HEAT AND MASS TRANSFER IN THE DESTRUCTION OF THERMAL PROTECTIVE MATERIALS WITH A DIFFERENT CONTENT OF A POLYMER BINDER IN A HIGH-ENTHALPY GAS FLOW

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With the aid of a complex experimental procedure, we consider the mechanism of thermal destruction of carbon-phenol thermal protective compositions with a different content of components in the interaction with a high-enthalpy gas flow. Thermophysical, thermokinetic, and structural properties of the thermal protective compositions are determined. The effect of the rate of heating on characteristics of the transfer coefficients, which is specified by a kinetic shift of the pyrolysis reactions to a high-temperature region, is ascertained.

The problem of thermal protection of landing aircraft is fairly complex, since many interrelated factors should be taken into account, such as pyrolysis of thermal protective materials (TPMs), heterogeneous reactions on the surface and in a porous coke layer, change in the structure and thermophysical properties due to thermomechanical and thermochemical processes, etc. The thermal state of structures and the efficiency of thermal protective coatings (TPCs) can be predicted after comprehensive experimental investigations that elucidate the physical pattern of the destruction, salient features of changes in the structure and coefficients of heat and mass transfer, and the kinetics of physicochemical transformations under different conditions of heat and mass transfer. At present, thermotechnical calculations suggest the use of dependences for the thermal conductivity $\lambda_s(T_s)$ and specific heat $c_{ps}(T_s)$ and a constant value of the density of the carbon residue ρ_c in solving the mass and energy equations. At the same time, these quantities are not constants at a specified temperature level [1, 2]. Their numerical values are determined by the current density (porosity) of TPM that is related to the temperature and the rate of heating, dT_s/dt. The dependence $\rho_c(T_s)$ is due to the multistage nature of physicochemical transformations. The number and character of the stages are determined by many factors; the chemical structure of the polymer, the activity of the composition components, the conditions of thermal action, etc. Each of them makes a contribution of its own to the formation of a carbon residue. Moreover, thermomechanical effects (such as expansion, shrinkage, and cracking) give rise to an additional porosity, which affects the thermophysical properties of TPMs.

The investigation procedure included a study of the properties of thermal protective compositions at different temperatures of thermal stabilization, determination of the kinetics of thermal destruction, and tests of TPCs in a high-temperature gas flow. To this end, standard (thermogravimetric) and original [3, 4] experimental methods were employed.

