A STUDY CONCERNING THE DECOMPOSITION OF VITROPLASTIC MATERIAL DURING DIFFERENTIATED CARBON BURNOUT

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The quasisteady decomposition of a vitroplastic material is analyzed in the case of carbon burnout both in the inner layers and at the surface.

Statement of the Problem. We consider a material which is a mechanical mixture of glass and phenolic resin, and its quasisteady decomposition near the critical point of an axially symmetric body with a blunted surface. Chemically the material will be assumed to consist of oxygen, carbon, and hydrogen only. It will also be assumed that all processes involving the pyrolysis of the binder (direct pyrolysis as well as decomposition of hydrocarbons [1]) occur along one front at a temperature T_f much lower than the temperature of the hot surface T_h. The content of the pyrolysis products will be limited to solid carbon (coke) with gaseous carbon monoxide and hydrogen, which corresponds to the case of maximum coke yield. The heterogeneous interaction between glass and carbon is a complex multistage process. According to the data in [2, 3], the most likely end products of this interaction are silicon monoxide and carbon monoxide, i.e., the total reaction can be described by the following equation

$$\mathrm{SiO}_2^s + \mathrm{C}^s \rightarrow \mathrm{SiO} + \mathrm{CO}. \tag{1}$$

The rate of reaction (1) will be expressed in terms of the Arrhenius equation with the kinetic coefficients corresponding to the upper limit of the test-values band in [2], namely:

$$\frac{dK_3^s}{dt} = -K_3^s \exp\left(-\frac{34720}{T} + 15.477\right). \tag{2}$$

If one assumes reaction (1) to be the only process which affects the weight content of the material ingredients in the y < 0 region, then the equations of mass conservation for the individual compounds within the region $[0, y_h]$ can be written as follows:

$$\frac{\partial G_2^s}{\partial y} = \frac{1}{x}\cdot\frac{\partial}{\partial x}(xK_2^s u_2^s) - \frac{M_2}{M_3}\cdot\frac{G_3^s}{v_3^s}\exp\left(-\frac{34720}{T} + 15.477\right), \tag{3}$$

$$\frac{\partial \ln G_3^s}{\partial y} = -\frac{1}{v_3^s}\exp\left(-\frac{34720}{T} + 15.477\right), \tag{4}$$

$$G_4 = \frac{M_4}{M_3}\left[G_{\Sigma,\infty}(1-\varphi)\nu_{C,1} - G_3^s\right], \tag{5}$$

$$G_5 = \frac{M_5}{M_3}\left[G_{\Sigma,\infty}(1-\varphi)\left(\nu_{C,1} - \nu_{O,1}\frac{M_3}{M_7}\right) - G_3^s\right], \tag{6}$$

$$G_6 = G_{\Sigma,\infty}(1-\varphi)\nu_{H,1}. \tag{7}$$

The flow of the viscous film of molten silicon dioxide due to shear forces induced by the oncoming gas stream is usually described by the equations of an incompressible boundary layer with the inertia terms omitted as negligibly smaller than the viscous terms [4]. If the variability of ξ across the molten film is also disregarded, then the x-component of the equation can be integrated once over the limits $[y, y_h]$

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and then written as

$$\frac{\partial}{\partial y}\left[\frac{1}{x}\cdot\frac{\partial}{\partial x}\,(xK_2^s u_2^s)\right] = -\frac{2\xi\rho_2^s}{\mu}\left[\tau_{w,x} - p_{e,xx}(y - y_{\mathrm{h}})\right]. \tag{8}$$

The velocity of solid carbon will be assumed equal to the decomposition rate of the material:

$$v_3^s = v_{\Sigma,\infty} = -G_{\Sigma,\infty}/\rho_{\Sigma,\infty}. \tag{9}$$

The energy equation for the $[0, y_{\mathrm{h}}]$ region can be expressed as

$$-\sum_{i=2}^{6} c_{p,i}\,G_i\,\frac{\partial T}{\partial y} = \frac{\partial}{\partial y}\left(\lambda\frac{\partial T}{\partial y}\right) + \Delta Q_2\frac{G_3^s}{v_3^s}\exp\left(-\frac{34720}{T} + 15.477\right). \tag{10}$$

