Degradation of Materials by High-Energy Atomic Oxygen*

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The degradation of materials exposed in LEO (low earth orbit) is one of the most important problems in space technology because the predominant component of the atmosphere in LEO is AO (atomic oxygen) which degrades some kinds of materials. This paper presents an experimental simulation on the ground for the degradation of carbon-based materials. In the experiment, AO produced at a plasma torch is accelerated fluid-dynamically with working gas. Graphite, C/C (carbon/carbon) composite and Si-C.C. (silicon impregnated C/C composite) were used as the target materials. The mass loss per unit area depends strongly on the temperature of the material surface. The eroded surfaces of materials were observed with SEM (scanning electron microscope) and laser focus displacement meter. In case of C/C composite, the matrix region erodes more than carbon fiber. The mass loss of Si-C.C. is less than that of corresponding C/C composite and only the C/C region erodes deeply with almost no erosion in Si and SiC regions. In order to investigate the degradation caused by the impact of AO, numerical simulation was also conducted for graphite using MD (molecular dynamics) method.

Key Words: Atomic Oxygen, Oxidation, Degradation, Graphite, Carbon, C/C Composite, Low Earth Orbit, Molecular Dynamics

1. Introduction

Space structures in LEO (low earth orbit) are traveling with the orbital velocity of approximately 7.8 km/s and affected by the bombardment of AO (atomic oxygen) which is the predominant component of the atmosphere in LEO. Furthermore, not only in LEO but also on the re-entry into the atmosphere of the earth, spacecraft structures are degraded by AO dissociated due to shockwave. In recent years, the necessity of extending the life of space structures has been enhanced by the increase of the utilization of the space environment. In long term missions in LEO, the degradation of the strength of the carbon-based materials due to the mass loss by the bombardment of

AO is one of the most serious problems. Regarding the problem, lots of experiments in space or the simulations on the ground have been conducted until now⁽¹⁾. However, the number of the data in space is not sufficient because of the extraordinary cost needed in space experiments and it is difficult to simulate the LEO environment perfectly by the ground experiments. Therefore, the mechanism of the degradation by AO has not been clarified sufficiently.

The purpose of this study is to elucidate the mechanism of the degradation of carbon-based materials due to the impact of AO. AO bombardment experiment was carried out using DC arc jet of the high temperature discharging type as the source of AO in the space chamber which simulates the vacuum environment. In this experiment, graphite, C/C (carbon fiber/carbon) composite and Si-C.C. (silicon impregnated C/C composite) were chosen as the target materials. The mass loss was measured with the surface temperature of the target material. After the bombardment, degraded surfaces were observed with

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SEM (scanning electron microscope) and the laser focus displacement meter. Normal oxidization experiment in the ambient atmosphere at high temperature was also carried out to compare with the degradation by AO. Furthermore, numerical simulation of the material degradation was carried out for crystalline graphite and amorphous carbon using MD (molecular dynamics) method. The mechanism of the material degradation by AO is discussed comparing the experimental results with the numerical simulation.

2. Experiment

Figure 1 shows the outline of the experimental apparatus. In the space chamber, the vacuum of approximately 2×10^{-3} Torr can be realized using two

Table 1 Experimental conditions

		This work	LEO
Incident Velocity	[km/s]	~ 2.3	~ 8
	[eV]	~ 0.44	~ 5.3
Flux [atoms/cm ² /s]		$\sim 10^{20}$	$10^{10} \sim 10^{15}$
Fluence [atoms/cm ²]		1.42×10^{23}	$0.65 \sim 3.5 \times 10^{20}$

Fig. 1 High-energy AO bombardment apparatus

Fig. 2 DC arc-heated atomic oxygen beam source

oil rotary pumps and a mechanical booster pump. Electric power, gas and cooling water are supplied through the upper flange. A DC arc jet system is used as the AO source as shown Fig. 2, which is supplied with power of approximately 1.6 kW. Ar (argon) is used as the working fluid. After the flow of Ar becomes uniform, high voltage is applied between both electrodes with direct current, so that arc discharging occurs, heating Ar gas. O₂ (molecular oxygen) is injected into the flow downstream of the arc, where O₂ is thermally dissociated into AO in the high temperature Ar atmosphere. AO is accelerated fluid-dynamically with Ar through the nozzle and collides with the target material. In this experiment, the flow rates of Ar and O₂ were controlled to be 6 slm and 1 slm respectively and each target material was exposed to AO for 20 minutes. The temperature on the material surface was controlled by changing the distance from the nozzle exit to the target material and by the cooling system. The temperature is measured by a thermocouple embedded in the target material. Table 1 shows the conditions in this experiment in comparison with those in LEO.

