PROBLEMS REGARDING THE TRANSIENT HEATING OF HEAT-SHIELDING MATERIALS

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UDC 536.212.3

An analysis of problems regarding the transient heating and breakdown of heat-shielding materials is presented. The limiting heating rates for which allowance for the processes taking place in the interior of the heat-shielding materials becomes decisive are established.

Considered from the point of view of heat physics, reinforced (composite) heat-shielding materials belong to the category of porous substances with variable structure and internal heat evolution. Both the manner in which the structure varies and the intensity of internal heat evolution depend very considerably on the temperature and the conditions of heating (magnitude of the thermal flux, its period of action, and so on). It is therefore very important to establish the accuracy with which the thermophysical properties of such materials should be determined and what parameters are likely to introduce increasing errors of measurement.

A special characteristic of reinforced heat-shielding materials is the existence of at least two "fronts" of mass loss: the losses at the surface, which determine the linear dimension (thickness) of the heat shield, and an internal front defining the depth of the layer within which the structure has been altered. The relationship between these thicknesses decides the order of importance of making precise determinations of particular parameters (physicochemical at the outer surface or thermophysical inside the heat-shielding material). In addition to the many external parameters such as the temperature and velocity of the incident gas flow, the ambient pressure, and the size of the actual body, we may also distinguish two internal parameters: the temperature of the disintegrating surface T_W and the rate of change of the temperature of the layer just under the surface $-b = (\partial T)/\partial\tau$; these may constitute characteristics of the external and internal problems at the same time.

For example, in the quasi-steady-state disintegration of the heat-shielding material, when the velocities of all the isotherms inside the material coincide with the linear rate of disintegration v_∞, we may estimate the maximum heating rate as

$$b \leqslant \left(\frac{\partial T}{\partial \tau}\right)_{\max} = (T_w - T_0)\,\frac{v_\infty^2}{a}.$$

The depth δ_T at which the isotherm $(T - T_0)/(T_W - T_0) = 0.05$ is located may be related to the thermal diffusivity a and the velocity v_∞ in the following way:

$$\delta_T = 3a/v_\infty.$$

Correspondingly, the thickness of the layer carried away $s = v_\infty\tau$ where τ is the period of quasi-steady-state disintegration. However, before the quasi-steady state of disintegration at a linear rate v_∞ is achieved, a time period of $\tau_V \approx a/v_\infty^2$ elapses.

Table 1 presents an estimate of all the parameters indicated for the following specified values: $T_W = 2300$°K, $a = 5\cdot 10^{-7}$ m^2/sec, and a total heating time of $\tau = 50$ sec.

Analysis of these results shows that for low rates of disintegration v_∞ a much greater thickness of the heat shield is raised to a higher temperature than that which is carried away by the flow. For loss rates

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 29, No. 1, pp. 39-44, July, 1975. Original article submitted January 27, 1975.

TABLE 1

v_∞, mm/sec	b, deg/sec	δ_T, mm	τ_V, sec	$s=v_\infty(\tau-\tau_V)$, mm
0,1	40	15	50	0
0,3	400	5	5	13,5
1,0	4000	1,5	0,5	49,5

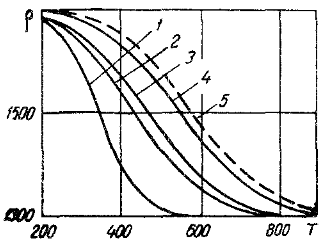

Fig. 1. Density of fiber glass-reinforced plastic as a function of the temperature in the decomposition zone of the organic binder for various heating rates. b (°K/sec): 1) b → 0; 2) b = 1; 3) 1.5; 4) 5.2; 5) 7. ρ, kg/m^3, T, °C.

of $v_\infty > 0.3$ mm/sec and, correspondingly, heating times of $b > 400$ deg/sec, errors committed in determining the depth of heating δ_T are not decisive in relation to the final choice of the thickness of the heat-resistant layer, since the thickness of the layer s carried away is almost three times as great.

Generalizing the situation, we may thus assert that, as regards heat-shielding materials, the effects of transient heating are important up to heating rates of $b < 200$-400 deg/sec.

Let us consider how the heating rate influences the way in which the thermophysical characteristics of such materials vary, namely the thermal conductivity λ_Σ, the volumetric specific heat $(\rho c)_\Sigma$, and the specific heat of the gas c_g. This influence is associated with a displacement of the zones characterizing the physicochemical transformations in the high-temperature direction as the heating time increases. Figure 1 shows some experimental data regarding the influence of heating on the position of the zone of thermal decomposition for an organic binder in fiber glass-reinforced plastic.

The displacement of the zones of physicochemical transformations inside the heated layer has the effect that the thermophysical properties corresponding to a specific temperature are no longer unique (Fig. 2a). This ambiguity is the more serious the more the corresponding thermophysical parameter depends on the structure or density of the material.