We will consider that the displacement rate of the hot surface is determined by the nonequilibrium evaporation (condensation) of silicon dioxide and that all the carbon reaching this surface transforms into gas while physically and chemically interacting with ingredients of the boundary layer. The boundary conditions can then be formulated as follows:

at $y = y_{\mathrm{h}}$

$$-\lambda\frac{\partial T}{\partial y} = q_{\mathrm{h}} \tag{11}$$

$$G_2^s = \frac{\eta\xi\,(p_{2,\mathrm{h}}^* - p_{2,\mathrm{h}})}{\sqrt{2\pi RT_{\mathrm{h}}/M_2}}; \tag{12}$$

at $y = 0$

$$T = T_f, \tag{13}$$

$$G_2^s = G_{\Sigma,\infty}\,\varphi, \tag{14}$$

$$G_3^s = G_{\Sigma,\infty}(1-\varphi)\left(\nu_{\mathrm{C},1} - \nu_{\mathrm{O},1}\frac{M_3}{M_7}\right), \tag{15}$$

$$\frac{1}{x}\cdot\frac{\partial}{\partial x}(xK_2^s u_2^s) = 0, \tag{16}$$

$$-\lambda\frac{\partial T}{\partial y} = G_{\Sigma,\infty}\left[c_{p,\Sigma,\infty}(T_f - T_\infty) + (1-\varphi)\Delta Q_1\right]. \tag{17}$$

The quantities q_{h}, $p_{2,\mathrm{h}}$, $\tau_{\mathrm{h},x}$ are determined from the solution to the equations of a laminar frozen boundary layer. One uses here the Reynolds analogy as well as the analogy between heat- and mass-transfer processes. The hot surface is assumed catalytic, i.e., under thermodynamic equilibrium.

Analysis of the Physical Aspects of Decomposition. If no heterogeneous interaction between glass and carbon occurs, and if the sole source of silicon in the boundary layer is the evaporation of SiO_2 molecules from the hot surface, then the oxidation of carbon causes a shift in the reaction

$$SiO_2 \rightleftarrows SiO + 0.5\,O_2 \tag{18}$$

toward the right and, therefore, an increase in the SiO_2 evaporation rate (12). The occurrence of reaction (1), as an additional means of transforming elemental silicon into a gas, does appreciably modify the mechanism of material decomposition (Fig. 1), because an injection of SiO vapor into the boundary layer shifts reaction (18) to the left. As a result, instead of the partial dissociation of glass molecules evaporating at the hot surface, for example, there may take place an opposite reaction: oxidation of SiO vapor to silicon dioxide. If reaction (1) is sufficiently intensive, furthermore, then the partial pressure of silicon dioxide on the hot surface may exceed the corresponding saturated-vapor pressure level and, instead of evaporating, silicon dioxide will condense (see formula (12)). The extent of reaction (1), i.e., the fraction of carbon $\Gamma_{3,\mathrm{r}}$ which has had time to react with silicon dioxide during heating depends on the temperature level within the reaction zone and on the time t_{R} the reagents have been there. This time t_{R} is inversely proportional to the decomposition rate squared because, as $G_{\Sigma,\infty}$ increases, the reaction zone becomes narrower and the velocity of reagents passing through it increases. According to Fig. 1 (curve 3), even under the most favorable conditions for reaction (1) assumed in this study, a change in t_{R} due to a decrease in $\overline{G}_{\Sigma,\infty}$ affects the reaction appreciably more than the simultaneous drop of the temperature

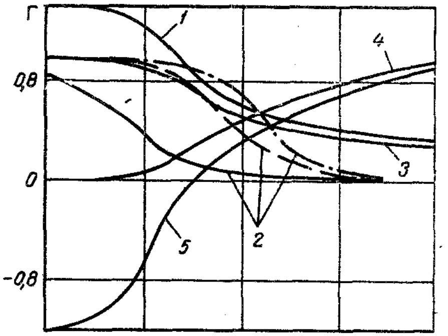

Fig. 1

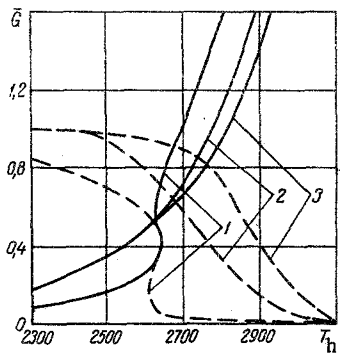

Fig. 2

Fig. 1. Gasification factor of carbon and silicon dioxide, as a function of the dimensionless decomposition rate of the material [solid lines) differentiated burnout of carbon; dashed line) surface burnout of carbon; dashed-dotted line) mechanical wear of carbon mass]: 1) $\Gamma_{2,r}$; 2) $(1-\Gamma_{2,\Sigma})$; 3) $\Gamma_{3,r}$; 4) $\Gamma_{3,h}$; 5) $\Gamma_{2,h}$.

