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Development of Advanced Carbon-Carbon Composite for Spaceplane Application

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Advanced carbon-carbon composites for spaceplane application have been developed which have high mechanical properties and good oxidation resistant coating. The C/C composites are reinforced with two-dimensional carbon fiber fabrics and coated with multiple SiC layers by chemical vapor deposition. After the evaluation of the mechanical properties, the C/C composites have been exposed to an oxidative atmosphere in a temperature range between 500℃ and 1700℃. The C/C composites have exhibited a tensile strength of 323 MPa, tensile modulus of 132 GPa, flexural strength of 417 MPa, flexural modulus of 119 GPa, compressive strength of 264 MPa, and compressive modulus of 129 GPa. The multilayer coating has been found capable of protecting the C/C composite against air oxidation up to 1700℃.

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1 Introduction

Ever since the Space Shuttle was launched, the potential of space and its future utilization has been looked forward to with a great interest by many countries. The space station program which was originally put forward by the United States has resulted in international cooperation between 12 countries, including Japan, the United States, Canada and the European Space Agency.

Including Japanese payload specialists, a maximum of 8 astronauts can stay in the space station. Since launching capability is estimated at five flights per year, the development of a successful and efficient space transportation system between the space station and the earth is required. Research and development programs for a number of space vehicles such as space shuttles, spaceplanes, and spaceships have been studied and some of them are already underway.

When a spaceplane is launched and enters the earth's atmosphere, its estimated surface temperature, due to aerodynamic heating between the body and atmosphere will be extremely high. Thus, the development of high temperature oxidation-resistant materials is essential.

A highly durable and oxidation-resistant advanced carbon-carbon (ACC) composite material which has high mechanical strength and stiffness was investigated for structural and thermal protection use in the spacecraft called "HOPE" which is currently on the drawing board of the National Space Development Agency of Japan (NASDA).

2 Background of Development on Advanced Carbon-Carbon Composites

Space development projects in Japan have reached a new stage of advanced technology. Concentrated efforts are being made toward space utilization following the development of the space station and new space vehicles, instead of exhaustive one-way transportation systems restricted to artificial satellites and a rockets.

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The 21st century will witness the development of completely-reusable manned space vehicles, which will be able to take off and land horizontally.

Several projects are currently under development; the spacecraft, HOPE, which will be launched with the H-II rocket of NASDA, the one-stage spaceplane called "JASP" by National Aerospace Laboratory (NAL), and the winged flying object called "HIMES" by Institute of Space and Astronautical Science (ISAS).

In the United states, a manned transportation system called "Shuttle-II" is planned as the post-Shuttle, and the two types that are presently being investigated are a vertical take-off and horizontal landing type and a horizontal take-off and landing type. In Europe, France took the initiative to develop the large ARIAN-V. A spaceplane called "HERMES" which is a mini-orbiter is planned to be launched with ARIAN-V and then glide back to the earth. This spaceplane is of the same vertical take-off and horizontal landing type as HOPE which is launched with rocket.

A horizontal take-off and landing, manned spaceplane called "HOTOL" in England and a two-stage horizontal take-off and landing, manned spaceplane called "ZÄNGER" in West Germany are also under development.

Furthermore, the New Orient Express, which will take about two hours at hypersonic speed to travel between Washington, D.C. and Tokyo, represents an advance in high speed transportation. In response to growing space activity expected during and after the 21st century, great efforts to develop spaceplanes are being conducted by each nation.

Photos 1 and **2** show conceptual illustrations of two types of spaceplanes, one is a horizontal landing type spaceplane launched with rocket, and the other a horizontal take-off and landing type.

When launching and reentering the Earth's atmosphere, the plane's surface reaches high temperatures.

