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BREAKDOWN OF AN ORGANICALLY BASED COMPOSITE MATERIAL IN A HIGH-TEMPERATURE GAS FLOW

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UDC 536.244

The authors analyze a mechanism for breakdown of a composite material of the textolite type, composed of the chemical elements H, C, N, and O in an air stream of stagnation enthalpy 14,000-73,000 kJ/kg. A comparison of the theory and the experimental data show that the accuracy of the theoretical model is 25%.

Recently, many papers have appeared with mathematical models for breakdown of heat shield materials in high enthalpy gas flow. The physics of the breakdown process have been analyzed in detail [1]. It has been established that the error in the theoretical model depends to a greater extent than had been suggested earlier on the accuracy of calculating the transfer coefficients of the mixture in the boundary layer, and on the use of a correctly chosen kinetic condition for breakdown of the material at the body surface.

The literature makes wide use of the boundary layer model with the approximation of frozen chemical reactions within the flow and under the hypothesis of a catalytic wall [2], lead-

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 50, No. 3, pp. 367-373, March, 1986. Original article submitted January 2, 1985.

ing to an equilibrium chemical composition of the gas at the body surface. In subsequent papers it has been established, from estimating the chemical reaction rates or from direct measurement of composition [3], that for normal or increased pressure the model of the equilibrium chemical boundary layer in the vicinity of the stagnation point is larger than the boundary layer model with frozen chemical reactions, and corresponds to the actual field of chemical composition of the mixture. However, it is more complex in mathematical formulation, since one cannot repeatedly solve a nonlinear algebraic system of equations to determine the equilibrium chemical composition at all points of the flow field. From theoretical estimates it was predicted that the actual value of the heat flux supplied to the body surface may not differ too much in the two cases.

It was established in [4] that for a dissociated air boundary layer in the absence of breakdown the difference is 7-8%. The same order of difference was observed in the heat flux supplied to the surface of a disintegrating body formed of the chemical elements H, C, and O in the vicinity of the stagnation point, if the material does not contain too much hydrogen [5, 6]. It is of practical interest to compare the theory and the experimental data on rate of breakdown of charring composite materials in high-temperature gas streams.

1. Theoretical Model of the Multicomponent Boundary Layer. The equations of the laminar multicomponent boundary layer in flow over an axisymmetric body of revolution of a gas mixture consisting of N chemical components, neglecting thermodiffusion and chemical reactions inside the layer have the form [7, 8]:

$$\frac{\partial}{\partial x}(\rho U r_1) + \frac{\partial}{\partial y}(\rho V r_1) = 0,$$

$$\rho U \frac{\partial U}{\partial x} + \rho V \frac{\partial U}{\partial y} = -\frac{dP}{dx} + \frac{\partial}{\partial y}\left(\mu \frac{\partial U}{\partial y}\right),$$

$$\rho C_p\left(U \frac{\partial T}{\partial x} + V \frac{\partial T}{\partial y}\right) = U \frac{dP}{dx} + \mu\left(\frac{\partial U}{\partial y}\right)^2 + \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial y}\right) - \sum_{i=1}^{N} C_{pi} m_i \frac{\partial T}{\partial y},$$

$$\rho U \frac{\partial C_i}{\partial x} + \rho V \frac{\partial C_i}{\partial y} = -\frac{\partial}{\partial y} m_i \quad (i = 2, \ldots, N - n),$$

$$\sum_{i=1}^{N} C_i = 1, \quad \sum_{i=1}^{N} \frac{e_i C_i}{\mu_i} = 0, \quad \text{if} \quad n = 1.$$

