INSIGHT INTO CHEMICAL REACTION KINETICS EFFECTS ON THERMAL ABLATION OF CHARRING MATERIAL

by

Jie XIAO, Lin JIANG^{*}, and Qiang XU

School of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing, China

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Thermal ablation plays an important role in the aerospace field. In this paper, to study the chemical kinetics effects on heat transfer and surface ablation of the charring ablative material during aerodynamic heating, a charring ablation model was established using the finite element method. The AVCOAT 5026-39H/CG material, one typical thermal protection material used in thermal protection system, was employed as the ablative material and heated by aerodynamic heating condition experienced by Apollo 4. The finite element model considers the decomposition of the resin within the charring material and the removal of the surface material, and uses Darcy's law to simulate the fluid-flow in the porous char. Results showed that the model can be used for the ablation analysis of charring materials. Then effects of chemical kinetics on ablation were discussed in terms of four aspects, including temperature, surface recession, density distribution, and mass flux of pyrolysis gas. The pre-exponential factor and activation energy have different effects on ablation, while the effect of the reaction order is little. This paper is helpful to understand the heating and ablation process of charring ablative materials and to provide technical references for the selection and design of thermal protection materials.

Key words: *ablation, charring material, finite element method, surface recession, chemical kinetics*

Introduction

For hypersonic vehicle and spacecraft, the design of thermal protection system is an important part to protect space vehicles from aerodynamic heating when they enter planetary atmosphere. The thermal protection system can effectively reduce or avoid the damage of the internal structural components of the vehicle by extremely high aerodynamic heating during hypersonic flight. For a typical low earth orbit re-entry vehicle, it can reach the maximum speed Mach 25 and maximum surface temperature 3000 K [1]. The AVCOAT 5026-39H/CG, an epoxy novolac resin with special additives in a fiberglass honeycomb, is often used as the thermal protection material. During the hypersonic re-entry, the charring ablative material is subjected to extremely high aerodynamic heating. On the one hand, it can avoid direct contact between the airframe or blunt body and the external heat flow, on the other hand, heat is consumed through the decomposition reaction of the ablative material, and the pyrolysis gas is released to the surface to reduce heat transfer, thus effectively protecting the internal structural components of the oxygen at the boundary of the material surface reacts with the solid carbon at high temperature, resulting in surface ablation, which can also effectively protect the internal structural components. In conclusion, the decomposition reaction within

^{*}Corresponding author, e-mail: ljiang@njust.edu.cn

the ablative material and the ablation of the surface carbon will eventually cause the material surface to recession and the initial thickness will be reduced [2-4].

A large number of researches were carried out on the charring ablation problem. Numerical methods such as CMA [5], FIAT [6], TITAN [7], and 3-D FIAT [8] are all based on the finite difference or finite volume methods. For example, Li et al. [9, 10] established a 1-D ablation model based on the central difference numerical method to study the thermal behavior of AVCOAT composites. Subsequently, Li et al. [11, 12] investigated the surface ablation of charring ablative materials during aerodynamic heating by thermal/fluid/chemical coupling analysis using central difference and upwind numerical schemes to discrete governing equations of surface ablation, and the effects of activation energy, frequency factor, composition of pyrolysis gas and diameter of single carbon fiber on surface ablation were analyzed. In addition, the effects of the gasification parameters and fiber volume fraction on coupling were also investigated. Moreover, Li et al. [13] calculated the effects of six different pore structures on ablation by thermal/fluid/chemical coupling analysis. Scoggins et al. [14] investigated the thermal and chemical non-equilibrium of ablation and pyrolysis of carbon-phenolic ablator by finite difference method. Based on the finite volume method, Lachaud et al. [15] developed a chemical equilibrium heat and mass transfer model for the porous ablative material, the boundary conditions and pyrolysis gas generated by heating of porous carbon-phenolic ablator were studied in details. Nowadays, finite element method has received more and more attention, because it has improved computational capability, better flexibility and applicability to complex geometries than finite difference and finite volume methods [16-18].