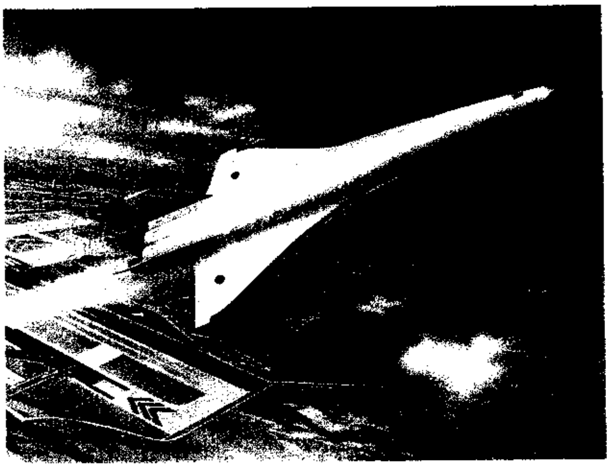

Photo 2 Spaceplane in the future illustrated by Kawasaki Heavy Industries, Ltd.

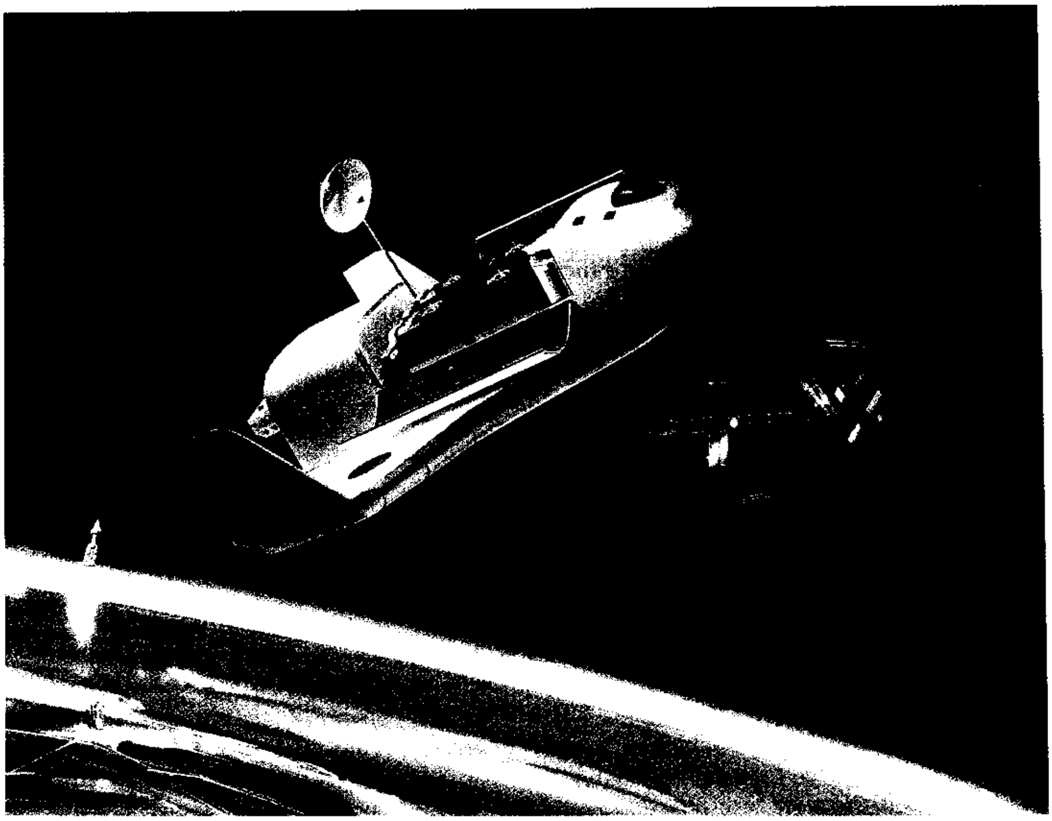

Photo 1 Conceptual illustration of "HOPE" proposed to NASDA by Kawasaki Heavy Industries, Ltd.

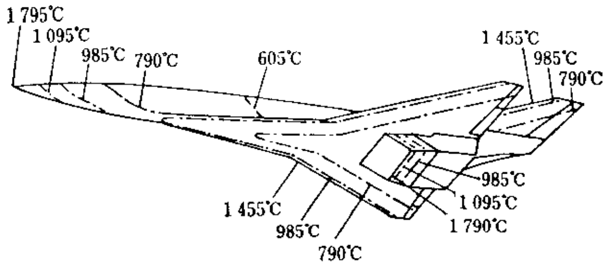

Fig. 1 Estimated temperatures on spaceplane surface

Horizontal take-off and landing spaceplanes, which will be equipped with an air-breathing engine accelerated at low altitudes, are exposed to more severe conditions due to aerodynamic heating in dense air. **Figure 1** shows an example of estimated temperatures on these spaceplane surfaces[1]. To build an effective spaceplane, development of a super-heat-resistant material is a vital prerequisite.

