FABRICATION AND CHARACTERIZATION OF ULTRA-LIGHTWEIGHT ABLATOR USING POROUS CARBON MATERIALS

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Abstract

We have fabricated a light-weight ablator with excellent erosion resistance in order to reduce the weight of TPS used for re-entry vehicles. Polyimide resin and porous carbon materials which can control the diameter of the pores were used as the raw materials. At first, manufacturing process was examined by changing impregnation, drying and curing condition. Then, new carbon ablators have been fabricated, and were evaluated thermal insulation properties and erosion resistance by thermal conductivity measurement and arc-jet tests. Experimental results showed that the thermal insulation properties became larger when the pore diameter decreased. In addition, they showed higher erosion resistance than the fiber-based ablator by suppressing the mechanical erosion in the high heating rate environment.

1 Introduction

Thermal protection systems (TPS) are an important technology in order to protect re-entry space vehicles from aerodynamic heating during re-entry into the atmosphere. Ablators are one of the TPS materials which have been used for the heat shield of many re-entry vehicles including Apollo spacecraft etc., and it has attracted attention even now because of its high reliability. Typical examples of an ablation material are char-forming ablators, which are manufactured by phenolic resin matrix carbon-fiber-reinforced plastics (CFRP). The thermal protection mechanism of ablators is schematically illustrated in Fig.1. These materials generate pyrolysis gas by ablating its own, and the gas blocks the heat convection [1]. This process is typically endothermic and the resin pyrolysis also produces a carbonaceous residue which showed the heat resistance [1]. Evaluation of ablators is difficult because re-entry environment is complex and involving various factors. Therefore, an arc-jet test is often used as a method of evaluating the ablators for simulating the re-entry environment. Insulation and erosion characteristics of heat shield materials can be examined by exposing a test piece to the high-enthalpy airflow in the arc-jet test.

Recent years, lightweight ablator for re-entry capsules of next-generation spacecrafts is attracting attention. It can introduce a large number of pores for reducing the weight and has low thermal conductivity: Phenolic Impregnated Carbon Ablator (PICA), which is manufactured by impregnating phenolic resin to the carbon fiber preform, is typical examples of lightweight ablators developed by NASA [2]. Such FRP lightweight ablators has been studied and developed actively in each country. However, FRP ablator cause mechanical erosion of fibrous material (ex. char spallation), and will not be able to achieve their full potential. The char spallation is an undesirable phenomenon because it consumes mass of the ablator with minimal loss of thermal energy [1]. Furthermore, this phenomenon makes it difficult to characterize and predict ablative behavior [1]. As a technique to prevent this phenomenon, densification of ablators is effective. However, in that case, a thermal conductivity and weight are increased. In fact, the surface recession rate, insulation and weight characteristics are trade-offs. As shown in Fig.2, optimum ablative TPS materials are categorized by density in terms of the re-entry environments [1]. Since one of the threshold is surface spallation, the development of ablators with lightweight and no-mechanical erosion will lead to a reduction in the weight of the TPS and improving the reliability in the high heating rate environment.

In this study, we focused on using a porous carbon material to the preform in order to suppress the mechanical erosion and aim to create an ablator with excellent erosion resistance and lightweight characteristics. Features of the porous carbon material are excellent strength, light weight, heat insulation, heat resistance and process ability. In the past studies, it was reported that ablation materials using carbon foam (GRAFOAM, Graf Tech International) showed heat insulating performance equivalent to lightweight CFRP ablators [3]. Our porous carbon materials are manufactured by carbonization of the porous phenolic resin and they have a three-dimensional network structure with continuous open pores. In addition, they have almost uniform pore diameter, which can be controlled in the range of 5~25μm. In this study, we tried to manufacture new porous carbon ablators using our porous carbon materials. These were evaluated its performance by arc-jet tests. In this paper, we summarize results of manufacturing process, relationship between pore diameter and thermal insulation performance and surface recession in comparison with fiber-based lightweight ablator.

