Study on plasma ablation behavior of C/C composite materials under particle erosion

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Abstract. In order to explore the ablation law and characteristics of carbon/carbon composite materials on the surface thermal protection of hypersonic vehicles under the condition of particle erosion, the ablation test of a 4D C/C composite was carried out based on a small plasma simulated ablation test system. Four sets of experiments were designed according to different temperature and particle concentration. After the test, two kinds of ablation rate were measured, and the microscopic ablation morphology was observed by scanning electron microscope (SEM) and the ablation behavior was analyzed. The results show that, under the equivalent test conditions, the rate of jet temperature increases, and the material ablation rate increases. With the increase of particle concentration, the two kinds of ablation rate of materials increased, the maximum mass ablation rate was 0.0363 g•s⁻¹, and the line ablation rate was 0.053 mm•s⁻¹. The temperature affects the thermal erosion rate of the material, while the particle mainly causes mechanical erosion. The particle has a coupling effect of heat transfer and mechanical destruction on the material, and the material ablation is intensified. Moreover, due to the strong corrosion resistance of carbon fiber, the overall corrosion resistance of materials has obvious anisotropy.

1. Introduction

The hypersonic vehicle is subjected to severe aerodynamic heating during the flight. With the improvement of equipment performance, the surface thermal protection problem becomes more prominent. In the air, there are raindrops, ice crystals, dust and other particles. The particle hits the surface of the material with relatively high relative speed, which seriously affects the service life of the thermal protection material. These problems require the materials not only have good thermal performance, but also have good corrosion resistance. All mentioned problems must be taken into consideration when conducting material assessment.

C/C composite materials have the characteristics of high ratio strength, high ratio modulus, high temperature mechanical properties and excellent ablation performance under low oxygen enrichment conditions, has been widely used in the fields of solid rocket motor nozzle, missile end, wing leading
edge, et al [1]. It is a key problem to test the ablation behavior of materials based on actual flight conditions in the field of thermal protection of hypersonic vehicle.

In order to study the ablation mechanism of C/C composite materials, a large number of ablation experiments were conducted on the ablation behavior of various C/C composite materials. There are several methods: actual flight test, numerical simulation calculation [2], simulation experiment of small solid rocket engine [3], simulated ablation experiment of liquid rocket engine [4], oxy-acetylene ablation experiment [5], radiation heating simulation experiment [6], arc heating the wind tunnel [8], thermal plasma ablation experiment [9] et al. However, in different application fields, the actual conditions are quite different, so the appropriate assessment scheme should be selected according to the specific situation. Flight tests are most accurate, but expensive. The theoretical calculation makes the simulation more economical and convenient, but because of the complex ablation process and numerous shadow factors, it is generally used as the auxiliary proof of the experiment. Solid rocket engine simulation ablation experiment provides the environment similar to the flow field in the rocket, but the oxygen enrichment degree is not suitable for hypersonic flight. Liquid rocket engine simulated ablation experiment and oxygen-acetylene ablation experiment can provide high temperature and high speed flow. There are more controllable variables, but the temperature still cannot meet the requirements. The radiation heating simulation experiment can heat the larger thermal structure parts, but can't provide the corresponding airflow and particle conditions. Arc heating wind tunnel can provide more comprehensive ablation conditions, but the power consumption is larger.

In this paper, the ablation test was carried out on a type 4D C/C composite based on a small plasma multi-phase flow simulation ablation test system developed by the research group. It has high heat flux density and can add erosion particles. The line ablation rate and mass ablation rate were measured after the test. The ablation behavior of materials was analyzed according to macroscopic and microscopic ablation morphology, which provides reference for the study of ablation failure mechanism of C/C composite.

2. Test materials and methods

2.1. Specimen preparation
The experimental materials are 4D C/C composite materials weaved with carbon fiber and axial carbon rod. They are made by bituminous high pressure impregnated - carbonized dense process. As a piece of materials, it uses a thin carbon fiber rigid rod to form an axial (Z-direction) reinforcement network. In the x and y plane perpendicular to the axial direction, it is composed of a three-dimensional four-way precast, which is composed of a soft and hard blend of carbon fiber. Then the high density composite materials were prepared by multiple asphalt impregnation, carbonization cycle dense and high temperature graphitization.

According to the size of the test bench, the sample is processed into 100 mm x 100 mm x 10 mm square. The density is about 1.95 g/cm³.