In the investigations by the method of stabilized states, the specimens were heated in an inert medium (nitrogen) to the specified temperature T_s and held under these conditions up to complete cessation of mass loss; afterwards, they were cooled to the initial temperature and weighed on an analytical balance, and their geometric dimensions were identified. From measurement results for the mass M and volume V_T, the density of carbon residue ρ_c was obtained that corresponds to a given annealing temperature T_s. In each subsequent experiment, the level of the dissociation temperature rose. Thermoanalytical tests of TPMs at rates of heating $dT_s/dt = 10$ K/min were performed on a Paulik, Paulik–Erdei derivatograph, and similar experiments under the
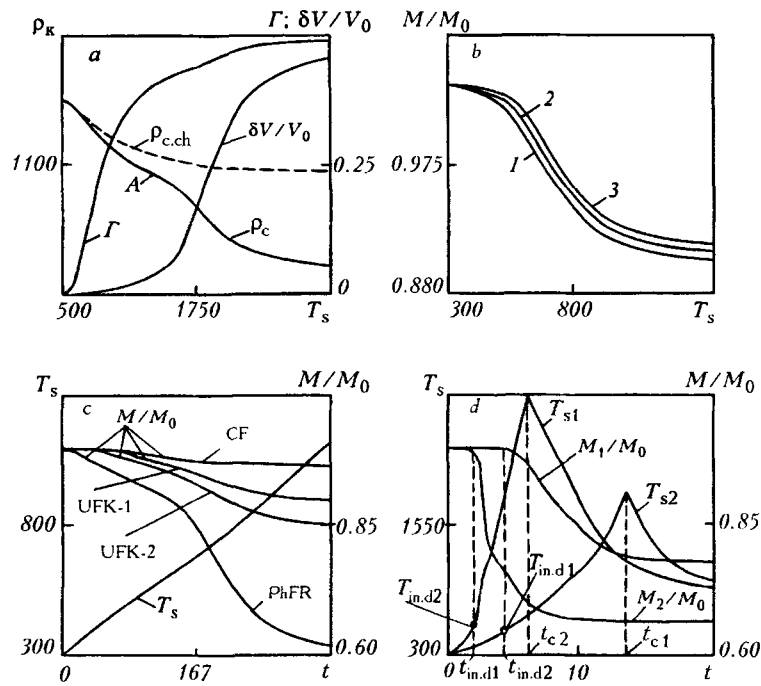
Fig. 1. Test data for thermal protective coatings: a) degree of gasification Γ, relative change in volume $\delta V/V_0$, and density of the carbon residue ρ_c (kg/m^3) vs. temperature T_s (K) for UFK-1 TPC; b) relative mass loss M/M_0 of UFK-1 vs. temperature T_s (K) at rates of heating dT_s/dt: 1) 2.5, 2) 5.0, 3) 10.0 K/min; c) temperature T_s (K) and relative mass loss M/M_0 vs. time t (min) for UFK-1, UFK-2, and their constituents; d) mass M/M_0 and temperature T_s (K) of UFK-1 specimens vs. time t (sec) at rates of heating equal to 50 and 150 K/sec.

conditions of high-rate (up to 1000 K/sec) heating were carried out using an original setup [3], where carbon-plastic specimens were heated by the electric current. Here, the required rate of heating was attained by varying the voltage applied to a specimen from a controlled power source, which provided the needed rate of heat release. On heating at the specified rate dT_s/dt to the annealing temperature T_s, the specimens were cooled under the conditions of free convection. In the regions of heating $0 < t < t_c$ (t_c is the time of completion of the annealing) and cooling $t > t_c$, the temperature and mass loss in the time t were measured continually. Subsequently, the dependences $M(t)$ and $T_s(t)$, obtained at the heating stage, were used for determining thermokinetic parameters of the pyrolysis reaction (the activation energy E, the frequency factor k_0, the order of reaction n, and the thermal effect Q), and from the $T_s(t)$ temperature curves for the specimen cooling we found the coefficients of thermal conductivity λ_s and specific heat c_{ps} of the TPMs considered.

The TPM tests under unilateral heating in a gas flow heated to the temperature T_e were performed on a setup [4] that consisted of the source of convective heating, an automatic weight meter, and recording equipment. The carbon-plastic specimens with thermocouples embedded at several points at distances y from the heated surface were exposed to a high-enthalpy gas flow, and simultaneously the temperatures $T_s(y, t)$ and the mass loss $\Delta M(t) = M_0 - M(t)$ were recorded (M_0 and $M(t)$ are the initial and current masses of the specimen). Figures 1-3 present results of testing the TPMs by various methods.

Figure 1a plots data for the degree of gasification $\Gamma = 1 - K_T$, the relative increase in the volume $\delta V/V_0 = (V_T - V_0)/ V_0$ (V_0 and V_T are the volumes of the specimen in the initial state and after thermal stabilization at the temperature T_s), and the density of the carbon residue ρ_c as functions of the annealing temperature T_s ($K_T = 1 - [M_0 - M(t)]/\varphi M_0$, where φ is the mass fraction of the binder). Clearly, the dependence $\rho_c(T_s)$