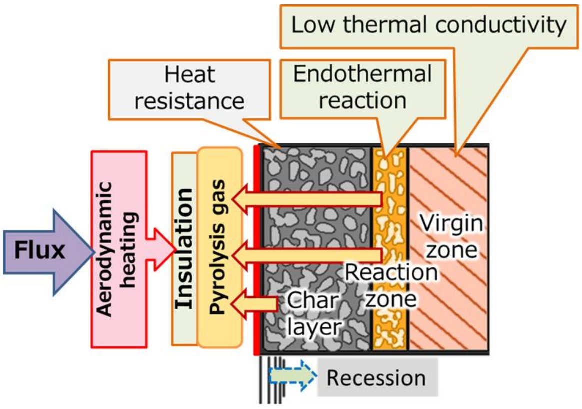

Fig.1 Mechanism of ablative TPS materials.

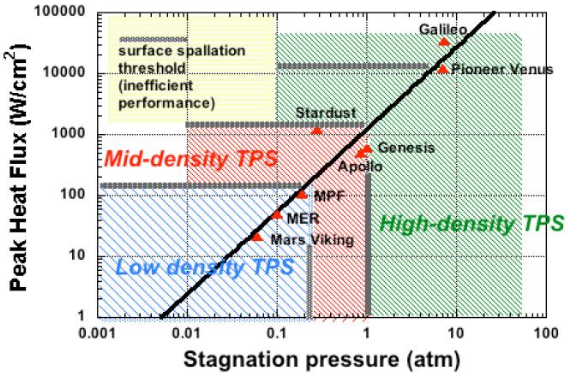

Fig.2 Limitations of ablative TPS classes [1].

2 Materials and Methods

2.1 Materials

Porous carbon materials were produced by carbonization of porous phenolic resin at 950ºC under Ar atmosphere. As shown in Fig.3, the porous carbon materials have uniform micro structures and nominal average pore diameters are 5, 10, and 25μm. The properties of the porous carbon were shown in Table 1.

2.2 Manufacturing Process

Porous carbon ablators were manufactured by impregnating the resin solution into the porous carbon preform, and drying solvent and curing resin. Polyimide was used as impregnated resin because it has excellent residual carbon ratio and high heat resistance. After adjusting the polyamic acid resin precursor, the preform was filled by the resin with pressure and vacuum impregnation. Impregnated preforms were dried and cured at RT-250ºC in a vacuum oven in order to fabricate ablators. Porous carbon preform has microscopic pore and is rigid material relative to fiber-based insulator material. Therefore, it is expected that it is more difficult to impregnate a resin to the porous carbon than fiber-based material. Thus, we improved manufacturing processes by changing impregnation step and drying/curing conditions. The shape of the test piece for the ablator was octagonal pillars of 55mm×55mm×50mm. Observation of center cross-section was carried out and the density of edge and center was measured and compared. The processing route of the porous carbon ablator was summarized in Fig.4.

2.3 Thermal conductivity evaluation

Thermal conductivity of porous carbon materials and ablators was measured at 50, 100, 150, 200 and 250 ºC in air by the steady state method (GH-1 ULVAC ASTM-E1530) in order to examine the pore size dependence of the thermal insulation property. Size of the test piece was 25mm×25mm×5mm. Bulk density of each material was shown in Table 2. Before thermal conductivity measurements, the test piece was dried at 120ºC using a hot plate in order to prevent the effect of moisture absorption.

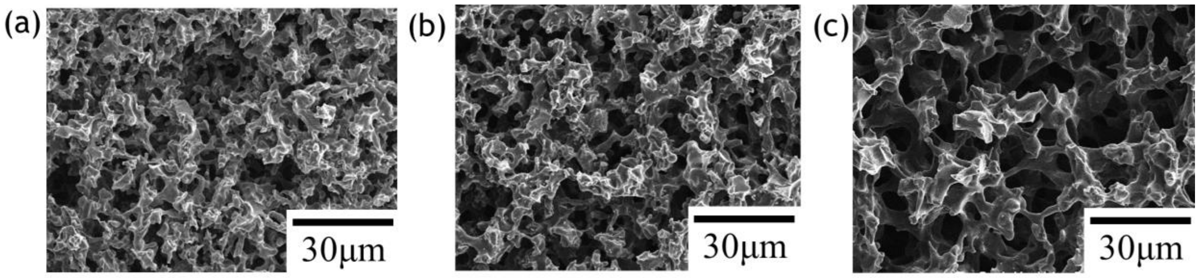

Fig.3 Microstructure of porous carbon: Average pore diameter of (a)5μm (b)10μm (c)25μm.