Charring ablative materials undergo decomposition during the heating process. Lattimer et al. [19] analyzed the decomposition process using Arrhenius law and heat conduction governing equations to obtain the mass change fraction, thermal properties and temperature distribution. However, the results of this method largely depend on the heating rate, which is different from the actual situation faced by aerodynamic heating. In addition, the recession of material surface cannot be obtained by this method. In order to obtain the recession of material surface, Li et al. [20] developed a model with a pyrolysis interface, which comprehensively considered the ablation of material surface and the internal pyrolysis, and the effects of different density distributions on ablation were analyzed. However, this model does not take into account the real situation between the virgin layer and the char layer, because the density and the enthalpy of pyrolysis gas change with heating time in this stage. In order to analyze the effect of this stage on ablation, Li et al. [21, 22] established a 1-D ablation model including the virgin layer, the pyrolysis layer, the char layer and the ablation layer and the effect of density on ablation was analyzed. It was found that not only external heat flux, moving interfaces and boundary affect the ablation result, but the change in density also affects the ablation, it was shown that the pyrolysis layer is essential in the 1-D ablation model.

In this paper, a 1-D charring ablation model was established using the finite element method, which considers the surface material removal and decomposition within material, and the sample was heated by aerodynamic heating experienced by Apollo 4 [23]. The decomposition reaction within the material can be analyzed using Arrhenius law to obtain the density distribution, heat and mass transfer can be represented by the heat conduction governing equation, thus the ablative material can be reasonably selected and used according to different needs. The energy balance on the material surface is due to the complex convection and radiation heat exchange between the material and the external flow, as well as the release of pyrolysis gas and the ablation of material surface. The basic mathematical model consists of four layers. It has been found through experimental and theoretical studies that the thermal properties of charring

materials change with the pyrolysis process [24-26]. In addition, the heat conduction equation with temperature dependent thermal properties are strongly non-linear [27-31].

Mathematical models

In the process of aerodynamic heating, the charring ablative material can absorb heat due to its own heat capacity. The surface temperature gradually increases with the heat absorption. When the temperature reaches the onset temperature, $T_{\rm bp}$, the resin within the material starts to pyrolyze. Subsequently, when the temperature increases to the complete pyrolysis temperature, $T_{\rm cp}$, the material is pyrolyzed completely, leaving a region of carbon fiber skeleton, resinous carbon, and coke as the main components, known as the char layer. When the temperature rises to the ablation temperature, $T_{\rm a}$, ablation and surface recession will occur on the material surface [9].

Since the temperature gradient perpendicular to the material surface is much larger than that in other directions [32, 33], a 1-D ablation model was established in this paper, as illustrated in fig. 1, which mainly studies the heat transfer process and the ablation characteristics.

In fig. 1, the charring material is heated by external heat flux. The L_0 is the initial thickness of ablator. From bottom to top, the charring ablator can be divided into four layers, which are the virgin layer, the pyrolysis layer, the char layer, and the ablation layer. The characteristics of each layer during ablation are briefly described below [23].

The virgin layer: the L_0 is the initial thickness of the virgin layer. The temperature of the layer is lower than T_{bp} and there is mainly heat conduction.



Figure 1. The 1-D ablation model

The pyrolysis layer: in this layer the temperature varies from $T_{\rm bp}$ to $T_{\rm cp}$. The main components of this layer are the porous deposited carbon and pyrolysis gases produced by the thermal decomposition of the resin, and to a lesser extent the permeable oxygen of the char layer and its oxidation reaction products, which is an unstable and complex region. In this layer, material pyrolyzes and releases mixed gases, among which solid carbon is gradually generating. The pyrolysis layer has two moving interfaces. There is heat conduction, pyrolysis gas-flow, and density change.