Carbon-carbon composite not only stands at temperatures above 2000°C, but it is also light. Compared with this material, the strength of heat-resistant super alloys and ceramics drops at temperatures over 1000°C.

In the atmosphere, the super-heat-resistant high strength and stiffness carbon-carbon composite is a vital prerequisite.

3 Fabrication Methods and Characteristics of High Strength and Stiffness Carbon-Carbon Composites

In the fabrication of carbon-carbon composites, suitable raw materials are selected and fabrication conditions are determined, with particular attention paid to the fabrication of obtuse-angled parts and curved surfaces such as the Space Shuttle's nose cap, leading edge, and panels for the thermal protection system (TPS).

3.1 Arrangements of Reinforcement Carbon Fiber

There are several ways to reinforce carbon-carbon composites using a UD (uni-directional) structure, 2D structure or 3D structure as in the case with general resin matrix composites. **Table 1** gives a classification of carbon-carbon composites according to their reinforcement structure.

The UD reinforcement structure shows the highest strength due to its high fiber volume fraction and lack of fiber deflection. Anisotropic properties can be used with the optimum ply arrangement, but complex 3D structure components are difficult to laminate. The UD reinforcement structure is suitable for simple angle forms and panels.

The 2D reinforcement structure has less design flexibility in angle ply arrangement. However, general quasi-isotropic laminates can take the same high in-plane strength as UD reinforcement structures, and it is easy to make complex structures because a deep-drawing forming process can be used.

The 3D reinforcement structure improves drastically the interlaminar shear strength as a result of being reinforced by fiber in the Z axis direction which is not strong enough in UD and 2D composites. However, in-plane strength decreases by increasing the Z axis fiber volume fraction. Furthermore, the 3D reinforcement structure is limited in application to complex structures and large components, because of difficulties in weaving the fiber into complex shapes.

Considering the points raised above, the 2D reinforcement has been chosen as an adequate fiber reinforcement structure for making complex shaped carbon-carbon composite parts for spaceplanes. In this study, carbon fiber fabric with a 2D structure was used.

3.2 Fabrication Processing

In typical fabrication of carbon-carbon composites, there are the hot press method, the HIP method, the CVI method and the resin impregnation method. The resin impregnation method was used in the present study, because other methods such as the hot press method, the HIP method and the CVI method are

Table 1 Classification of carbon-carbon composites by reinforcement structure

Reinforcement structure	Advantage	Limitation	Total evaluation
UD (Uni-directional)	· High fiber volume fraction · Highest in-plane strength · Fiber orientation flexibility (easily get some anisotropic composites)	· Conformability for complex shaping	Fair
2 D (Two-directional)	· Formability and conformability for complex shaping by wringing technique · High in-plane strength as UD in case of quasi-isotropic stacking	· Fiber orientation possibility	Excellent
3 D (Three-directional)	· High interlaminar shear strength · High fracture toughness	· In-plane strength · Preformability and conformability for shaping	Good

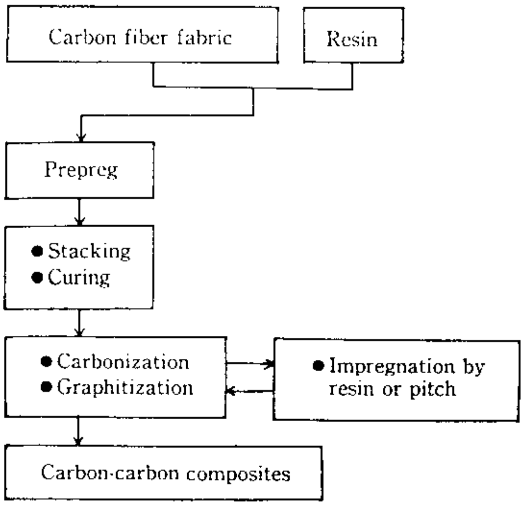

Fig. 2 Production scheme of the carbon-carbon composites by resin impregnation process

limited in conformability of shaping, fabrication capability of large components, and cost of manufacturing.

