

New discrimination method for ablative control mechanism in solid-propellant rocket nozzle

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Received November 21, 2009; accepted June 17, 2010

A reasonable discrimination method for ablative control mechanism in solid-propellant rocket nozzle can improve the calculation accuracy of ablation rate. Based on the different rate constants for reactions of C with H₂O and CO₂, a new discrimination method for ablative control mechanism, which comprehensively considers the influence of nozzle surface temperature and gas component concentration, is presented. Using this new discrimination method, calculations were performed to simulate the nozzle throat insert ablation. The numerical results showed that the calculated ablation rate, which was more close to the measured values, was less than the value calculated by diffusion control mechanisms or by double control mechanisms. And H₂O was proved to be the most detrimental oxidizing species in nozzle ablation.

nozzle, Ablation, diffusion control mechanism, chemical kinetics control mechanism, discrimination method

Citation: Zhang B, Liu Y, Wang C H, et al. New discrimination method for ablative control mechanism in solid-propellant rocket nozzle. *Sci China Tech Sci*, 2010, 53: 1–7, doi: 10.1007/s11431-010-4081-6

1 Introduction

At present, carbon-carbon composites, which have a serial excellent performances, are widely used as materials for rocket-nozzle ablative thermal protection. The ablation of carbon-carbon composites can be mainly classified into two categories: thermo chemical ablation and mechanical ablation. The former is about chemical reactions occurring between the carbon-carbon composites and oxidizing species (H₂O, CO₂ and OH) in the combustion stream under high temperature environment. The latter is referring to the mechanical process associated with the impingement of metal oxide particles on to the nozzle surface and the thermal-stress-induced structural failure [1, 2].

The ablative rate of carbon-carbon composites materials is mainly depended on two factors. The first one is the diffusive speed of the oxygen-bearing components in the

boundary layer toward wall surface. The second one is the speed of chemical reaction under high temperature. Generally speaking, if the wall surface temperature is high and the reactive speed is so high that the oxygen-bearing components diffusing to wall surface are rapidly exhausted in short supply, then the ablation is restricted by the diffusion process. Contrarily, if the wall surface temperature is low and the diffusion process is so rapid that oxygen-bearing components can sufficiently supply a need of chemical reaction, then the ablation is controlled by kinetics of chemistry. Due to the maximized heat-transfer rate in the throat, many people assumed that ablation in that region is controlled by the diffusion [3, 4]. And other people believe that the ablation is controlled not only by diffusion but also by chemical kinetics. And it is called the double control mechanism [5, 6]. Both the two discrimination mechanisms give a relatively reasonable ablation calculation method. However, Huang [7] argued that both the two discrimination method are both too subjective. He believes that the discrimination for ablative control mechanism is dependent

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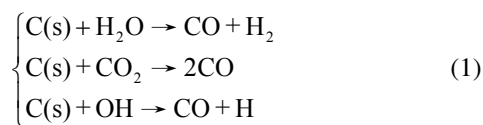
on both concentration and activation energy of H_2 . We also agree with that choosing ablation control mechanism only by the temperature is arbitrary. Any other factors should be considered, for example, gas component concentrations?

There is a disagreement concerning the importance of the reaction between C and H_2 at home and abroad. Some people [8, 9] believe that the reaction should be excluded because of the experimentally observed decrease in the nozzle recession rate with increasing concentration of H_2 . The reactions of C with H_2O and CO_2 have been extensively investigated. The kinetics data compiled by Libby and Blake [10] considered the specific rates of both reactions to be equal. It has been suggested in previous studies that at high temperature, H_2O was the most detrimental oxidizing species responsible for nozzle ablation. Consequently, the rate constants for the reactions of C with H_2O and CO_2 should not be treated identically.

Based on different rate constants for the reactions of C with H_2O and CO_2 , a new discrimination method, which considers the influence of nozzle surface temperature and gas component concentration, is presented in this paper. The rationality of this new discrimination method is verified by some ablation examples.

