SM/SEED Experiments of Carbide and Nitride Ceramics for Three Years

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Space exposure tests of five ceramic samples have been carried out from October 15, 2001 to August 19, 2005 at the Service Module of the International Space Station; aluminum nitride, two kinds of silicon carbides fabricated by hot-pressing and reaction-sintering, and ion-plated titanium nitrides on aluminum and alumina plates. The samples were fixed on three sets of sample trays, which were set on to the external wall of the Service Module, which were retrieved after 315 days, 865 days and 1403 days, respectively. In the present experiments, the tested samples in the three series were examined to evaluate property changes due to atomic oxygen, cosmic-ray radiation, solar light exposure, thermal cycle, etc. As a result, the oxygen content of the surface of space-exposed samples was confirmed to be increased markedly compared with those of non-tested and atomic oxygen-irradiated ones, and the oxidized layers of the samples exposed in space were thicker than those irradiated by atomic oxygen.

Keywords: Exposure Test, Atomic Oxygen, Non-Oxide Ceramics, LEO, Surface

1. Introduction

Ceramic materials have advantages in their properties such as high specific strength, tolerance in high temperature, high hardness, low friction, etc. Such ceramic materials are useful for heat shield and/or insulator materials in fields of space explorations, where there exist many environmental factors, such as particles, radiations, gravity, pressure, temperature, etc. The factors are sometimes harmful to spacecrafts or materials consisting of a spacecraft. Large particles of centimeter order are catastrophic for spacecraft and small ones, which exists some kinds such as gas molecule, atom, heavy ion particle, etc, make small but cumulative damages. Radiations affect on electronic device and life. Low pressure causes out-gassing from materials. On orbit, temperature of a spacecraft changes in the range between 100 K and 400 K, resulting in thermal fatigue. It is also necessary to verify that the materials have enough tolerance for these factors and have enough life in space environments.

The research regarding the characteristic change of ceramics due to long period of exposure in space environment has been limited, although several space environment exposure missions haven performed in the past by NASA and JAXA. In the present work, five kinds of tests have been carried out with three ceramic materials: aluminum nitride (AlN), hot-pressed silicon carbide (SiC), reaction-sintered silicon carbide (SiC), titanium nitride (TiN) ion-plated on alumina plate, and titanium nitride (TiN) ion-plated on aluminum plate. The ceramic materials exposed in a space environment for three years on the surface of the International Space Station (ISS) have been evaluated through an SM/SEED (Service Module / Space Environment Exposure Device) mission. In the SM/SEED mission, it is unique that three exposed samples with three different durations of exposure have been obtained. Five tests with three ceramic materials have been proposed in the present experiments, and reference experiments on ground have also been carried out through the SM/SEED missions. By analyzing each tested sample, the influence of exposure duration has been investigated with respect to the material resistance against the environment in durations. Such an environmental effect would be classified in two categories: dynamic effect and static effect. The dynamic effect occurs with high force in short time and the static one with low force in long time.

The main focus of the present SM/SEED mission is measuring the degradation of materials exposed to the environment. Since the orbit of ISS is LEO (Low Earth Orbit), the amount of atomic oxygen is much higher compared to that in higher orbit. Atomic oxygen (AO) generates through the dissociation of molecular oxygen under UV-ray. With the data of AO flux with altitude, the AO flux can be estimated to be 10^{13} atoms/cm^2-sec at the ISS altitude of about 400km, where the spacecraft goes round with the period of 90 minutes (8 km/s). This corresponds to a mean AO energy of about 5 eV. When the collision occurs between the surface of material and AO, the material would be damaged through its oxidation or erosion. The energy of sunlight at the ISS orbit is about 1.4 kW/m^2, which includes strong UV-ray under low pressure of 10^{-5}Pa resulting in some serious degradation of material surface characteristics.

2. Experimental Procedure

2.1 Samples

All samples have been sized in the same dimension of 17mm x 17mm x 2mm as shown in Fig. 1. AlN is characterized with its high heat conduction, electrical insulation and translucency, which give the high potential to AlN as integrated circuit substrate, heater base, heating sink and light-emitting devise-package material. Grain sizes of the hot-pressed SiC are uniform, and those of the reaction-sintered SiC are not uniform. There exist some impurities in grain boundaries of the hot-pressed SiC because the hot-pressing process needs additives. SiC has been applied to bearing balls, refractory materials, mechanical seals and turbine blades. Recently, its potential as power devices has been highly assessed and actively investigated world-widely. TiN is characterized with its hardness and low friction. The samples in the present work are ion-plated on Al and Al_2O_3 plates. With its superior thermal properties, the surface treatment of cutting tool is a popular application.