For a quasisteady rate of breakdown for the case of a perfectly catalytic wall, the boundary conditions may be writtin in the form:

$$\text{for} \quad y \to \infty \quad U \to U_e(x), \quad T \to T_e, \quad C_i \to C_{ie} \ (i = 2, \ldots N - n),$$

$$\text{for} \quad y = 0 \quad U = 0, \ \rho V = \rho_1 \dot{l},$$

$$\sum_{k=1}^{N} (\rho V C_k + m_k) C_{lk} - \rho V C_l^* = 0 \quad (l = 1, \ldots, r - 1 - n),$$

$$\sum_{k=1}^{N} C_k = 1, \quad C_r = 0, \quad \text{if} \quad n = 1,$$

$$\frac{P_i}{\prod_{l=1}^{r-n} P_l^{\nu_{li}}} = k_{Pi} \quad (i = r + 1, \ldots, r + q),$$

$$C_i = 0 \quad (i = r + q + 1, \ldots, N),$$

$$\lambda \cdot \frac{\partial T}{\partial y} - \sum_{k=1}^{N} h_k m_k = \rho V(\delta + I_w - I_{-\infty}) + \rho V(h_w - h^{(1)}) + \varepsilon \sigma_r T_w^4.$$

The diffusion fluxes for flow regimes with ionization are found from the system of equations of ambipolar diffusion [8]. The coefficients of viscosity and heat conduction of the partially ionized mixture, required to solve the problem, are calculated from formulas of the kinetic theory of gases, which takes account of pair interactions and is rigorous in the tem-

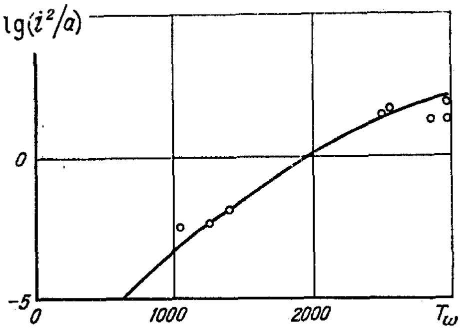

Fig. 1

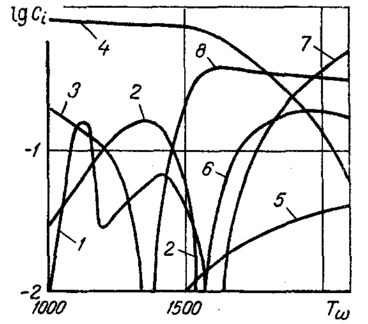

Fig. 2

Fig. 1. Dependence of the group lg (i^2/a) on the surface temperature T_W, °K, during breakdown of the material; a) for the original material.

Fig. 2. Mass concentrations of gases at the body surface as a function of the surface temperature T_W: 1) H_2O; 2) CO_2; 3) O_2; 4) N_2; 5) H_2; 6) HCN; 7) C_2H_2; 8) CO.

perature range 8000-14,000°K at pressures below 10^{-3} atm. At higher pressures (on the order of 1 atm and above) this theory is approximate. The transport and thermophysical coefficients were determined from the Hirschfelder theory for the first approximation, and from the Chapman–Enskog theory in calculating the coefficients of viscosity and heat conduction of multicomponent mixtures. The interaction of neutral particles was calculated by a (6-12) Lennard–Jones potential. The interaction of neutral particles with charged particles was described by the hard sphere model. The effective diffusion cross section Q for electrons with all neutral particles was assumed to be the same and equal to $9 \cdot 10^{-16}$ cm², and for all the ion-neutral particle pairs it was determined from the Pen Tszai Chen and Pindrokh dependences to be

$$Q = 1{,}08 \cdot 10^{-12} T^{-0{,}4}, \text{ cm}^2.$$

The transport coefficients for charged particles were calculated from formulas based on the principle of Coulomb interaction with the radius of interaction of the forces b limited by the Debye screening radius h^0. In the case where h^0 becomes less than the mean distance between the charged particles b^0, then b is assumed to equal b^0.

As is shown by the calculations, the breakdown process depends strongly on the material surface temperature, since this determines the chemical composition of the mixture in the boundary layer and the energy radiated by the material and the specific heat of the original material up to the breakdown temperature. It is known that the laws of conservation of mass, momentum, and energy are not enough to close the boundary conditions, and that one must assign an additional condition controlling the breakdown rate of the material. Relations which can be assumed as such a condition are discussed in several publications.

