



Modeling ablative behavior and thermal response of carbon/carbon composites



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ABSTRACT

Carbon/carbon composites usually work in complex thermo-chemical environments, surface recession is thus inevitable due to chemical ablation and further affects the system stability and safety. In this paper, a model for chemical ablation of the materials which accounts for the effects of non-uniform temperature and pressure is proposed. As an application, the surface recession of a carbon/carbon composites leading edge structure are simulated in detail. The results show that the non-uniform distributed pressure plays an important role in the final ablation configuration. The effects of altitude and oxidation protection on the chemical ablation are discussed as well.

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1. Introduction

Carbon/carbon composites, due to their excellent thermo-physical properties and low densities, have found extensive applications in rocket nozzles, aero plane braking disks, and thermal protection systems of atmospheric re-entry vehicles [1–3]. Use of such composite components would reduce the structure weight for increased payload and enhance the reliability of the system. However, a challenge arises from the complex thermo-chemical environments in which the structures are working. The hostile thermo-chemical constraints give rise to heterogeneous oxidation reactions between carbon and oxidizing species such as H₂O, CO₂, and O₂ from the hypersonic flow, causing undesirable surface recession [4–8], degradation or micro-damage [9,10] of the materials by chemical erosion or ablation. In addition, the surface and interface defects produced by the chemical reaction may result in mechanical erosion. Existing studies indicate that thermo-chemical ablation is the primary cause for surface recession [11], while the effect of mechanical erosion is secondary for advanced carbon/carbon composites with high-density. Accordingly, understanding the mechanism of thermo-chemical ablation is a key from the view point of structure design.

Great efforts have been made to minimize chemical ablation so as to improve the system stability and safety. In addition to experimental explorations [12], numerical models have also exploited to predict the oxidation erosion of carbon/carbon composite materials and structures. A thorough literature review on numerical characterization of ablative materials used for different military and aerospace applications was given in Ref. [13]. To solve the chemical ablation problem for charring or carbon based materials, several approaches [14–16] were developed to calculate the temperature of body and the surface recession caused by chemical ablation. These studies essentially regarded the oxidation reactions of chemical ablation as equilibrium processes, implying that the oxidation species are consumed completely at the gas–solid surface and thus the reactions are fully controlled by the diffusion rate of the reactants. However, experiments [1,2,17] confirmed that the oxidation reaction of carbon/carbon materials at lower temperatures is a non-equilibrium process with the reaction rate in the Arrhenius form. Only at higher temperatures the oxidation reaction is controlled by the diffusion rate of the reaction species. This fact was simulated by some later researches where the non-equilibrium nature of reaction process was taken into account [18]. In particular, by distinguishing the kinematics and diffusion-controlled regimes, the whole chemical reaction process of carbon/carbon materials was formulated [19].

Besides the correlation with temperature, the oxidation reactions in the chemical ablation of carbon/carbon composites are also

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dependent on the concentration of reaction gases at the surface, which is related to the local pressure [20–22]. In practical applications, the complex local fluid field near the composite structure leads to non-uniform temperature and gas pressure on the surface, thereby giving rise to non-uniform chemical reaction. Nevertheless, most of the existing models are focused on one-dimensional cases [14–16,19] in which the temperature effect is involved but the pressure is presumed constant. Though these models can provide the thermal and ablation information at some positions such as where being most seriously ablated, they are hard to be used to predict the overall erosion configuration of the structure.

Motivated by the above reasons, a chemical ablation model for carbon/carbon composites is developed in this paper to incorporate both effects of non-uniform temperature and pressure. As the application, the thermal and ablation behaviors of a leading edge structure are simulated. Quantitative evaluation of the structure response at different altitudes is performed, and the influence of a possible oxidation protection is discussed.

