Spectroscopic Measurements of SiC Ablations in Air Plasma Freejets

By Masahiro Ozawa1), Masato Funatsu1), Ryota Onozawa1), Ryuji Shibata1), Hiroyuki Shirai2) and Fumio Takakusagi3)

1) Graduate School of Engineering, Gunma University, Kiryu, Japan
2) The Open University of Japan, Chiba, Japan
3) School of Engineering, Gunma University, Kiryu, Japan
(Received June 16th, 2011)

In order to investigate silicone carbide (SiC) ablations in detail, the test pieces of SiC were ablated using air plasma freejets, and spectroscopic measurements were performed at three points around the ablating SiC. It was found that spectra measured at each point were quite different with each other both in distribution and in intensity. At the point just upstream of the tip of the test piece, the molecular bands of CN, N2, and the atomic lines of Si were observed, and in the downstream region, that is, in the pale greenish flow region, strong molecular bands of C2 appeared. It was suggested that the C2 molecules were generated by recombination reaction of C atoms originated from the ablation of SiC. Experimental spectra of radiation from the heated test piece were fitted with the black body radiation function to estimate its surface temperature. The brightness temperature thus measured was 3,600K and this was considerably higher than the decomposition temperature of SiC.

Key Words: Ablation, Silicon Carbide, Spectroscopic Measurement, Plasma, Freejet

Nomenclature

\[ x \quad : \quad \text{distance from nozzle exit, mm} \]
\[ q \quad : \quad \text{heat flux, MW/m}^2 \]
\[ T \quad : \quad \text{temperature, K} \]
\[ t \quad : \quad \text{elapsed time (heating time), sec} \]
\[ W \quad : \quad \text{weight loss per unit area, kg/m}^2 \]
\[ m \quad : \quad \text{weight loss rate per unit area, kg/m}^2\cdot\text{sec} \]

1. Introduction

When a spacecraft enters the atmosphere of a planet at a hypersonic speed, an extremely strong shock wave forms over the vehicle. Because the vehicle is seriously heated aerodynamically, the thermal protection system is required. Ablation method has been proved to be very effective to protect the vehicle from such heating. However, the property of ablating material and the behavior during ablation have not been clarified enough yet. For carbonaceous material, studies have been partly performed, for example, for spalled particles from the ablating surface, the speed of nitridation reaction on the ablating surface, and so on.

In our laboratory, the ablation experiments of SiC have been performed using air plasma jets and air plasma freejets, because it was thought to be a likely candidate as an ablating material for the next generation. Measurements of weight loss and weight loss rate, observation and chemical analysis of the surface of test pieces after heating were performed in our previous studies using air plasma freejets. It was found that the weight loss rate of SiC changes a little with heat flux and that its ablation needs a longer time to be steady than C material. The process how the oxide of Si attached to the surface of the test piece was formed was also proposed. However, the behavior of SiC ablation and detailed processes proceeding in the ablation gases are still unknown.

In this study, in order to investigate SiC ablations in detail, spectroscopic measurements were performed at three points around the SiC test piece ablating in air plasma freejets. Main chemical species were identified from the experimental spectra. The properties of the spectra at each point and the differences among the spectra at the three points were discussed in detail. Brightness temperature of the surface of
the test piece was also estimated by fitting the black body radiation function to experimental spectra. In addition, the cause of time-variation of weight loss rate was also discussed.

2. Experimental Setup

Figure 1 shows the experimental setup. This consists of two parts, one of which is for SiC ablation, and the other for spectroscopic measurements. The former contains plasma freejet generator, calorimeter, and automatic test-piece positioning control system. Figure 2 shows a layout of nozzle section of the plasma freejet generator. As seen in Fig. 2, the generator has a plasma torch which functions as a cathode, 1st-nozzle of 0.7mm in diameter and 2nd-nozzle of 2mm in diameter. The top of the cathode is made of hafnium. The 2nd-nozzle works as an anode outside of the torch and is made of brass. Air was arc-heated between the 1st and 2nd-nozzle, and micro-air plasma freejet was generated by spurring the plasmajets from the 2nd-nozzle. The calorimeter measured the heat flux by temperature elevation of water which flows in it. This was used as a test piece holder, too, namely, the test piece was inserted in the calorimeter and was set on the center line of plasma freejets. Because the tip of the test pieces was recessed by heating, its position was controlled using the automatic test-piece positioning control system.