As the target materials, graphite, C/C composite and Si-C.C. were used. As graphite, high-density graphite manufactured by Toyo Tanso Co. Ltd., Japan was used. C/C composite used in this experiment was manufactured by Across Co. Ltd., Japan through the preformed yarn method⁽²⁾. Si-C.C. is silicon impregnated C/C composite developed by NGK Insulators, Ltd., Japan⁽³⁾. This material is made from the same C/C composite used in this experiment and composed of three phases; C/C, Si and SiC. The densities of graphite, C/C composite and Si-C.C. are 1.8, 1.7 and 2.0 g/cm³ respectively.

3. Results and Discussions

3.1 Mass loss

The temperature on the material surface was controlled within the range 320 – 830 K. Figure 3 is the photograph of the AO bombardment experiment. Figure 4 shows the mass loss vs. the surface temperature on the target materials, i.e., graphite, C/C and Si-C.C. In this graph, considering the fluctuation of the specimen and the condition of the plasma, the average value of 3 – 5 data is plotted for each condition. As the results, it has been clarified that the mass loss depends strongly on the temperature of the material surface though the tendency is small at high temperature. The mass loss of Si-C.C. is much smaller than that of C/C under the same condition; therefore, it can be mentioned that the oxidization resistance of Si-C.C. to AO is improved much comparing with C/C.

Park⁽⁴⁾ has found that the logarithm of the reac-

tion probability (the number of reacted carbon atoms per one atomic oxygen) is in proportion to the reciprocal of the surface temperature of the target material by space experiments. Arnold et al.⁽⁵⁾ has found that the similar relationship holds on amorphous carbon by the ground experiment. Considering them, Arrhenius plot was conducted for the data obtained by this experiment of graphite, which is shown in Fig. 5. In this figure, obtained data are nearly on one straight line, which is consistent with the results by Park⁽⁴⁾ and

Fig. 3 Photograph of DC arc jet

Fig. 4 Mass loss vs. surface temperature

Fig. 5 Arrhenius plot of the reaction probability of graphite

Arnold et al.⁽⁵⁾

Comparing the present experiment with space experiment, although the fluence of AO in this experiment is 10^3 times larger than that in LEO, the reaction probability is smaller by one or two digits. This matter can be explained by the difference of the impact velocity of AO. The kinetic energy in this experiment is less than 10% of that in LEO. However, Arnold et al.⁽⁵⁾ concluded that the reaction probability is not affected so much by the velocity of AO if it has the kinetic energy more than 1.0 eV. Anyway, it is anticipated that in the experiment, the velocity of AO is much increased. Furthermore, because it is assumed that all O_2 molecules are dissociated in this study, the flux of AO may be estimated larger than the actual one. Moreover, in this experiment, as mentioned above, the surface temperature of the target material is controlled with changing the distance from the nozzle, which may affect the velocity and the flux of AO.

3.2 Observation of material surfaces

Figures 6-8 are the SEM photographs of the surfaces of graphite, C/C and Si-C.C. The left and the right of each figure show the photographs before and after AO bombardment respectively. The surface of graphite degraded almost uniformly because this material is homogeneous macroscopically. Regarding C/C, fibers of the surface layer became tattered and fibers of the internal layer are exposed. The matrix region is degraded more than the fibers. Regarding

(a) Top view

(b) Cross-sectional view

Fig. 6 SEM photographs of graphite before (left) and after (right) the bombardment of AO

(a) Top view

(b) Cross-sectional view

Fig. 7 SEM photographs of C/C composite before (left) and after (right) the bombardment of AO

(a) Top view

(b) Cross-sectional view

Fig. 8 SEM photographs of Si-C.C. before (left) and after (right) the bombardment of AO

Si-C.C., Si and SiC phases are scarcely degraded though the C/C phase exposing on the surface is degraded considerably. The SiC phase does not play a role of oxidation resistant coating layer because the C/C phase is exposed to AO directly and even the internal layer is eroded.

(a) Graphite

(b) C/C composite

(c) Si-C.C.

Fig. 9 SEM photographs of materials after the normal oxidation (top view (left) and cross-sectional view (right))

3.3 Comparison with normal oxidization

The normal oxidization experiment in the ambient atmosphere at high temperature was carried out to investigate the difference from the oxidization by AO. Figures 9(a), (b) and (c) are the SEM photographs of graphite, C/C and Si-C.C. respectively. The left and the right of each figure are the top view and the cross-sectional view respectively. In graphite, there is little difference between the normal oxidization and the oxidization due to AO while in C/C and Si-C.C., the tendency that the matrix is eroded more than fibers is pronounced in the normal oxidization condition. In the experiment of AO bombardment, fibers are bored or broken in some places due to the impact of AO. However, in case of the normal oxidization, the degradation is such that fibers are getting thinner uniformly instead of breaking. The difference in the behavior of the degradation can be explained by the energy of O_2 and AO. In case of the normal oxidiza-

tion, the energy of O_2 is not so large that O_2 erodes mainly the matrix the bonding energy and the density of which are small. On the other hand, in case of AO bombardment, the kinetic energy of AO is so large that AO erodes both the matrix and the fibers.