2.2. Ablation test system and apparatus
The plasma multiphase flow ablation system uses argon as starting gas. Nitrogen is the main gas and carrier gas, hydrogen is auxiliary gas. The control cabinet regulates the mixed gas flow and delivers it to the plasma generator. After the gas is breakdown by the high-voltage electric spark, a large current with steep drop characteristics is output from the power cabinet to generate a plasma arc. Then it is accelerated by the Laval nozzle to form a stable plasma jet. The simulated particle (Al₂O₃ powder) is injected into the jet center through the powder injection component of the nozzle. The particle is mixed, heated and accelerated to form a test condition. The particle concentration can be adjusted within the range of 0 to 30%, and the ablation angle can be set to any value from 0 to 90° as required. The overall schematic diagram is shown in figure 1.

Al₂O₃ particles were prepared by crushing, and the size is about 50 μm to 70 μm. Figure 2 shows the micro-morphology of Al₂O₃ powder. The powder has irregular shape but relatively uniform size.
Experimental material analysis instruments include high-precision electronic balances, depth gauges, and scanning electron microscopes produced by the Czech company TESCAN with an accuracy of 3 nm.

![Schematic diagram of the experiment system](image1.png)

**Figure. 1 Schematic diagram of the experiment system**

![Morphology of the alumina powder](image2.png)

**Figure. 2 Morphology of the alumina powder (×500)**

### 2.3. Ablation test parameters

The test parameters are determined according to the characteristics of the aircraft re-entry environment. According to the atmospheric profile of the CIRA of Stickland A, the atmosphere at 25 km altitude is mainly \( \text{N}_2, \text{O}, \text{O}_2 \) and a small amount of \( \text{He}, \text{H}, \text{Ar}, \text{N} \). In flight, the tip material withstands a heat flux density up to 400 kW/m\(^2\), a temperature up to 8000 K, a surface gas temperature up to 3400 K, and erosion caused by cloud particles [10].

The particle concentration is the proportion of particles in the jet stream, and its calculation formula is as equation (1).

\[
\eta = \frac{G}{Q_1 \rho_1 + Q_2 \rho_2 + Q_3 \rho_3 + Q_4 \rho_4 + G}
\]  

(1)

\( Q_1 \) is the argon volumetric flow, \( \rho_1 \) is the argon density, \( Q_2 \) is the nitrogen flow, \( \rho_2 \) is the nitrogen density, \( Q_3 \) is the hydrogen volume flow, \( \rho_3 \) is the hydrogen density, \( Q_4 \) is the carrier gas volumetric flow, and \( \rho_4 \) is the carrier gas density. \( G \) is the mass flow rate of the injected jet particles.

Select the equivalent assessment parameters as shown in table 1. After calibration and simulation calculation, under the most severe conditions, the center temperature of the jet can reach 11500 K at a distance of 20 mm from the exit of the plasma generator, and the velocity of particles (at a particle size of 60 μm) is 226 m/s. In the latter two groups of experiments, \( \text{Al}_2\text{O}_3 \) simulated particles were added. The cooling water flow remained 1.02 m\(^3\)/h, and the main gas and auxiliary gas pressure were 0.8 MPa. Taking into account heat flux and particle erosion, the heat flow environment provided by the test system is basically in line with the test requirements of this heat-proof material.

### Table 1 Ablation test scheme for materials

| Samples | Ar flux(slm) | H2 flux(slm) | carrier gas flux(slm) | Arc current (A) | Arc voltage (V) | Particle conveyor voltage(V) | Ablation angle(°) | Test time(s) |
|---------|-------------|-------------|-----------------------|-----------------|-----------------|-------------------------------|------------------|-------------|
| 1       | 40          | 4.4         | 0                     | 452             | 69.2            | 0                            | 90               | 35          |
| 2       | 40          | 6.1         | 0                     | 452             | 69.2            | 0                            | 90               | 35          |
| 3       | 40          | 6.1         | 3.6                   | 452             | 69.2            | 7                            | 90               | 35          |
| 4       | 40          | 4.4         | 3.6                   | 452             | 69.2            | 7                            | 90               | 35          |

### 3. Results and discussion

#### 3.1. Ablation rate measurement

The line ablation rate \( R_d \) and mass ablation rate \( R_m \) of the material are calculated as:
\[ R_d = \frac{(d_1 - d_2)}{t} \]  \hfill (2) 
\[ R_m = \frac{(m_1 - m_2)}{t} \]  \hfill (3)

\(d_1\) and \(d_2\) indicates the thickness before and after ablation of the center of the sample. \(m_1\) and \(m_2\) indicates the mass before and after the ablation of the sample; \(t\) indicates the ablation time.