at T_s = 1300 K has the inflection point A, which conventionally separates two stages of the formation of the carbon residue. When $500 < T_s < 1000$ K, $\rho_c(T_s)$ varies mainly due to the thermal decomposition of the carbon-phenol composition (CPhC) accompanied by the liberation of gaseous reaction products. When $T_s > 1000$ K, volumetric expansion begins due to the thermomechanical effects in the composite material and the weakening of bonds between the components as a consequence of pyrolysis of the phenol-formaldehyde resin (PhFR). This process prevails in the formation of the structure of the carbon residue in the temperature range of 1300 $< T_s < 2900$ K. So, for each temperature T_s there is a corresponding coke number K_T, and the TPM is formed in two stages; due to the PhFR pyrolysis and due to the irreversible thermomechanical processes leading to a volumetric expansion. Thus,

$$\rho_c = \rho_{c.ch}/[1 + \delta V/V_0] , \tag{1}$$

where $\rho_{c.ch} = \rho_0[1 - \varphi(1 - K_T)]$. For a material with mass content of the binder ρ_0 = 1350 kg/m^3 at T_s = 2900 K, calculation by Eq. (1) with account for the data of Fig. 1a yields ρ_c = 720 kg/m^3, which checks with experimental data. The results of thermogravimetric tests of the UFK-1 (CPhC) composition at rates of heating dT_s/dt = 2.5, 5.0, and 10.0 K/min (curves 1, 2, and 3, respectively) are presented in Fig. 1b. Assuming that the thermal destruction of the TPM is described by the equation of chemical kinetics

$$dM/dt = (M - M_c)^n k_0 \exp(-E/RT_s) , \tag{2}$$

at n = 1 for two rates of heating dT_{s1}/dt and dT_{s2}/dt and the corresponding dependences of the change in the masses M_1 and M_2, and the derivatives dM_1/dt and dM_2/dt it is easy to find

$$M_c/M_0 = [M_1 (dM_2/dt) - M_2 (dM_1/dt)]/[(dM_1/dt) - (dM_2/dt)] . \tag{3}$$

The dependence $M_c(T_s)/M_0$, obtained from Eq. (3) with account for data of the thermogravimetric experiment, defines the mass of the carbon residue formed on completion of thermochemical processes in the TPM. As ensues from Fig. 1a (dashed curve), this dependence describes only the first stage of the formation of the carbon residue. Figure 1c presents data of the thermogravimetric experiment at the rate of heating dT_s/dt = 2.5 K/min for UFK-1 (φ = 42%, ρ_0 = 1350 kg/m^3) and UFK-2 carbon plastics (φ = 35%, ρ_0 = 1380 kg/m^3), phenol-formaldehyde resin (PhFR), and carbon fabric (CF). An analysis of the obtained dependences $M(T_s)/M_0$ reveals that the entrainment of the UFK mass is determined not only by the thermal expansion of the polymer binder but also by the pyrolysis of the carbon fabric (CF). The liberation of gaseous products starts at fairly low temperatures of 350–370 K (see the $M(t)/M_0$ curve for PhFR). The low-temperature mode of gasification up to T_s = 450–470 K, when a horizontal plateau is formed on the M/M_0 curves, is generally associated with the liberation of bound water and evaporation of highly volatile components remaining after solidification [6]. With $T_s > 450$ K, thermal decomposition of the material begins. The inflection point on the horizontal plateau conventionally separates these two stages, which are accompanied by the liberation of gaseous products but are different in nature, and can serve as a characteristic point defining the initial instant of decomposition $t_{in.d}$ of the polymer or the composition as a whole. When heated to a temperature of 1200 K, the filler (CF) loses up to 3%, the binder (PhFR) up to 40%, the UFK-1 composition up to 10%, and the UFK-2 composition up to 15% of its mass. Thus, the increase in the mass content of the carbon filler in a composition enhances the gas liberation. Such behavior of the material at elevated temperatures may be caused by the increase in the structural defects of the polymer, which serve as micronuclei of a new phase [2], and by the additional porosity brought about by the cracking as a consequence of thermomechanical effects. Moreover, the increase in the rate of heating leads to a more profound TPM decomposition. This follows from the results of thermoanalytical tests of UFK-1 obtained by the methods of [3] (high-rate heating with transmission of the electric current through a carbon plastic) and presented in Fig. 1d. Thus, at T_s = 1100 K, the mass loss of the specimen M/M_0 heated at the rate dT_s/dt = 50 K/sec (the T_{s1} and M_1/M_0 curves) amounted to 15%, while at dT_s/dt =
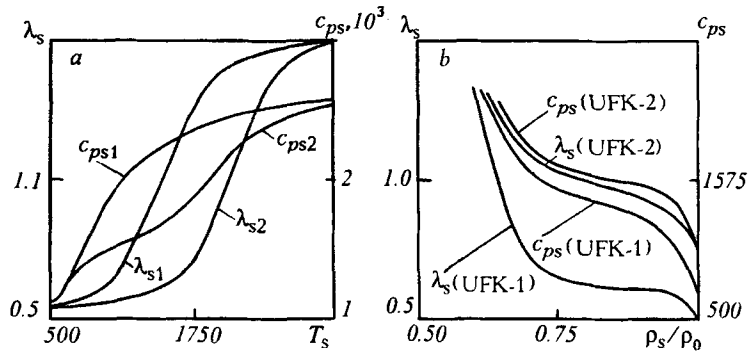
Fig. 2. Thermal conductivity λ_s (W/m·K)) and the specific heat c_{ps} (J/(kg·K)) vs. temperature T_s (K) for UFK-1 at dT_s/dt = 1, 150 K/sec (a) and vs. relative change in density ρ/ρ_0 for UFK-1 and UFK-2 (b) in pyrolysis.