In the spectroscopic measurements, images of ablating SiC were focused on a slit of the spectrometer with optical lens. The radiation was detected by a photomultiplier, and the signals from it were amplified by a lock-in amplifier. The amplified signals were recorded on X-Y recorder and personal computer. The spectrometer used in the measurements had the grating of 1,200 grooves/mm, its focal length was 500mm.

In the experiments, the distance between the 1st and 2nd-nozzle was kept at 3.0mm, discharge current was 10A, discharge voltage was 180-185V and, reservoir pressure was 0.6MPa in absolute pressure. The heat flux of the present air plasma freejets decreased with increasing distance from the 2nd-nozzle exit. The distance from nozzle exit to the tip of the test piece was set at 5mm. The test piece of SiC used in the measurements was a circular cylinder of 5mm in diameter.

3. Properties of Air Plasma Freejets

Figure 3 shows a photograph of the air plasma freejet. The long bright region from side to side is air plasma freejet. It was exhausted from the 2nd-nozzle exit and expands. Its size was up to about 10mm in the radial direction and about 40mm in the flow direction. In the figure, the strong radiation of the freejet can be seen in the region of about 10mm from the 2nd-nozzle exit, and the radiation became week downstream. Figure 4 shows cold wall heat flux and stagnation temperature distributions along the center axis of the freejet. Here, the horizontal axis is the distance from 2nd-nozzle exit to the tip of the calorimeter, the left vertical axis is temperature, and the right one is heat flux. Heat flux and temperature was measured using a calorimeter of double annular type and thermocouple, respectively. The temperature was measured in the range of 20 to 60mm from the nozzle exit, since in the upstream region flow temperature was too high to use a thermocouple.
The heat flux was measured at 1 to 60mm. The heat flux was calculated by Eq. (1),

\[ q = \rho_w C_p f \Delta T / A, \]

where \( \rho_w \) is the density of water, \( C_p \) is the specific heat at constant pressure of water, \( f \) is the flow rate of water, \( \Delta T \) is the temperature rise of water, \( A \) is the cross sectional area of a calorimeter. The error bars in Fig. 4 were determined from the maximum and minimum values in all the heat flux data. The heat flux at 1, 3, and 5mm was 5.92, 5.24, and 4.56MW/m², respectively, as seen in Fig. 4. The heat flux decreased considerably with the distance from the nozzle exit in the upstream region of the jet. The temperature of the freejet decreased gradually in the range from 20 to 60mm. The temperature near the nozzle exit was estimated using the relation between the temperature and the heat flux. As a result, the temperature at the position of 1, 3, and 5mm near the nozzle exit was estimated at 7,500, 6,500, and 5,500K, respectively5).

4. Results and Discussion

4.1. Observations of SiC ablations

In order to know the behavior of SiC in air plasma freejets, the test pieces was observed during the ablation experiment. Figure 5 shows the photos of the test pieces under ablation. Each photo is one flame of a movie taken by applying a neutral density (ND) filter to a video camera. The elapsed time since heating started and the optical density (O.D.) of a filter used are indicated below the underside. The O.D. value used in the experiments was 3.0 and 5.0. As shown in Fig. 5, the freejet flows from left to right along the center axis. The region near the tip of the test piece is shining very brightly, and in addition, one can see the pale greenish radiation clearly in the downstream region. The radiation seems to change with the position and/or the size of a deposit attached to the test-piece surface. In the photo at 5sec, the intense zone of radiation spreads widely vertically. On the contrary, at 10sec, such a zone spreads much less widely. This may be due to the shift of the deposit and/or the change of its size. At the elapsed time of 30sec, the situation is almost the same as at 10sec. The difference in color of the radiation by position is closely related to the difference of chemical species existing there, and also chemical processes happening there. Photos in the bottom of Fig. 5, which were taken with much dense ND filter, the shape of the test piece, the position of the deposit and size of the deposit can be seen clearly. These varied sizably
between the elapsed time of 5 to 10 sec. During the elapsed time of 10 to 30 sec, the situation is almost kept the same except the tip shape of the test piece changed from round to roughly flat. Therefore, it was assumed that SiC ablation was almost steady after the elapsed time 10 sec.