For charring materials forming a crust of carbon at the breakdown surface, it is customary to use an expression for the rate of sublimination of carbon. For polymers we use the dependence of reaction rates of depolymerization on temperature. There are regimes where the kinetics of breakdown are controlled by the rate of diffusion of the chemical components in the boundary layer.

For complex composite materials containing constituents with different breakdown physics the hypothesis has been suggested that one could experimentally link the surface temperature with a linear breakdown rate. It has turned out that, from a comparatively small set of experimental data for a material examined, one can construct an experimental link between the linear breakdown rate i and the surface temperature T_W that gives good accuracy:

$$\lg (i^2/a) = \alpha T_w^2 + \beta T_w + \gamma. \tag{1}$$

Equation (1) can be used to close the system of boundary conditions.

Figure 1 shows the dependence of lg (i^2/a) on T_W, constructed for a textolite that we examined, containing 8.4% hydrogen, 68% carbon, 6.6% nitrogen, and 17% oxygen, from experimental data in an electric arc facility. We note also that a rather smooth curve of the type of Eq. (1) can be constructed from a comparatively small number of points. For example, one could use the results of a thermal weight analysis [9], which is comparatively simple to conduct, together with one point obtained on the electric arc.

TABLE 1. Parameters of the Electric Arc Heater Flow

Regime of operation	Flow coordinates, mm	P_0, atm	q_0, kW/m²	q_{rad}, kW/m²	T_0, K	I_0, kJ/kg	$(\alpha/C_p)_0$, kg/m²·sec	M
I	10	1,6	$8{,}9\cdot10^4$	$6\cdot10^3$	12400	$7{,}2\cdot10^4$	1,2	0,99
II	17	1,53	$7{,}5\cdot10^4$	$3\cdot10^3$	11800	$6{,}3\cdot10^4$	1,16	0,93
III	27	1,48	$6{,}05\cdot10^4$	$1\cdot10^3$	10700	$5{,}2\cdot10^4$	1,14	0,88
IV	37	1,2	$3{,}3\cdot10^4$	$0{,}4\cdot10^3$	7750	$3{,}5\cdot10^4$	0,97	0,59
V	47	1,1	$1{,}95\cdot10^4$	—	6700	$2{,}2\cdot10^4$	0,93	0,41
VI	57	1,02	$1\cdot10^4$	—	5750	$1{,}45\cdot10^4$	0,74	0,18

The literature data on chemical compounds formed by combustion of breakdown products are very contradictory, and we therefore calculated the gas composition at the body surface, consisting of the chemical elements H, C, N, and O disintegrating in air. It was assumed that on the surface of the disintegrating body the following components could be present: H, H_2, C, C_2, C_3, N, N_2, O, O_2, NO, OH, H_2O, CO, CO_2, CH_4, CN, C_2H_2, HCN, C_2H_4, and NH_3. With the aid of a special computer program to solve the problem of breakdown of the material in the simplified formuation described in Sec. 4 of [7], we obtained the result that of the 20 postulated compounds on the body surface only 4 or 5 were present.

Figure 2 shows the logarithms of mass concentrations C_i as a function of the surface temperature T_w. There are two temperature zones differing substantially in chemical composition. With low-temperature combustion with $T_w \leq 1300$°K the quantities CO_2, H_2O, N_2, and O_2 are present on the body surface, and for $T_w \geq 1600$°K we have the high temperature combustion zone with H_2, HCN, CO, C_2H_2, and N_2 at the surface. All the experiments in the acr facility, for which the calculations were discussed above, relate to the regime with a high-temperature surface.

Allowing for the seven components: H_2, HCN, CO, C_2H_2, N_2, O, and N and dissociation of the incident stream, and the nine components: H_2, CO, HCN, C_2H_2, e^-, O, N, O^+, and N^+ with ionization of the incident stream, we used the numerical method of [8] to calculate the multicomponent boundary layer on a body with a given velocity gradient dU_e/dx at the outer edge of the boundary layer in the vicinity of the stagnation point.