2. Model and algorithm

The ablation of carbon/carbon composites is a coupled thermo-chemical process which involves complex heat and mass transfers. Toward a quantitative modeling, the following aspects will be confronted with. First, a transient thermal analysis is needed to provide the temperature field due to incoming heat flux in any time. Next, a chemical ablation model is required to predict the surface recession rate. Finally, a suitable numerical approach is necessary to tackle the evolution of the moving boundaries.

2.1. Transient thermal analysis

A carbon/carbon composite structure may suffer complicated thermal conditions such as aerodynamic heating and radiation flux. To analyze the chemical ablation, the first step is to obtain the transient temperature field T . In the rectangular Cartesian coordinate system (x, y, z) , the general form of differential equation governing the transient temperature is given by

$$\rho_c C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[k_x \frac{\partial T}{\partial x} \right] + \frac{\partial}{\partial y} \left[k_y \frac{\partial T}{\partial y} \right] + \frac{\partial}{\partial z} \left[k_z \frac{\partial T}{\partial z} \right] \quad (1)$$

where ρ_c is the material density, C_p is the heat capacity, and k_x, k_y, k_z are the heat conductivity components in the global directions.

The associated boundary conditions for (1) can be specified according to energy balance on the structure surface. Fig. 1 illustrates the current configuration of the receding surface of the structure during ablation, where the dashed line stands for a control volume of infinitesimal thickness [7,23]. The energy fluxes leaving the control volume include the conduction q_N into the materials and the radiation $q_{rad-out}$ away from the surface. The latter takes away by the ablation mass ejector heat flux $\dot{m}_w h_w$, with \dot{m}_w being the materials oxidation rate and h_w the gases enthalpy of reaction product. The inputting energy fluxes involve the conduction q_w from the gas boundary layer, the radiation q_{rad-in} from the

gas boundary layer, and the enthalpy flux $\dot{m}_w h_{cs}$ absorbed by oxidation reaction. Here h_{cs} is the reaction enthalpy. Therefore, the conduction energy fluxes q_N which provides the link to the in-depth heat transfer equation can be written as

$$-k \frac{\partial T}{\partial S} = q_N = q_w - [\dot{m}_w h_w - \dot{m}_w h_{cs}] + q_{rad-in} - q_{rad-out} \quad (2)$$

where the term in the square bracket means energy variation caused by the chemical reaction and the values of h_w and h_{cs} can be gathered from literature [23]. In most cases the influence of the radiations q_{rad-in} and $q_{rad-out}$ on the ablation process is not significant and thus is neglected. In contrast, the conduction q_w is a vital parameter which varies with the wall temperature and can be expressed by [20].

$$q_w = C_h (T_r - T_w) \quad (3)$$

Here, C_h is the convective heat transfer coefficient, T_r is adiabatic wall temperature, and T_w is the solid wall temperature. The value of C_h and T_r can be obtained from the flow field analysis with the help of computational fluid mechanics software (FLUENT). Consequently, q_w can be updated dynamically with the wall temperature in the heating and ablation process.

2.2. Model of oxidation ablation

Following Refs. [1,19], the oxidation reaction is controlled at low temperatures by reaction kinematics rate, while at higher temperatures by the diffusion rate of gaseous oxygen. Thus, the chemical ablation of carbon/carbon composite should be divided into two regimes [19], reaction kinematics rate controlled and diffusion rate controlled regime.

In the kinematics rate controlled regime, the oxidation reaction rate is determined by

$$\dot{m}_{C, ch} = 12 \times A \times \exp\left(-\frac{E_a}{RT_w}\right) \times C_{O_2} \quad (4)$$

where A is a constant, T_w is the solid wall temperature, C_{O_2} is the concentration of oxygen, E_a is the activation energy, which changes depending on the level of oxidation protection. In the diffusion rate controlled regime, the oxidation rate is determined by the diffusion rate of gas species as [19],

$$\dot{m}_{C, d} = 12 \left(\frac{2\varphi + 1}{\varphi + 1} \right) N \quad (5)$$