150 K/sec (the T_{s2} and M_2/M_0 curves) this magnitude attains 20% (the rate of heating was determined from the $T_s(t)$ temperature curves at the instants $t_{in.d1}$ and $t_{in.d2}$ corresponding to the initiation of the reaction). When $0 < t < t_{in.d}$, the specimen is heated as an inert body. At the instant $t_{in.d}$, the gaseous products of TPM destruction start to be liberated. The thermal decomposition of the material is of a pronounced multistaged character. Thus, for $8 < t < 10$ sec (the M_1/M_0 and T_{s1} curves) and $3 < t < 4$ sec (the M_2/M_0 and T_{s2} curves) there is a decrease in the rate of liberation of the pyrolysis gases, which is linked to the completion of the first stage and transition to the second stage that leads to a more profound decomposition at $T_s > 1100$ K. Interestingly, this temperature corresponds to the onset of structural changes in TPC (Fig. 1a). The temperature $T_s = 1100–1200$ K is a limiting temperature of heating attained on a standard derivatograph, and therefore the data on thermal decomposition of TPM in Fig. 1b describe only one of the stages of the multistage process of thermochemical destruction of carbon-phenol compositions. For the initial instants of thermal decomposition $t_{in.d1}$ and $t_{in.d2}$ on the $T_{s1}(t)$ and $T_{s2}(t)$ curves there are corresponding temperatures $T_{in.d1}$ and $T_{in.d2}$, at which the pyrolysis reaction of a thermal protective composition begins.