The final ablation rate of the test is shown in table 2.

| Samples | Average mass ablation rate. (g·s\(^{-1}\)) | Average line ablation rate(mm·s\(^{-1}\)) |
|---------|------------------------------------------|------------------------------------------|
| 1       | 0.0339                                   | 0.032                                    |
| 2       | 0.0352                                   | 0.043                                    |
| 3       | 0.0363                                   | 0.053                                    |
| 4       | 0.0346                                   | 0.039                                    |

Comparing groups 1, 2 and groups 3, 4, the results show that with the increase of the temperature and the speed of the plasma jet, the ablation rate of the material increase. Comparing groups 2, 3 and groups 1, 4, the results show that the erosion effect of particles on the material is obvious under the same temperature conditions. The line ablation rate and the mass ablation rate of the additive particle samples are both greater than the samples without particle addition.

In particular, the line ablation rate and mass ablation rate of the third group of specimens are larger than other groups, and are larger than the linear sum of the temperature increase and the particle addition alone. Analysis believes that firstly the state 3’s ablation/erosion coupling environment is harsher than the state 1’s pure jet environment, secondly the carbon fibers are distributed on the XY plane along 120°, 240°, and 360°. Its anti-ablation performance is better than that of the parallel-distribution fine carbon fiber rigid rod XZ plane.

3.2. Microscopic morphology analysis

3.2.1. The xy plane morphology analysis under state 1. Because the working gas of the plasma generator is argon and hydrogen, the ablation behavior of C/C composite in the jet environment is dominated by thermodynamic ablation under non-oxidizing conditions. Figure 3 as sample 1 ablation area SEM figure, there is an obvious pit on the surface of the ablation area. According to the ablation surface morphology characteristics, the ablation surface can be divided into four zones: ablation center, transition zone, marginal zone and external thermal influence area. In this case, the ablation center area is the center of the sample surface, which corresponds to the plasma jet center. The center has the highest temperature and the most severe ablation. Around the center is a transition zone, where the plasma jet’s affect is weakened.

![Figure 3 sample 1 ablated area SEM image](image)

The samples of the ablation center area and the ablation edge area were selected for SEM morphology observation.

In the ablative center region, the matrix carbon has been ablated firstly (figure 4(a)). The ablated end of the axial carbon fiber becomes blunt, irregular in shape, and the diameter of the fiber is
significantly reduced. The surface XY fiber shows relatively smooth, pits were generated, and the fiber gap become larger (figure 4(b)). The main cause of the pit is the microporous defect of fiber itself, which burns faster during ablation.

In the ablation edge region, there is an obvious interface preference ablation phenomenon and an obvious interfacial gap between carbon fiber and the surrounding carbon matrix (figure 5 (a)). Z-axis carbon fiber top is flat. The surface XY fibers are severely ablated, sharpened sharply, and they are tapered. The surface of the fibers becomes rough (figure 5(b)).

![Figure 4](image1.png)

**Figure 4** Sample 1 Ablation Center Area

![Figure 5](image2.png)

**Figure 5** Sample 1 ablation marginal zone

3.2.2. The xy plane morphology analysis under state 2. Figure 6 and figure 7 show the microstructure of the ablated central region and the ablated edge region of the sample 2 in the jet 2 state respectively.

In the ablative center region, the interface is ablated preferentially. There is a clear interface gap between the carbon fiber and the surrounding carbon matrix and the carbon ablation surface of the substrate is relatively flat. The carbon fiber end of axial fibers bundle are irregular, with many pits (figure 6(a)); The surfaces of XY fibers are severely ablated, the remaining fiber diameters become significantly smaller, appearing as needles and cones, the spacing between the fibers is significantly enlarged (figure 6(b)).

In the ablative edge region, the substrate carbon ablation is a little serious, and the interfacial interface between the fibers and the matrix is ablated. A pit appears at the end of the z-axis carbon fiber tip (figure 7(a)). The XY fibers in the surface layer are severely ablated, most of the fibers are burnt away, and the remaining fiber ends are in cone shape (figure 7(b)).
3.2.3. The xy plane morphology analysis under state 3. In state 3, Al$_2$O$_3$ particles were injected into the plasma jet, and the sample is subjected to ablation and erosion. Figure 8 and figure 9 show the microscopic appearance of the ablation center area and edge area of the sample respectively.