in which φ is the ratio of produced CO and CO₂ and N is the diffusion rate of oxygen through boundary layer. The expressions of φ and N are given by

$$\varphi = \frac{\sqrt{1 + 0.3215 \exp(868/T_w)} - 1/0.7656 \exp(868/T_w)}{0.21 - \sqrt{1 + 0.3215 \exp(868/T_w)} - 1/0.7656 \exp(868/T_w)} \quad (6)$$

$$N = 2.07 \times 10^{-6} \frac{P}{P_i} \frac{P_{og}}{R} \frac{T_w^{0.8}}{d} \left[\frac{2422.77 (\rho du)^{0.7}}{T_w^{0.55}} + 3.95 \right] \quad (7)$$

where P is the total pressure, P_{og} is the pressure of oxygen in the bulk air, P_i is the logarithmic pressure of inert, R is universal gas constant, d is characteristic dimension, u is flow velocity of air around the body, and ρ is the density of air. Some of the parameters are functions of altitude.

In the whole ablation process, the lower one of the reaction kinematics rate and the diffusion rate plays the dominating role and is used as the oxidation rate. Depicted in Fig. 2 is the variation of the oxidation rate with temperature at $P = 1$ atm. It is clear that the critical temperature appears at about 1150 K, implying that the

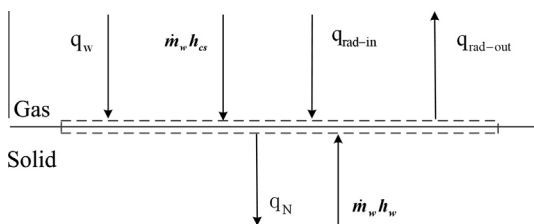


Fig. 1. Energy fluxes over the ablation interface layer.

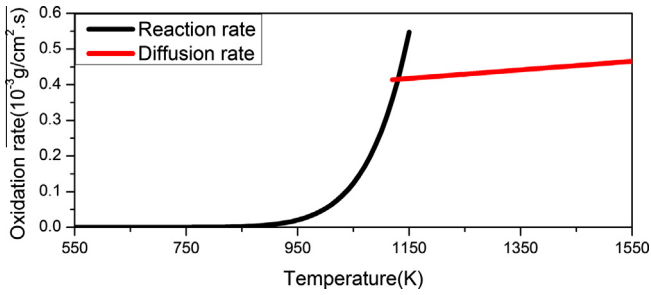


Fig. 2. The relation between oxidation rate and temperature.

oxidation reaction is controlled by reaction kinematics rate and diffusion rate, respectively, at temperatures lower and higher than 1150 K. As mentioned before, the pressure on the structure surface is non-uniform and also affects the chemical ablation behavior. In light of (4) and (5), it can be assumed that the oxidation rate is linearly dependent on the pressure in both regimes. Therefore, once the temperature and pressure distribution on the surface are determined, the oxidation behavior of the carbon/carbon composites can be calculated.

2.3. Tackling of moving boundary

With the calculated oxidation rate, the surface recession rate can be obtained from

$$\dot{R}_w = \frac{\dot{m}}{\rho_c} \quad (8)$$

where ρ_c is the density of material and \dot{m} is the mass ablation rate. To tackle the moving boundary, the surface recession depth at a surface node ΔR_w is obtained by the product of recession rate \dot{R}_w and the time increment Δt at each time step. Then the boundary nodes are moved inward along the normal to the surface by the amount of ΔR_w . By remeshing the elements, the new configuration of structures can be determined.

The FEM analysis is performed by using the commercial FEM software ABAQUS. The value of ΔR_w is passed into the user subroutine UMESHMOTION in ABAQUS to update the new positions of the surface nodes. The new position of each surface node is given by

$$\begin{aligned} \text{new } x &= x - \Delta R_w \times l_x \\ \text{new } y &= y - \Delta R_w \times l_y \\ \text{new } z &= z - \Delta R_w \times l_z \end{aligned} \quad (9)$$

where l_x , l_y , l_z are the direction cosines.