The char layer: the temperature of the layer is higher than T_{ep} , but lower than T_a . The layer is mainly composed of carbon fiber skeleton and resinous carbon remaining after pyrolysis and residual coke deposited after the secondary cracking of pyrolysis gas. Pyrolysis gas-flows through the porous carbon the material surface and releases. In addition, surface carbon and external oxygen undergo oxidation reaction at high temperature.

The ablation layer: the temperature of the layer is higher than T_a . The layer includes aerodynamic heating with convection and radiation, radiant heat dissipation from the ablation surface to the boundary-layer, and thermochemical ablation reaction heat between the flowing gases in the boundary-layer and the wall carbon and pyrolysis gases, respectively. The thermal blocking effect caused by the pyrolysis gas effectively reduces aerodynamic heating. In addition, the pyrolysis gas and combustion products change the temperature and velocity of the gas-flow. To facilitate the calculation, two assumptions are employed as:

- when the pyrolysis gas-flows through the porous char layer, there is no chemical reaction
 occurs between the pyrolysis gas and the porous char and
- there is no secondary cracking of the pyrolysis gas.

For 1-D ablation problem, the in-depth heat conduction equation that considers both material decomposition and surface ablation [34-38] can be expressed:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \left(h_g - \overline{h} \right) \frac{\partial \rho}{\partial t} + \dot{s} \rho C_p \frac{\partial T}{\partial x} + \dot{m}_g'' \frac{\partial h_g}{\partial x}$$
(1)

where ρ , C_p , and k are the density, specific heat, and thermal conductivity of the material, respectively, h_g – the enthalpy of the pyrolysis gas, \overline{h} – the mass weighted average of the enthalpy of the charring material, \dot{s} – the surface recession rate, m_g'' – the mass flux of pyrolysis gas, x – the co-ordinate, T – the temperature, and t – the time.

In eq. (1), both specific heat and thermal conductivity are temperature-dependent, and the temperature-dependent properties of the virgin and char layer can be calculated according to the mixture rule:

$$k = \delta k_{\rm v} + (1 - \delta) k_{\rm c} \tag{2}$$

$$C_p = \delta C_{p,v} + (1 - \delta) C_{p,c}$$
(3)

where subscripts v and c represent the virgin layer and the char layer, respectively, and δ – the volume fraction of the ablative material without decomposition:

$$\delta = \frac{\rho_{\rm v}}{\rho_{\rm v} - \rho_{\rm c}} \left(1 - \frac{\rho_{\rm c}}{\rho} \right) \tag{4}$$

As the ablative material is a composite material, it causes the density variation during decomposition, which follows the Arrhenius equation [23]:

$$\frac{\partial \rho}{\partial t} = -A \exp\left(-\frac{E}{RT}\right) \rho_{\rm v} \left(\frac{\rho - \rho_{\rm c}}{\rho_{\rm v}}\right)^n \tag{5}$$

where A is the pre-exponential factor, E – the activation energy, R – the universal gas constant, and n – the reaction order.

In addition, the mass weighted average of material enthalpy, \overline{h} , can be expressed:

$$\overline{h} = \frac{\rho_{\rm v} h_{\rm v} - \rho_{\rm c} h_{\rm c}}{\rho_{\rm v} - \rho_{\rm c}} \tag{6}$$

where h is the enthalpy of the charring material.

The enthalpy of pyrolysis gas can be described as the function of temperature:

$$h_{\rm g} = \int_{T0}^{T} C_{p,\rm g} \mathrm{d}T \tag{7}$$

On the basis of conservation of mass [19], assuming that the solid mass is much larger than that of the gas within the charring material, and the sample volume remains constant during the heating, there is:

$$\frac{\partial \dot{m}_{g}''}{\partial x} = -\frac{\partial \rho}{\partial t}$$
(8)

Therefore, the mass flux of pyrolysis gas at any location x during the heating can be written:

$$\dot{m}_{g}'' = -\int_{x}^{L_{0}} \frac{\partial \rho}{\partial t} dx$$
(9)