The resin impregnation method is a common method for processing carbon-carbon composites, and was applied to components of the Space Shuttle.[2)] **Figure 2** shows the fabrication process of the carbon-carbon composites by resin impregnation. In this method, plastics reinforced with carbon fiber fabric (CFRP) is carbonized in an inert gas atmosphere. Then, a pore which is produced by vaporization of a part of the resin is impregnated with resin or pitch. After that, carbonization and graphitization are required. Impregnation, carbonization and graphitization are repeated. This method is easy to apply to large components and has a cost advantage, because a lamination process with prepreg can be used and also a conventional carbonization furnace, a graphitization furnace and impregnation equipment can be utilized.

3.3 Mechanical Properties

As a result of this study for improving the strength of carbon-carbon composites, high strength and high modulus carbon-carbon composites were obtained by the selection of reinforcement fiber arrangements and fiber types and by the investigation of processing. **Table 2** shows the mechanical properties of composite. Of particular note is that a high flexural strength of 417 MPa was achieved.

Table 2 Mechanical properties of the carbon-carbon composite

Density	(g/cm^3)	1.63
V_f	(%)	54.8
Tensile strength	(MPa)	323
Tensile modulus	(GPa)	132
Flexural strength	(MPa)	417
Flexural modulus	(GPa)	119
Compressive strength	(MPa)	264
Compressive modulus	(GPa)	129
Short beam shear strength	(MPa)	23

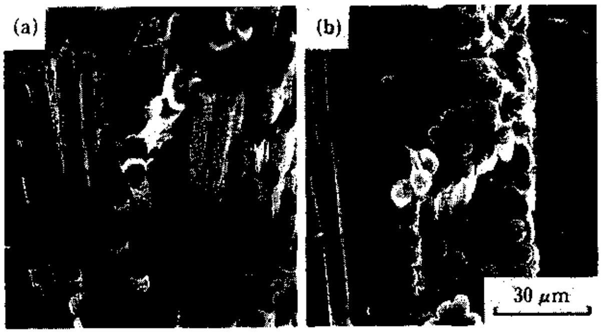

Photo 3 Comparison of fractured surface of the developed C/C composites of 417 MPa flexural strength (a) with a trial product of 137 MPa (b)

Not only properties of raw materials but also bonding behavior between the carbon fibers and matrix have a great influence on the strength of carbon-carbon composites. Since crack propergation sensitivity increases when the bonding force between the carbon fibers and matrix is too strong, brittle fractures occur easily and the strength of the carbon-carbon composites decreases. Also, if the adherence between the carbon fibers and matrix is too weak, high strength cannot be maintained because carbon fibers do not work effectively enough to hold the load. Therefore, optimum control of the bonding force is required for high strength carbon-carbon composites. **Photo 3** shows a comparison of fractured surfaces of the developed carbon-carbon composites. The fractured surface of the low strength specimen (flexural strength of 137 MPa) is comparatively smooth. In the fractured surface of the specimen under controlled bonding (flexural strength of 417 MPa), adequate pull-out of fiber was observed.

4 Oxidation-Resistant Coating on Carbon-Carbon Composites

Carbon-carbon composites retain their typical mechanical properties and chemical stability at around 2000°C in an inert atmosphere. Therefore, they are expected to be used as the structural components of spacecraft.

A serious defect, however, is that carbon-carbon composites readily react with oxygen and burn away rapidly at temperatures as low as 500°C in the atmosphere. On the other hand, the study of arc-tunnel tests performed by using aerodynamic models, and the data of temperature distribution on the Space Shuttle's surface during reentry into the atmosphere shows that temperatures of bottom surfaces of the body, main wings rudders, flaps and so on and the surface of outer side of the tip fin will reach up to 1300°C, and those of the nose cap and wing's leading edges will reach up to 1600°C.3) Therefore, it is necessary to coat these carbon-carbon composites with highly oxidation-resistant materials.