Fig. 2. Dimensionless decomposition rate of the material and extent of glass melting, as functions of the surface temperature (°K) [solid lines) $\bar{G}_{\Sigma,\infty}$; dashed lines) $(1-\Gamma_{2,\Sigma})$]: 1) differentiated burnout of carbon; 2) surface burnout of carbon; 3) mechanical wear of carbon.

level due to this decrease in $\bar{G}_{\Sigma,\infty}$ (Fig. 2). For this reason, at a sufficiently low value of $\bar{G}_{\Sigma,\infty}$ the interaction between glass and carbon has usually time to proceed till completion (i.e., till the carbon is completely burned out). As the wear rate increases, however, the magnitude of $\Gamma_{3,r}$ gradually decreases with more and more carbon burning out as a result of surface reactions. At rather low values of $\bar{G}_{\Sigma,\infty}$ the earlier mentioned possibility of condensation of SiO_2 molecules becomes real (Fig. 1, curve 5). The decomposition of the material is shown schematically in Fig. 3. It is evident here that, as glass molecules condense, carbon passes through the molten film emerging from the boundary layer and continues to migrate toward the gas-condensate interphase boundary. A mode of decomposition is possible, therefore, where more glass interacts with carbon than is contained in the worn layer of material (Fig. 1, curve 1). The practical sense of this is that some SiO_2 molecules have time to react with carbon several times (after entering into the boundary layer as silicon monoxide, which oxidizes into silicon dioxide, they precipitate on the surface and again interact with carbon). Moreover,

$$\Gamma_{2,r,\max} = \frac{1-\varphi}{\varphi} \cdot \frac{M_2}{M_3} \left(\nu_{C,1} - \nu_{O,1} \frac{M_3}{M_7} \right).$$

In order to evaluate the role of reaction (1) in the mechanism of the material decomposition, we have plotted in Figs. 1, 2 curves representing the surface burnout of carbon ($\Gamma_{3,r} = 0$, $\Gamma_{3,h} = 1$) and the mechanical wear of carbon mass ($\Gamma_{3,r} = 0$, $\Gamma_{3,h} = 0$). Reaction (1) is highly endothermal: it requires approximately 52,000 kJ/kg combustible carbon. As a consequence of that, the temperature profile becomes significantly distorted and this in turn affects the rate of glass melting, inasmuch as the viscosity of the melt is strongly temperature-dependent [4] (Fig. 1, curves 2). The occurrence of reaction (1) may also distort the relation between decomposition rate and surface temperature, the latter having a significant effect on the effective enthalpy of the material. The simultaneous rise in the SiO_2 gasification rate and drop in the melting rate cause the decomposition to proceed slower within the temperature range where melting of glass predominates and to proceed faster where melting is negligible (Fig. 2). The burnout of carbon makes the $\bar{G}_{\Sigma,\infty}(T_h)$ relation become bivalent (Fig. 2). The explanation for this is that, beginning at a sufficiently high decomposition rate (and at a corresponding surface temperature T_h' based on Eq. (12)) the oxidation of carbon results in a complete single-stage dissociation of glass molecules. Meanwhile, at low wear rates and under high pressure in the boundary layer or during appreciable injection of SiO vapor, reaction (18) may become "inhibited" up to temperatures much above T_h'.

A Study Concerning the Effect of Reaction (1), Based on the Material Decomposition Characteristics. In this study a body with a 0.007 m radius at the blunt end was placed in a supersonic air stream with a

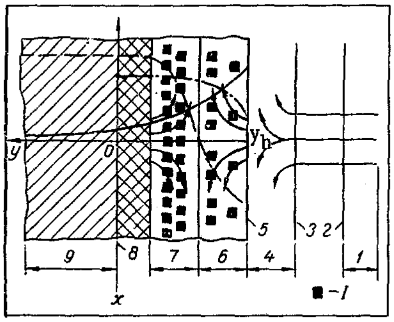

Fig. 3

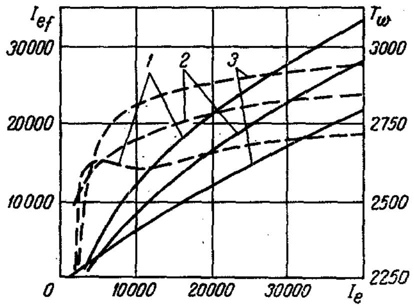

Fig. 4

Fig. 3. Schematic diagram of material decomposition: 1) oncoming air stream; 2) shock wave; 3) outer edge of boundary layer; 4) boundary layer; 5) hot surface; 6) molten SiO_2 condensate; 7) molten original SiO_2; 8) front of binder pyrolysis; 9) original material; I) carbon; solid line) T(y) curve; dashed line) $G_2^s(y)$; dashed-dotted line) $G_3^s(y)$ curve.