The pyrolysis gas generated during the heating is released outside of the material through the char layer. For fluid-flow in the porous media, the effect of the frictional resistance in the pores on gas-flow is considered using the gas-phase mass conservation equation:

$$\frac{\partial}{\partial t} \left(\rho_{\rm g} \varphi \right) + \frac{\partial}{\partial x} \left(\rho_{\rm g} \varphi \vec{\rm v} \right) = \rho_0 \dot{\omega}_{\rm g} \tag{10}$$

where φ is the porosity, \vec{v} – the velocity vector, and $\dot{\omega}_g$ – the gas reaction rate. According to eq. (10), the variation of pressure within the ablative material can be derived from Darcy's law.

Surface ablation will occur when the surface temperature of the charring material reaches the ablation temperature, T_a , and resulting in surface recession. In this paper, the grid moving speed is used to study the variation of the physical field when the material geometry changes with the parameters. During the ablation process, the linear ablation rate of the ablative material is constantly changing, which does not allow the surface to recede uniformly with time. The characterization of the linear ablation rate is usually done by dividing the ablated surface recession by the ablation time to get the average linear ablation rate, but this is not the true process of surface recession during the ablative material AVCOAT 5026-39H/CG based on the reaction-rate-control regime, which is obtained by fitting reasonable ground test data [23]. The removal of surface material can be obtained by combining the relationship of surface recession rate with temperature and eq. (1).

The initial temperature, pressure, and density are listed as follows, where the initial temperature and pressure are both ambient atmospheric values:

$$T_0 = 300 \text{ K}, P_0 = 1.013 \cdot 10^5 \text{ Pa}, \rho_0 = \rho_v$$
 (11)

For the upper surface of the ablative material:

$$-k_{\rm c}\frac{\partial T}{\partial x} = \lambda q - \sigma \varepsilon T_{\rm s}^{4} + \dot{m}_{\rm com}^{\prime\prime} h_{\rm com}$$
(12)

where σ is the Stefan-Boltzmann constant, ε – the surface emissivity, T_s – the surface temperature, m''_{com} – the mass flux of combustion of surface carbon, h_{com} – the enthalpy of combustion of surface carbon, and λ – the thermal blockage coefficient, which can be expressed [9]:

$$\lambda = 1 - 0.58 \left(\dot{m}_{gc}'' + \dot{m}_{com}'' \right) \frac{h_r}{q_{cold}}$$
(13)

where h_r – the recovery enthalpy, which can be expressed [9]:

$$h_{\rm r} = 3 \cdot 10^{-5} q_{\rm cold}^2 - 146 q_{\rm cold} + 2 \cdot 10^8 \tag{14}$$

The hot wall heat flux q can be given [9]:

$$q = q_{\text{cold}} \left(1 - \frac{h_{\text{s}}}{h_{\text{r}}} \right) \tag{15}$$

where h_s is the wall enthalpy [9].

On the basis of conservation of mass:

$$\frac{\partial \rho_p}{\partial t} = -\frac{\mathrm{d}\dot{m}_{\mathrm{gp}}''}{\mathrm{d}x} \tag{16}$$

$$\dot{m}_{\rm gc}'' = \dot{m}_{\rm gp}'' \Big|_{x = x_{cp}}$$
 (17)

The mass flux of combustion of surface carbon can be written:

$$\dot{m}_{\rm com}'' = \rho_{\rm c} \frac{\Delta x}{\Delta t} = \rho_c \dot{s} \tag{18}$$

For the lower surface of the ablative material:

$$-k_{\rm v}\frac{\partial T}{\partial x} = 0\tag{19}$$

In addition, the two moving interfaces are:

$$T = T_{\rm bp}, \ x = x_{\rm bp} \tag{20}$$

$$T = T_{\rm cp}, \ x = x_{\rm cp} \tag{21}$$

The incident heat flux adopts the aerodynamic heating condition experienced by Apollo 4. The heat flux is a function of time with two peaks. The first peak is 3.6 MW/m^2 at 75 senconds and the second peak is 0.8 MW/m^2 at 420 seconds [23].

