101), reaction-sintered silicon carbide (RS-SiC, Toshiba Ceramics Co. Ltd. TPSS), aluminum nitride and ion-plated titanium nitride on aluminum or alumina...
plate. The HP-SiC was made from solid-state sintering mechanism, and consisted from shows extra high thermal conductivity and high electric resistivity within several kinds of SiC, and consisted from mostly silicon carbide single phase except for about 1.0 wt% BeO particles distributed along the grain boundary. The RS-SiC was made from reaction-sintering mechanism via the reaction of liquid Si and carbon distributed in a SiC powder compact. Therefore, the RS-SiC contained large amount of metallic silicon (~17 wt%) and show high electric conductivity. In this experiment, these two different kinds of silicon carbide ceramics were examined.

The size of these specimens was 17 mm square and 2 mm in thickness, and the surface of each specimen was polished. These specimens (two plates each) were fixed on the sample tray which was fixed onto the external wall of the Russian SM of the ISS. An average flight altitude of the ISS was 371 km and the orbital inclination was 51.6 degree. The exposure periods were 315 day (0.86 year, first set), 865 day (2.4 year, second set) and 1386 day (3.8 year, third set), respectively. Specimen surface was faced normal to the moving direction 54 ~59%, depending on the flight position of the ISS. The specimens exposed for 0.86 year in space were labeled as ISS-1 and these exposed 2.4 year and 3.8 year were labeled as ISS-2 and ISS-3, respectively.

Table 1 Irradiation fluences of ground experiments. AO-irradiated (AO-0.5, AO-1 and AO-3), UV-irradiated (UV-0.5, UV-1 and UV-3) and EB-irradiated (EB-0.5, EB-1 and EB-3) specimens.

<table>
<thead>
<tr>
<th></th>
<th>AO-0.5</th>
<th>AO-1</th>
<th>AO-3</th>
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<tbody>
<tr>
<td></td>
<td>1.38 E21 atoms/cm²</td>
<td>3.70 E21 atoms/cm²</td>
<td>6.39 E21 atoms/cm²</td>
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<tr>
<td></td>
<td>UV-0.5</td>
<td>UV-1</td>
<td>UV-3</td>
</tr>
<tr>
<td></td>
<td>3.47 E4 J/cm²</td>
<td>7.04 E4 J/cm²</td>
<td>2.12 E5 J/cm²</td>
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<tr>
<td></td>
<td>EB-0.5</td>
<td>EB-1</td>
<td>EB-3</td>
</tr>
<tr>
<td></td>
<td>1.64 E12 electrons/cm²</td>
<td>3.86 E12 electrons/cm²</td>
<td>9.89 E12 electrons/cm²</td>
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</table>

About the AO-irradiated specimens, those irradiated by AO up to a fluence corresponding to 0.5 year, 1.0 year and 3.0 year on the orbital were indicated as AO-0.5, AO-1 and AO-3, respectively. Similarly, the specimens irradiated by UV-rays up to a fluence corresponding to 0.5 year, 1.0 year and 3.0 year on the orbital were indicated as UV-0.5, UV-1 and UV-3, respectively. The EB-irradiated specimen was similarly labeled as EB-0.5 which was EB-irradiated up to a fluence corresponding to 0.5 year on the orbital, EB-1 and EB-3 corresponding to 1.0 and 3.0 year on the orbital, respectively.

These specimens were characterized with the following equipments; a surface roughness tester (Dektak3030, ULVAC Ins. Japan), a thermo-optical measuring unit (DB-100, Gier Dünkell, Germany), a wavelength-dispersive type X-ray spectrometer (WDX, Microspec WDX400, Oxford Instr. USA) using 25 kV incident electron beam for micro elemental analysis, and a X-ray photoelectron spectroscopy (XPS, PHI 5600, ULVAC-PHI INC. Japan) using 14 kV incident X-ray and 3 kV Ar beam for sputtering during depth analysis. A secondary ion mass spectrometer (SIMS) for depth analysis was conducted on the IMF-4F, Cameca Instr. France using 10 kV accelerated Cs primary ion beam and 4.5 kV secondary ion accelerating voltage. Actual depth of SIMS analysis was obtained from the surface profile measurement after SIMS observation. The roughness average of each specimen surface was measured along 10 mm in length and ten different positions near the center of each specimen. An averaged value for ten measurements was obtained as a roughness average. WDX measurement was performed for five positions (12.8 μm × 9.6 μm square) of each specimen and an averaged value was obtained. For space exposed specimen, five positions at the center exposure part and five surrounding positions covered by a fixture jig were observed.

3. Results and Discussion

Fig. 1(a) and 1(b) show the oxygen concentration of the specimen surface of the HP-SiC and RS-SiC specimen detected by WDX. The oxygen content of the RS-SiC surface of the space-exposed specimens (detection range ~1 μm in depth), where was not covered by the fixture jig, increased with increasing exposure period, and obviously higher than those of the blank specimens. The surface oxygen content of the specimens irradiated by AO was also increased, but less than the case of space-exposed one, and not significantly influenced by the AO fluence. It is thought that AO is a principal factor of the oxidation of the specimen. On the contrary, oxygen content of surface where was covered by the fixture jig was comparable or slightly higher values from those of the blank specimens, and far lower values compared with the exposed parts of the space-exposed specimens. Measurement errors of each specimen were small as indicated in the figure, thus the
Fig. 1  Oxygen content of specimens measured by EDX. (a) HP-SiC: hot-pressed SiC and (b) RS-SiC: reaction-sintered SiC. (AO: atomic oxygen irradiated, ISS: space-exposed)

Fig. 2  Depth profile of oxygen of (a) HP-SiC and (b) RS-SiC specimens measured by SIMS. HP-SiC: Hot-pressed SiC and RS-SiC: Reaction-sintered SiC

difference in each specimen was clear. Therefore, direct bombardment of AO with energy of 5 eV (8 km/s) is seemed to be essential for the surface oxidation of SiC. Carbon should become volatile components and be lost from the specimen surface. The oxygen contents of HP-SiC were slightly higher than those of RS-SiC in each condition. This difference can be attributed to the larger original oxygen content in HP-SiC due to the presence of BeO sintering additive.

