DECOMPOSITION OF TEFLON HEAT PROTECTIVE COATINGS AT HYPERSONIC FLIGHT VELOCITIES

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We consider the decomposition of a teflon thermal protective coating along the generatrix of a blunted solid of revolution for various Mach numbers and pressures of the incident flow. On the basis of preliminary parametric study of the equations of a laminar boundary layer with pressure gradient, calculation of the teflon decomposition parameters is reduced to solution of a system of nonlinear and transcendental equations. It is shown that the temperature distribution and decomposition rate along the generatrix of the solid of revolution have a monotonic character, and that the effective enthalpy of the material remains constant along the body. A simple approximate formula is proposed for calculation of the teflon decomposition rate.

1. Teflon can serve as a strongly ablative low enthalpy coating material, which almost completely blocks convective thermal flux because of the draft of material in the vapor state into the boundary layer. It is assumed that decomposition does not disturb the laminar flow mode in the boundary layer.

A study of teflon decomposition at the critical point with simplifications was performed in [1, 2]. Experimental studies of effective enthalpy values were made in [1, 3]. Numerical calculations of the decomposition of sublimating coatings along the generatrix of a sphere were performed for graphite and a textolite type material in [4, 5].

We will now consider the formulation of the problem of decomposition of an ablative coating along the generatrix of a blunted solid of revolution. The problem of the decomposition of a thermal protective coating which does not form a liquid phase reduces to simultaneous solution of the system of boundary layer equations and the thermal conductivity equation in the solid. Boundary conditions are set at the outer edge of the boundary layer, at the decomposition front, and within the depths of the solid phase. The conditions at the decomposition front are derived from the laws of conservation of mass, momentum, and energy, adapted to a surface of strong discontinuity [6]. For completion of the problem the equations of chemical equilibrium and conditions defining the kinetics of coating decomposition are used. For materials decomposing by pyrolysis, such a condition is

$$\dot{S} = \int_0^{-\infty} K(T)\,dy \tag{1.1}$$

where $K(T) = B \exp(-E/RT)$ is the pyrolysis reaction constant, and S is the decomposition front displacement rate. It may be said that in light of the low thermal conductivity of the material and the sharp dependence of pyrolysis rate on temperature, that decomposition is localized in a narrow subsurface layer and all chemical reactions may be referred to the body surface. Assuming that $\partial T/\partial y \gg \partial T/\partial x$, we will consider the equation for thermal conductivity in the one-dimensional formulation. For the established decomposition regime the boundary problem describing the propagation of heat within the solid phase has the form

$$\begin{gathered}\lambda_1 \frac{d^2T}{dy_1^2} = -\rho_1 c_{p_1} \dot{S} \frac{dT}{dy_1} + \Delta\rho_1 K(T) \\ T(0) = T_0, \quad T(-\infty) = T_{-\infty}\end{gathered} \tag{1.2}$$

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Here $y_1 = y - St$ is the coordinate connected with the decomposition front, and Δ is the heat liberated upon pyrolysis of a unit mass of the material. Integrating Eq. (1.2), we have a formula for the thermal flux passing into the solid phase

$$-\lambda_1 \frac{dT}{dy_1} = \rho_1 \dot{S}\,[\Delta + c_{p_1}(T_0 - T_{-\infty})] - \Delta\rho_1 \int\limits_0^{y_1} K(T)\,dy \tag{1.3}$$

Further integration of the thermal conductivity equation may be performed with the thin reaction zone approximation. Using the first two terms of an expansion in a Taylor series of the function $1/T$ we obtain the temperature profile within the solid and the relationship between the decomposition rate and the material surface temperature

$$\frac{T - T_{-\infty}}{T_0 - T_{-\infty}} = e^{-k_1 y^1} + \frac{C}{T_0 - T_{-\infty}}\left(e^{k_2 y_1} - e^{-k_1 y_1}\right) \tag{1.4}$$