### 4.2. Spectroscopic measurements

The spectroscopic measurements were performed around the test piece during the steady ablation. Measuring points in the present experiments are shown in the upper-middle photograph of Fig. 5, where \( x \) is the longitudinal distance from the nozzle exit, \( y \) is the vertical distance from the centerline. The point [a] is at \( x = 4 \) mm on the axis, just upstream of the test piece, the point [b] is at \( x = 7 \) mm on the test piece, the point [c] is off axis, namely, at \( x = 8.5 \) mm and \( y = 1.5 \) mm, where the pale greenish radiation can be seen.

Figure 6 shows the experimental spectra, which were measured broadly near point [a] in the wavelength region of 250 to 900 nm. Here, horizontal axis is the wavelength and vertical axis is the radiative intensity in an arbitrary unit. It is composed of continuum band, molecular bands, and atomic lines. In the short wavelength region, Cu and Si atomic lines, and CN molecular bands are seen. Cu atomic line is an impurity caused by vaporization of nozzle material. In the long wavelength region, O atomic line is seen. This shows that the radiation consists of one from gasses generated by ablation and from plasma freejet itself.

In the short wavelength region, many atomic lines and molecular bands appeared. Therefore, spectroscopic measurements were performed in detail in the wavelength region from 250 to 600 nm. Figure 7 shows the experimental spectra at point [a], where the black-solid line in the figure indicates the experimental spectra of air plasma freejet itself, and the blue-solid line is that of SiC ablation. The spectra of SiC ablation are very similar to those of the freejet. In both the spectra, continuum appeared comparatively weakly. Many chemical species were identified and shown in the figure. In the short wavelength region, one can see OH, NH, CN, and \( \text{N}_2 \) molecular bands, and Cu, Zn, and Pb atomic lines, all of which are common to the both. Cu, Zn, and Pb atomic lines are impurities caused by vaporization of the nozzle material. It was supposed that OH molecular band was originated from small amount of water contained in the freejet. One can see some differences between the results of SiC ablation and freejet. In the ablation spectra, the continuous spectra were relatively stronger than those of plasma freejet, particularly in the long wavelength region, Si atomic lines appeared, and complex spectra, which look like bands, can be seen in the wavelength region of 450 to 600 nm. The strength of the Si atomic line is sufficiently strong, and hence it was concluded that Si decomposed by heating spurted upstream.

Figure 8 shows the experimental spectra at point [b]. It should be noted that though the relative intensity is plotted in an arbitrary unit, it is comparable to those of Fig. 7. It can be seen that the relative intensity at point [b] is much stronger than at [a]. From Fig. 8, the continuum spectra, atomic lines and molecular bands appeared just like in Fig. 6 in the shorter wavelength region to about 400 nm. However, in the range over 400 nm, the relative intensity decreased suddenly. The reason why this phenomenon happened has been unknown,
yet. Si atomic line appeared around 290nm is about 10 times as strong as that in Fig. 7. This means that Si atoms are plentiful in the side region of the test piece.

Figure 9 shows the experimental spectra at point [c]. They are much different from those at point [a] and [b]. The radiative intensity at point [c] is, in general, stronger than that at point [a], but much weaker than those at point [b]. Unlike in Fig. 7, strong continuum spectra appeared, especially in the long wavelength region. Si atomic lines, OH, CN, and C$_2$ molecular bands were identified, though many other peaks are still unknown. OH molecular band would be caused by small amount of water contained in the freejet. Strong C$_2$ Swan bands appeared at 470nm and 520nm. Therefore, it was supposed that the pale greenish radiation around ablating SiC was originated from these bands. The C$_2$ molecules might be formed through recombination reactions of C which generated by decomposition of SiC. The pale greenish radiation was very strong behind the deposit on the surface of ablating SiC test piece. It is sure that many C$_2$ molecules were generated there by recombination reactions because of relatively low temperature due to the expansion of gas which flows around the deposit.