Table 1. Properties of Porous carbon.

	Porous Carbon Materials		
Bulk density (g/cm^3)		0.36-0.38	
Pore diameter (μm)	5	10	25
Compressive Strength（MPa）	13.4	13.2	18.1
Compressive Modulus(GPa)	1.08	1.23	1.83
CTE (10^{-6}/ºC)	3.20	3.28	2.83
Porosity (%)		70-80	

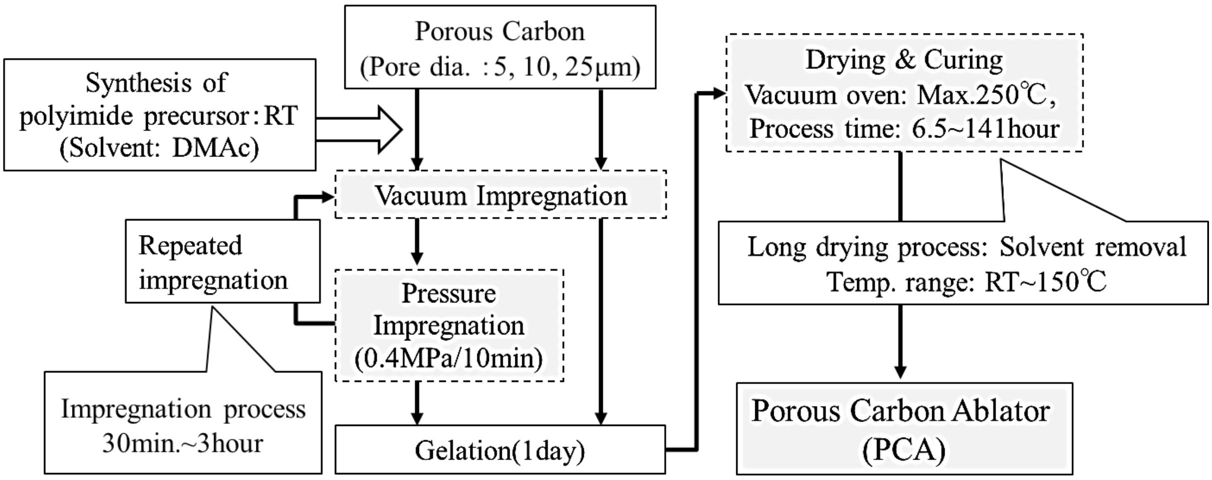

Fig.4 The processing route of Porous Carbon Ablator.

Table 2. Test specimen for thermal conductivity measurement.

	Bulk density (g/cm^3)		
Pore size	5μm	10μm	25μm
Porous carbon	0.374	0.369	0.376
Ablator	0.481	0.482	0.483

2.4 Arc-jet Test

The shape of the test piece for an arc-jet test is shown in Fig.5. K-type thermocouples were embedded in the ablator specimen, and they were located at the depth of 20mm or 30mm from the surface. Side surface of the specimens were covered with glass cloth and Bakelite holder to prevent heating on the side surface. Internal temperature, surface temperature and surface recession amount have been measured in the arc-jet tests with three different heating conditions of 1.8, 3.2 and 6.0MW/m^2. In addition, we prepared a fiber-based ablator which has been fabricated by impregnation of same polyimide into the carbon-fiber insulation in order to compare of surface erosion behavior. Test conditions of the arc-jet tests were listed in Table 3.