2 Discrimination of control mechanism

According to thermodynamic calculation results, gas component concentration changes very little with the variational pressure and it can be seen as constant value. The main species in the combustion stream are H_2O , CO_2 , CO, HCl, N_2 , and H_2 , along with small amounts of OH and H and negligible concentrations of O_2 and O. In the case of a metallized propellant, a condensed-phase species of Al_2O_3 is also presented. Generally, it is assumed that HCl, N_2 and Al_2O_3 are not involved in the gas-phase chemical reactions. The 3-equation model can be expressed as



Because the concentration of OH is low, the reaction between C and OH can be ignored usually. Then the 3-equation model is transformed into the 2-equation model. In the current study, the kinetics parameters are adopted from the experimental data compiled by Bradley [11]. These parameters were used successfully by other scholars [12–14].

Considering the different rate constants for the reactions of C with H_2O and CO_2 , the ablation induced by H_2O and CO_2 are calculated separately. It is assumed that the two equations are mutually independent. For example, when calculating the ablation caused by H_2O , the reaction between C and CO_2 is frozen. The ablation velocity due to

H_2O is obtained appropriately as

$$r_{H_2O} = \min(r_{H_2O\text{-diff}}, r_{H_2O\text{-chem}}). \quad (2)$$

The ablation velocity due to CO_2 can be obtained in the identical method.

$$r_{CO_2} = \min(r_{CO_2\text{-diff}}, r_{CO_2\text{-chem}}). \quad (3)$$

The total ablation velocity is determined by

$$r = r_{CO_2} + r_{H_2O}, \quad (4)$$

where the subscripts diff and chem denote diffusion control mechanism and chemical control mechanism, respectively, and r is the linear ablation rate.

3 Ablation model

3.1 Linear ablation velocity of C/C composites under chemical kinetics control mechanism

The mass conservation equations can be deduced from the continuity equations of i component near the surface.

$$(1 + B')P_{iw} = P_{ie} + \beta w_i, (i = 1, 2, \dots, 7). \quad (5)$$

Applying eq. (5) to every gas component, we have

$$(1 + B')P_{1w} = P_{1e} - \beta w_1, \quad (6a)$$

$$(1 + B')P_{2w} = P_{2e} - \beta w_2, \quad (6b)$$

$$(1 + B')P_{3w} = P_{3e} - \beta w_3, \quad (6c)$$

$$(1 + B')P_{4w} = P_{4e} + \frac{M_4}{M_1}\beta w_1 + 2\frac{M_4}{M_2}\beta w_2 + \frac{M_4}{M_3}\beta w_3, \quad (6d)$$

$$(1 + B')P_{5w} = P_{5e} + \frac{M_5}{M_1}\beta w_1, \quad (6e)$$

$$(1 + B')P_{6w} = P_{6e} + \frac{M_6}{M_3}\beta w_3, \quad (6f)$$

$$(1 + B')P_{7w} = P_{7e}. \quad (6g)$$

The mass consumption rate of carbon is

$$B' = \beta M_c \left(\frac{w_1}{M_1} + \frac{w_2}{M_2} + \frac{w_3}{M_3} \right). \quad (7)$$

The ablation velocity of C/C composites under chemical control mechanism is given as follows:

$$\dot{r}_{\text{chem}} = \dot{m}_c / \rho_c = B' / (\beta \rho_c), \quad (8)$$

where the subscript w and e denote wall and main stream, respectively, P is pressure, M is molecular weight, w is the mass generating rate. B' and β are two dimensionless parameters. We convert the inert components which do not

occur in the reaction into N_2 , H_2O , CO_2 , OH , CO , H_2 , H , N_2 are orderly denoted by $i=1, 2, \dots, 7$, respectively.

The thermo-chemical reaction velocity is given by Arrhenius equation.

$$k_i = A_i T_w^b \exp(-E_i / (RT_w)), \quad (9)$$

where A_i and E_i represent respectively pre-exponential factor and activation energy in the reaction of procedure between C/C composites and i component. R is molar gas constant and T_w is the temperature of throat surface. The kinetics data for 3-equation model are given in Table 1.