Since the density of the charring material changes during aerodynamic heating, resulting in the uneven density distribution and the stepwise change in thermal conductivity, it is assumed that the following relationships should be satisfied on the moving interfaces:

$$-k_{\rm v} \frac{\partial T}{\partial x} = -k_{\rm p} \frac{\partial T}{\partial x}, \quad x = x_{\rm bp}$$
 (22)

$$-k_{\rm p}\frac{\partial T}{\partial x} = -k_{\rm c}\frac{\partial T}{\partial x}, \quad x = x_{\rm cp}$$
(23)

Assume that there is no mass exchange, as well as inflow and outflow of gas at the bottom boundary, which is denoted:

$$\rho_{\rm v} \left(-\frac{\kappa}{\mu} \nabla P \right) = 0 \tag{24}$$

where κ is the permeability, μ – the dynamic viscosity, and P – the pressure.

The initial thickness of the sample in the verification simulation was selected as 0.0394 m, which is the same as [9]. All calculation were performed using $4 \cdot 10^{-4}$ m average grid size and 0.1 second time step. Increasing or decreasing these integration parameters by a factor of 2 did not produce any significant changes in the results of the simulations indicating convergence of the numerical solutions. The external heat flux action time is about 550 second and calculation time was selected as 600 second.

The parameters of the virgin layer and the char layer can be obtained through experiments [9, 23]. In these two layers, some property parameters such as density, thermal conductivity of the virgin layer, the onset temperature, the complete pyrolysis temperature, and emissivity of the ablation surface are constant. The property parameters of the pyrolysis layer are temperature dependent [9].

Model verification

The numerical calculation was performed according to the method provided in last section, and the results were compared with the thermal analysis of the charring ablation material AVCOAT 5026-39H/CG using the finite difference method [9] to verify this finite element method.

The comparison of surface temperature calcul ated by finite difference method and finite element method is shown in fig. 2. It can be seen that the tendency of two temperature curves are similar. The surface temperature rises rapidly before 80 seconds due to the significant increase of the external heat flux, which actually rises to 2865 K, while the reference temperature is 2753 K [9]. Subsequently, due to the decrease of the external heat flux, the pyrolysis behavior within the material and the ablation of the surface carbon consume heat, then the surface temperature decreases until 200 seconds, at which point the actual and reference temperature are 1613 K and 1503 K, respectively. Then the temperature remains essentially constant until 340 seconds. As the external heat flux increases again, the surface temperature curves rise again to the second peaks, the actual temperature is 2033 K at 420 seconds, while the reference value is 1928 K. Then the surface temperature decreases with the decrease of the external heat flux. The actual and reference temperature are 1125 and 1029 K at 550 seconds, respectively. Because the actual calculation time is 600 seconds, so the actual temperature curve exists from 550-600 seconds. Since the external heat flux has stopped heating the sample, the temperature slowly decreases over this period of time, and finally reaches 1077 K. At each time point, the actual temperature is slightly higher than the reference value, which is mainly caused by the different selection of enthalpy of the pyrolysis gas. There is a fixed value of $8.77 \cdot 10^4$ kJ/kg in [9], while the enthalpy of pyrolysis gas related to temperature [19] was selected in this paper, it can be seen in fig. 3, which is less than the fixed value at each time point and position. Therefore, the actual heat consumption due to the heat convection by the pyrolysis gas and the decomposition within the material is less, so the corresponding surface temperature at each time point in actual calculation is higher. Noting that between 9-22 seconds, there is a difference between the actual and reference surface temperature curves due to the rapidly increase in thickness of the pyrolysis layer and the formation of the char layer, resulting in the oscillation of the temperature curves.