4.1 Coating Materials

There are many factors which must be considered in developing a successful oxidation resistant coating for carbon-carbon composites. As shown in **Fig. 3**, coating materials must possess low volatility, good heat resistance and good anti-oxidation properties. Moreover, good adherence and good mechanical and chemical compatibility between the coating and the carbon-carbon composites must be achieved.4) Furthermore, in applying an anti-oxidation coating to carbon-carbon composites in the aerospace field, reasonable cost and lightweight by reducing the thickness of the coating area also indispensable. Some ceramics can meet these requirements and in this study silicon carbide (SiC) was applied as an oxidation-resistant coating because of its practicability.

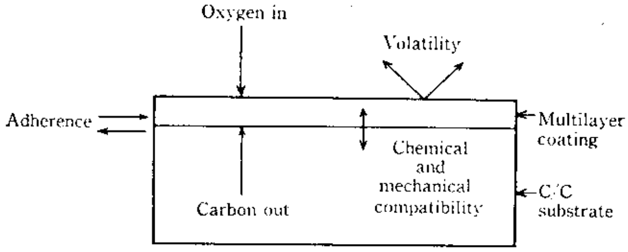

Fig. 3 Critical factors for oxidation-protection coating for carbon-carbon composites

4.2 Method of Oxidation-Resistant Coating

Typical ceramic coating techniques are shown in **Table 3**. Especially by using CVD (chemical vapor deposition), stoichiometric nucleation can be occured and pure and dense ceramic coating can be obtained on the surface of base materials with raw material gases including less impurities. Therefore, objective materials such as ceramics are directly deposited by thermal decomposition of pure raw gaseous precursors. Dense and uniform CVD-SiC is stable at temperatures up to 1700°C in the atmosphere5).

Table 3 Techniques for ceramic coating

Glass-type ceramic coating
Ceramic/metal coating
Solution ceramic coating
Plasma spray
CVD
PVD

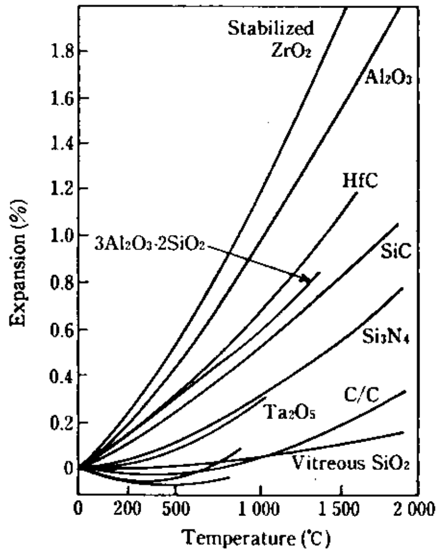

Fig. 4 Thermal expansion of ceramics

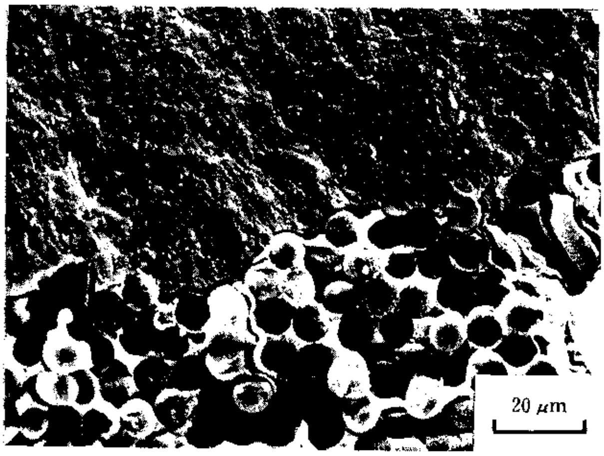

Photo 4 Delamination caused by direct deposition of CVD-SiC on the carbon-carbon composite

Because of the thermal expansion mismatch between CVD-SiC and carbon-carbon composites as shown in **Fig. 4**, however, direct deposition of CVD-SiC on the surface of the carbon-carbon composites resulted in forming delaminations at their interface, as shown in **Photo 4**. Consequently, when applying CVD-SiC to carbon-carbon composites, it is necessary for a good oxidation-resistant coating to release the thermal stress created by their thermal expansion mismatch.