The energy conservation equations on the surface are given as follows:

$$\dot{q}_{\text{int}} = q_{\text{conv}} + \dot{q}_{\text{rad}} - \dot{q}_{\text{chem}}, \quad (10a)$$

$$\dot{q}_{\text{conv}} = h_c (T_e - T_w), \quad (10b)$$

$$\dot{q}_{\text{rad}} = \varepsilon_{\text{eff}} \sigma (T_e^4 - T_w^4), \quad (10c)$$

$$\dot{q}_{\text{chem}} = \sum_{i=1}^3 \frac{\dot{W}_i}{M_i} \cdot \Delta H_i, \quad (10d)$$

where \dot{q}_{int} , q_{conv} , \dot{q}_{rad} , \dot{q}_{chem} respectively represent net heat flux, convective heat flux, radiative heat flux, chemical heat flux; h_c is convective heat transfer coefficient; T_e is the gas temperature; ΔH_i is the standard enthalpy of formation in the reaction procedure between C and i component; ε_{eff} is the surface radiation factor of throat material; σ is the Stefan-Boltzmann constant.

One dimension axial symmetry heat conduction equation can be described as

$$\frac{\rho_c c}{\lambda_c} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r}, \quad (11)$$

initial condition: $T(r)=T_0$,

internal boundary condition: $-\lambda \frac{\partial T}{\partial r} = q_{\text{int}}$,

external boundary condition: $-\lambda \frac{\partial T}{\partial r} = 0$,

where ρ_c and λ_c represent the density of throat material and the heat conductivity coefficient of throat material. The solving process of the heat conduction equation can be found in ref. [15].

The solution procedure can be divided into several parts. Firstly, with the initial condition and boundary condition, T_w

at $t = n$ can be obtained by solving heat conduction equation. Secondly, the linear ablation velocity and the net heat flux can be calculated with the substitution of T_w into mass conservation equations and Arrhenius equation. Thirdly, by substituting the calculated net heat flux into heat conduction equation, T_w at $t = n+1$ can be iteratively solved.

3.2 Linear ablation velocity of C/C composites under diffusion control mechanism

According to the diffusion theory and the chemical kinetics theory, the ablation velocity of C/C composites under diffusion control mechanism is given as follows:

$$r_{\text{diff}} = \frac{h_c \left(\frac{M_C}{M_{H_2O}} P_{1e} + \frac{M_C}{M_{CO_2}} P_{2e} + \frac{M_C}{M_{OH}} P_{3e} \right)}{C_p \rho_c}, \quad (12)$$

where C_p denotes the specific heat of gas.

4 Results and discussions

The parameters for cases in sections 4.1 and 4.2 are given as follows: combustion average pressure is 4.9 MPa, the density and thickness of throat is 1900 kg/m³ and 80 mm respectively, and the diameter of nozzle throat is 25.4 mm.

4.1 The calculation and analysis of linear ablation velocity induced by H₂O

It is assumed that the concentration of H₂O is 15% and the gas temperatures are 3200, 3500 and 3800 K, respectively. The numerical results are given in Figure 1. At the beginning of ablation, the kinetics-controlled ablation velocity

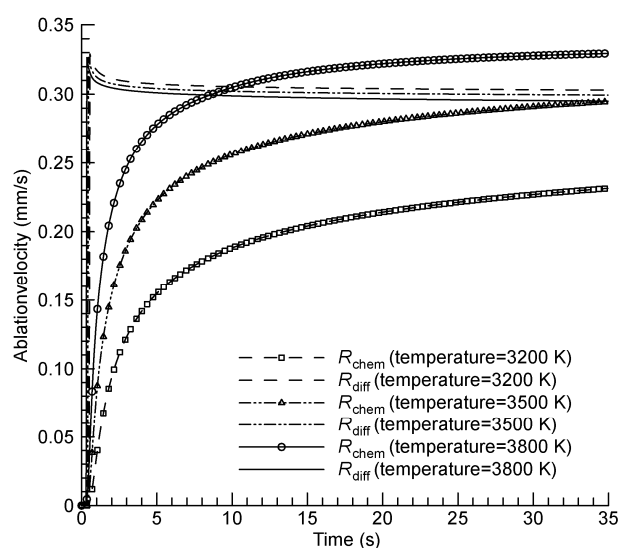


Figure 1 The ablation velocity histories with different temperatures (induced by H₂O).