2. Comparison of Theoretical Results and Experimental Data. The experimental setup was a group of gasdynamic, electric, and measuring systems. The high-temperature stream was generated with the aid of an electric arc heater, in which the high-power arc was stabilized by means of a liquid air vortex. With this method of arc stabilization, we could solve two complex problems while using a relatively simple electric-arc heater scheme: firstly, obtain a high-temperature flow of a chemical composition corresponding to the real case; and secondly, considerably expand the range (by a factor of two or more) of variation of temperature and stagnation enthalpy.

Table 1 shows the gasdynamic and thermophysical parameters of the facility. The diagnosis of these parameters was done with particular care. Each of the parameters was determined by a minimum of two or three independent methods, which ensured a high reliability of the data obtained with small mean square errors. On this facility we tested the above-mentioned texolite to determine the breakdown parameters and compare the experimental data with theory.

The test models were cylinders of various diameters from 14 to 30 mm, consisting of the test material and inserts protecting it from side heating and made of the same material. The technique for testing specimens corresponded to quasisteady conditions. During the experiment as material is lost the specimen takes the form of an ellipsoid of revolution with a certain ratio of the semiaxes: a':b':b'. The rate of recession was measured when the ratios a':b' were steady over time. The recession at the specimen stagnation point was determined using the method of [7, 8] for an axisymmetric body with the same velocity gradient dU_e/dx at the outer edge of the boundary layer as for the test specimen. In most experiments the surface temperature was also measured by optical methods. The results of the measurements were used to construct the kinetic curve described in Section 1.

We now turn to comparison of the experimental and calculated data. The results of one variant of boundary layer calculation with a stagnation enthalpy I_0 = 73,000 kJ/kg are shown in Fig. 3.

Figure 4 shows the effective enthalpy of the material obtained by calculation and by experiment. The calculations were performed for the same values of stagnation enthalpy I_0

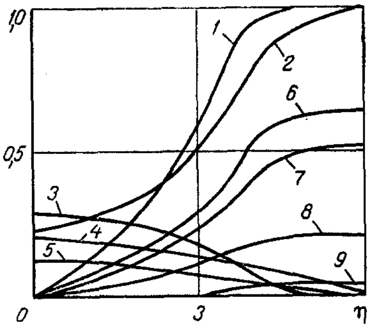

Fig. 3

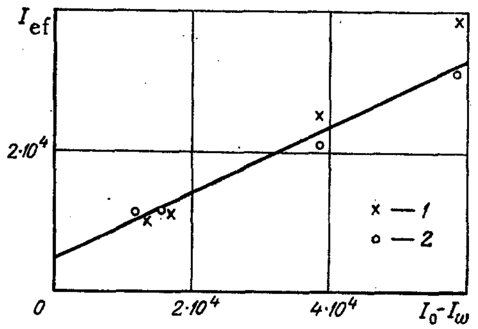

Fig. 4

Fig. 3. Profiles of dimensionless velocity U/U_e, dimensionless temperature T/T_e and mass concentration of components across the boundary layer in dimensionless coordinate η: 1) U/U_e; 2) T/T_e; 3) $C(C_2H_2)$; 4) $10 \cdot C(H_2)$; 5) $C(HCN)$; 6) $C(N)$; 7) $10^5 \cdot C(e^-)$; 8) $C(O)$; 9) $C(O^+)$.

Fig. 4. Effective enthalpy I_{ef} obtained by calculation (1) and experimentally (2) as a function of the enthalpy drop across the boundary layer I_0-I_w, kJ/kg. The straight line is $I_{ef} = 4600 + 0.475\ (I_0-I_w)$.

achieved in the experiments. The surface temperature in the calculations were chosen from the kinetic curve, and therefore in some cases the calculated value of gas enthalpy at the wall I_w did not coincide with the experimental value, and as a result the calculated points corresponding to some experimental conditions are displaced along the abscissa axis.

The difference between the calculated results and the experiments does not exceed 25%, which is evidence that in this work we have used a good mathematical model of the physical essence of the process.