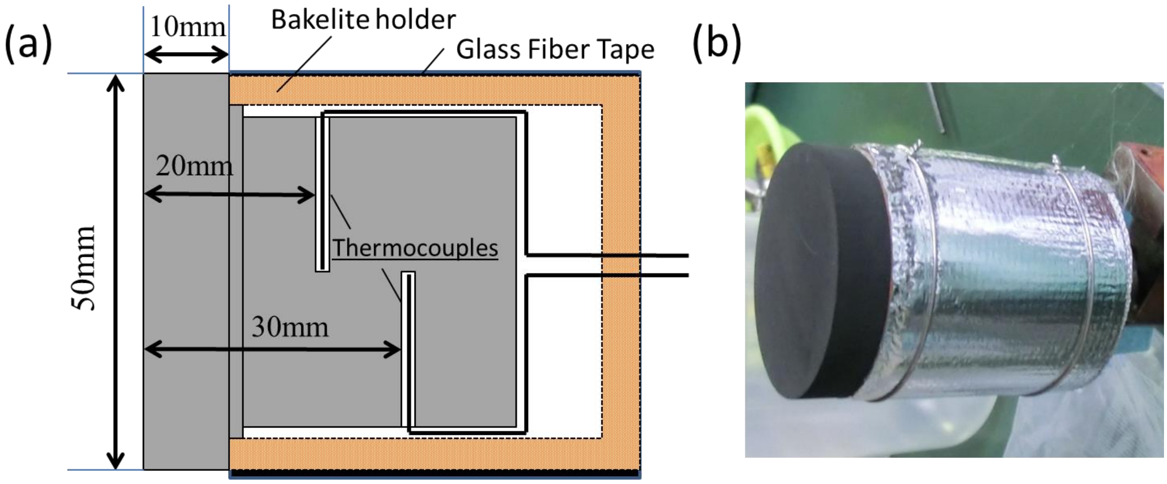

Fig.5 Arc-jet test specimen: (a)Specimen configuration (b)Specimen appearance

Table 3. Specimens and testing conditions.

Test specimen	Pore size (μm)	Base material density (g/cm^3)	Ablator density (g/cm^3)	Heating rate (MW/m^2)	Impact Pressure (kPa)	Exposure Time (sec.)
PCA5-1	5	0.36	0.478	1.8	4.5	30
PCA10-1	10		0.478			
PCA25-1	25		0.474			
PCA5-2	5		0.478	3.2	12.8	
PCA10-2	10		0.484			
PCA25-2	25		0.477			
PCA5-3	5		0.476	6.0	19.4	
PCA10-3	10		0.481			
PCA25-3	25		0.481			
CF-3	N/A	0.3	0.467	1.8	4.5	
CF-2			0.469	3.2	12.8	
CF-1			0.442	6.0	19.4	

※PCA: Porous carbon ablator, CF: Carbon Fiber based ablator .

3 Result and discussion

3.1 Manufacturing Process

Cross-sectional views of the ablators prepared under several processing conditions were shown in Fig.6-(a). Fast and short drying conditions caused uneven distribution of cured resin: Fig.6-(a-i). Although low-density area was reduced by the slow and long drying process, it was still remained at the center of the specimen as shown in Fig.6 (a-ii). Such difference might be caused during removal process of the solvents. Finally, long time impregnation processes with repetitive pressurization and depressurization improved uneven distribution as shown in Fig.6-(a-iii). Then, the effect of the drying and curing time on the difference between density of edge and center portion was examined as shown in Fig.6-(b). From this figure, when the drying and curing time is long, the density difference is reduced and the resin is able to fill the inside. The density difference could be suppressed to less than 10% when drying and curing time was extended to 141 hours, and variability by the pore diameter difference became small.

It was indicated that the long time drying and repeated impregnation process was effective in manufacturing of porous carbon ablator. On the other hand, it was suggested that changing impregnation method and resin component is necessary for upsizing the ablator and improving manufacturability.

3.2 Thermal conductivity evaluation

A thermal conductivity of porous carbon materials and porous carbon ablators are shown in Fig.7-(a). In addition, Fig.7-(b) showed microstructure of porous carbon ablator after measurement of thermal conductivity. From Fig.7-(a), thermal conductivity decreased with decreasing pore diameter. Thus, it was confirmed that thermal conductivity depends on the pore size.