Table 1 Kinetics data for surface reactions

Surface reaction	A_i (kg/m ² /s)	b	E_i (kcal/mol)	W_i (kg/m ² /s)
$C(s)+H_2O \rightarrow CO+H_2$	4.8×10^5	0	68.8	$k_i P_{H_2O}^{0.5}$
$C(s)+CO_2 \rightarrow 2CO$	9.0×10^3	0	68.1	$k_i P_{CO_2}^{0.5}$
$C(s)+OH \rightarrow CO+H$	3.61×10^2	-0.5	0.00	$k_i P_{OH}$

increases rapidly, than the increasing trend decreases gradually, finally the chemical ablation velocity tends to be a stable value. The diffusion-controlled ablation velocity slightly decreases at the initial stage and then tends to be stable. The ablation velocity controlled by chemistry kinetics increases obviously with the temperature increasing. This is because temperature has great influence on the chemical reaction rate. While the ablation velocity under diffusion control mechanism decreases slightly with the increment of temperature. The reason for this trend is that convective heat transfer coefficient decreases slightly with the temperature increasing. And it can be found from the eq. (12) that the diffusion-controlled ablation velocity is proportional to the convective heat transfer coefficient. When the temperature is 3200 or 3500 K, the ablation velocity under diffusion control mechanism is always larger than the ablation velocity under kinetics control mechanism within the calculation time. However, when the temperature is 3800 K, the kinetics-controlled ablation velocity overtakes the diffusion-controlled ablation velocity at about $t=8$ s. At the beginning of ablation, the surface temperature is low and the ablation is controlled by chemistry kinetics. With the increasing surface temperature, the ablative control mechanism may convert to the diffusion control mechanism.

Suppose that the gas temperature is 3500 K and the concentration of H_2O are 5%, 15% and 25%, respectively. It can be seen from Figure 2 that both the kinetics-controlled ablation velocity and diffusion-controlled ablation velocity increase obviously with the increasing concentration of H_2O . The ablation velocity controlled by chemistry kinetics overtakes the ablation velocity controlled by diffusion at $t=4$ s in the case in which the concentration of H_2O is 5%. However, the diffusion-controlled ablation velocity is always larger than the kinetics-controlled ablation velocity in the other two cases. The results have indicated that it is difficult for the kinetics-controlled ablation velocity to overtake the dif-

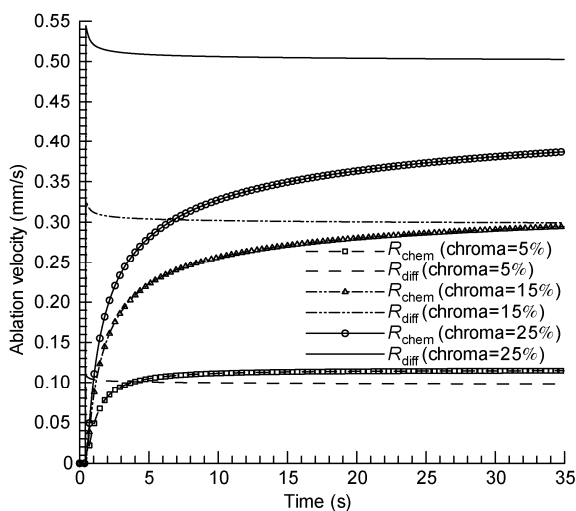


Figure 2 The ablation velocity histories with different concentration (induced by H_2O).

fusion-controlled ablation velocity with the increasing concentration of H_2O .

To sum up, a reasonable ablative control mechanism for ablation induced by H_2O should comprehensively consider the influence of temperature and component concentration.

4.2 The calculation and analysis of linear ablation velocity induced by CO_2

Suppose that the concentration of CO_2 is 15% and the gas temperatures are 3200, 3500 and 3800 K, respectively. The results are shown in Figure 3. As shown in Figure 3, the trend of the kinetics-controlled or diffusion-controlled ablation velocity are similar to those shown in Figure 1. The most obvious difference between Figure 1 and Figure 3 is that diffusion-controlled ablation velocity is much larger than the kinetics-controlled ablation velocity in Figure 3. It is also found that the kinetics-controlled ablation velocity induced by CO_2 is far less than the kinetics-controlled ablation velocity induced by H_2O . This is because the rate constants for the reactions of C with H_2O and CO_2 are different. The result shows that H_2O is the most detrimental oxidizing species in nozzle ablation.

