STUDY OF THE EFFECT OF DIFFERENT FACTORS ON THE THERMOPHYSICAL
CHARACTERISTICS OF CHARRING MATERIALS BY SOLVING AN INVERSE
(COEFFICIENT) HEAT-CONDUCTION PROBLEM

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A great many charring-type thermally protective materials (TPM) have now been developed. They are distinguished from one another by the type and content of the binder, the nature and structure of the filler, etc. These materials are used under the most diverse conditions, in turn differentiated by pressures, enthalpies, chemical composition of the media, etc. All of these factors in a certain way affect the thermophysical characteristics of these materials at temperatures above the temperature at which the binder begins to decompose.

We used the method in [1] to determine the thermophysical characteristics of the pyrolysis and char (coke) zones of a TPM. The theoretical relations for determining these characteristics have the form:

pyrolysis zone

$$\overline{C}_{v2} = C_{v0} = \rho_0 c_0, \tag{1}$$

$$\overline{\lambda}_2 = \frac{V\psi_2}{\ln[(T_c - T_0)/(T_p - T_0)]}\rho_0 c_0; \tag{2}$$

coke zone

$$\overline{C}_{v1} = \frac{\rho_0 \ln \dfrac{T_w - T_0}{T_c - T_0}\{c_0(T_c - T_0) + \varphi[\Delta H + \Gamma c_g(T_w - T_c)]\}}{(T_w - T_c)\left[1 + \dfrac{T_w - T_c}{T_w - T_0}\varphi\Gamma\left(\dfrac{c_g}{c_0} - 1\right) + \dfrac{\varphi\Delta H}{c_0(T_c - T_0)}\right]}, \tag{3}$$

$$\overline{\lambda}_1 = \frac{\rho_0 V\psi_1\{c_0(T_c - T_0) + \varphi[\Delta H + \Gamma c_g(T_w - T_c)]\}}{T_w - T_c}. \tag{4}$$

The materials were tested in the focus of a solar furnace [2] ($q = (0.42-1.26)\cdot10^4$ kW/m²; $P = 10^5$ Pa); in a jet of products of the combustion of kerosine and oxygen [3] ($q = (0.4-1.26)\cdot 10^4$ kW/m², $P_e = (1.2-2.4)\cdot10^5$ Pa, $I_e = 2100-4000$ kJ/kg, $T_e = 1700-2800°K$); in jets of air ($q = (0.13-1.3)\cdot10^4$ kW/m², $P_e = 10^5$ Pa, $I_e = 2000-14,000$ kJ/kg, $T_e = 2000-6000°K$) and nitrogen ($q = 0.63\cdot10^4$ kW/m², $P_e = 10^5$ Pa, $I_e = 11,000$ kJ/kg, $T_e = 5500°K$) plasmas [4]. The materials were tested on the unit described in [4] with combined radiative—convective heating.

Type of Heating. We will examine the effect of this factor on mean thermophysical characteristics using the example of asbestos- and glass-reinforced plastics. Figure 1 shows the effect of different types of unidirectional heating and heating rate on mean thermal conductivity in the zone of pyrolysis of the asbestos—plastic. It can be seen from the figure that the thermal conductivities of the pyrolysis zone of the asbestos—plastic lie almost on a single curve (points 1, 3, 6) in the tests in the jets of plasma (air and nitrogen) and products of kerosine combustion. The increase in $\overline{\lambda}_2 = f(\partial T/\partial\tau)$ in the range 100-300°K/sec is evidently connected with a shift in the process of decomposition of the binder to a region of higher temperatures with an increase in heating rate, as well as with a certain
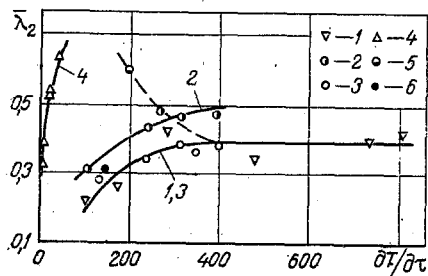
Fig. 1   Fig. 2