About the thermal conductivity of porous insulation materials, Williams et al assume the following expressions [4].

$$\lambda = (1-\phi)\lambda_S + \phi\lambda_G + (1-\phi)^{-1}\lambda_R \tag{1}$$

Where ϕ is the porosity, λ_S the thermal conductivity of the solid, λ_G the thermal conductivity of the gas, and λ_R the thermal conductivity of the internal radiation. In other words, the thermal conductivity of porous carbon can be considered the sum of the thermal conductivity of the solid, the internal gas and radiation heat transfer. In our experiments, the density of the porous carbon materials was almost the same regardless of the pore size. Therefore, it is implied that λ_S, λ_G and ϕ are assumed independent of pore size. The difference in thermal conductivity due to pore structure as shown in Fig.3 and Fig.7-(b) is considered as the influence of λ_R which is radiant heat transfer in the air gap. In porous materials, reflection of radiation in the cell wall increased with decreasing pore diameter [5]. Therefore, λ_R by radiation heat transfer decreased with decreasing the pore diameter in the porous carbon materials. This might be the reason for the pore diameter dependence shown in Fig.7-(a). Moreover, there was tendency that a thermal conductivity difference between the different pore diameter is increased with increasing temperature. This fact also suggests that λ_R contributes to the difference in thermal conductivity because λ_R is proportional to the cube of the absolute temperature. Thus, it is thought that the porous carbon material having small pore diameter is promising as an insulation material in the environment of the high temperature.

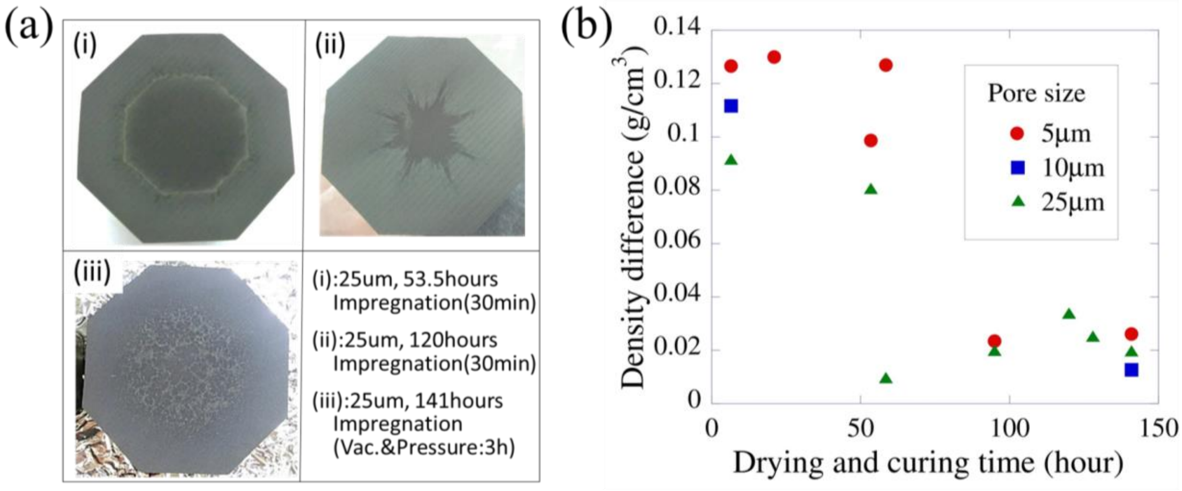

Fig.6 Effect of processing condition: (a) Cross-sectional observation and (b) Influence on the density of the dry & curing time.