It is assumed that the temperature is 3500 K and the concentrations of CO_2 are 5%, 15% and 25%, respectively. As shown in Figure 4, the concentration of CO_2 has a great influence on the diffusion-controlled ablation velocity, but has little influence on the kinetics-controlled ablation velocity. This leads to the increase of the gap between the kinetics-controlled ablation velocity and the diffusion-controlled ablation velocity with the increasing concentration of CO_2 . The diffusion-controlled ablation velocity induced by H_2O is about 2.5 times larger than the diffusion-controlled ablation velocity induced by CO_2 . This is because M_{CO_2} / M_{H_2O} is about 2.5 and other relative parameters in eq. (12), such

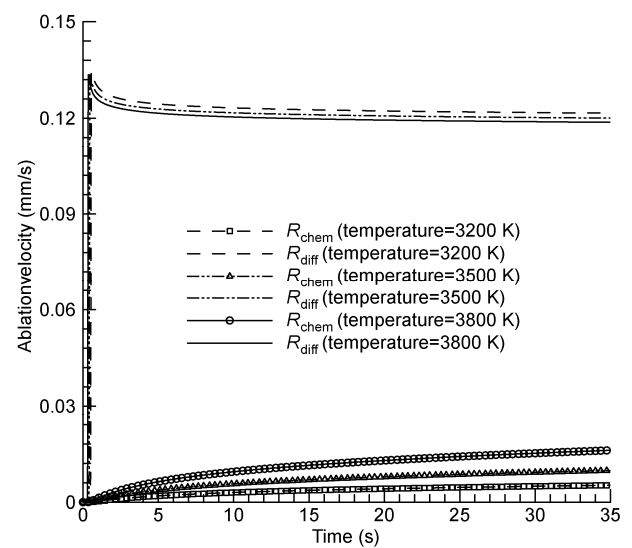


Figure 3 The ablation velocity histories with different temperatures (induced by CO_2).

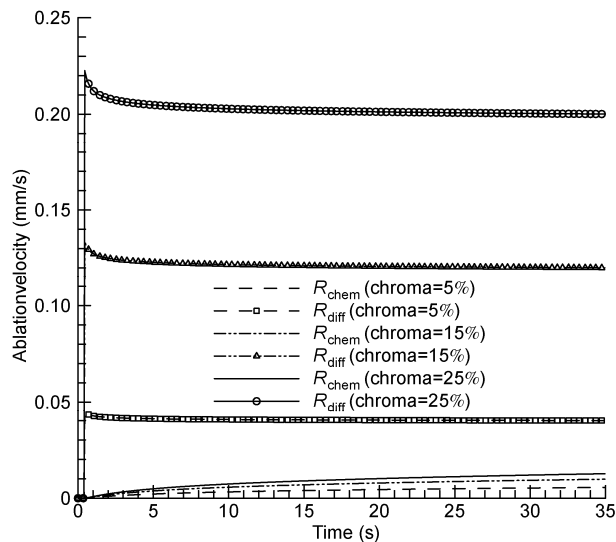


Figure 4 The ablation velocities history with different concentrations (induced by CO₂).

as h_c , C_p , ρ_c , K_{1e} , K_{2e} , are the same at any arbitrary time. To sum up, the ablative control mechanism for ablation induced by CO₂ can be always chemical kinetics control mechanism because the diffusion-controlled ablation velocity is always larger than the kinetics-controlled ablation velocity.

4.3 Ablation example

To validate the current model, calculations using diffusion control mechanism (Model 1), double control mechanism (Model 2) and current model respectively were performed to simulate the nozzle-ablation experiments by Geisler [16]. A BATES (Ballistic Test and Evaluation System) engine was developed in the early 1960s and was intensively used to analyze SRM carbon nozzle ablation. It was found that the onset of ablation was between 1 and 2 s. In practice, because it takes about a second to attain the steady-state operating condition, there exists a corresponding time delay in the commencement of the nozzle surface recession. In this paper, there is no delay time because it is assumed that the operating condition is reaches the steady state at the beginning of calculation. Some parameters for calculation are given as follows: the density and thickness of throat are 1830 kg/m³ and 80 mm, respectively, the diameter of nozzle throat is 25.4 mm. Other parameters are listed in Table 2.