It is well known that a reduction in the density of fiber glass-reinforced plastic by 10% reduces the thermal conductivity by 20-30%. With increasing temperature the influence of porosity on the thermal conductivity also increases.

The specific heat of nondisintegrating substances depends very little on the porosity; however, in the case of composite heat-shielding materials there is not only an increase in porosity in the reaction zone, but also a change in the chemical composition (in particular, the high-molecular components of greater specific heat may volatilize). This is, of course, to a certain extent reflected in the specific heat of the material (Fig. 2b). We must also allow for the fact that the specific heat enters into the heat-conduction equation in the form of a product with the density $(\rho c)_\Sigma$.

Thus for composite materials both thermophysical parameters form a characteristic "hysteresis loop" on the graph relating them to temperature (Fig. 2, a and b); the width of this loop corresponds to the possible displacement of the reaction resulting from a change in the heating rate from zero to several hundreds of degrees per second (when the role of surface disintegration becomes dominant).

Finally, the specific heat of the gaseous decomposition products c_g may vary considerably as a function of the conditions of filtration of these products within the porous heated layer. The composition of these products varies continuously, as indicated by the deposit of pyrolytic carbon on the sides of the pores close to the decomposing surface. However, calculations based on the assumption of thermodynamic equilibrium may yield results far removed from the truth if we remember the comparatively low decomposition temperature of the organic binder and the high rate of outflow of the gases so formed.

Summarizing all these phenomena, we may conclude that the study of the thermophysical parameters should be regarded as a complex problem, involving the simultaneous determination of many interrelated characteristics. Remembering the high temperature levels and heating rates, experiments in high-temperature aerodynamic tubes are probably best for this purpose.

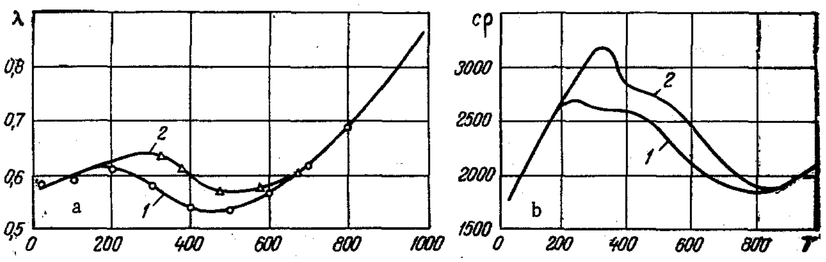

Fig. 2. Temperature dependence of the thermal conductivity (a) and specific heat (b) of asbotextolite for various heating rates: 1) b → 0; 2) b = 5. λ, W/(m·°K); ρc, kJ/(m^3·°K).

The complexity and interrelated nature of the physical processes taking place during the transient heating of heat-shielding materials presents the research worker with the problem of determining a large number of thermophysical properties at the same time. Correspondingly, it is essential to develop special methods of analyzing the results of the measurements capable of providing such complex information.

In the early years of research into high-temperature heat-shielding materials, methods based on the so-called "equivalent" thermophysical properties were widely developed. The essence of these methods amounted to the fact that the many physicochemical processes and transformations taking place inside the heat-resistant composite materials were described by the classical Fourier equation, although the thermal diffusivity had the formal significance of a matching coefficient. It is not difficult to show that the difference between the equivalent thermal diffusivity a_{eq} and the real one $a = (\lambda/\rho c)$ may be extremely substantial, and also different in different temperature ranges.

Thus even for constant values of the true thermal conductivities λ, density ρ, and specific heat c within the coke-encrusted layer of the heat-shielding material $T^* \leq T \leq T_W$ (where T^* is the coking temperature and T_W is the temperature of the disintegrating surface) we have the following in the case of quasi-steady-state heating and disintegration:

$$\frac{a}{a_{eq}} = 1 + \Gamma \frac{T - T^*}{T - T_0}\left(\frac{c_g}{c} - 1\right) + \frac{\Delta H^*}{c(T - T_0)}. \tag{1}$$

Here Γ is the mass proportion of material passing into the gas on coking and ΔH^* is the thermal effect of this process (for $T \leq T^*$ $\Gamma = \Delta H^* = 0$).

Equation (1) shows that the effects of the individual components of heat transfer differ in both extent and character.

Whereas the thermal effect of the coking reaction ΔH^* affects the equivalent thermal diffusivity most of all close to the temperature of the reaction front $T = T^*$, the absorption of heat by the filtering gases intensifies on moving in the high-temperature direction.

We note that under conditions of transient heating the role of heat absorption by filtration, and also the thermal effect ΔH^*, may be intensified by a large number of times, since the velocity of the coking front may greatly exceed the quasi-steady-state value. Hence the difference between a_{eq} and a, or, in general, the difference between the "equivalent" thermophysical parameters of the materials and their real values, may be very considerable.

Nevertheless, the introduction of the equivalent properties is justified in all cases in which they characterize the actual heat-shielding material (its structure or state) and not the heating process.