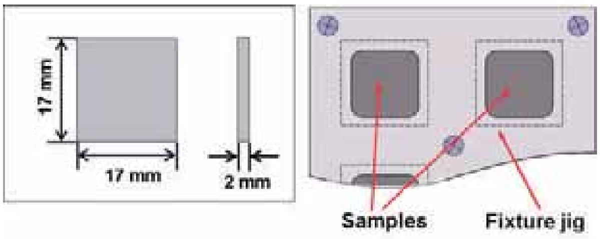

Fig. 1 Sample arrangement in the SM/SEED tests.

2.2 Experimental procedure

Samples are installed on sample trays which are inserted into the SM/SEED frame. Three SM/SEEDs were launched together by a Russian Progress Supply Ship from Kazakhstan in August, 2001. After the arrival at ISS, the SM/SEEDs were installed outside Service Module "Zvezda" on 15th of October in 2001 by an EVA (Extravehicular Activity) of an astronaut aboard on ISS, and the exposure tests have started in space environment. On 26th of August in 2002, astronauts on ISS collected only one set of sample trays by EVA from the SM/SEEDs, which means the first exposure duration 315 days. The collected sample trays returned to the earth by a Soyuz. The second sample trays were also collected on 27th of February in 2004(865 day exposure), and the third ones were collected on 19th of August in 2005(1403 day exposure).

Ground experiments were also conducted for comparing with the data of the space-exposed ones. Each kind of samples was irradiated by AO, UV ray and electron beam (EB) separately at room temperature under vacuum on the ground. Actual fluxes were roughly corresponding to half, one and three year exposures on the orbital as follows; AO: 1.38×10^{21}, 3.70×10^{21} and 6.39×10^{21} atoms/cm^2, UV ray: 401.2, 814.2 and 2448.5 mW/cm^2 and EB: 1.64×10^{12}, 3.86×10^{12} and 9.89×10^{12} electrons/cm^2, respectively. The AO irradiation was conducted using the FAST^{TM} atomic oxygen irradiation apparatus (Physical Sciences Inc. USA) under vacuum of the order of 10^{-2} Pa. Energy of AO was 5 eV, corresponding to the speed of 8 km/s, and an average flux of 1.17×10^{15} atoms/$cm^2 \cdot s$ at room temperature. The EB irradiation was conducted using an electron beam irradiation apparatus (Nisshin high-voltage Corp. Japan). The accelerating voltage of electron was 200 kV and the sample was irradiated at RT under $<10^{-8}$ Pa. The UV irradiation was conducted using the ultraviolet-ray irradiation apparatus (Yamashita Electronic Inc.). Light source was 6 kW xenon lamps under vacuum of $<10^{-8}$ Pa at lower temperature than 80°C.

The samples exposed for 315 days in space were labeled as ISS-1, for 865 days as ISS-2 and for 1403 days as ISS-3. About the AO-irradiated samples, those irradiated by AO up to the fluence corresponding to 0.5 year, 1.0 year and 3 years on the orbital were indicated as AO-0.5, AO-1 and AO-3, respectively.

The tested samples were characterized with an electric micro-balance for mass change, a thermo-optical measuring unit for solar absorptance and IR emissivity, and a surface roughness. With a field-emission type scanning electron microscope (FE-SEM) and a wavelength-dispersive-type X-ray spectrometer (WDX) and a secondary ion mass spectrometer (SIMS) on exposed surfaces, the changes of composition are measured. The roughness average of each sample surface was measured along 10 mm in length and ten different positions near the center of each sample. An averaged value for ten measurements was obtained as a roughness average. The WDX measurement was performed for five positions (12.8 mm x 9.6 mm) of each sample and an averaged value was obtained.

3. Results and Discussion

3.1 Surface roughness

Change in roughness average of the SiC sample surfaces after the space exposure and the AO irradiation is shown in Fig. 2. Irradiation of AO increased surface roughness average with increasing the AO irradiation, although no correlation was found between the effect of AO irradiation and that of the space exposure. 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 sample after 2.4 year exposure, and again increased after 3.8 year exposure. Surface roughness average of the RS-SiC samples was generally larger than that of the HP-SiC samples.

