STUDY OF THE HEAT-TRANSFER CHARACTERISTICS OF A THERMALLY PROTECTIVE COMPOSITE MATERIAL

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Results are presented from a theoretical—experimental study of the thermal conductivity of a thermally protective composite for different models of heat transfer.

Serious methodological errors usually attend the use of traditional methods of conducting thermophysical studies to determine the heat-transfer characteristics used in calculation of the temperature fields in thermally protective coatings based on composite materials which undergo degradation. The errors result mainly from the practice of analyzing empirical data with algorithms based on the solution of linear boundary-value problems of heat conduction for the simplest models of heat transfer, which ultimately makes it necessary to have idealized heating regimes in thermophysical experiments.

The approach based on the use of methods employing inverse problems [1] to analyze empirical data offers important advantages over traditional methods of studying the heat-transfer characteristics of a thermally protective composite material (TPM) under nonsteady conditions — especially thermal conductivity. Use of this approach not only removes limitations on the heating regime in the thermophysical experiment, but also permits determination of heat-transfer characteristics for the mathematical models in which they are to be later used.

The main goal of the studies completed is comparative analysis of the temperature dependences of the thermal conductivity $\lambda(T)$ of a composite TPM determined from the solution of an inverse problem for different heat-transfer models on the one hand and data obtained by a traditional method in thermophysical studies — the method of monotonic heating — on the other hand. We analyzed the effect of the temperature measurement error in the experiment on the accuracy of the results obtained.

The inverse problem of heat and mass transfer (IPH) consisted of determining the function $\lambda(T)$ from the condition of the minimum of the object functional

$$I = \sum_{i=2}^{N-1} \int_0^{\tau_m} [T_i(X_i,\ \tau,\ \lambda(T)) - f_i(\tau)]^2\, d\tau, \tag{1}$$

where T and f are the calculated and measured values of temperature at the specimen points with the coordinates $0 < X_i < b$.

In the general case, the mathematical model of heat and mass transfer in the material is described by the following system of equations:

$$c(T)\frac{\partial T}{\partial \tau} = \frac{\partial}{\partial x}\left(\lambda(T)\frac{\partial T}{\partial x}\right) - k(T,\ \eta)\frac{\partial T}{\partial x} - Q(T,\ \eta),\ x \in (0,\ b),\ \tau \in (0,\ \tau_m], \tag{2}$$

$$T(x,\ 0) = \varphi_0(x),\ x \in [0,\ b], \tag{3}$$

$$m(T,\ \eta) = \begin{cases} \int_0^x (1 - k_T)\rho_0(A + \Delta A\eta) z^n \exp\left(-\frac{E}{RT}\right) d\xi, & T > T_r, \\ 0, & T \leqslant T_r, \end{cases} \tag{4}$$

$$T(0,\ \tau) = f_1(\tau),\ T(b,\ \tau) = f_N(\tau),\ \tau \in [0,\ \tau_m], \tag{5}$$

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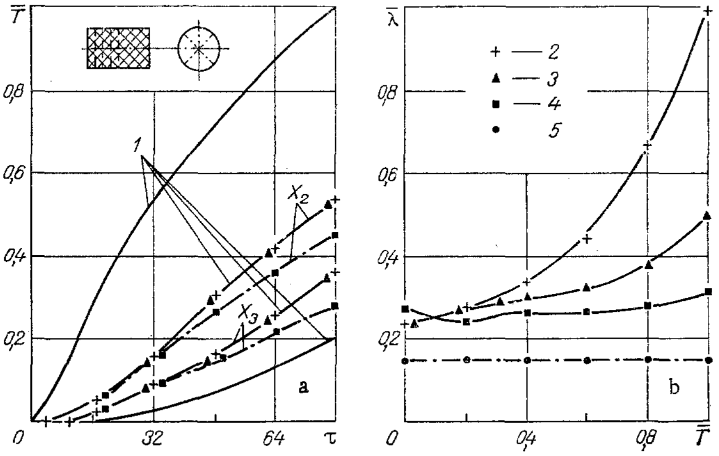