The new meshes are determined by the mesh smoothing algorithm based on the Arbitrary Lagrangian–Eulerian (ALE) adaptive meshing technique. It is noted that in remeshing the elements this technique helps controlling element distortion but sacrifices the accuracy. For example, the node movement with velocity of 1 mm/s for 1 s should be 1 mm, which is different from the computed result of 0.026 mm after remeshing by ALE. The problem

can be resolved by adjusting the time increment Δt . Indeed, as shown in Table 1, with decreasing values of Δt , the computed node displacement becomes continuously closer to 1 mm.

3. Results and discussions

3.1. The thermal and ablation response of the leading edge structure

The proposed model now is used to analyze the ablation behavior of a carbon/carbon composite leading edge structure. As shown in Fig. 3, the structure owns a blunt leading with curvature radius of 0.125 mm and included angle 13° , suffering a hypersonic flow with $Ma = 6$. The related materials parameters are taken as $\rho_c = 1800 \text{ kg/m}^3$, $C_p = 840 \text{ J/(kg K)}$ and $k_x = k_y = 15 \text{ W/(m K)}$. The parameters of coming air conditions are coming from that at the altitude of 24 km. By using FLUENT, the convective heat transfer coefficient C_h and adiabatic wall temperature T_r are obtained. At each time step, the heat flux q_w calculated by C_h , T_r and T_w is input to the FEM model (ABAQUS) to solve the heat transfer equation of the leading edge structure. In the meantime, the non-uniform pressure on the structure surface is calculated to gather the oxidation reaction rate. Then the surface nodes are moved to new positions along the normal to the surface to form the new surface configuration. For comparison, the results based on the existing one-dimensional model will also be given, where the ablation rate is assumed only dependent on the wall temperature and the pressure is set to be that at stagnation point (the most serious ablative position).

Fig. 4(a) plots the calculated morphology of the leading edge structure after the ablation of 10 s. It is seen that serious erosion occurs mainly in the region near the stagnation, in accordance with the prediction relying on an empirical model [6]. If the pressure is assumed constant, the whole ablation surface, including the leading edge and the side, is eroded seriously, as illustrated in Fig. 4(b). Similar phenomenon can be found for the recession depth as depicted in Fig. 5, where the result of the present model and that based constant pressure assumption are compared. Note that the abscissa in the figure means the node index numbered from 1 to 165 along the upper surface path, with the number 1 denoting the stagnation point and the number 165 the other end.

Given in Fig. 6 are the surface temperature distributions at different times. The predictions by the present model (solid lines) and by that assuming uniform pressure (dashed lines) exhibit similar feature and almost coincide at $t = 0.5 \text{ s}$ and 1 s . The difference between them is not large even for longer time. Because more energy is taken away due to more serious erosion, the temperature is a little lower for uniform pressure case. At $t = 10 \text{ s}$ the temperature is above 1150 K in most part of the surface, thus the oxidation rate is diffusion rate controlled there. In this regime the reaction rate is not sensitive to temperature, as demonstrated in Fig. 2, but depends on the gas pressure. Fig. 7 shows the distribution of the pressure on the ablating surface, obtained from the present model via FLUENT. The pressure is much higher near the stagnation point than elsewhere. This explains why the final ablation morphology predicted by the present model (Fig. 4(a)) differs from that based on uniform pressure assumption (Fig. 4(b)). In other

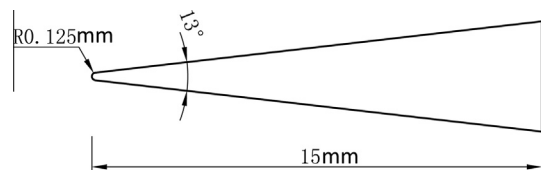


Fig. 3. The schematic sketch of the carbon/carbon composite leading edge structure.