The kinetic shift of the pyrolysis reaction to a high-temperature region with an increase in dT_s/dt has an effect on the temperature dependences $\lambda_s(T_s)$ and $c_{ps}(T_s)$, since the material structure remains unchanged until the temperature of the initiation of thermal decomposition is attained. For studying the effect of the rate of heating dT_s/dt on the change in $\lambda_s(T_s)$ and $c_{ps}(T_s)$, the specimens were heated at different rates to a specified temperature and thereafter cooled in an inert atmosphere, which precluded the effect of oxidation processes on the readings of the thermocouples. The temperature of heating varied within $400 < T_s < 300$ K. For the interval of $300 < T_s < 400$ K, λ_s and c_{ps} were obtained on IT-λ-400 and IT-c-400 standard thermophysical instruments. Figure 2a plots $\lambda_s(T_s)$ and $c_{ps}(T_s)$ at dT_s/dt = 1 K/sec and dT_s/dt = 150 K/sec for UFK-1 carbon plastic as function of the annealing temperature T_s. Clearly, the increase in dT_s/dt leads to a rightward shift of the dependences $\lambda_s(T_s)$ and $c_{ps}(T_s)$ on the temperature scale. Thus, the change in $\lambda_s(T_s)$ and $c_{ps}(T_s)$ as a function of the thermochemical and structural transformations in TPC in heating is governed by the kinetics of the proceeding processes. Representing the thermophysical characteristics in the form of the functions $\lambda_s(\rho_s)$ and $c_{ps}(\rho_s)$ [3], where ρ_s is the current density of the material, yields universal dependences relating these quantities to the kinetics of decomposition, the temperature, and the rate of heating (Fig. 2b). Evidently, with the kinetic constants of pyrolysis E, k_0, and n known, from Eq. (2) it is easy to determine the current density of the TPM $\rho_s = M/V_T$ as a function of T_s and dT_s/dt, and hence the effect of the kinetic shift of the reaction on the TPC structure and the parameters $\lambda_s(T_s)$ and $c_{ps}(T_s)$. By processing the experimental $T_s(t)$ and $M(t)/M_0$ curves using the methods of [3] at n = 1, the following values were found for the kinetic constants of the reaction of thermal destruction of UFK: E = 83 kJ/mole, k_0 = $3.15 \cdot 10^4$ sec^{-1}, and Q = $3.35 \cdot 10^5$ J/kg. The results of testing UFK-1 and UFK-2 carbon plastics in unilateral heating in the flow of a high-temperature inert gas (nitrogen)
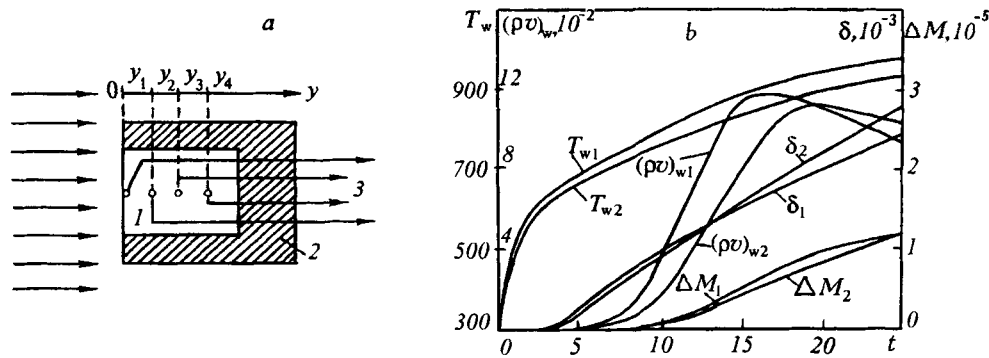
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Fig. 3. Test data for UFK-1 and UFK-2 in a heated nitrogen flow: a) diagram of the flow past a specimen and its fittings (1) specimen, 2) heat insulation, 3) thermocouples); b) surface temperature T_w (K), mass change ΔM (kg), velocity of mass entrainment $(\rho v)_w$ (kg/($m^2 \cdot$sec)), and thickness of coke layer δ (m) vs. time t (sec).