Fig. 1. Effect of the type and rate of heating on the mean thermal conductivity of the pyrolysis zone of an asbestos–plastic: 1) products of combustion of kerosine in oxygen; 2) air plasma + radiative heating (q = $0.42 \cdot 10^4$ kW/m^2); 3) air plasma; 4) radiative heating; 5) air plasma + radiative heating (q = $0.84 \cdot 10^4$ kW/m^2); 6) nitrogen plasma. $\bar{\lambda}_2$, W/m·K; $\partial T/\partial \tau$, K/sec.
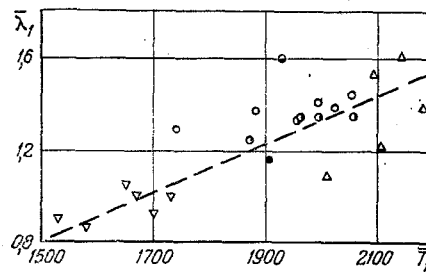
Fig. 2. Effect of type of heating and temperature on the mean thermal conductivity of asbestos–plastic coke (same notation as in Fig. 1). $\bar{\lambda}_1$, W/m·K; $\bar{T}_1$, °K.

reduction in the porosity of the pyrolysis zone at these temperatures. Shifting of the process of decomposition of a phenol formaldehyde binder to a higher temperature range also occurs at a heating rate of about 170°K/sec [5].

With a further increase in $\partial T/\partial \tau$, the phenomenon of a shift in the decomposition of the binder may weaken; the porosity of the pyrolysis zone decreases, although there is a simultaneous change in the orientation of the pores. Whereas the pores are mainly randomly oriented at low (up to 200-300°K/sec) heating rates (in the tests of the asbestos–plastic in kerosine combustion products), with an increase in heating rate more and more pores are oriented parallel to the heating surface and, with $\partial T/\partial \tau$ = 800°K/sec (P_e = $2.4 \cdot 10^5$ Pa), nearly all of them are so oriented. These pores are connected to each other by smaller pores.

Porosity was evaluated by the stereometric method using a metallographic microscope. The heating rate in the pyrolysis zone was determined from the relation

$$\frac{\partial T}{\partial \tau} = \frac{V(T_c + T_p - 2T_0)}{2\psi_2} \ln \frac{T_c - T_0}{T_p - T_0}.$$

This relation represents the mean heating rate in the pyrolysis zone and was obtained by differentiation of the exponential temperature distribution [1] at the boundaries of this zone.

In the tests of the asbestos–plastic in the focus of the solar furnace, an increase in heating rate (an increase in the incident radiative heat flux) led to a sharp increase in thermal conductivity in the pyrolysis zone (curve 4 in Fig. 1). Since $\partial T/\partial \tau$ changes negligibly for this type of heating compared to other types, then the sharp increase in $\bar{\lambda}_2$ = $f(\partial T/\partial \tau)$ is evidently connected with the penetration of heat radiation through the pores and channels in the coke to the pyrolysis zone. Meanwhile, for this type of heating, an increase in heat flux is accompanied by an increase in the porosity of the coke, and it is possibly as a result of this that the coke becomes more "transparent" to the incident radiation.

That the radiation penetrates to the pyrolysis zone is confirmed by the path of the dashed curve in Fig. 1 — an increse in the radiative component of combined (radiative–convective) heating leads to an increase in $\bar{\lambda}_2$, although the heating rate decreases in this case. This curve was constructed from values of the thermal conductivity of the pyrolysis zone obtained from the results of tests of asbestos–plastic with a change in the ratio of the convective (air plasma) and radiative heat fluxes. Here, their sum remained constant and was equal to $1.26 \cdot 10^4$ kW/m^2.

For the glass–plastic with an epoxy binder, tested under the same conditions, an increase in the radiative component of combined heating did not lead to an increase in thermal

TABLE 1. Effect of Ratio of Convective and Radiative Heat Fluxes on the Mean Thermal Conductivity of the Pyrolysis Zone and Coke of a Glass—Plastic on an Epoxy Binder

№	Heat flux $q \cdot 10^{-4}$, kW/m^2		$\overline{\lambda_2}$, W/m·K	$\overline{T_2}$, K	$\frac{\partial T}{\partial \tau}$, K/sec	$\overline{\lambda_1}$, W/m·K	$\overline{T_1}$, K
	convective	radiative					
1	1,26	—	0,23	750	690	0,81	1750
2	0,84	0,42	0,24	750	570	0,82	1815
3	0,42	0,84	0,24	750	470	1,03	1790

conductivity in the pyrolysis zone (Table 1) for two reasons. First, the structure of the coke pores of this glass—plastic is different from the structure of the coke pores in the asbestos—plastic in that there are no channels. The pores in the glass—plastic are oriented mainly along the fibers of the fabric. Such a structure impedes penetration of radiation deep into the material. Second, a porous melt of the filler forms on the surface of the epoxy glass—plastic during the tests, and this melt absorbs and scatters the incident radiation.