In this study, a relaxation layer was adopted for releasing thermal stress. Low density SiC was employed as the relaxation layer and CVD-SiC was deposited on the relaxation layer. Consequently, there were less microcracks at the interface between CVD-SiC and carbon-carbon composites. Subsequently, a SiO_2 glass layer was coated upon the CVD-SiC layer. This viscous layer acts as an oxygen barrier and seals microcracks in the CVD-SiC layer.

4.3 Anti-Oxidation Properties

4.3.1 Dynamic oxidation test by plasma flame equipment

As the reentry speed of the spacecraft into the atmosphere is almost Mach 25, the surface of the spacecraft is exposed not only to high temperatures but also to erosive circumstances by aerodynamic heating. Therefore, a plasma flame equipment was employed for evaluating erosion and oxidation performances of oxidation resistant carbon-carbon composites in the atmosphere.

A sketch of the plasma flame equipment is shown in **Fig. 5**. The speed of the Ar plasma was about Mach 2 and the diameter of the plasma flame was about 10 mm. The specimen (50 mm x 30 mm x 1.5 mm) was fixed 20 mm away from the plasma gun and the temperature of the specimen was measured with a thermocouple fixed at the back of the specimen. The testing temperatures were 1300°C, 1500°C and 1700°C. The test was repeated ten times for each specimen under an exposure time of 6 minutes per cycle. The weight and the thickness of the specimen were measured following each exposure. **Figure 6** shows the weight loss of the carbon-carbon composites with an oxidation resistant coating after the plasma flame test. After ten cycles' exposure at each temperature, the carbon-carbon composites with an oxidation-resistant coating showed a slight weight loss of less than 0.6 wt.%. The weight loss was thought to result from a scattering loss of SiO_2 created by oxidation of SiC and the oxidative loss of carbon. Though the color of the specimen's surface in the center changed after the plasma flame test as shown in **Photo 5**, the thickness change was negligible as shown in **Fig. 7**.

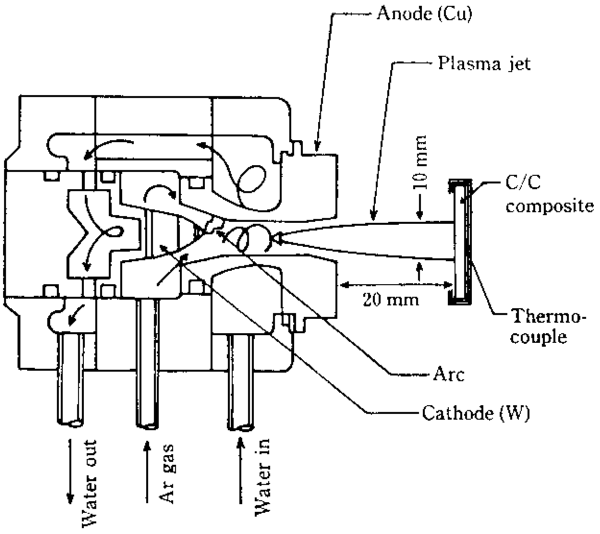

Fig. 5 Sketch of the plasma flame test equipment

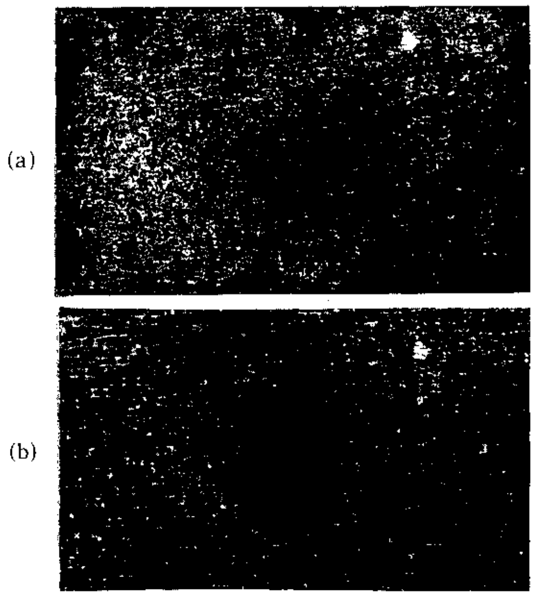

Photo 5 Carbon-carbon composites with multilayer coating before (a) and after (b) the plasma flame test at 1 700°C