are illustrated in Fig. 3, which also presents a diagram of the flow past a specimen and its fittings in the experiment. An analysis of the data indicated that, under identical heat transfer conditions, a decrease in the mass content of the polymer binder in the composite material does not, in fact, reduce the blowing of the gaseous products of pyrolysis into the boundary layer. At the initial instants ($0 < t < 19$ sec), the velocity of mass entrainment $(\rho v)_w = S^{-1}(dM/dt)$ of UFK-1 (the $(\rho v)_{w1}$ curve) is higher than the velocity of mass entrainment of UFK-2 (the $(\rho v)_{w2}$ curve, S is the area of the heated surface). At the instant $t = 19$ sec, the $(\rho v)_{w1}$ and $(\rho v)_{w2}$ curves intersect, and subsequently $(\rho v)_{w2} > (\rho v)_{w1}$. Similar data were obtained for the heating of the surface of carbon-plastic specimens for 60 sec on a radiant-heating device of the URAN-1 type (with a heat flux of $2 \cdot 10^6$ W/m^2) [7]. As ensues from the above results of thermogravimetric and thermophysical investigations, such behavior of TPMs with a different mass content of the polymer binder is linked to both the higher degree of decomposition of UFK-2 in comparison with UFK-1 and the difference in the thermophysical characteristics of the materials (Fig. 1c and Fig. 2b). Indeed, the reduction in the resin content in a composition and the related increase in the thermal diffusivity leads to thickening of the heating zone and the involvement of an additional mass of the reactive substance in the pyrolysis. Calculations of the thickness of the reactive layer from the position of the $T_{in.d} = 635$ K isotherm in the depth of the TPC, conducted in [7] in a laboratory experiment, demonstrated that, up to the instant $t = 13$ sec, the destruction zone for UFK-1 is deeper than for UFK-2 (see Fig. 3b, where the $\delta_1(t)$ and $\delta_2(t)$ curves describe the position of the boundary of the pyrolysis zone for UFK-1 and UFK-2, respectively). Up to this instant, the higher resin content in UFK-1 composition results in $(\rho v)_{w1} > (\rho v)_{w2}$. When $t > 13$ sec, $\delta_2(t)$ becomes larger than $\delta_1(t)$ because of the differences in thermophysical characteristics, which leads to a gradual increase in $(\rho v)_{w2}$, and when $t > 19$ sec the velocity of mass entrainment for UFK-2 begins to exceed that for UFK-1. The same behavior of the $(\rho v)_{w1}$ and $(\rho v)_{w2}$ curves is also observed for elevated thermal loads, which model the conditions of heat transfer for the aircraft motion along the trajectory [7].

Thus, a reduction in the mass content of a binder has an indefinitive effect on the characteristics of heat and mass transfer and destruction of a TPC, which should be taken into account in developing new TPM modifications.

NOTATION

t, time; T, temperature; M, mass; y, coordinate; λ, thermal conductivity; c_p, specific heat; k_0, preexponent; ρ, density; V, volume; Γ, gasification factor; K_T, coke number; R, universal gas constant; $(\rho v)_w$, velocity

of mass entrainment. Subscripts: s, solid; e, gas; 0, initial value; c, values of parameters at the instant of completion of the annealing (coking); w, surface; ch, chemical.

REFERENCES

1. Yu. V. Polezhaev and F. B. Yurevich, *Thermal Protection* [in Russian], Moscow (1976).
2. O. F. Shlenskii, N. V. Afanas'ev, and A. G. Shashkov, *Thermal Destruction of Materials. Polymers and Composites at High-Rate Heating* [in Russian], Moscow (1996).
3. V. V. Nesmelov, *Fiz. Goreniya. Vzryva*, **29**, No. 6, 53-58 (1996).
4. V. I. Zinchenko, V. V. Nesmelov, and A. S. Yakimov, *Fiz. Goreniya. Vzryva*, **31**, No. 1, 80-88 (1995).
5. A. V. Luikov, *Theory of Heat Conduction* [in Russian], Moscow (1967).
6. V. V. Korshak, *Thermally Stable Polymers* [in Russian], Moscow (1969).
7. V. I. Zinchenko, V. V. Nesmelov, A. S. Yakimov, and G. F. Kostin, *Fiz. Goreniya. Vzryva*, **34**, No. 6, 48-55 (1998).