Under the current discrimination method, the ablation velocities induced by H₂O and CO₂ for the first two cases are shown in Figures 5 and 6, respectively. It can be seen from Figure 6 that the ablation induced by CO₂ for this two cases are always controlled by kinetics of chemistry because the diffusion-controlled ablation velocity is always larger than the kinetics-controlled ablation velocity. As shown in Figure 5, the ablation velocity should also be controlled by chemical kinetic velocity due to the same reason. In case 2,

Table 2 Parameters for simulating experiments by Geisler

Case	Case 1	Case 2	Case 3	Case 4	Case 5
P (MPa)	6.9	6.9	6.9	6.9	6.9
T (K)	3580	3655	3715	3750	3745
Al	15%	18%	21%	24%	27%
Y_{CO_2}	0.04	0.025	0.015	0.005	0.0015
Y_{H_2O}	0.145	0.105	0.07	0.045	0.025
Y_{H_2}	0.02	0.02	0.02	0.02	0.02
Y_{HCL}	0.24	0.23	0.195	0.190	0.190
$Y_{AL_2O_3}$	0.28	0.34	0.40	0.44	0.47

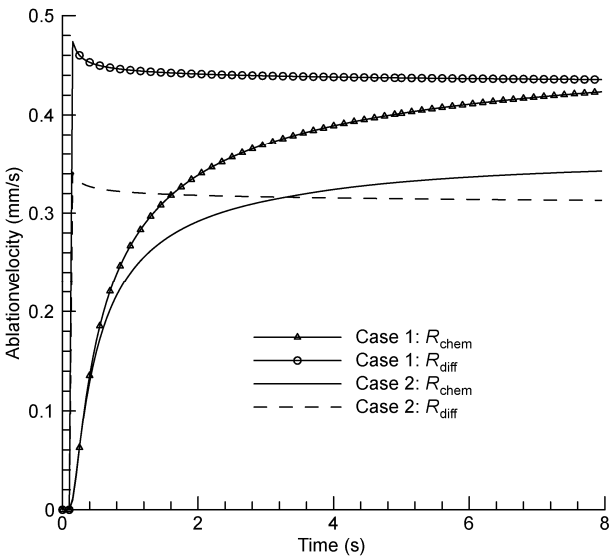


Figure 5 The ablation velocity histories for cases 1 and case 2 (induced by H₂O).

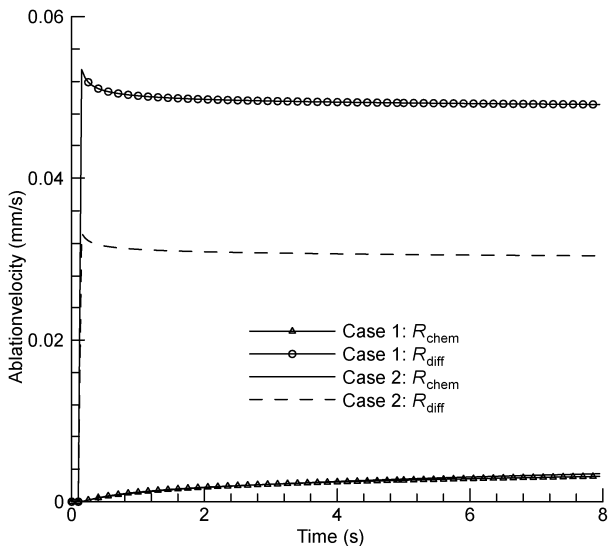


Figure 6 The ablation velocities history for cases 1 and case 2 (induced by CO₂).

the kinetics-controlled ablation velocity overtakes the diffusion-controlled ablation velocity at about 3.2 s. It is indicated that the ablation is restricted by chemical process be-

fore 3.2 s and is restricted by diffusion process after 3.2 s, respectively. The else cases (case 3–case 5) have the same ablation control mechanism as case 2. By comparing the ablation velocities in Figures 5 and 6, it can be found that the ablation induced by H₂O is larger than the value caused by CO₂.

The recession histories for different cases are given in Figure 7, where the recessions for different cases change approximately linearly with time. The recession decreases gradually from case1 to case 5. The reason for this trend is that the concentrations of CO₂ and H₂O decreases with the increasing concentration of Al.