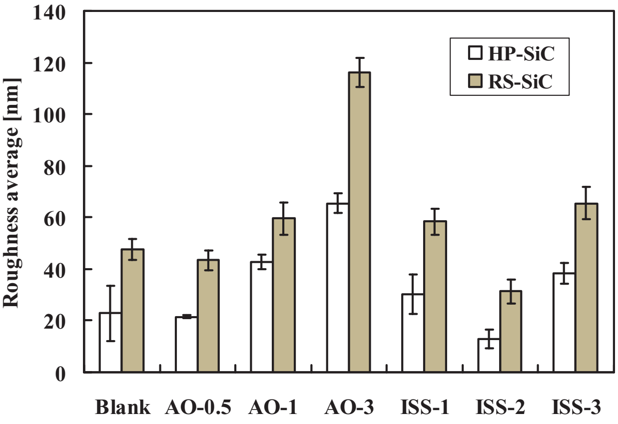

Fig. 2 Roughness of HP-SiC and RS-SiC samples.

3.2 Surface morphology

According to the SEM observation of the HP-SiC and the RS-SiC samples, the polishing damage which existed on the SiC surface before the space exposure gradually diminished with increasing space exposure duration. As shown in Fig. 3, the tiny particles which were thought to be SiC particles were observed for RS-SiC ceramics at the grain boundary silicon phase of the space-exposed samples. But it was rarely or never observed at the grain boundary of the sample irradiated by AO on the ground. In the cases of TiN/Al and TiN/Al_2O_3 tests, the morphologies exposed in space were much different from those irradiated by AO as shown in Fig. 4.

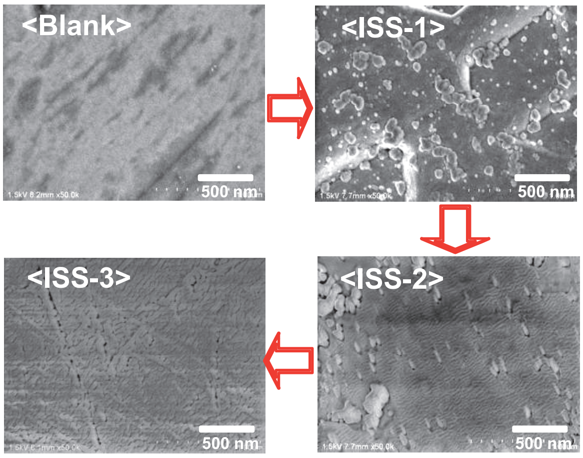

Fig. 3 Surface morphorogy changes of the RS-SiC samples during the exposured periods.

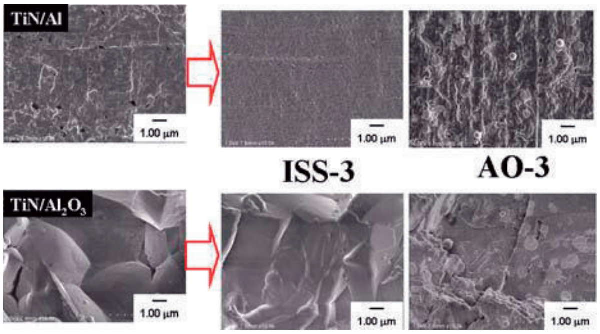

Fig. 4 Surface morphorogy changes of the TiN/Al and TiN/Al$_2$O$_3$ samples.

3.3 Surface composition

Figs. 5(a) and 4(b) show the oxygen concentration of the sample surface of the HP-SiC and RS-SiC sample detected by WDX. The oxygen content of surface of the space-exposed samples (detection range ~1 mm in depth), where was not covered by a fixture jig, increased markedly compared with those of the blank samples. The surface oxygen content of the samples irradiated by AO was also increased. Therefore, it is thought that AO is a principal factor of the oxidation of the sample. 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 samples, and far lower values compared with the un-covered parts of the space-exposed samples. Therefore, direct bombardment of AO with 5 eV energy (8 km/s) is seemed to be essential for the surface oxidation of SiC. Carbon should become volatile components and be lost from the sample surface.

Figs. 6(a) and 5(b) show the depth profiles of the O/Si ratio observed by SIMS for the HP-SiC and RS-SiC samples. The 15 keV O$_2^+$ or 10 keV Cs$^+$ was used as a primary ion, and the beam current was about 10 nA or 100 nA, respectively. Its scanned area was 250 mm square. The measuring depth was more than 1.5 mm. Energy distributions of molecular ions were measured with secondary ion energy windows of 10 eV. The most candidate species for the present measurements are neutral atomic and molecular ions, so the secondary ions measured are both in positive and negative treatments.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 sample (ISS-1) and 1.0 year AO-irradiated sample (AO-1), the O/Si ratio profiles are mostly resemble each other, and the thickness of the oxygen-rich layer was less than 15 nm in both the HP-SiC and RS-SiC samples. In past years, two chemical vapor deposited SiC mirrors were exposed to the 5eV fast atomic oxygen environment in low Earth orbit on NASA’s Long Duration Exposure Facility(LDEF) which remained in space for nearly 6 years. The XPS results showed the presence of SiO$_2$-like species on surface with the thickness varing from 1 to 8 nm depending the location of the samples on the spacecraft.

