EFFECT OF NONEQUILIBRIUM DECOMPOSITION ON THE THERMAL REGIME OF COMPOSITE ABLATIVE COATINGS

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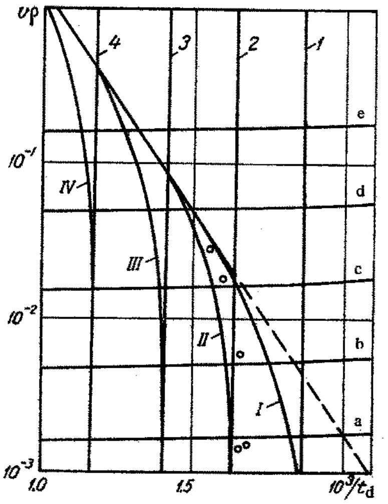
The decomposition of an ablative material under a refractory facing is examined for an arbitrary reaction regime. It is shown that the decomposition rate can be calculated from well-established equilibrium parameters.

A composite coating consists of a refractory facing and a substrate with low thermal conductivity. When the substrate is heated, it decomposes, and the gases formed create a layer with high thermal resistance. Consequently, the temperature of the facing increases, and the external heat load is reduced. Part of the heat passing through the facing is carried away by the decomposition products. In [1] it was shown that such a system operates more efficiently than homogeneous coatings and the rate of decomposition of the substrate was determined:



Nomogram for determining the decomposition parameters of ammonium chloride (P in bars; t_d in °K; q_* in kW/m^2; $v\rho$ in kg/m$^2\cdot$sec): 1) 535° K 2) 611; 3) 705; 4) 850; a) $q_* = 10$; b) 50; c) 10^2; d) $5\cdot10^2$; e) 10^3; I) $p = 10^{-1}$; II) 1; III) 10; IV) 10^2.

$$(v\rho)_n = \frac{q_*}{F}\exp(-k_*). \qquad (1)$$

The parameters F and k_* depend on the decomposition temperature t_d, which is known in advance only for the equilibrium decomposition regime, when the rates of the forward and reverse reactions are the same. However, in the case of polymer materials, for example, the decomposition is practically irreversible. Accordingly, the temperature t_d is determined from the condition that the "thermal" decomposition rate $(v\rho)_n$ be equal to the "kinetic" rate of the forward reaction:

$$\overrightarrow{(v\rho)} = \Phi_1\rho_1 a_1. \qquad (2)$$

The parameters of the forward reaction have been thoroughly investigated. Thus, for teflon $\Phi_1 = 2.25\cdot10^5$ m/sec, $\rho_1 = 2.15\cdot10^3$ kg/m^3, $E_1 = 1.7\cdot10^5$ J/mole, and the decomposition temperature t_d is found by solving (1) and (2).

We will consider the most complicated general case in which the decomposition regime cannot be foreseen in advance. This situation often occurs when traditional inorganic subliming compounds, NH_4Cl, NH_4HS, etc., are used as substrate. In the general case the decomposition rate is the resultant of the forward and reverse reactions:

$$(v\rho)_n = \overrightarrow{(v\rho)} - \overleftarrow{(v\rho)}. \qquad (3)$$

The reverse reaction rate

$$\overleftarrow{(v\rho)} = \Phi_2 P a_2. \qquad (4)$$

As a rule, the values of Φ_2 and a_2 are not known. Accordingly, we will determine them in terms of the investigated parameters of the forward reaction and the equilibrium decomposition pressure P_d.

At equilibrium

$$\overrightarrow{(v\rho)} = \overleftarrow{(v\rho)}, \quad P = P_d,$$

so that

$$\Phi_2 a_2 = \frac{\Phi_1\rho_1 a_1}{P_d}. \qquad (5)$$

From (2)–(5) we obtain

$$(v\rho)_n = \Phi_1\rho_1 a_1\left(1 - \frac{P}{P_d}\right). \qquad (6)$$

The figure shows values of $(v\rho)_n$ calculated from this relation for ammonium chloride NH_4Cl ($\Phi_1 = 0.60$ m/sec, $\rho = 1.53\cdot10^3$ kg/m^3, and $E_1 = 0.55\cdot10^5$ J/mole). For comparison, the dashed line indicates the irreversible decomposition rate (kinetic regime), while the vertical solid lines represent the equilibrium decomposition isotherms at various pressures (diffusion regime). The curves representing the true rate $(v\rho)_n$ are denoted by values of P and gradually degenerate into the limiting variants. The circles correspond to the experimental data on decomposition at P = 1 bar [2]. Clearly, an incorrect prediction of the reaction at a given temperature would involve serious errors.

For composite coatings the temperature t_d must be determined by solving (1) and (6). The almost horizontal lines in the figure, denoted by values of q_*, correspond to the decomposition rate calculated from (1) for NH_4Cl beneath an impermeable facing with the typical parameters

$$t_* = 2000° K, \quad \delta/\lambda_0 < 10^{-4} \text{ deg}\cdot m^2/W.$$

The points of intersection of these lines and the other curves determine the decomposition temperature and decomposition rate in various reaction regimes—kinetic, diffusion, and true regimes.

It is worth noting that only the decomposition temperature depends sharply on the regime. Owing to these temperature changes the rate is almost the same for different decomposition models. Only at $t_* < 1000°$ K is the temperature unresponsive to the reaction mechanism, whereas the rate $(v\rho)_n$ is very sensitive. However, the designer is interested in heat-resistant facings, so that in the investigated range of pressures and heat loads the rate $(v\rho)_n$ may be regarded as independent of the decomposition regime. In the calculation of composite coatings the temperature t_d is an intermediate parameter, and the ultimate aim is correctly to determine the decomposition rate $(v\rho)_n$. Hence the designer is not bound by the reaction mechanism and can use equilibrium values of the decomposition temperature in his solution.

NOTATION

$v\rho$ is the mass reaction rate; ρ is the density of the substrate; P is the pressure in the gap; P_d is the equilibrium pressure of the decomposition products; t_d is the substrate decomposition temperature; F is the heat of decomposition at temperature t_d; t_* is the permissible facing temperature; q_* is the heat load at temperature t_*; k_* is the root of the characteristic equation calculated in [1]; δ/λ_0 is the thermal resistance of the facing; Φ is the frequency factor; a is the decomposition coefficient equal to $\exp(-E/rt_d)$; E is the activation energy; r is the universal gas constant. The parameters Φ, a, E with subscript (1) relate to the substrate material, those with subscript (2) to its decomposition products.

REFERENCES

1. Yu. A. Dushin, IFZh [Journal of Engineering Physics], 8, no. 3, 330–335, 1965.
2. R. F. Chaiken et al., J. Chem. Phys., 37, no. 10, 2311–2318, 1962.

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