Table 1
The effect of time increment on the ALE adaptive meshing.

Δt (s)	Displacement(mm)	Errors(%)
1	0.026	97.4
0.1	0.874	12.6
0.01	0.964	3.6
0.001	0.973	2.7

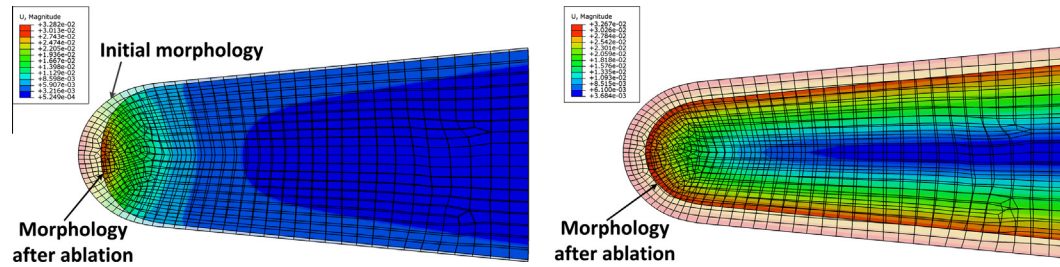


Fig. 4. The ablation morphology of (a) the temperature and pressure-dependent ablation model; (b) the temperature-dependent ablation model(uniform pressure).

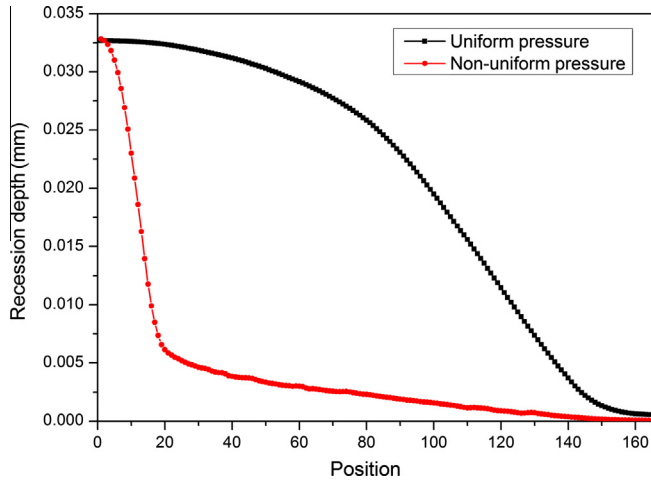


Fig. 5. The recession depth along the surface of carbon/carbon composite leading edge structure.

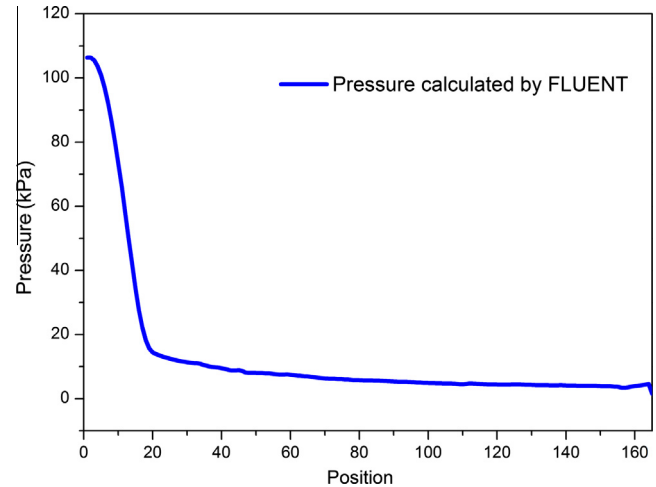


Fig. 7. Pressure distributions along the surface of the carbon/carbon composite leading edge structure.