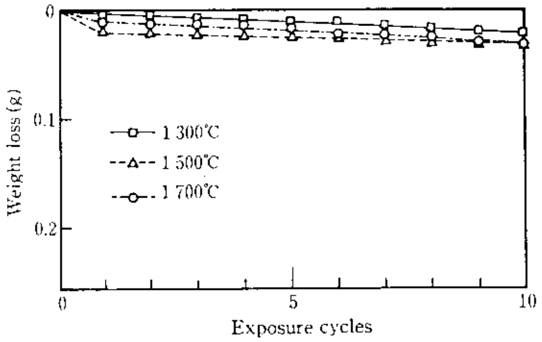

Fig. 6 Weight loss of the carbon-carbon composites with multilayer coating after the plasma flame test

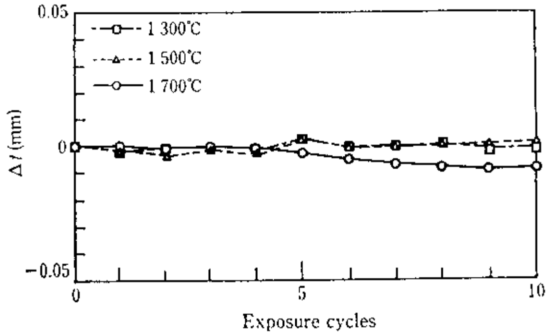

Fig. 7 Thickness changes of the carbon-carbon composites with multilayer coating after the plasma flame test

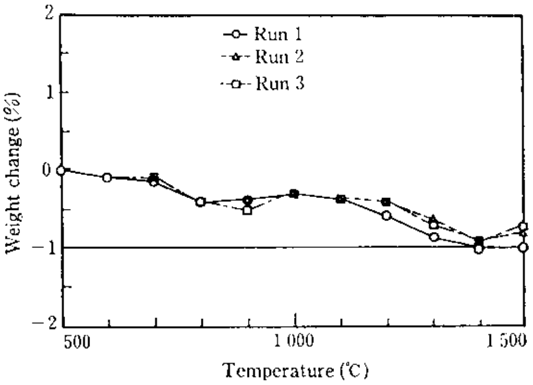

Fig. 8 Weight changes of the carbon-carbon composites with multilayer coating after the oxidation test by stagnant air

4.3.2 Static oxidation test by stagnant air

Anti-oxidation properties of oxidation resistant carbon-carbon composites were also evaluated by the static oxidation test in the stagnant air. The specimen, which was 50 mm × 50 mm × 1.5 mm, was put into the reactor tube fitted with 8-kW electric furnace heated in Ar at a flow rate of 5 *l*/min and heating rate of 6°C/min. After reaching the specified temperature, Ar gas was replaced with air and the specimen was oxidized for 30 min. After 30-min oxidation, air was purged with Ar and the specimen was cooled to room temperature and weighed. The test was conducted every 100°C from 500°C to 1500°C.

Figure 8 shows the relationship between oxidation temperature and the weight changes of the specimens after the oxidation test by stagnant air. The weight changes of the specimens were less than 1 wt.% at every temperature between 500°C and 1500°C. This result shows that this multilayer coating is an efficient barrier to oxidation of carbon-carbon composites caused by oxygen diffusion through cracks of coating layer.

5 Conclusions

The carbon-carbon composites have been investigated as attractive structural and oxidation protection materials for spaceplanes, especially HOPE. The following results were obtained:

(1) The present ACC reinforced with 2D carbon fiber fabric showed excellent mechanical properties including high tensile strength and modulus, high flexural strength and modulus, and high compression strength and modulus.

(2) Adhesive property of the interface between the carbon fiber and matrix had a significant influence on the mechanical properties of carbon-carbon composites as well as properties of raw materials and processing.

(3) New multiple SiC layers which include a relaxation layer for releasing thermal stress were developed to protect carbon-carbon composites for oxygen. Evaluations of multiple SiC layers under dynamic and static heating were carried out in an oxidation atmosphere. Weight loss with oxidation was below 1 wt.%. This experiment suggests that the present ACC has superior oxidation protection properties.

Acknowledgements

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