A change in the amount of convective heating with a constant radiative component (q = $0.42 \cdot 10^4$ kW/m^2) leads to some increase in $\overline{\lambda_2} = f(\partial T/\partial \tau)$ for the asbestos—plastic compared to the same function for purely convective heating, and they are nearly equidistant (curves 1, 3, 2, Fig. 1).

The thermal conductivity of the coke of the asbestos—plastic $(\overline{\lambda_1})$, i.e., of the zone where the decomposition of the binder has already been completed, is independent of the heating rate. Thus, in Fig. 2 this characteristic is represented as a function of the mean temperature of the coke: $\overline{T_1} = (T_w + T_c)/2$.

For all of the types of heating examined here, the values of the mean thermal conductivity of the coke of the asbestos—plastic are grouped around a straight line (Fig. 2), within the limits of the error of the determination of this characteristic.

In calculating the mean thermophysical characteristics of the coke of the asbestos—plastic, in Eqs. (3) and (4) we took into account the effect of the loss of water of crystallization by the asbestos fabric and the heat absorbed by water vapor.

The mean thermal conductivity of the coke of the glass—plastic with an epoxy binder increases somewhat with an increase in the proportion of radiative heating during combined heating (Table 1), although this increase lies within the error of this characteristic.

An increase in the stagnation pressure (by a factor of about 2.4) does not affect the mean thermal conductivity of the pyrolysis zone of the asbestos—plastic (points 1 and 3 in Fig. 1) or the glass—plastics on phenol-formaldehyde (Table 2, Nos. 3 and 8) and epoxy binders (Table 1, No. 1 and Table 2, No. 2). The mean thermal conductivity of the coke of these glass—plastics increases with an increase in the stagnation pressure, despite the fact that the mean temperature of the coke decreases (Table 2, Nos. 3 and 8; Table 1, No. 1; Table 2, No. 2). This evidently is the result of an increase in the density of the coke with an increase in the stagnation pressure [6]. Since the glass—plastics with a siliciferous filler form a molten film on their surface in the tests in a jet of kerosine combustion products, the mean thermophysical characteristics under these conditions were determined with allowance for this film, i.e., in Eqs. (3) and (4) we replaced T_w with the melting point of the filler.

The fact that we see the opposite pattern for the mean thermal conductivity of the coke of the asbestos—plastic (Fig. 2, points 1 and 3) is evidently explained by a difference in the pore structures of the coke formed in tests of the asbestos—plastic in the air-plasma jets and kerosine combustion products.

Within the framework of the adopted mathematical model of heat transfer [1], the mean volumetric thermal conductivities of the coke and pyrolysis zones are slightly dependent on the type of heating and the temperature (Fig. 3 and [7]).

Effect of the Type and Concentration of the Binder. Composite coking materials contain different binders having different decomposition parameters (specific heat of pyrolysis, coefficient of vaporization, etc.).

TABLE 2. Effect of Certain Factors on the Mean Thermal Conductivities of the Pyrolysis Zone and Coke of a TPM

№	Filler	Binder	$\bar{\lambda}_2$, W/m·K	$\bar{T}_2$, K	$\frac{\partial T}{\partial \tau}$, K/sec	$\bar{\lambda}_1$, W/m·K	$\bar{T}_1$, K	Factor
1	Multilayer siliciferous fabric	Organo-silicon	0,36	1050	550	1,14	1650	Type of binder
2	Same	Epoxy	0,23 (0,19*)	750	780	1,32 (1,20*)	1500	Same
3	»	Phenol-formaldehyde	0,50 (0,47*)	900	290	1,85 (1,10*)	1600	
4	Alumoboro-silicate fiber glass	Same	0,47 (0,53†)	900	760	0,72	1720	Nature of filler
5	Carbon fiber	»	0,35 (0,53‡)	900	220 / 0,13	0,83 (0,48‡)	1850	Same
6	Siliciferous fabric: single-layer (⊥)	»	0,20 (0,45‡)	900	880 / 0,13	0,81 (1,40‡)	1920 (1600)	Fiber orientation
7	single-layer (∥)	»	0,46	900	390	1,14	1890	Same
8	multilayer(⊥)	»	0,42	900	550	1,22	1870	»
9	multilayer (∥)	»	0,47	900	540	1,22	1850	»

*[8].
†[12].
‡[10].