Figure 10 shows the comparison of experimental spectra of the points [a], [b], and [c]. Here, the vertical axis is logarithmic scaled relative intensity. Each spectrum shows characteristic distribution and they are much different mutually. In the whole wavelength region measured, spectral intensity at point [b] is much stronger than the other points. This reflects the fact that the intensity at this point contains strong radiation from test piece itself heated to high temperature. The spectra at point [a] consist mostly of atomic lines and molecular bands. In the downstream region, most of the atomic lines disappeared, and at the point [c] molecular band like C$_2$ Swan bands dominated. Si atomic lines appeared at every point. The differences of the spectra by position and characteristics of radiation from chemical species generated in SiC ablation are the problem to be solved.

### 4.3. Estimation of temperature

Surface temperature of the test piece was estimated using the continuum spectra of SiC ablation at point [b] and black body radiation function. Figure 11 shows the spectra at the point compared with the black body function for three brightness temperatures. It is apparent that the agreement is very well for $T = 3,600K$ in the wavelength region of 250 to 400nm. Therefore, the temperature was estimated to be 3,600K at the present time. This is higher than the decomposition temperature of SiC, 2,818K$^7$. Further investigation is needed to obtain more precise temperature.

### 4.4. Weight losses and weight loss rates

In our previous studies, weight loss and weight loss rate were measured to know the ablation properties of SiC in air plasma frejett. The weight loss and weight loss rate were calculated from Eqs. (2) and (3), respectively,

\[
W = (w_1 - w_2) / A, \quad (2)
\]

\[
\dot{m} = W / t, \quad (3)
\]

where $W$ is the weight loss per unit area, $w_1$ is the weight of a test piece before experiment, $w_2$ is the weight of the test piece
after experiment, $A$ is the cross-sectional area of a test piece before experiment, $m$ is the weight loss rate per unit area, and $t$ is the elapsed time since the heating started. Figure 12 and 13 show the weight losses and weight loss rates measured, respectively, at the distance of 5mm from nozzle exit. Here, the horizontal axis is the elapsed time, common to both the figures. The vertical axis is weight loss in Fig. 12 and weight loss rate in Fig. 13. The weight loss in the figure increases almost linearly to elapsed time. In contrast, the weight loss rate is almost constant until elapsed time of 15sec, but increases gradually from 15 to 20sec. The changes in the weight loss rates are thought to be due to initial temperature elevation of the test piece, change of the flow field by nonuniform ablation of the test piece and change of the surface condition of the test piece by attachment of ablation products. As mentioned in the spectroscopic measurements, $C_2$ molecular bands were observed. The $C_2$ molecule is formed by a recombination reaction of two $C$'s produced by the decomposition of SiC. Thus there may be some correlation between the weight loss rate of SiC and the intensity of $C_2$ bands. If it is true, it will be valuable to measure the time-variation of the band intensity of $C_2$ molecule spectroscopically.

5. Conclusions

In order to investigate SiC ablations in detail, spectroscopic measurements were performed at three points around ablating SiC in air plasma freejets. At first chemical species were identified and the relation between chemical species and measuring point were discussed. The brightness temperature of the surface of the test piece was also estimated by fitting the black body function to the experimental continuum spectra from the test piece. In addition, it was pointed out that time-variation in the weight loss rate of SiC may be due to the some factors relevant to heating process, flow change, surface condition of the test piece, and so on.

Main conclusions were as follows.

(1) During SiC ablation, strong radiation around the heat of the test pieces and the pale greenish radiation in the rear of it were observed.

(2) Spectra measured at each point were quite different with each other in distribution and in intensity. Continuum and Si atomic line appeared in common. The other molecular bands and atomic lines observed were different by measuring point.

(3) The spectra obtained just upstream of the tip of the test piece was considerably similar to those of air plasma freejet but contained the chemical species originated from the test piece too.

(4) The spectral intensity obtained at the point $x = 7$mm was much stronger than those at the other points in the whole wavelength range measured. It was interpreted that the spectral intensity contained mainly the spectra from the test piece heated to high-temperature. From fitting between the spectra at this point and the black body radiation function, brightness temperature of the surface of the test piece was estimated at 3,600K.

(5) Strong $C_2$ molecular bands appeared around 470 and 520nm at $x = 8.5$mm and $y = 1.5$mm. It was suggested that this molecular band was the cause of pale greenish radiation and that $C_2$ molecules were formed through recombination reaction of two $C$'s originated from SiC ablation.

References