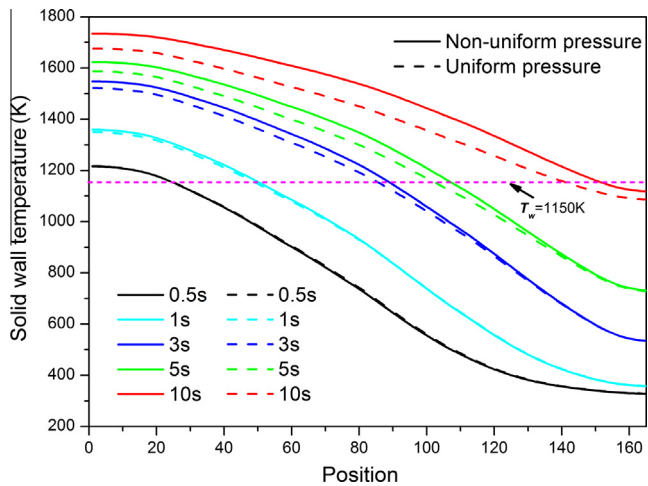


Fig. 6. The wall temperature along the surface of the carbon/carbon composite leading edge structure (The solid lines represent the predictions by the present model and dashed lines by that assuming uniform pressure).

words, it can be concluded that the non-uniformity of pressure strongly affects the process of ablation.

3.2. Effect of altitude

As shown in Table 2, the ambient temperature, pressure of air would change with altitude [24], which have greater influence on the chemical ablation. A study is carried out to focus on the ablation behaviors of carbon/carbon composite at different altitude.

The ablation morphologies of the leading edge at $H = 0, 10$ and 24 km are shown in Fig. 8. It is observed that the erosion is quicker at lower altitudes, and the surface recession depth reduces with increasing altitude. The erosion in the case of $t = 0.312$ s and $H = 0$ is even of the same order as that in the case of $t = 10$ s and $H = 24$ km. The calculated temperature, pressure and the recession depth at the stagnation point at $t = 0.312$ s are shown in Table 3. It can be shown that the temperature and pressure of the structure surface increase with decreasing altitude, finally leading to more serious erosion.

3.3. Effect of oxidation protection

As discussed above, the unprotected carbon/carbon composite will be ablated severely at relatively lower temperatures. This causes insecurity of the structure for continuing usage. Accordingly, to enhance the oxidation resistance, some strategies for oxidation protection are usually utilized. In the following, the present model will be applied to analyze the chemical ablation behavior of the oxidation protecting materials through matrix modification [17,25].

In the thermal-oxidative condition, the modifiers react with oxygen to form oxides which inhibit reaction. The usage of the matrix modifiers slow down the oxidation reaction kinematics rate. The difference between matrix-modified and unprotected carbon/carbon composites comes from the activation energy. The activation energy when using modifiers ($E_a = 56$ kcal/mol) is larger than that of the bare carbon/carbon composite ($E_a = 35.7$ kcal/mol), meaning that the reaction with modifiers is difficult to happen. The oxidation rate is shown in Fig. 9, where the critical temperature is at about 1780 K for the matrix-modified carbon/

Table 2

The air temperature, pressure at different altitude.

Flight altitude (km)	Temperature (K)	Pressure (kPa)
0	288.15	101.32
10	223.15	30.96
24	220.65	2.93

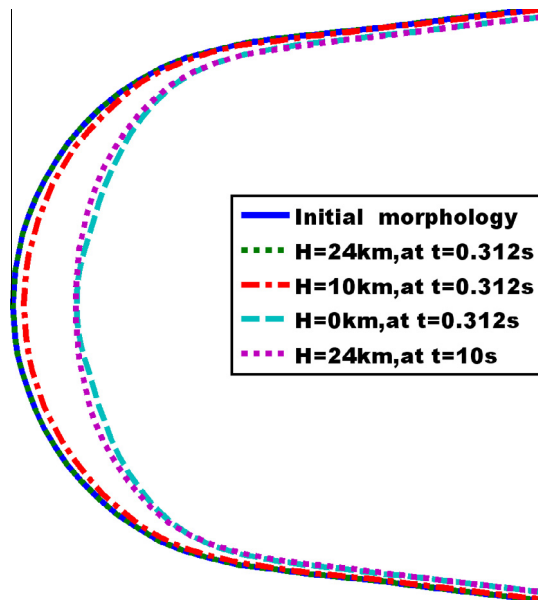


Fig. 8. The ablation morphology of carbon/carbon composite leading edge structure at different altitude.