We will examine the effect of the type of binder on the mean thermal conductivity of the coke and pyrolysis zones using the example of glass—plastics with phenol-formaldehyde, epoxy, and organosilicon binders with a multilayer siliciferous fabric (Table 2, Nos. 1-3). These glass—plastics were tested in a jet of products of kerosine combustion under the same conditions ($q = 1.26 \cdot 10^4$ kW/m^2).

The difference in the thermal conductivity of the pyrolysis and coke zones of these glass—plastics is connected with a difference in the pore structures, the percentage content of carbon in the coke, and — for the pyrolysis zone, apparently — a difference in the decomposition parameters of these binders.

For comparison, Table 2 (Nos. 2 and 3) presents results of [8]. The divergence of the thermal conductivity data has to do with a difference in stagnation pressures, as well as with the fact that in determining thermal conductivity in [8] no allowance was made for heat absorption due to decomposition of the binder and gaseous products of pyrolysis.

Due to possible deviations in the manufacturing process, the resulting composites may have different concentrations of binder. Here, an increase in the content of the binder leads to a decrease in the thermal conductivity of the coke in tests of the material in kerosine combustion products [9], which is evidently connected with an increase in the porosity of the coke accompanying an increase in the content of the binder for this type of heating. With radiative heating, although there is again an increase in the porosity of the coke with an increase in the content of the binder, the mean thermal conductivity of the coke increases [9]. This may be connected with the penetration of the radiation through the pores and channels into the coke. The latter result is qualitatively in agreement with the data in [10].

The type of binder and its concentration also affect the volumetric specific heat of the coke and pyrolysis zones of a TPM. An increase in the content of binder leads to an increase in the volumetric specific heat of both the pyrolysis zone and coke for different binders [11], the actual specific heat being determined by the binder. Here, the lowest volumetric specific heat for the coke is seen in glass—plastic on an organosilicon binder, which is explained by the small amount of carbon in the coke of this material.
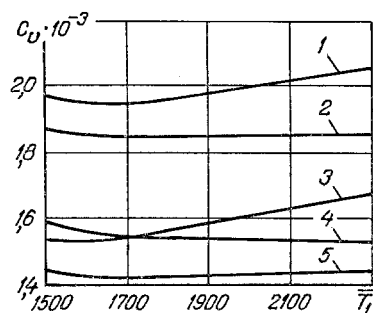
Fig. 3. Effect of the nature of
the filler and the temperature
on the volumetric specific heat
of the coke of materials with a
phenol-formaldehyde binder: 1)
carbon—plastic (data from [10]
with the actual specific heat);
2) glass—plastic (3); 3) carbon—
plastic (data from [10] with the
mean specific heat); 4) glass—
plastic (data from [14]): 5)
carbon—plastic (3). C_v, kJ/m$^3 \cdot$
K; $\overline{T}_1$, °K.

Effect of the Nature, Structure, and Orientation of Fibers of a Fabric Filler.

A TPM, besides different binders, has different fillers. They are differentiated from one another by their nature (for example, asbestos and siliciferous fabric), structure (single-layer or multilayer cloth), fiber orientation relative to the incident heat flow, etc. All of these differences in the fillers in some way affect the thermophysical characteristics of a TPM.

First we will examine the effect of the nature of the filler on the mean thermal conductivity of the coke and pyrolysis zones (asbestos—, glass—, and carbon—plastics on a phenol-formaldehyde binder, tested in a jet of kerosine combustion products with q = $1.26 \cdot 10^4$ kW/m^2).

Despite the fact that the carbon—plastic contains carbon fibers with a higher thermal conductivity than the asbestos fabric and alumoborosilicate glass fibers, its mean thermal conductivity in the pyrolysis zone is lower than the same characteristic for the asbestos— and glass—plastics (Fig. 2, $\partial T/\partial \tau$ = 810°K/sec, and Table 2, Nos. 4 and 5) because coarse cracks and channels, running mainly parallel to the heating surface, are formed in the carbon—plastic during the unidirectional heating. Thus, the mean conductivity of the coke of the carbon—plastic occupies an intermediate position between the analogous values for the asbestos—plastic (maximum value) and the glass—plastic (minimum value) (Fig.2, $\overline{T}_1$ = 1730°K, Table 2, Nos. 4 and 5).