Fig. 1. Analysis of empirical data: a) temperature at points of installation of thermocouples; b) established temperature dependences of thermal conductivity (1 — experimental values; 2, 3 — determined from the solution of the IPH for model (2-5) and a homogeneous heat-conduction equation; 4 — the function λ(T) obtained by the method of monotonic heating; 5 — initial approximation). $\lambda_{\max}=0{,}343$ W/(m·K); $T_0=T_{\min}=303$ K; $T_{\max}=663$ K; $\bar{T}=(T-T_0)/(T_{\max}-T_0)$; $\bar{\lambda}=\lambda/\lambda_{\max}$; τ, sec.

where

$$\eta=\frac{\partial T}{\partial \tau},\ T_r=T_{r_0}+a_1\eta^{a_2},\ z=(\rho-\rho_0)/(\rho_0-\rho_k),\ k(T,\ \eta)=m(T,\ \eta)\frac{dh(T)}{dT},\ Q(T,\ \eta)=\frac{\partial m}{\partial x}h(T).$$

In Eqs. (2)-(5), the functions $\lambda(T);\ c(T);\ \varphi_0(x);\ f_i(\tau),\ i=\overline{1,\ N},$ and the parameters of thermal degradation of the material were considered to be known. We solved the above inverse problem by means of the iterative numerical algorithm described in [2].

By subjecting the sought function to parametrization in the form

$$\lambda(T)=\sum_{k=1}^{M+1}\lambda_k B_k(T),$$

where $B_k(T)$ is a system of basis functions constructed on the grid $\omega=\{T_{\min}+kH,\ k=\overline{-1,\ M+3};\ H=(T_{\max}-T_{\min})/M\}$ with the use of cubic B-splines, we reduce the initial nonlinear variational problem to an extreme finite-difference formulation. The new problem consists of finding the (M + 1)-dimentional vector of the parameters $\bar{\lambda}=\{\lambda_k\}_1^{M+1}$ from the condition of the minimum of the object functional (1) with limitations (2)-(5). The functional was minimized by the method of conjugate gradients.

Figure 1 shows the composite specimens used in the studies. Temperature was measured with KhA_{68} Chromel—Alumel thermocouples (GOST 3044-77) of diameter $d = 0.1\cdot10^{-3}$ m. The thermocouples were butt-welded. The coordinates of the thermocouples in the specimen were determined from x-ray photographs. The ratio of the length of the isothermal section of the thermocouple to the diameter of the thermoelectrode $l/d = 50$. To ensure a uniform temperature field, the cylindrical specimen was inserted in a hole in a square plate made of the same material. The rear and lateral surfaces of the assembled model were thermally insulated. The tests were conducted on a thermally evacuated radiant-heating stand.

Two models of the above-described design were used in experimental studies. The function λ(T) of the material was determined from measurements of temperature in model No. 1. The measurements in the second model were for control purposes and were used to compare the experimental and theoretical values of temperature at an internal point of the specimen with a known coordinate X_2 in the solution of heating problem (2-5) with the function λ(T) found from the solution of the IPH.

The coordinates of the thermocouples in the models were as follows ($X\cdot10^3$ m):

TABLE 1. Variants for which Calculations Were Performed in Analyzing Errors from Analysis of Experimental Data

No. of variant	Error of thermocouple location, $\Delta X\cdot10^3$, m		Coordinates of thermocouples, $X\cdot10^3$, m		ε_{max}, %
	ΔX_2	ΔX_3	X_2	X_3	
1	0	0	2,6	4,2	5
2	−0,2	+0,2	2,4	4,4	5
3	+0,2	−0,2	2,8	4,0	5

Number of model	X_1	X_2	X_3	X_4
1	0	2,6	4,2	5,6
2	0	2,2	3,5	—

As the nominal external boundary (X_1 = 0) we took the plane passing through the thermocouple closest to the heated surface.

The function $\lambda(T)$ of the material was determined in three stages: mathematical modeling to evaluate the possibility of using the IPH to reliably determine the thermal conductivity; analysis of experimental data; evaluation of the accuracy of the solution.