3.4 Surface profiles

Surface profiles were observed with laser focus displacement meter. Figures 10(a), (b) and (c) are the measured surface profiles of graphite, C/C and Si-C.C. respectively after AO bombardment. The measurement pitch is $10\text{ }\mu\text{m}$. Degradation of graphite is relatively uniform with little roughness on its surface because the material itself is uniform. On the surface of C/C, the deep bottoms are located periodically with a constant interval, which correspond to the boundary between yarns of fibers. In case of Si-C.C., periodic parts with little damage are observed. These parts correspond to the Si or SiC phase which is not degraded by AO easily. It is noteworthy that the depths of the peak of Fig. 10(b) and the bottom of Fig. 10(c) are of the same order. The reason is because the peaks of Fig. 10(b) correspond to the yarns of carbon fibers in C/C and the bottoms of Fig. 10(c) correspond to the residual C/C phase in Si-C.C.

Fig. 10 Surface profiles of materials after the bombardment of AO

4. Theoretical Analysis

4.1 Numerical method

In order to elucidate the degradation mechanism of materials by AO bombardment, numerical simulation was carried out for crystalline graphite and amorphous carbon using MD method with a simple model of chemical reaction. In MD method, Newton's equation of motion is formulated on each particle composing the system and integrated numerically in order to pursue the motion of each particle. In the numerical integration, velocity Verlet algorithm is utilized because this algorithm is superior in stability and precision. In this analysis, equations of motion are normalized into non-dimensional forms for the convenience.

For crystalline graphite, three layers consisting of 864 carbon atoms (288 atoms per one layer) with the size $29.51 \times 25.56 \times 6.8\text{ }\text{\AA}$ are calculated. In each layer, periodic boundary condition is applied. In the calculation for amorphous carbon, 500 carbon atoms are located at random in the domain of the size $29.51 \times 25.56 \times 13.6\text{ }\text{\AA}$. Lennard-Jones potential is assumed between AO and each carbon atom. On the other hand, harmonic potential is assumed between carbon atoms in crystalline graphite the interatomic force of which is large while Lennard-Jones potential is assumed between carbon atoms in amorphous carbon the interatomic force of which is not large. The initial velocities of carbon atoms are given from the uniform random number series so as to fit the Maxwell distribution at the given temperature; 400 K, 600 K or 800 K.

In the analysis, the chemical reaction of atomic oxygen with carbon is assumed to be restricted to the process

with the following necessary condition

$$E > E_0$$

where E is the kinetic energy in the direction of impact and E_0 is the activation energy of reaction. The actual reaction process is assumed to occur under the following statistical condition

$$P > R$$

where P is the reaction probability determined by a value proportional to overlapping volume between two atoms and R is a random number distributed between 0 and 1.

By the abovementioned method, the effect of the temperature of the target material and the impact energy of AO on the reaction probability can be evaluated qualitatively. Figures 11(a) and (b) show the models for the numerical simulation.

Fig. 11 Models for numerical simulation

4.2 Numerical results

In Figs. 12(a) and (b), calculated reaction probability is shown as the function of the impact energy of AO. It can be seen that the reaction probability increases with the impact energy or the initial velocity of AO. However, the larger the impact energy of AO becomes, the smaller the increment of the reaction probability is. Comparing crystalline graphite with amorphous carbon, the reaction probability of amorphous carbon becomes a little larger than that of crystalline graphite. Especially when the energy of AO is small, amorphous carbon is eroded more seriously than crystalline graphite. This is because the threshold value of the reaction energy E_0 is smaller in amorphous carbon than in crystalline graphite. Furthermore, it has been clarified that the reaction probability becomes larger as the temperature of the

Fig. 12 Calculated reaction probability vs. atomic oxygen energy

material becomes higher in both materials.

5. Conclusions

Experiments of AO bombardment to carbon-based materials were carried out on the ground using DC arc jet as the source of AO. As the results, the followings are clarified regarding the mechanism of the degradation of graphite, C/C and Si-C.C. due to the impact of high-energy AO.

- 1) In every material, the mass loss increases with the temperature of the material surface; however, the tendency is small at elevated temperature.
- 2) In case of C/C, matrix region degrades more seriously than fibers; however, the difference is small comparing with the normal oxidation.
- 3) Si and SiC phases in Si-C.C. are scarcely affected by AO; therefore, the oxidation resistance of Si-C.C. is improved in comparison with C/C. However, these phases play no role as the oxidation resistant coating material.
- 4) For crystalline graphite and amorphous carbon, numerical simulations of material degradation were carried out using MD method. The numerical results agree with the experimental results qualitatively.

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