Thus it is desirable to describe the thermal conductivity of a porous structure by means of a single coefficient λ_Σ incorporating the thermal conductivity of the solid matrix and the thermal conductivity of the gas filling it, and allowing for radiative transfer inside the pores. This is due to the fact that all three phenomena are mainly dependent on the temperature and less on the pressure. Thus a completely specific quantity λ_Σ may be ascribed to each state of the material, quite independently of the heating prehistory.

On the other hand, heat transfer by virtue of the filtering gases or heat absorption in the chemical reactions depends not only on the particular state of the material, but also on the heating rate or, in general, on the previous states. In this case the introduction of the equivalent parameters cannot provide a proper account of all the multitide of physical phenomena taking place inside the heat-shielding material.

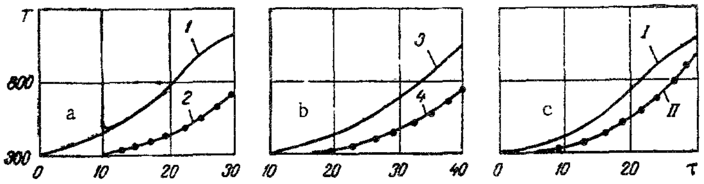

Fig. 3. Comparison between experimental data relating to the temperature inside fiber glass-reinforced plastics with different contents (Γ) of gaseous binder decomposition products: a) $h_0 = 5$ mm; b) 7 mm; 1) material No. 3; 2) No. 1; 3) No. 3; 4) No. 2; c) with different structures of the filler (glass fiber), material No. 3, $h_0 = 5$ mm; I) three-dimensional structure of the filler; II) one-dimensional (h_0 is the depth of the thermocouple relative to the decomposing surface) τ, sec.

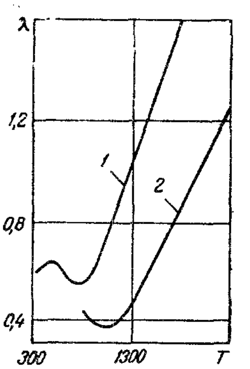

Fig. 4. Comparison between experimental data relating to the thermal conductivity of asbotextolite obtained under conditions of uniform (1) and unilateral (2) heating.

On the other hand, the importance of correctly allowing for all these extra components of heat transfer is demonstrated by the results of direct measurements of the temperature field in heat-shielding materials of like initial composition.

Figure 3a,b, and c illustrates the results of temperature measurements at a depth $h = h_0$ from the heated surface in fiber glass-reinforced plastic with differing values of Γ, the mass proportion of material passing into the gas during thermal decomposition. The quantity Γ was 0.5 for material No. 1, 0.25 for material No. 2, and 0.15 for material No. 3. For comparison Fig. 3c shows the results of temperature measurements on material No. 3 under the same experimental conditions for a three- and one-dimensional structure of the glass-fiber filler. We see that the influence of the filtration of the gaseous coking products (for $\Gamma > 0.15$) is far stronger than the influence of the direction of the glass fibers in the fiber glass-reinforced plastic.

In conclusion, we may consider one further problem regarding the thermophysical study of heat-shielding materials which undergo coking. This is the problem of matching the data obtained under conditions of uniform and unilateral heating. It is well known that the majority of thermophysical investigations are carried out on small samples of the particular material placed in a thermostated volume, a furnace, in which the coking products are able to leave the sample in all directions with an almost equal probability. For the practical operating conditions of heat-shielding materials, however, the gaseous products are only able to leave in a direction opposite to the thermal flow, and they have to overcome the hydrodynamic resistance of the coked layer. In addition to this, the heating time in furnaces is usually much greater than the actual working time of the heat-shielding materials. All this probably has the effect that the thermal conductivity measured in the furnace differs from the real value not only inside the zone of decomposition of the organic constituent, but also over a wider temperature range (Fig. 4).

An analysis of all the foregoing problems of transient heat transfer in heat-shielding composite materials leads to the conclusion that the solution of such problems will require new methods of processing experimental data. Whereas in earlier treatments of many thermophysical problems attention could be restricted to analytical relationships obtained by standard or regular methods of heating, in the present case the solution of the inverse problems is often required. It is simply important that the formulation of the inverse problems should start from a fairly general physical model, allowing for the most important physicochemical transformations inside the heat-shielding material which accompany its heating [4].

The advantage of carrying out thermophysical measurements during the actual course of transient decomposition lies in the fact that in this way the question of modeling the structure of the material or the character of the internal processes taking place is eliminated. However, a whole series of difficulties of a methodical nature arises, and, in particular, that of the discreteness of the temperature data. That is, the measured temperature field fails to provide a continuous profile of the temperature in the solid. This impedes the solution of the reciprocal problems of heat conduction and requires the use of various special mathematical devices [5, 6, 7]. As data regarding the physics of the processes taking place and the thermophysical properties of heat-shielding materials accumulate, we shall probably discover the answer to the main question, namely, whether such properties are uniquely related to the temperature, or at least to what extent this assertion is valid.

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