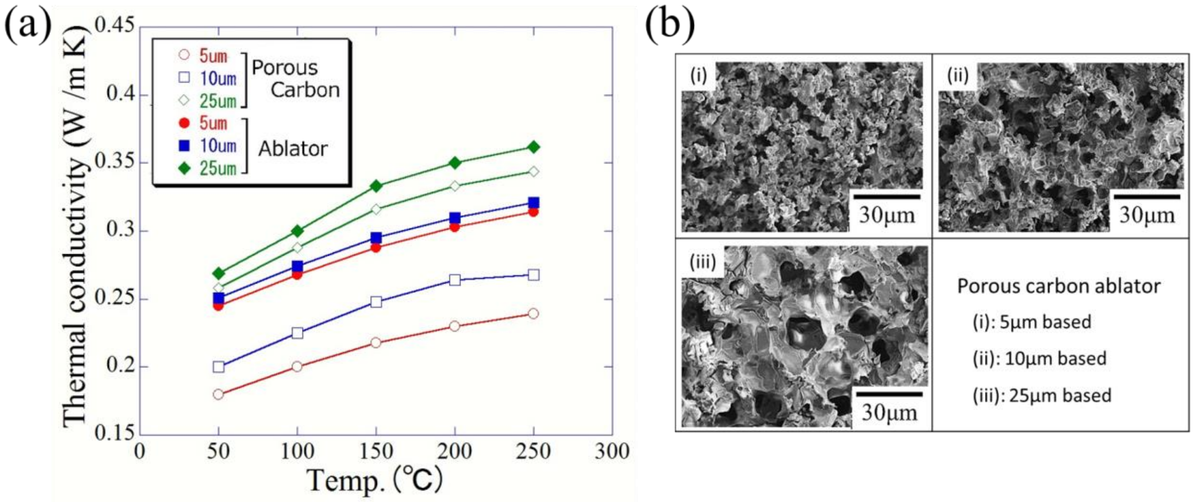

Fig.7 Thermal conductivity evaluation: (a) Pore size dependence of the thermal conductivity and (b) Microstructure of porous carbon ablator.

3.3 Arc-jet Test

The surface temperature during arc-jet tests were approximately 1900ºC at 1.8MW/m^2, approximately 2300ºC at 3.2MW/m^2 and approximately 2600ºC at 6.0MW/m^2. Furthermore, mass loss rate of surface recession was calculated by the following expressions in order to assess erosion resistance from quantity of surface recession after the examination.

$$\begin{matrix}\text{Mass loss rate of} \\ \text{Surface recession}\end{matrix}\ (\mathrm{g/m^2/s}) = \frac{\text{Resession (m)}}{\text{Exposure Time (s)}} \times \begin{matrix}\text{Ablator} \\ \text{density}\end{matrix}\ (\mathrm{g/m^3}) \qquad (2)$$

The summarization of mass loss rate of surface recession by each heating rate was shown in Fig.8-(a). It was shown in Fig.8-(a) that the porous carbon ablator has better erosion resistant property than that of carbon fiber-based lightweight ablator. This tendency was shown more significantly in a higher heating rate. Char spallation phenomenon was confirmed in carbon fiber ablator as shown in Fig.9 (b). On the other hand, it was not found in porous carbon ablator. From this result, it was suggested that erosion resistant characteristics was improved by employing new porous carbon material to the base material of the ablator. In addition, the fiber-based ablator showed large deformation in the heating direction, but porous carbon ablator showed no such deformation. Therefore, it is considered that actual surface recession of fiber-based ablator was larger than the measured value. It suggests that porous carbon ablator has higher erosion resistance than that of the fiber-based ablator.

The summary of maximum internal temperature by each heating rate was also shown in Fig.8-(b). This figure showed that internal temperature is suppressed with decreasing the pore diameter. This tendency is strongly related to the results of the thermal conductivity evaluation. From the fact that the temperature difference got larger when the heating condition is higher, it is suggested that reduction of the radiation by the smaller pore diameter resulted in the reduction in the temperature inside the ablator.