Fig. 2(a) and 2(b) show the depth profiles of the O/Si ratio observed by SIMS for the HP-SiC and RS-SiC specimens. The oxygen ion detection ratio was calculated as follows; (1) $^{28}$Si silicon intensity was recorded at start and finish of the measurement. (2) These silicon intensities were averaged. (3) $^{16}$O oxygen intensities were divided by the averaged silicon intensity, giving the O/Si ratio. Compared with the O/Si ratio along depth change of the 0.86 year space-exposed
AO-irradiation does not proceed oxidation for deeper part. Only after AO-1 and AO-3 irradiations, oxygen concentration tailed off ~50 nm in depth, as same as the case of ISS-1. Again, the difference between AO-irradiation and the space-exposure is obvious.

Fig. 3a) ~3c) show the binding energy changes along depth direction of the HP-SiC specimen space-exposed for 2.4 year (ISS-2) measured by X-ray photoelectron-spectroscopy (XPS). The C-1s electron binding energy was not largely changed from surface to inside specimen up to ~150 nm, and mostly corresponding to the carbide origin (SiC). The intensity of C-1s was very low up to ~75 nm, i.e., the SiC was not exist. From middle region (about 75 nm~) the C-1s was detected at high intensity, indicating SiC (Fig. 3a)).

The binding energy of O-1s electron (Fig. 3b)) of near surface region through middle region (about ~65 nm) were detected as a energy corresponding that of silicon dioxide (silica) with very high and mostly constant intensity. The binding energy of O-1s at deeper region (about 75 nm~) were close to that of carbides but intensity was very low. Furthermore, the binding energy of Si-2p changed from ~104 eV to 100.5 eV (Fig. 3c) at around 70 nm, former corresponding to the silica origin energy and latter corresponding to the carbide (SiC) origin. Up to ~70 nm from the surface, only Si and O were detected, therefore surface layer should be mostly pure SiO2. The change is Si-2p and O-1s energies close to the interface is relatively gradual, so that a thin intermediate layer or a mixed layer of oxide (SiO2) and carbide (SiC) should be existed.

Fig. 4 shows the solar absorptance change of the HP-SiC and RS-SiC specimens. Solar absorptance of the 0.86 year space-exposed (ISS-1) HP-SiC and RS-SiC specimens increased and was almost the same as those of the AO-irradiated specimens. Solar absorptance of the 2.4 year space-exposed (ISS-2) specimens and 3.8 year space-exposed (ISS-3) specimens increased markedly compared to those of 0.86 year exposed specimens in both SiC specimens. In addition, solar absorptance of the SiC obviously increased by the AO-irradiation after corresponding 0.5 year exposure, but not significantly changed for further AO-irradiation. According to the reports, thin silica layer has higher solar absorptance (0.90)\(^{13}\) than that of the present SiC specimens (0.68 ~0.70)\(^{14}\). This suggested the formation of silica layer on SiC during the present space exposure. It is also suggested that the AO-irradiation was one possible factor for increase in solar absorptance of the space-exposed specimens, but the increase in long time space exposure cannot be explained by the AO-irradiation. UV and EB irradiations did not significantly modify the solar absorptance of the specimens.

Change in roughness average of the specimen surface after the space exposure up to 3.8 year and the AO irradiation is shown in Fig. 5. Irradiation of AO increased surface roughness average with increasing...
Solar absorptance change ($\alpha_S$) of space-exposed (ISS-1, ISS-2 and ISS-3), AO-irradiated (AO-0.5, AO-1 and AO-3), UV-irradiated (UV-0.5, UV-1 and UV-3) and EB-irradiated (EB-0.5 and EB-1) specimens. HP-SiC: Hot-pressed SiC and RS-SiC: Reaction-sintered SiC

Fig. 4

Roughness average of specimens. HP-SiC: Hot-pressed SiC and RS-SiC: Reaction-sintered SiC

fluence, but no correlation was found between the effect of AO irradiation and that of the exposure in space. In the case of the space exposure, slight increase in roughness average was observed after 0.86 year exposure, but it decreased less than the blank specimen after 2.4 year exposure, and again increased after 3.8 year exposure. These roughness changes were supported from the microstructure observation. Surface of SiC grains obviously smoothen after 2.4 year space-exposure (ISS-2). The reason of increase in roughness after 3.8 year exposure is not clear at present. Surface roughness average of the RS-SiC specimens was generally larger than that of the HP-SiC specimens, due to the original larger roughness average which was artificially introduced by the polishing process.

4. Conclusions

Surface characteristics change of two types of SiC ceramics due to the space exposure up to 3.8 year was evaluated. The results were summarized as follows. (1) Surface of the SiC ceramics were oxidized continuously by the space exposure up to 3.8 year. (2) Degree of oxidation was quite different between the exposed part and the covered part of the same space-exposed specimens. (3) Chemical formula of surface oxidized layer is SiO$_2$ and thin intermediate layer or mixed layer with SiC is existed. (4) Oxidation should be caused by the collision of atomic oxygen, but another effect should be considered for accelerated oxidation in the present space exposure condition.

References

14) JAXA material database; http://matdb1n.tksc.jaxa.jp/main_e.html