Figure 2. Comparison of surface temperature calculated by finite difference method and finite element method

Figure 3. Enthalpy of pyrolysis gas related to temperature

The comparison of surface recession rate calculated by finite difference method and finite element method is shown in fig. 4. It can be seen that the surface recession rate relates



Figure 4. Comparison of surface recession rate calculated by finite difference method and finite element method

closely with the surface temperature, the actual and reference surface recession rate curves have similar trends. In the first 25 seconds, the actual surface temperature does not reach the ablation temperature T_a , so the surface recession rate is 0. As for the reference temperature curve, there is no surface recession before 37 seconds. Subsequently, the increase in external heat flux causes the surface temperature significantly increasing to the ablation temperature T_a , thus the surface recession rate also increases sharply. The actual and reference surface recession rates at the first peak are 0.027 mm/s and 0.023 mm/s, respectively. Subsequently, due to the decrease of the surface temperature, the surface recession rate

also decreases, and it remains basically unchanged from 160-360 seconds. Then the surface recession rate increases with the increasing of surface temperature. The actual and reference surface recession rates reach $6 \cdot 10^{-3}$ mm/s and $4.2 \cdot 10^{-3}$ mm/s at 420 seconds, respectively. After that, they decrease with the decreasing of surface temperature till 523 seconds, at which time the surface temperature is lower than T_a . The actual surface recession rate at two peaks and between 160-360 seconds are significantly greater than the reference value, because the actual surface temperature corresponding to this period of time is higher than the reference value.

Results and discussion

Effect of pre-exponential factor on ablation

In this section, the effect of the pre-exponential factor $\ln A$ on ablation characteristics, which are the temperature, surface recession rate, density distribution, and mass flux of pyrolysis gas, were discussed. Taking *E* and *n* as constants, 100 kJ/mol and 2, respectively, but $\ln A$ as a variable changing from 10-20 1/s. The external constant heat flux, calculation time and initial material thickness are 1.5 MW/m², 600 seconds and 40 mm, respectively.

When $\ln A$ is 10, 12, 14, 16, 18, 20 1/s, respectively, the temperature history of the ablative material is shown in fig. 5. It can be seen that when pre-exponential factor $\ln A$ changes from 10-20 1/s in fig. 5(a), it has little effect on surface temperature. Because the chemical



Figure 5. Temperature history of six different pre-exponential factors for the ablative material; (a) surface temperature and (b) bottom temperature

kinetics mainly affects the decomposition reaction within the material. The most important factor affecting the surface temperature is the external heat flux, which can be seen in fig. 6. The surface temperature increases with the increase of external heat flux. When external heat flux is 0.5 MW/m^2 and 3.0 MW/m^2 , the surface temperature is 1781.1 K and 2896.9 K at heating time 600 seconds, respectively. The temperature corresponding to each time point is the highest when $\ln A = 10 \text{ l/s}$ in fig. 5(a). It increases sharply after heating and reaching 2268.5 K at 60 seconds, due to the heating by external heat flux, resulting in a sharply increase in surface temperature. Because of the thermal conductivity of the material, heat conduction occurs within the material with the internal temperature increasing. The decomposition reaction within the material and surface ablation consume heat, as well as the complex convection and radiation, which eventually lead to surface energy balance and the surface temperature gradually tends to be stabilize, which reaches 2419.6 K at 600 seconds.

The bottom temperature history are shown in fig. 5(b). As $\ln A$ increases, the corresponding temperature decreases at the same time. The temperature under these pre-exponential factors are controlled by the chemical kinetics. Because there is a positive correlation between decomposition reaction rate and $\ln A$, which can be seen in eq. (5), so the larger the pre-exponential factor $\ln A$, the faster the decomposition reaction, which results the more heat is absorbed, so the less heat is transferred to the bottom. When $\ln A$ is 10 1/s and 20 1/s, the bottom temperature stays at 300 K for the first 200 seconds, then they gradually increase to 359.6 K and 324.4 K at 600 seconds, respectively.