The need to perform preliminary numerical modeling of the process of analyzing the experimental data was based on the results in [3]; the procedure used was detailed in [4], and calculations were performed for model No. 1. Here, as the exact value of thermal conductivity we used the function $\lambda(T)=6{,}7\cdot10^{-7}T^2-6{,}1\cdot10^{-4}T+0{,}22$, W/(m·K) while as the boundary conditions we used experimental values of temperature at the points X_1 = 0, $X_4 = 5.6\cdot10^{-3}$ m (Fig. 1). The values of the rest of the coefficients and parameters describing heat and mass transfer in Eqs. (2)-(5) and required for the calculations were assumed to be known and corresponded to a typical semiorganic polymer.

The results of the numerical modeling confirmed the feasibility of reliably determining the sought function for the specified regimes of thermal loading and scheme of thermocouple placement in model No. 1.

Figure 1 shows results of analysis of experimental data within the framework of a mathematical model considering the occurrence of thermal degradation in a thermally protective material during heating. Also shown are the functions $\lambda(T)$ and the temperatures found at the thermocouple locations obtained from analysis of test data for a homogeneous heat-conduction equation $(k(T,\eta)=Q(T,\eta)\equiv0)$. For comparison, we show the relation for thermal conductivity obtained by the method of monotonic heating.

Errors connected with inaccurate determination of the thermocouple coordinates and errors incurred during measurement, recording, and interpretation of temperature were considered when we analyzed the effect of measurement errors on the accuracy of the IPH solution.

The total error for the first group was made up of the error incurred in determining the position of the thermocouples from x-ray photographs and their displacements connected with contraction and expansion of the specimen during heating. According to estimates, the maximum value of this error for the experiment was $\Delta X = 0.2\cdot10^{-3}$ m. In the numerical modeling we assumed that the deviations of the thermocouple coordinates from the nominal values had different signs.

We did not perform special calculations to evaluate the errors connected with measurement and recording of temperature or interpretation of the thermograms. The literature data (see [5, 6], for example) permits us to conclude that these errors amount to no more than 4-6% of the running value of the measured temperature. The total error for this group was modeled on a computer with a standard random-number generator with a uniform probability density for perturbations. Here, the perturbed value of temperature at the points X_i, i = 2, 3, was calculated from the formula

$$\tilde{f}_i(\tau)=f_i(\tau)+\omega_i(\tau)\,\varepsilon_{max},$$

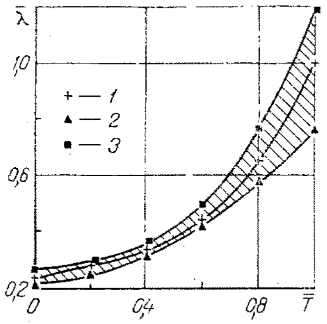

Fig. 2

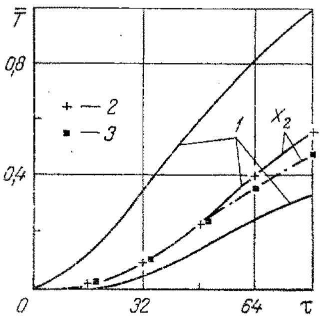

Fig. 3

Fig. 2. Estimate of the error of the thermal conductivity function: 1) nominal value; 2, 3) estimate for variants 2 and 3 in the table. $\lambda_{max} = 0.343$ W/(m·K); $T_0 = T_{min} = 303$°K; $T_{max} = 663$°K.

Fig. 3. Comparison of temperatures at the control point of model No. 2: 1) experimental values; 2) calculation with the function $\lambda(T)$ determined from the solution of the IPH for model (2-5); 3) calculation with the function $\lambda(T)$ obtained by the method of monotonic heating, $T_0 = T_{min} = 303$°K; $T_{max} = 556$°K.

where f_i is the exact value of temperature; ω_i is the random variable distributed according to a uniform law with a zero expectation value and a single dispersion; ε_{max} is the maximum possible temperature measurement error.

Figure 2 shows the results of the modeling and Table 1 shows the variants for which the calculations were performed. As the nominal value of $\lambda(T)$ in the calculations we took the function determined from the solution of the IPH for variant 1 in Table 1 with $\varepsilon_{max} = 0$ (curve 1 in Fig. 2); the hatched region in the figure corresponds to variants 2 and 3.