Comparison of the data on the mean thermal conductivities of the pyrolysis zones of these materials with the data from [10, 12] shows good agreement with the values in [12] for the glass—plastic (Table 2, No. 4), while the values in [10] for the glass—plastic are higher (Table 2, No. 5).

For the coke of the carbon—plastic, a low value of thermal conductivity was obtained in [10] compared to the results we obtained (Table 2, No. 5). This discrepancy is not quite understandable, since the heating rate in [10] was low (less than 1.0°K/sec) and graphitization of the material was quite possible. It was shown in [13] that the conductivity of a carbon—graphite material with a porosity of 78% is ~5 W/m·K at 1950°K. However, it must be considered that the heating rate is very high (hundreds of deg K/sec) in the intensive unidirectional heating of carbon—plastic and, evidently, graphitization of the coke cannot occur. Thus, with unidirectional heating, the conductivity of the coke of the carbon—plastic is lower than the conductivity of the carbon—graphite material. It is evidently for this reason that the volumetric specific heat of the coke of the carbon—plastic is lower than the actual volumetric specific heat of this material [10] (Fig. 3, curves 1 and 5). The data in [14] and [10] (in the latter, with a mean specific heat) are closest to $\overline{C}_{V1} = f(\overline{T}_1)$ (Fig. 3, curves 3-5).

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Comparison of the mean volumetric specific heats of the carbon– and glass–plastics (Fig. 3, curves 2 and 5) shows that, despite the fact that the carbon fibers have a greater specific heat than the glass fibers, the latter have a greater mean volumetric specific heat. This is connected with the difference in the densities of the cokes of these materials. The coke of the glass–plastic is denser.

We will examine the effect of the structure and orientation of the fibers of the fabric using the example of phenol glass–plastics containing single- and multilayer siliciferous fabrics. These materials were tested in a jet of air plasma ($q = 1.16 \cdot 10^4$ kW/m^2).

Table 2, Nos. 6-9, shows that the orientation of the fibers of the fabric is important only for the glass–plastic with a single-layer fabric. Here, with parallel orientation of the fibers relative to the thermal effect ($\parallel$), the mean thermal conductivity of both the pyrolysis zone and the coke of this glass–plastic is nearly the same as the conductivity of the pyrolysis zone and coke of the glass–plastic containing a multilayer fabric.

Effect of Density. As was shown in [15], an increase in the density of a glass–plastic with a phenol-formaldehyde binder leads to an increase in both the thermal conductivity of the material as a whole and the mean thermal conductivities of the pyrolysis and coke zones in tests in a jet of kerosine combustion products ($q = 1.26 \cdot 10^4$ kW/m^2). Such behavior of the mean thermal conductivity of the coke in relation to the density of the initial material indicates that the conductive component is the main contributor to the thermal conductivity of the coke of this glass–plastic, while the radiative component (due to reradiation in the pores) is insignificant under the given test conditions with convective heating.

The mean volumetric specific heats of the pyrolysis zone and coke increase with an increase in the density of the original material, which is important for materials of uniform composition (Eqs. (1) and (3)).

Thus, comparison of the data on the mean thermal conductivities of the pyrolysis zone and coke of TPM's with data from works in which thermal conductivity was determined by solution of an inverse (coefficient) problem of heat conduction with unidirectional heating shows that they agree well. Comparison with data obtained by the "method of limiting decomposition" [10] shows that this method gives exaggerated values of thermal conductivity (except for the conductivity of the coke of the carbon–plastic), which has to do with the difference in the heating rates and times [16] and, evidently, with the difference in the structures of the pores in the coke and pyrolysis zones with three-dimensional and intensive unidirectional heating.

The factors examined in this article mainly affect the formation of the pore structure of the pyrolysis zone and coke, which in turn affects the mean thermal conductivities of these zones.

The mean volumetric specific heat of the coke of a TPM depends mainly on the type of binder and its concentration in the material, as well as on the density of the material.