The surface recession rate is shown in fig. 7. It can be seen that the pre-exponential factor $\ln A$ has little effect on surface recession rate, which is due to the selection of the surface recession rate of AVCOAT 5026-39H/CG based on the reaction rate control mechanism [23], thus the surface recession rate is mainly affected by surface temperature. The surface recession rate is slightly greater when $\ln A = 10$ 1/s, because the surface temperature is higher under this condition, which can be seen in fig. 5(a). It increases sharply when surface temperature reaches the ablation temperature, which is 0.0101 mm/s at 60 seconds.



The density distribution is illustrated in fig. 8. With the increase of $\ln A$, the range of density changes within the material increases, which means that the larger range of the decomposition reaction occurs, the greater the depth of heat transfer. So the heat consumed increases and heat transferred to the bottom decreases, which can be seen in fig. 5(b). The position of

density change is the position of the pyrolysis layer and the char layer. Another interesting finding is that the magnitude of the pyrolysis layer increases as $\ln A$ decreases. The pyrolysis layer is 4.9, 4.8, 4.0, 2.5, 1.3, and 0.7 mm for six different $\ln A$, respectively. This is because the heat transferred to the bottom increases as $\ln A$ decreases. In addition, there is 7.3 mm has been ablated. The pre-exponential factor mainly affects the position of the pyrolysis layer and the char layer. When $\ln A = 20$ 1/s, the density is basically unchanged at 512.59 kg/m³ between 0 m and 0.0223 m. Then the density decreases rapidly from 0.0223-0.0264 m. The large density gradient is caused due to the temperature increases in this range with pyrolysis gas generated and char layer formed. Finally, it remains unchanged until 0.0332 m. In addition, the density gradient is greatest for $\ln A = 20$ 1/s, indicating that the most drastic decomposition reaction occurs.

The mass flux of pyrolysis gas within the ablative material at heating time 600 seconds is shown in fig. 9. It can be seen that with the increase of $\ln A$, the peak of the pyrolysis gas mass flux increases correspondingly, but the co-ordinate position where the peak appears is farther from the surface. This is due to the increase of the pre-exponential factor $\ln A$, the density changes with time faster, the decomposition reaction is more intense, the more pyrolysis gas is generated, as a result, the more pyrolysis gas-flows through the area per unit time. In addition, since the decomposition reaction occurs closer to the bottom with increasing $\ln A$, the location of mass flux of pyrolysis gas is further away from the surface. When $\ln A$ is 20 1/s, the peak of the mass flux appears at 0.0253 m, which has a value of 0.038 kg/m²s, and when $\ln A$ is 10 1/s, the peak appears at 0.0264 m with a value of 0.009 kg/m²s.



Effect of activation energy on ablation

The effect of the activation energy, E, on ablation was discussed in this part. Taking $\ln A$ and n as constants, 15 1/s and 2, respectively, but E as a variable with the range from 100-200 kJ/mol.

Figure 10(a) shows the surface temperature of the ablative material. It can be seen that the activation energy, E, has little effect on surface temperature, just like the pre-exponential factor. After heating the ablator by external heat flux, the surface temperature rises rapidly. When E = 200 kJ/mol, the temperature reaches 2139.4 K at 5 seconds, then it gradually stabilizes and reaches 2426.9 K at 600 seconds because of the surface energy balance. The energy balance on the material surface is due to the complex convection and radiation heat exchange between the

material and the external flow, as well as the release of pyrolysis gas and the ablation of material surface, which can be expressed by eq. (12).



Figure 10. Temperature history of six different activation energies for the ablative material; (a) surface temperature and (b) bottom temperature

The bottom temperature curves are shown in fig. 10(b). It can be seen that as the activation energy increases, the bottom temperature at each time point also increases accordingly. This is because as the activation energy increases, the rate of density with time decreases, which results the heat consumption decreases, thus heat transferred to the bottom increases. When the activation energy, *E*, is 100 kJ/mol and 200 kJ/mol, the bottom temperature remain basically unchanged at 300 K in the first 200 seconds, then they increase gradually, which is 339.2 K and 372.5 K at 600 seconds, respectively. It should be pointed out that the activation energy is influenced severely by the kind of the carbon fiber. So the selection of the kind of the carbon fiber of the charring material has significant influence on the mechanism of surface ablation.