Table 3

The temperature, pressure and recession depth of the stagnation point at different altitude.

Altitude (km)	Temperature (K)	Pressure (kPa)	Recession depth (mm)
0	1584	4128.5	3.0×10^{-2}
10	1199	1322.8	5.1×10^{-3}
24	932	135.1	5.7×10^{-6}

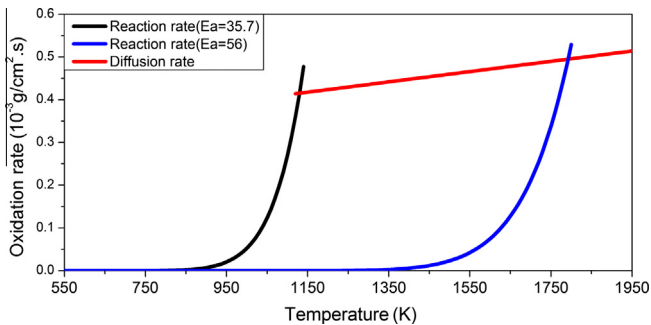


Fig. 9. The oxidation rate of matrix-modified carbon/carbon composites.

carbon composite. Hence the oxidation reaction is controlled by reaction kinematics rate when the temperature is lower than 1780 K, and by diffusion rate when the temperature is higher than 1780 K.

As shown in Fig. 10, the surface recession of the carbon/carbon composite with modifiers is much smaller than that of the bare one. When using modifiers, the largest erosion at the stagnation point is reduced about 73.8%, from 2.4×10^{-2} mm to 6.3×10^{-3} mm. The result clearly shows the efficiency of applying oxidation protection to improve the ability of erosion resistance.

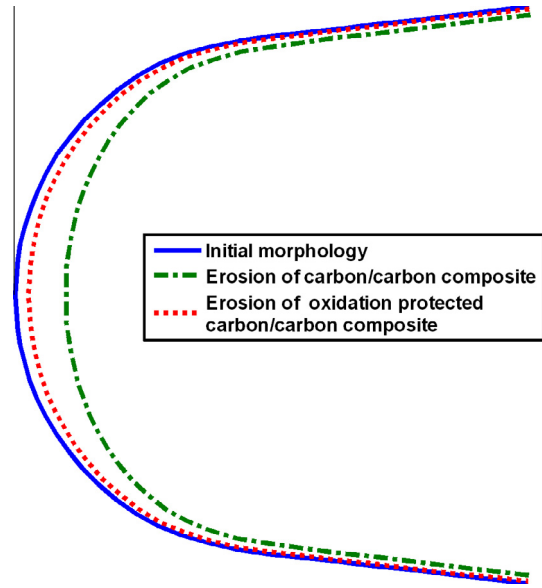


Fig. 10. The effect of matrix modifiers on the ablation of carbon/carbon composite leading edge structure.

4. Conclusion

A new model for chemical ablation of carbon/carbon composite structures has been proposed. The outstanding feature of the model that differs from the previous ones is that both effects of non-uniform temperature and pressure are incorporated. Numerical example for surface recession of a carbon/carbon composites leading edge, indicates that the region near the stagnation point of the leading edge is eroded more seriously than elsewhere. This is consistent with the existing experimental observation and shows the reasonability of the present work. The model has also been applied to examine the effect of altitude on ablation and the efficiency of oxidation protection by matrix modifiers. The results are believed of significant importance in practical applications.

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