Fig. 4. Main parameters of material destruction versus stagnation enthalpy of incident air flow (kJ/kg): solid curve) I_{ef}; dashed curve) T_h (°K); 1) differentiated combustion of carbon; 2) surface combustion of carbon; 3) mechanical combustion of carbon mass.

pressure of 1 bar in the boundary layer. The flow mode in the boundary layer was assumed laminar. The characteristic curves in Figs. 1 and 2 correspond to these conditions of decomposition as well. The thermodynamic properties of the chemical ingredients were calculated according to [5] and, in addition, the following values of the material constants were used: $\rho_{\Sigma,\infty} = 1700$ kg/m^3, $c_{p,\Sigma,\infty} = 1.0$ kJ/kg·deg, $\lambda = 0.003$ kW/m·deg, $\Delta Q_1 = 1200$ kJ/kg of resin; $\Delta Q_2 = 52{,}000$ kJ/kg of carbon; $\eta = 1$; $\xi = 0.7$; $\nu_{O,1} = 0.17$, $\nu_{C,1} = 0.77$, $\nu_{H,1} = 0.06$. The following relation in [6] was used for the viscosity of the melt:

$$\ln \mu = \frac{68800}{T} - 22.29 \ \mathrm{N \cdot sec/m^2}.$$

The essential calculated results are shown in Fig. 4. It will be noted here that at high values of the stagnation enthalpy, when the injection effect is the main contributor to the heat balance at the surface, taking into account the carbon burnout yields a lower surface temperature (especially in the case of differentiated burnout), because then a lower temperature T_h is necessary for ensuring the required gasification rate of the material (Fig. 2). At low values of the stagnation enthalpy, most pronounced becomes the heat of carbon oxidation which is released at the surface and which causes the surface temperature to rise. A drop in the decomposition rate, which occurs under these conditions of mass wear while reaction (1) is in progress, has a more appreciable effect on reducing this temperature rise at the surface than during mechanical wear of carbon. Since the melting rate of glass is reduced by reaction (1), when the latter occurs, and this should result in a higher effective enthalpy of the material, hence an appreciable increase in the latter is to be expected at $\bar{G}_{\Sigma,\infty} \sim 0.5$ (Fig. 1). The reduction of $\Gamma_{2,\Sigma}$ which accompanies a reduction in the decomposition rate, compensates to a large extent the positive effect of reaction (1), and the effective enthalpy appears to depend rather little on the mode of carbon burnout.

NOTATION

x, y	are the coordinates referred to the surface of binder pyrolysis: x-axis directed along this surface from the critical point as origin, y-axis normal to it into the cold material;
u, v	are the x and y components of the velocity vector;
T	is the temperature;
p	is the pressure;
ρ	is the density;
τ	is the frictional stress;
K	is the weight content per unit volume;
$G = -vK$	is the mass rate of flow toward hot surface;
Γ	is the gasification factor;
M	is the molecular mass;

φ	is the weight content of glass in the original material;
$\nu_{j,i}$	is the weight content of j-th chemical element in i-th ingredient of the material;
ΔQ_1	is the thermal effect of resin pyrolysis;
ΔQ_2	is the thermal effect of reaction (1);
ξ	is the fraction of material surface filled with glass;
η	is the accommodation coefficient;
t	is the time;
μ	is the dynamic viscosity;
λ	is the effective thermal conductivity;
c_p	is the specific heat;
α/c_p	is the heat-transfer coefficient;
$\bar{G} = G/[(\alpha/c_p)_0]$	is the dimensionless rate;
R	is the universal gas constant;
q_h	is the thermal flux into the material through the hot surface;
I_e	is the stagnation enthalpy of the oncoming air stream;
I_{ef}	is the effective enthalpy of the material.

Subscripts

h	denotes the hot surface;
f	denotes the front of resin pyrolysis;
∞	denotes the cold material;
Σ	denotes the mixture;
O	denotes the impermeable surface;
r	denotes the internal process;
x	denotes the differentiation with respect to x;
1	denotes the resin;
2	denotes the silicon dioxide SiO_2;
3	denotes the carbon C;
4	denotes the carbon monoxide CO;
5	denotes the silicon monoxide SiO;
6	denotes the hydrogen H_2;
7	denotes the oxygen O.

Superscripts

*	denotes the saturated vapor;
s	denotes the condensate phase of the material.

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