To check the correspondence of the established thermal conductivity function of the material to other experimental conditions, we analyzed the agreement between the theoretical and empirical temperatures for model No. 2 at the point with the coordinate $X_2 = 2.2 \cdot 10^{-3}$ m. We used the function $\lambda(T)$ obtained from solution of the IPH with the nominal values of thermocouple location in model No. 1. The thermal boundary conditions were the empirical values of temperature at the points $X_1 = 0$ and $X_3 = 3.5 \cdot 10^{-3}$ m. The results shown in Fig. 3 indicate good agreement between the theoretical and experimental temperatures at the control point of model No. 2. Also shown are the values of temperature calculated with the function $\lambda(T)$ obtained by the method of monotonic heating.

The completed analysis of the experimental data and analysis of the accuracy of the results showed that the function $\lambda(T)$ obtained by the method of monotonic heating in the case of intensive thermal degradation in a composite may differ significantly from that which should be used in calculations of temperature fields with mathematical model (2)-(5).

NOTATION

T, temperature; τ, time; x, ξ, space coordinates; τ_m, b, right boundary values of the time and space intervals; c, λ, volumetric specific heat and thermal conductivity; m, h, mass rate and enthalpy of gaseous products of thermal degradation; $k_T = \rho_k/\rho_0$, limiting value of the coke number; ρ_0, ρ, ρ_k, initial, running, and final values of the density of the material; a_1, a_2, A, ΔA, n, E, parameters of thermal degradation; η, heating rate; T_{r_0}, T_r, temperatures of the beginning of physicochemical transformations in the material with $\eta = 0$ and $\eta \neq 0$, respectively; φ, initial temperature distribution; T_{min}, T_{max}, minimum and maximum temperatures; R, universal gas constant; N, number of temperature measurement points; M, number of sections of the spline approximation.

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MATHEMATICAL MODEL OF THE KINETICS OF THERMAL DEGRADATION OF POLYMERS WITH INTENSIVE HEATING

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A modified equation is proposed to describe the kinetics of the thermal degradation of polymers with allowance for temperature limits for the polymers. A physical interpretation of the model is given.

The need to mathematically model thermal degradation processes arises in the solution of both direct and inverse problems of heat transfer, since the thermophysical characteristics of the materials undergoing degradation are dependent on the completeness of the chemical reactions. It is difficult to perform such modeling because a large number of chemical and physical processes are taking place simultaneously in the material. Thus, if 20 substances are formed as a result of degradation, this corresponds to 20 kinetic equations including 60 parameters. Accompanying the chemical reactions are complex physical processes: mass transfer (diffusive and molar) of the degradation products and their interaction — dissolution, sorption, and desorption, etc. Even for a simple composition during thermal degradation, a complete system of equations describing the transformations in polymers has not yet been solved. Given this situation, the development of simple mathematical models adequate to the physics of the phenomena in question is very important for engineering calculations.

Studies of polymers of different classes by the methods of thermal analysis conducted in a broad temperature range have shown that the regions of thermal degradation of polymers are limited. The upper boundary of the degradation region was first fixed in tests with heating rates of 1-10 deg/sec. Later tests conducted at heating rates up to $5\cdot10^4$ deg/sec confirmed the conclusions made. It was established for linear polymers that thermal degradation is completed upon attainment of a limiting temperature T_{mt} = 500-540°C, regardless of the heating rate. The limiting temperatures are higher for cross-linked polymers. Tests with high heating rates were conducted on specimens up to 5-7 μm thick. The particulars of the methods used for tests are described in [1, 2].

In engineering applications, the kinetics of the thermal degradation of high-molecular-weight compounds is usually described by the equation of an n-th-order chemical reaction

$$d\omega/dt = -k(\omega - \omega_\infty)^n, \tag{1}$$

where it is assumed that

$$k = k_0 \exp(-E/RT). \tag{2}$$

It cannot be expected that system (1)-(2), containing three parameters in all, will adequately characterize the larger number of complex processes that occur in thermal degradation. However, it has been empirically established that this system well reflects the kinetics of the thermal degradation of polymers with a single heating rate. With another heating rate, the parameters k_0, E, and n turn out to be quite different [3]. Here, k_0 may change by several orders of magnitude when heating rate increases by several factors [3]. A serious

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