$$\begin{gathered} k_1 = \frac{\rho_1 c_{p_1}}{\lambda_1}\dot{S}, \quad k_2 = \frac{ET_0'}{RT_0^2}, \quad \dot{S} = \left\{\frac{\lambda_1 BR/E}{\rho_1\,[c_{p_1}(T_0 - T_{-\infty}) + \Delta]}\right\}^{1/2} T_0 e^{-E/2RT_0} \\ C = -\frac{\rho_1 \Delta \dot{S}/\lambda_1}{k_2 + k_1} = \frac{\Delta RT_0^2/E}{c_{p_1}(T_0 - T_{-\infty} - RT_0^2/E) + \Delta}, \\ \frac{k_2}{k_1} = -\frac{E}{RT_0^2}\left(T_0 - T_{-\infty} + \frac{\Delta}{c_{p_1}}\right) \end{gathered} \tag{1.5}$$

For a surface temperature $T_0 \sim 800\text{-}1000°\mathrm{K}$ ($E = 8 \cdot 10^4$ kcal/mole, $\Delta = 411$ cal/g; $c_{p1} = 0.4$ cal/g · deg) $k_2/k_1 \gg 1$, $C/(T_0 - T_{-\infty}) \ll 1$, and thus, consideration of chemical reactions within the depths of the body has a weak influence on the temperature profile within the solid phase.

Using Eq. (1.3) at $y_1 = 0$, we write the boundary conditions on the decomposition front [6] in Dorodnitsyn–Lize variables

$$\xi = \int\limits_0^x \rho_e \mu_e u_e r^2\,dx, \quad \eta = \frac{u_e r l_e^{1/2}}{\sqrt{2\xi}} \int\limits_0^{y - \dot{S}t} \rho\,dy \tag{1.6}$$

These conditions have the form

$$\frac{\alpha(\xi)}{l_e^{1/2}} \frac{\xi_x r^{-1}}{\sqrt{2\xi}} = \rho_1 \dot{S} = \rho_1 \int\limits_0^{-\infty} K(T)\,dy_1 \tag{1.7}$$

$$\alpha(\xi)(c_l^* - c_l^{*(1)}) + \sum_{k=1}^{N} m_{lk} S^{-1}{}_k \left(\frac{\partial c_k}{\partial \eta}\right)_0 = 0, \qquad l = 1, 2, \ldots, N - 1 \tag{1.8}$$

$$\sum_{k=1}^{N} c_k = 1 \tag{1.9}$$

$$\begin{gathered} \sum_{k=1}^{N-N^*} Q_k \left[\alpha(\xi)(c_k - c_k^{(1)}) + \frac{1}{S_k}\frac{\partial c_k}{\partial \eta}\right]_0 + \sum_{k=1}^{N} h_k{}^T \frac{1}{\sigma_f}\left(\frac{\partial c_k}{\partial \eta}\right)_0 + \\ + \alpha(\xi)[\Delta + c_{p_1}(T_0 - T_{-\infty})] + \frac{1}{\sigma_f}\left(\frac{\partial h^T}{\partial \eta}\right)_0 = (\varepsilon\sigma_r T_0{}^4 - q_r)\frac{r\sqrt{2\xi}}{\xi_x} l_e^{1/2} \end{gathered} \tag{1.10}$$

Here x, y, are coordinates directed along the generatrix of the solid of revolution and normal to the body; r is the distance of a point on the body surface from the axis of symmetry; u, v are the projections of the velocity vector on the axes x and y; $l = \rho\mu/\rho_0\mu_0$; $\alpha = (\rho v)_0 \; 2\xi r l_e{}^{1/2}/\xi_x$ is the dimensionless draft parameter; c_k, $c_l{}^*$ are the mass concentration of the k-th component and the l-th element; m_{lk} is the mass fraction of the l-th element and k-th component; Q_k is the heat of reaction for formation of the k-th component from N^* independent components; σ_f is the effective Schmidt number; h^T is the enthalpy of the ideal gas state. The indices 0 and e denote the surface of the body and the external edge of the boundary layer while the upper index (1) denotes parameters in the solid phase. The transfer coefficient notation is that generally employed.