NOTATION

x, y, Coordinates, directed along the body surface and along the normal to it; U, V, velocity components in the directions of these coordinates; r_1, distance to the body axis of symmetry; P, ρ, T, μ, C_p, λ, pressure, density, temperature, viscosity, heat capacity, and thermal conductivity of the gas; P_0, stagnation pressure; U_e, T_e, velocity and temperature at the outer edge of the boundary layer; C_i, μ_i, e_i, C_{pi}, and m_i, mass concentration, molecular weight, electric charge, heat capacity and diffusion flux of the i-th conponent; n = 1 corresponds to flow of an ionized gas; n = 0 corresponds to flow without ionization; N, number of chemical components in the mixture; C_{lk}, weight fraction of the l-th element in the k-th component; C^*_l, concentration of a chemical element in the material; h_w, enthalpy of the gas at the body surface; P_i and h_i, partial pressure and enthalpy of the i-th component; I_0, flow stagnation enthalpy; I_w, enthalpy of the material heated to the surface temperature; T_w, surface temperature; T_0, stagnation temperature; $I_{-\infty}$, enthalpy of the unheated material; $h^{(1)}$, enthalpy of the injected gases; δ, heat of vaporization of the material; $\varepsilon\sigma_r T^4_w$, specific radiative flux emitted by the body; k_{p_i} equilibrium reaction constant for formation of component i from the basic components $l(1 \le l \le r - n)$; r, number of chemical elements; ρ_1, material density; i, linear rate of disintegration; v_{li}, stochiometric coefficients; Q, effective diffusion cross section; h_0, Debye screening radius; b_0, mean distance between charged particles; b, radius of action of charged particle interaction forces; a, thermal diffusivity of the material; α β, γ, approximation coefficients; dU_e/dx, velocity gradient at the outer edge of the boundary layer in the vicinity of the stagnation point; a', b', semiaxes of the ellipsodal shape of the specimen surface; e^-, symbol for the electron component of the mixture; I_{ef}, effective enthalpy; I^t_{ef}, I^e_{ef}, theoretical and experimental values of the effective enthalpy; q_0, convective heat flux; q_{rad}, radiative heat flux; $(\alpha/C_p)_0$, heat-transfer coefficient for the nondisintegrated specimen; M, flow Mach number.

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THERMAL DESTRUCION OF POLYMERS IN NONSTEADY HEATING IN A STREAM OF HOT GAS

V. V. Nesmelov and G. N. Isakov

UDC 541.6:536.24

The method of laser probing was applied in determining the characteristics of thermal destruction in dependence on the heating rate and the magnitude of the heat flux, and a method was suggested for calculating the kinetic parameters of the reaction of thermal dissociation of polymers.

The application of polymer materials in industry entails ever more stringent requirements concerning the durability of these materials under the effect of intense thermal fluxes. One of the principal requirements is increased heat resistance of polymers; when they are used as structural materials, it is possible to reduce the weight of industrial installations and special structures per unit power [1].

Thermal destruction of polymers is at present investigated by methods of thermogravimetry and of differential thermal analysis involving heating rates not exceeding 10°K/sec [2, 3]. The low rates of change of temperature in linear programmed heating are used because it is necessary to heat the test specimens uniformly throughout their bulk. Under real operating conditions, where the heating rates attain tens or even hundreds of degrees per second, the temperature distribution over the section of the specimen is important, and the method of determining the thermokinetic characteristics used in thermogravimetry are inapplicable. In addition, the recorded parameters (e.g., the temperature and the time of onset of thermal destruction) are substantially affected by the temperature of the gas stream T_e, the heat transfer coefficient α, and the heating rate dT_w/dt. For that reason the properties of polymers have to be studied under conditions that are close to the operating conditions of heat insulating materials [4]; this makes it possible to obtain reliable data on the kinetics of the investigated processes.

1. Method of Carrying Out the Experiment. One of the methods of investigating the thermal destruction of polymers and of composites based on them during rapid heating is the method

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Tomsk State University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 50, No. 3, pp. 373-379, March, 1986. Original article submitted January 30, 1985.

0022-0841/86/5003-0266$12.50