NOTATION

T, temperature; C_v, volumetric specific heat; c, specific heat; λ, thermal conductivity; V, steady-state linear rate of material entrainment (ablation); ψ, thickness of the zone; φ, concentration of binder in the material; ΔH, specific heat of decomposition of the binder; Γ, coefficient of vaporization of the binder; q, calorimetric heat flux; P, pressure; I, enthalpy; $\bar{T}_2 = (T_c + T_p)/2$, mean temperature in the pyrolysis zone; $\perp$, $\parallel$, fabric fibers normal and parallel to the heat flow, respectively. Indices: 0, original material; 2, pyrolysis zone; 1, coke; p, c, beginning and end of decomposition of the binder, respectively; w, surface; g, gaseous products of decomposition of the binder; e, stagnation parameters.

LITERATURE CITED

1. K. B. Isaev, V. S. Dvernyakov, and V. V. Pasichnyi, "Determination of the mean high-temperature thermophysical characteristics of a degenerate layer of material with unidirectional heating," Teplofiz. Vys. Temp., 17, No. 3, 650-652 (1979).
2. V. V. Pasichnyi and V. S. Dvernyakov, "Unit for high-temperature studies of heat-resistant aviation materials and coatings," in: Samoletostr. Tekh. Vozdushn. Flota, No. 10, 77-83 (1967).

3. V. S. Dvernyakov, G. F. Gornastaev, K. B. Isaev, et al., "Theoretical and experimental study of the fracture kinetics of high-temperature materials," in: Heat and Mass Transfer VI. Methods of Experimental Investigation [in Russian], Naukova Dumka, Kiev (1980), pp. 124-131.

4. G. A. Frolov, V. S. Dvernyakov, and V. V. Pasichnyi, "Some results of an experimental study of heat exchange on a surface with combined radiative and convective heat flow," Teplofiz. Vys. Temp., 15, No. 1, 221 (1978).

5. R. W. Farmer, "Phenolic resin char-formation during hyperthermal ablation," Thermochim. Acta, 4, No. 3, 223-238 (1972).

6. V. V. Kuz'mich, "Study of the fracture of glass—plastic based on a filler of siliciferous fiber and an epoxy binder in a quasisteady regime," in: Features of Heat and Mass Transfer [in Russian], ITMO Akad. Nauk BSSR, Minsk (1979), pp. 194-197.

7. K. B. Isaev, "Study of the effect of certain factors on the high-temperature thermophysical characteristics of glass—plastics," in: Structural Studies of New Materials [in Russian], IPM Akad. Nauk Ukr. SSR, Kiev (1979), pp. 194-198.

8. Yu. G. Narozhnyi, Yu. V. Polezhaev, and V. N. Kirilov, "Some results of a study of the thermal conductivity of glass—plastics," Inzh.-Fiz. Zh., 29, No. 1, 77-80 (1975).

9. K. B. Isaev, A. A. Korol', and G. S. Elicheva, "Effect of the content of the constituents and the types of unidirectional heating on the thermophysical characteristics of glass—plastics at high temperatures," Kosm. Issled. Ukr., 15, 37-41 (1981).

10. A. G. Shashkov and V. I. Tyukaev, Thermophysical Properties of Decomposing Materials at High Temperatures [in Russian], Nauka i Tekhnika, Minsk (1975).

11. K. B. Isaev, "Effect of different binders and the content of the constituents on the volumetric specific heat of glass—plastics at high temperatures," in: Development and Investigation of New Materials and Composites Based on Them [in Russian], IPM Akad. Nauk Ukr. SSR, Kiev (1980), pp. 21-25.

12. V. M. Yudin, "Heat and mass transfer in glass—plastics," Inzh.-Fiz. Zh., 24, No. 4, 618-626 (1973).

13. É. A. Bel'skaya and A. S. Tarabanov, "Experimental studies of the thermal conductivity of carbon—graphite materials of high porosity," Inzh.-Fiz. Zh., 18, No. 4, 696-701 (1970).

14. A. L. Laganelli, T. P. Harper, and R. P. Fogaroli, "Integral solution for thermal performance of a charring ablator," Heat Transf. Therm. Contr. Appl., New York (1975), pp. 375-393.

15. K. B. Isaev, "Effect of the density of the original material on the thermal conductivity of the coke of glass—plastics at high temperatures," in: Study of Heat and Mass Transfer [in Russian], Naukova Dumka, Kiev (1979), pp. 85-88.

16. Yu. V. Polezhaev, V. E. Killikh, and Yu. G. Narozhnyi, "Problems of nonsteady heating of thermally protective materials," Inzh.-Fiz. Zh., 29, No. 1, 39-44 (1975).