The first equation of the system is a combination of the law of convervation of mass and the equation for decomposition kinetics. Equation (1.8) is the law of conservation of elements. Equation (1.10) is the law of conservation of energy at the decomposition front. To this system we must add the equations of chemical equilibrium for the reactions occurring at the decomposition front

$$K_{p_i} = \prod_i p_{A_i}^{\nu_i} \Big/ \prod_i p_{B_i}^{\nu_i'}, \quad i = 1, \ldots, N_0 - N \tag{1.11}$$

In the system (1.8)-(1.10) the effective Schmidt number $S_k = \mu\rho/D_k$, appears defined by the effective diffusion coefficients D_k in the multicomponent mixture; $\rho D_i = J_i/\nabla c_i$ [7]. The coefficients of heat mass transfer $(\partial h^T/\partial\eta)_0$, $(\partial c_k/\partial\eta)_0$ are obtained by factual solution of the system of boundary-layer equations.

We will divide the problem of determining mass loss parameters into two parts. We shall integrate the boundary-layer equations with fixed values of draft, temperature, and composition at the decomposition front. By parametric study of the boundary-layer system of equations it is possible to obtain formulas approximating the coefficients of heat mass transfer as functions of the defined parameters of the problem. Using such an approach heat mass transfer in the boundary layer is described by parameters subject to definition such as the draft α, wall enthalpy, etc. As a result, the problem of determination of mass loss parameters is reduced to solution of a system of $N_0 + 3$ nonlinear equations (1.7)-(1.11) for the unknown quantities S, α, T_0, c_{i0} ($i = 1, ..., N_0$). The basic system includes the supplementary equation (1.3) or (1.4) for definition of the temperature profile in the solid and calculation of the linear displacement rate of the decomposition front as a result of pyrolysis of the solid phase (1.1), (1.7).

2. We will now consider heat and mass transfer in a laminar boundary layer with arbitrary pressure gradient distribution in the presence of a draft of some other gas through the body surface. The basic system of boundary-layer equations was considered in the local self-similarity approximation. This permits examination in the most general form of the dependence of the heat mass transfer coefficients on pressure gradient, draft, and wall temperature, while not setting concrete flight conditions and the form of the body.

There exists a large number of studies which indicate the applicability of the local self-similarity model for calculation of heat mass transfer coefficients even in the case of flows with sharp change in the pressure gradient [8].

By solving the system of boundary-layer equations [9] for the heat mass transfer coefficients the following approximate functions are obtained

$$\theta_0'(\alpha) = \theta_{0*}'(\alpha)\,\psi, \quad \psi = \left(\frac{l_{e0}}{l_{e*}}\right)^{1/2}\left\{1-\left[1-\left(\frac{\sigma_0}{\sigma_*}\right)^m\right] b\right\} \tag{2.1}$$

Here $\theta_{0*}'(\alpha)$ is the heat-transfer coefficient with a draft of a gas mixture close in its properties to the gas flowing around the body, while ψ is a correction for the differences in properties between draft and flow gases. The parameters m and b are functions of the pressure gradient and draft

$$m = 1.05 + (1.6 - 0.7\sqrt{\Lambda})\,\alpha, \quad b = 0.075 + g_0^{1/4} - 2.04\alpha - (4.51-4g)\alpha^2 \tag{2.2}$$

$$\Lambda = 2\frac{d\ln u_e}{d\ln\xi}, \quad g = \frac{H^T}{H_e^T} = \frac{h^T + u^2/2}{h_e^T + u_e^2/2}, \quad \theta = \frac{g - g_0}{1 - g_0} \tag{2.3}$$