The comparison between the experimental and the computed ablation velocities are reported in Table 3. The error of calculated ablation velocity under diffusion control mechanism is larger than the value controlled by double mechanism model or by current model. With the increasing concentration of Al, the error of calculated ablation velocity under diffusion control mechanism decreases gradually. This behavior can be explained by analyzing the ablation caused by H₂O and CO₂. As for case1, the ablation induced by H₂O and CO₂ should be controlled by chemical kinetics.

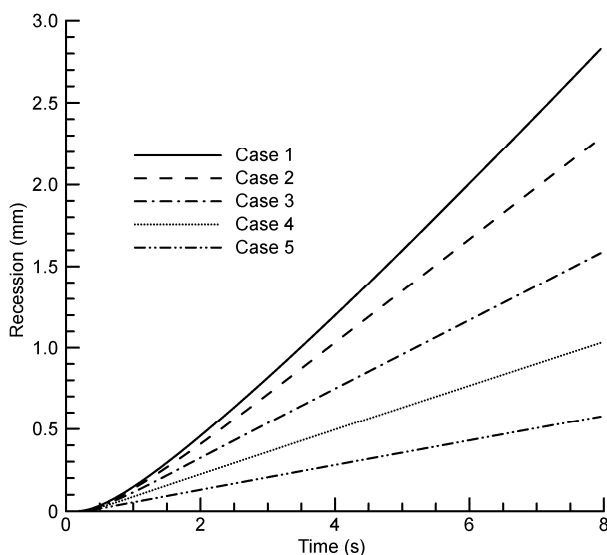


Figure 7 The recession histories for different cases.

Table 3 Comparison between calculated and measured nozzle ablation velocities (mm/s)

	Model 1	Model 2	Current model	Exp
Case 1	0.493	0.363	0.362	0.353
Err	40.0%	2.8%	2.5%	–
Case 2	0.349	0.302	0.292	0.284
Err	22.9%	6.3%	2.8%	–
Case 3	0.229	0.214	0.202	0.200
Err	14.5%	7.0%	1.0%	–
Case 4	0.141	0.135	0.131	0.124
Err	13.7%	8.9%	5.6%	–
Case 5	0.077	0.075	0.073	0.069
Err	11.6%	8.7%	5.8%	–

The ablation velocity will be aggrandized if the calculation is under diffusion control mechanism. The ablative control mechanism for ablation induced by H₂O in other four cases changed from kinetics-control mechanism to diffusion-control mechanism. The onset of control mechanism transformation from case 2 to case 5 is about 3.2, 1.5, 0.9 and 6 s, respectively.

The calculated ablation velocity under double control mechanism and current model are similar to the experimental value. In case 1, the ablation velocity under these two models are nearly the same because the ablation velocity is only controlled by chemical kinetics. As for the other four cases, the ablation caused by CO₂ will be aggrandized if calculation is under diffusion control mechanism. However, because the ablation induced by CO₂ is small, the difference between double control mechanism and current model is small too. The error of ablation velocity under double control mechanism is increasing gradually with the increasing concentration of Al. However, this trend will not appear in the current model.

5 Conclusions

1) A new discrimination method for ablative control mechanism in solid-propellant rocket nozzle is presented:

$$r = \min(r_{\text{H}_2\text{O-diff}}, r_{\text{H}_2\text{O-chem}}) + \min(r_{\text{CO}_2\text{-diff}}, r_{\text{CO}_2\text{-chem}}).$$

2) The ablative control mechanism for ablation induced by H₂O should comprehensively consider the influence of temperature and component concentration. However, the ablative control mechanism for ablation induced by CO₂ can be always chemical kinetics control mechanism.

3) The ablation velocity induced by H₂O is larger than the value caused by CO₂. Consequently, H₂O is the most detrimental oxidizing species responsible for ablation.

4) Under the different ablative control mechanisms (diffusion control model, double control model and current model), the calculations were performed to simulate the nozzle-ablation experiments by Geisler. It is found that the diffusion-control velocity is much larger than the experimental value. However, the calculated ablation velocities under double control mechanism and current model are similar to the experimental value.

5) With the increasing concentration of Al, the error of the ablation velocity under double control mechanism is increasing and the error of the ablation velocity under diffusion control mechanism is decreasing. However, this trend will not be occurred in the current model.

This work was supported by the National Hi-Tech Research and Development Program of China ("863" Project) (Grant No. 2008AA7020508).

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