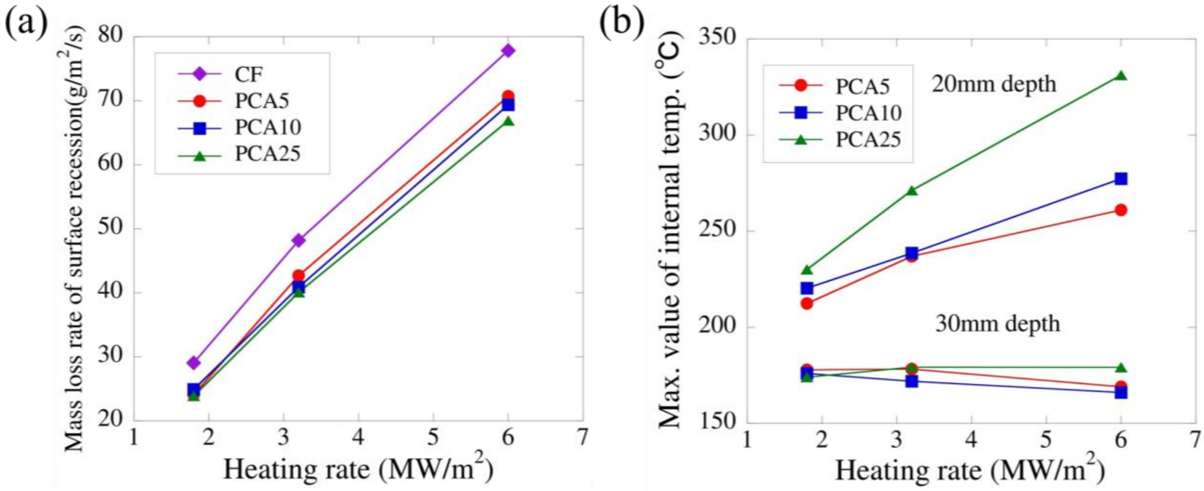

Fig.8 Result of arc-jet test in each heating rate: (a) Mass loss rate of surface recession and (b) Maximum value of internal temperature.

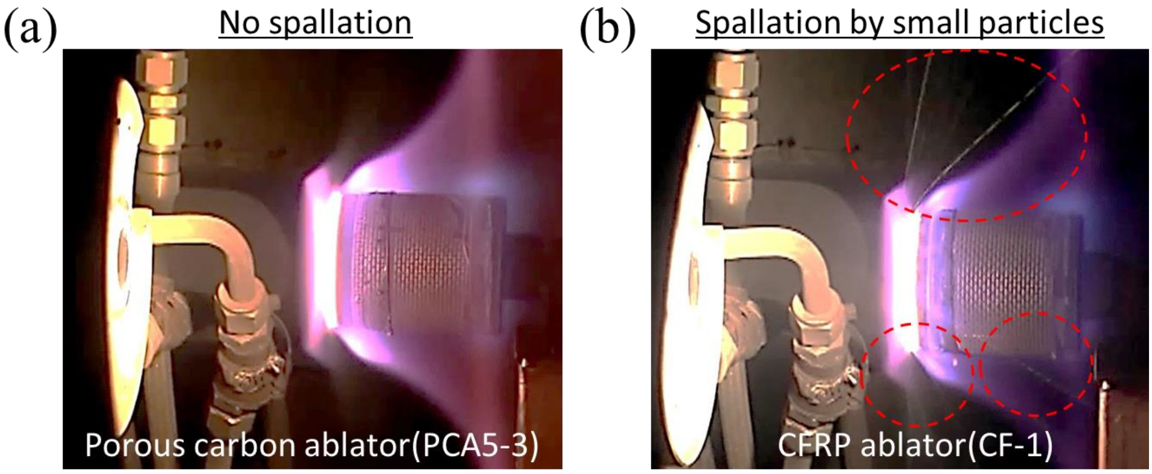

Fig.9 Existence of spallation in each specimen at 6.0MW/m^2.

4 Summary

It was suggested that a repeated impregnation process and long-time drying process were effective to manufacturing of porous carbon ablator. Porous carbon ablator showed higher erosion resistance than the fiber-based ablator by suppressing the mechanical erosion in the high heating rate environment. In addition, it was confirmed that thermal insulation property of porous carbon materials was improved by decreasing pore diameter which is attributed to the effect of pore size on the thermal conductivity.

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