The values of $\theta_0{*}'(\alpha)$ may be calculated from the equation

$$\begin{aligned}
&\theta_{0*}'(\alpha) = [\theta_{00}' + \varphi_1(\alpha)\varphi_2(\Lambda)\varphi_3(\sigma)]\left(1 - \frac{u_e^2}{2H_e^T}\,\frac{1-\sqrt{\sigma_*}}{1-g_0}\right)\\
&\theta_{00}' = [0.4696 + (0.0253 + 0.0867g_0 - 0.195g_0^2)\sqrt{\Lambda}]\,\sigma_*^{0.355}\,l_{e_*}^{0.386-0.162l_e}\\
&\varphi_1(\alpha) = \alpha(0.568 + 0.176\alpha), \quad \varphi_2(\Lambda) = 1 - 0.15\Lambda^{(2.5+\Lambda)^{-1}},\\
&\varphi_3(\sigma) = \left(\frac{\sigma_*}{0.7}\right)^{0.73+0.08\sqrt{\Lambda}}
\end{aligned} \tag{2.4}$$

Comparison with numerical solutions shows that in the interval $0.5 \geq \alpha \geq -1$, $0 \leq \Lambda \leq 1$, $0.4 \leq \sigma \leq 1$, $0.2 \leq l_e \leq 1.2$ the accuracy of Eqs. (2.1)-(2.4) is no less than 5%.

For the case of a draft of a gas mixture with different properties a generalized analogy between the heat mass transfer coefficients is established in a formula analogous to the case of draft of a mixture with similar heat capacities [9]

$$\left(\frac{\partial}{\partial\eta}\,\frac{c_i}{c_{ie} - c_{i0}}\right)_0 \left[\frac{\partial\theta}{\partial\eta}(\xi, 0)\right]^{-1} = L_{i0}^{-k} \tag{2.5}$$

$$k = 0.35 + (1.35g_0^{-0.173} - 0.67\,\Lambda^{(3.05+\Lambda)^{-1}})\,\alpha\,(0.325 - 1.35\,\alpha) \tag{2.6}$$

The functions for determination of the dimensionless heat-transfer coefficient θ'_0 and the generalized analogy are obtained from the example of a draft into air of gases with various numbers of atoms and various molecular weights (H_2, He, N, CH_4, H_2O, O, C_2H_6, HCl, C_3H_8, C_2H_5OH, CF_4, Br_2). Equation (2.1) is uniformly accurate for all draft gases and agrees with calculations of the heat mass transfer coefficients for the forward critical point [5, 11].

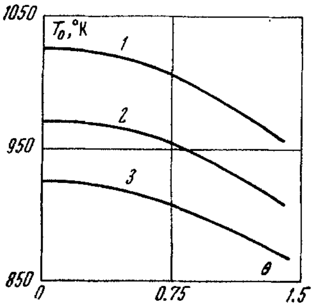

Fig. 1

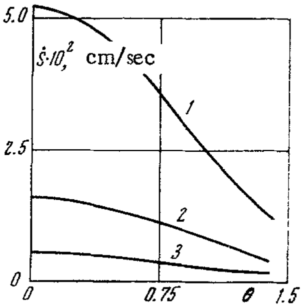

Fig. 2

To calculate the effective Schmidt and Lewis numbers the method of [7] is used. The components existing in the boundary layer and on the wall may be divided into four groups, at the limits of which the binary diffusion coefficients for each group differ by no more than 1%. As a result, for given composition and draft from the body surface the problem of determining effective diffusion coefficients on the wall reduces to solution of a system of nonlinear algebraic equations.

The general method of finding mass-loss parameters reduces to solution of Eq. (1.10) by the iteration method by selection of surface temperature T_0. For a fixed value of T_0 from Eq. (1.7) we define the draft into the boundary layer. The system (1.8), (1.9), (1.11) together with the equations defining the effective diffusion coefficients and heat mass transfer coefficients (2.1)-(2.6) permits calculation of the gas composition on the wall, and thus determination of the left side of Eq. (1.10).