The surface recession rate history is illustrated in fig. 11. It can be seen that the activation energy, *E*, has little effect on the surface recession rate. With the activation energy increases, the corresponding rate at each time point increases slightly. When the activation energy E = 200 kJ/mol, the surface recession rate increases sharply from 0 to 0.0077 mm/s, then it gradually stabilizes, which is 0.0136 mm/s at 600 seconds.

Figure 12 shows the density distribution history of the ablative material at heating time 600 seconds under different activation energies. As the activation energy, E, increases, the range of density change decreases. When E = 200 kJ/mol, the density remains unchanged at 512.59



Figure 11. Surface recession rate history of the ablative material with heating t = 600 s under six different activation energies

kg/m³ from 0-0.0245 m, then it drops sharply, because the resin within the material is decomposed by heating and causing the density of this segment to change. In addition, the ablated thickness is 7.2 mm, which is the same as the value in fig. 13.



The mass flux of pyrolysis gas within the ablative material at heating time 600 seconds under different activation energies is shown in fig. 13. It can be seen that the larger the activation energy, E, the smaller the peak of mass flux and the farther the position from the bottom. This is because the larger the activation energy, E, the lower the decomposition reaction rate and the less pyrolysis gas is generated. When E = 100 kJ/mol, the peak of pyrolysis gas mass flux is 0.0222 kg/m²s and the corresponding co-ordinate position is 0.0256 m. When E =200 kJ/mol, the value is 0.0078 kg/m²s and the corresponding co-ordinate position is 0.0276 m.

Effect of reaction order on ablation

The effect of the reaction order, n, on ablation was discussed when n as a variable with the range from 1-3, but $\ln A$ and E as constant, which are 15 1/s and 100 kJ/mol, respectively.

The surface temperature history of the ablative material under different reaction orders is shown in fig. 14. It can be seen that reaction order, *n*, has little influence on surface temperature. This is because the value in the brackets of $[(\rho - \rho_c)/\rho_v]^n$ in eq. (5) is between 0.37 and 0, the overall change of this term is inconspicuous, thus the reaction order, *n*, has little effect on decomposi-



Figure 14. Surface temperature history of five different reaction orders for the ablative material



the ablative material with heating t = 600 s under five different reaction orders

tion. When n = 3, the surface temperature rises sharply from 300-2125.9 K in the first 30 seconds, then it tends to be stabilize and reaches 2417.1 K at 600 seconds due to the surface energy balance.

The surface recession rate history is illustrated in fig. 15. The reaction order, n, also has little influence on surface recession rate, which is closely related to surface temperature. When n = 3, the surface recession rate increases sharply to 0.0074 mm/s at 30 seconds, then it gradually stabilizes and reaches 0.0136 mm/s at 600 seconds.

Conclusion

In this paper, a 1-D charring ablation model was established by finite element method, taking into account the density change within the material and the removal of surface material. The difference between the calculation results and the non-linear analysis results of the thermal behavior of the charring material is mainly due to the different enthalpy of the pyrolysis gas produced by thermal decomposition, which results in the heat convection of the pyrolysis gas consuming less external aerodynamic heat and absorbing less heat from the decomposition of the virgin material, so the surface temperature at each time point in this paper is higher and the surface recession rate is larger. However, the trends of the curves are generally similar and can be used for the analysis of the ablation characteristics of charring ablative materials. Then the effects of three chemical kinetics on ablation energy have significant effects on ablation, both of which have significant effect on the bottom temperature, density distribution, and mass flux of pyrolysis gas, but have less effect on surface temperature and the surface temperature-dependent recession rate because the surface temperature changes less after the surface energy reaches equilibrium. In addition, the reaction order has little effect on ablation.

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