In the ablation/erosion center area, the carbon in the matrix is basically abrogated. The carbon fiber ends in the axial fiber bundle are irregular, and most of the fiber edges are washed away (figure 8 (a)). The XY-direction fiber ablation/erosion of the surface layer is more serious than that of the state 2, the inter-fiber spacing is significantly enlarged, the bottom fiber is rough and the image is gloomy, and the grooves left by the particles can be seen (figure 8(b)). In the ablative edge region, the carbon erosion of the matrix is most serious, the ablation/erosion of the Z-direction carbon fiber is uneven (figure 10(a)). After the XY-direction fibers are ablated/eroded, they become needle-pointed, and part of the surface fibers are washout by particle jet. Lamellae-like residues are attached to the surface of the XY transverse fiber bundles. They were caused by the stripping of the fibers (figure 9(b)).
3.2.4. The xz plane morphology analysis under state 4. Figure 10 and figure 11 are the microscopic morphology of the ablation center area and the ablation edge area under the state 4. The total ablation degree is between state 1 and state 3. In contrast to the foregoing conditions, due to multi-point ablation/erosion, the fibers arranged perpendicular to the jet are more likely to be broken off under the Complex multiphase flow. However, end-face ablation/erosion occurs when the fibers are parallel to the jet.

Some white particles can be observed on the ablation surface. With the help of EDS spectrum analysis, we find they are a small amount of deposits formed by Al₂O₃ particles melting and accelerating in a high-temperature and high-speed plasma jet, striking the ablated surface, and then combining with carbon substrates or fibers.

In particular, as shown in figure 12, cracks were observed on the ablated surface after ablation/erosion of the XZ plane. This is because during the flushing process, the particles obtain kinetic energy in the jet, then violent collision occurs between the particles and the matrix, the surface destruction of the carbon matrix is intensified, and cracks are generated. At the same time, the thermal stress in the flushing process will aggravate the crack propagation.
3.3. Material ablation/erosion results and mechanism analysis

Comparing the ablation results of state 1 and state 2, we find that by increasing the flow of hydrogen gas (increasing the velocity and temperature of the plasma jet), the carbon fiber and the matrix carbon were ablated more severely, and pits appeared on the axial surface of the axial carbon fiber. The lateral fibers became significantly thinner and sharper under the state 2.

Comparing the ablation results of the XY surface of the C/C composite materials in state 2 and state 3 (particles injected), we can find that as a result of the erosion of the particles, the ablation degree of the matrix carbon and carbon fiber in state 3 is significantly increased. The matrix carbon is essentially ablated. The diameter of the Z-direction fiber is significantly reduced, and the shape of the end face is irregular. The mechanical destruction of particles cannot be ignored. The erosion of particles in high-temperature and high-speed jets is even dominant.

As shown in figure 13, it is generally considered that the ablation begins with the interface between the carbon matrix and the carbon fiber. In the atmosphere, the central area is mainly thermodynamically ablated, and from the center to the edge, it is gradually transformed into thermochemical ablation, accompanied by the dissociation of nitrogen and the reaction of carbon and nitrogen [11]. Due to the diversity in the physical and mechanical properties of the carbon fiber and the matrix carbon, thermochemical ablation and particle erosion of the surface of the materials will lead to varying degrees of increase of the surface roughness. Meanwhile, as the decrease of jet’s radial temperature and velocity, the momentum of the particles in the jet also decreases. Therefore, the mechanical fragility of the particles decreases. However, the plasma jet is parallel to the ablated surface in this area, and the aerodynamic shearing effect is increased. Therefore, the shearing and erosion effect of the material in the jet is obvious in this region.

At the same time, the entrained oxygen in high-velocity jets also participates in the oxidation reaction with carbon, consuming part of the carbon matrix and carbon fibers [12]. Since a small amount of hydrogen is added to the plasma jet, there may also be a certain thermochemical reaction of carbon and hydrogen in the area.
4. Conclusion

The plasma ablation/erosion behavior of C/C composites under particle erosion conditions includes thermochemical reaction between the surface of the material and the ambient air flow, sublimation of carbon, high-speed particle erosion, and airflow mechanical erosion. The maximum mass ablation rate was $0.0363 \text{ g s}^{-1}$, and the line ablation rate was $0.053 \text{ mm s}^{-1}$.

Because the density of carbon fiber is larger than that of carbon matrix, and the density of carbon rod is larger than that of carbon fiber yarn, the material's axial (Z-direction) ablation/erosion resistance is obviously better than that of XY direction. This type of material reflects the anisotropy of ablation resistance.

The role of particles in the test process can be divided into particle heat transfer and particle mechanical destruction. The mass transfer of particles in the jet depends on the energy of the jet itself. When the velocity and temperature of the jet are high, the ablation/erosion process of the particles is accompanied by the combined effect of heat transfer and mechanical damage.

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