3. We will consider in further detail the results of teflon mass loss calculations. Teflon (Ftoroplast-4) is a polymer of tetraflorethylene $(C_2F_4)_n$, a typical low enthalpy ablative material. It has been established that teflon decomposition commences at temperatures above 415° C. The thermophysical properties of teflon are as follows: density $\rho_1 = 2.14$ g/cm^3, thermal conductivity $\lambda_1 = (5.5\text{-}6)\cdot 10^{-4}$ cal/cm·sec·deg; heat of pyrolysis, $\Delta = 411$ cal/g. The thermal capacity of teflon is temperature dependent and may be calculated from the equation

$$c_{p_1} = 0.1539 + 3.36\cdot 10^{-4}\, T \text{ cal/g}\cdot\text{deg}$$

Teflon decomposition occurs according to the formula $(C_2H_4)_{nT} \rightarrow C_2F_{4g}$, while the pyrolysis reaction constant is described by the equation

$$K = \dot{B}\exp(-E/RT), \quad E = 8.3\cdot 10^4 \text{ kal/mole} \quad B = 3\cdot 10^{19}\ \text{сек}^{-1} \tag{3.1}$$

The composition of the pyrolysis products depends on pressure, however, there are no reliable experimental data. It is known that at low pressure over the entire temperature range the monomer C_2F_4 is formed. In pyrolysis in mixtures with an oxygen excess the final reaction products will be CO_2 and CF_4. It follows from analysis of the equilibrium constants of the group of reactions possible that in the surface temperature range up to 1200° K the monomer appearing as a result of thermal destruction will participate in two reactions

$$\begin{gathered} C_2F_4 + O_2 \rightleftarrows CO_2 + CF_4 \\ CO_2 + CF_4 \rightleftarrows CF_2O \end{gathered} \tag{3.2}$$

Thus, in decomposition in a flow of dissociated air on the wall seven components may participate, O_2, N_2, C_2F_4, CF_4, CO_2, CF_2O, Ar.

Numerical calculations were performed for the decomposition of a teflon thermal protective coating on a sphere 1 m in diameter over the Mach number range 10-20 and incident flow pressures $p_\infty = 0.001$-0.1 atm. Figures 1 and 2 present typical dependences of surface temperature and decomposition rate along the generatrix of the sphere for various pressures in the incident flow at M = 15. Curves 1-3 correspond to pressures p = 0.1, 0.01, 0.001 atm. It is evident that with removal from the critical point the surface temperature and decomposition rate decrease monotonically. Calculations performed show that the dimensionless decomposition rate $\alpha/l_e^{1/2}$ and effective enthalpy $H_{ef} = q_0/\rho_1 S$ are constant along the lateral surface and independent of pressure. The dependence of $\alpha/l_e^{1/2}$ on Mach number is shown in Fig. 3. The results of numerical calculation of the quantity $\alpha/l_e^{1/2}$ in the range $10 < M < 20$ may be approximated to an accuracy of 3% by the formula

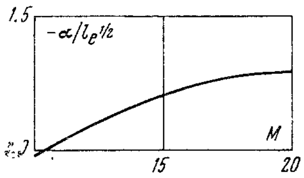

Fig. 3

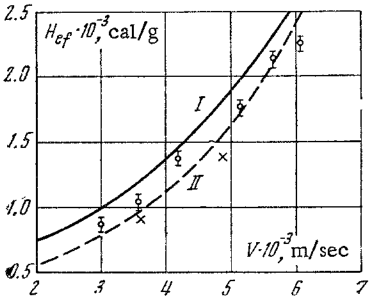

Fig. 4

$$\frac{\alpha}{l_e^{1/2}} = 0.314M^{0.52-0.002M}$$

Comparison of the results of this calculation with theoretical and experimental data for the forward critical point [1, 2] was made for the effective enthalpy values. The dependence of effective enthalpy on flight velocity is presented in Fig. 4. Also shown are the data of [2] (curve 1) and the results of experiments on teflon decomposition in instruments with electric arc heating, used in [1]. The dashed line II is the computed curve of the present study. From Fig. 4 it is evident that theory and experiment agree satisfactorily.

We offer an approximate formula for calculation of the decomposition in the vicinity of the critical point

$$\dot{S} = \frac{3\cdot 10^{-2}}{\sqrt{R}} M^{3/2}\sqrt{P_\infty} \text{ cm/sec} \qquad [R] = \text{cm} \qquad [P_\infty] = \text{atm}$$

The formula approximates the decomposition rate well over the range of calculated parameters $0.001 \leq P_\infty \leq 0.1$ atm and $M_\infty < 12$.

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