It is obvious that the O/Si ratio of the space-exposed sample for 2.4 year (ISS-2) kept high values until depth of about 50 nm, which was deeper than that of the ISS-1 samples. The O/Si ratio of the ISS-1 sample until ~15 nm was higher than that of the blank sample. The high oxygen concentration layer in the 3.8 year exposure (ISS-3), HP-SiC sample was thicker than that of the sample after 2.4 year exposure (ISS-2).

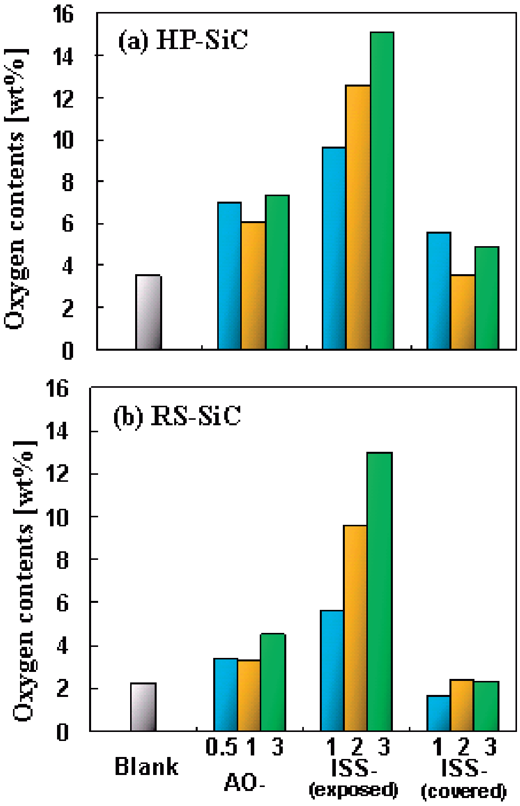

Fig. 5 Changes of oxygen contents in the HP-SiC and RS-SiC tested samples.

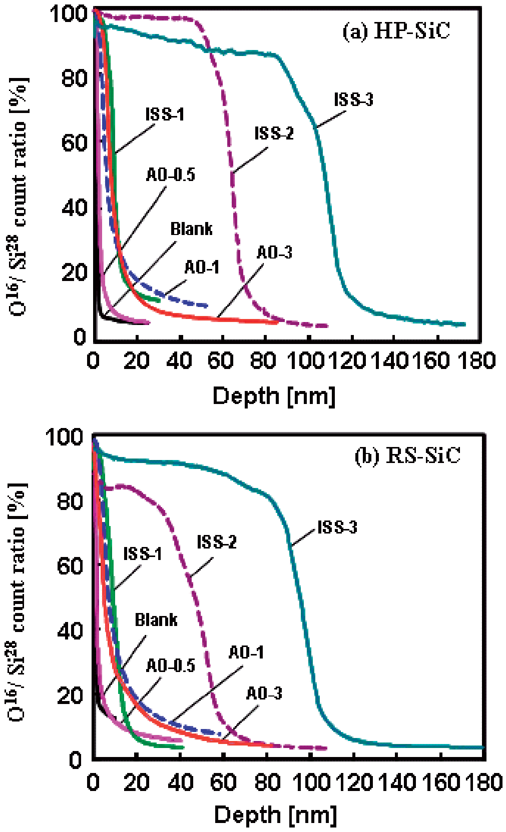

Fig. 6 **Oxygen depth profiles from the surfaces of the HP-SiC and RS-SiC tested samples.**

4. Conclusion

As space utilization becomes broader, space activities not only on science and technology but also on culture and social applications have been designed. Therefore, greater technological development can make more reliable set-up for space infrastructures, which grow ideas of applications much more. A key technology would be in material development. Ceramic materials have advantages such as high specific strength, tolerance in high temperature, high hardness, low friction, etc. These properties must be useful to apply for spacecraft or payload.

Surface characteristics change of two types of SiC ceramics due to the space exposure up to three years was evaluated. The results were summarized as follows. (1) Surface of the SiC ceramics were oxidized continuously by the space exposure up to three years. (2) Degree of oxidation was quite different between the exposed part and the covered part of the same space-exposed samples. (3) 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.

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