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THERMAL DIFFUSIVITY OF COMPOSITE MATERIALS AT HIGH TEMPERATURES

A. G. SHASHKOV, V. I. TYUKAEV and A. T. NIKITIN
Heat and Mass Transfer Institute, BSSR Academy of Sciences, Minsk, USSR

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ТЕМПЕРАТУРОПРОВОДНОСТЬ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ ПРИ ВЫСОКИХ ТЕМПЕРАТУРАХ

Аннотация—Рассматривается теория экспериментального определения температуропроводности квазистационарным и монотонным методами.

Приводится техника эксперимента в восстановительной среде до температур порядка 3300°K, описывается специально созданное фотоэлектрическое устройство.

Проводится анализ результатов по температуропроводности фенольных пластиков, устанавливается зависимость температуропроводности асбопластиков от состава. Определяются границы применимости дифференциального уравнения теплопроводности без источников (стоков) тепла.

NOMENCLATURE

a,	thermal diffusivity;
A_n,	initial heat amplitudes;
$A_0(\tau)$,	first term of power series;
$A_{2n}(\tau)$,	coefficients of even power series;
b,	heating rate;
c,	specific heat capacity;
d,	sample diameter;
Bi,	Biot number;
Fo,	Fourier number;
H,	dimensionless heat transfer coefficient;
J_0,	first kind Bessel function of the zeroth order;
Ki,	Kirpichev number;
l,	sample length;
n,	serial number;
Pd,	Predvoditelev number;
q_s,	heat flux at body surface;
q_v,	density of internal heat sources;
R,	cylinder radius;
r,	radius as variable;
T,	temperature;
T_0,	initial temperature of body;
T_m,	temperature of medium;
X,	phenolic resin concentration in initial plastic;
γ,	bulk mass;
δ,	correction for change of thermophysical parameters with temperature;
ε,	correction for variability of heating rate;
λ,	thermal conductivity;
μ_n,	roots of characteristic equation;
τ,	time;
$\Delta\tau$,	time of temperature retardation at cylinder axis from mean mass temperature.

BECAUSE of their specific properties, different plastics based on organic and inorganic resins become of ever-increasing use in advanced technology at conditions of high heat fluxes [1–4].

Judging from literature data, investigations of thermal diffusivity of poor heat conductors were carried out at temperatures up to 1300 K [5, 6] and up to 1800 K [7]. Chromel–alumel and tungsten–rhenium thermocouples were used as temperature probes; this was reasonable since the test materials had been metal oxides or their mixtures. In a recovery medium containing carbon, use of a platinum–platinum rhodium thermocouple is undesirable. The other known thermocouples for high temperature measurements such as tungsten, molybdenum, tungsten–rhenium, tungsten–tantalum, tantalum–molybdenum are recommended for use only in vacuum, nitrogen or insert gases [8]. Besides, at 2100–2300 K recrystallization occurs in refractory materials together with intense mass transfer at a hot junction resulting in a change of thermoelectromotive force and disturbance of stability of thermocouple readings. The plastics under test are recognized as a media of strong heat recovery, therefore application of thermocouples for temperatures above 1300 K is unreliable, the more so as there is no high-temperature insulation and shielding armature for such a medium. The way out was found in constructing a special photoelectric device designed for measurement of temperatures above 1300 K or its variation with time.

The non-stationary methods used allow for quick and accurate measurement of thermal diffusivity of poor heat conductors, in particular of composite materials based on phenolic resins and asbestos, glass and carbon fibres.

DEVELOPMENT OF EQUATIONS

The differential heat-conduction equation may be written in a general form as

$$c\gamma \frac{\partial T}{\partial \tau} = \operatorname{div}(\lambda \operatorname{grad} T). \tag{1}$$

Since higher temperatures and more uniform temperature fields may be achieved in a tube heater, the cylinder method has been chosen. For an infinite cylinder with symmetric heating of the lateral surface, the differential heat-conduction equation is of the form

$$\frac{\partial T(r,\tau)}{\partial \tau} = a\left[\frac{\partial^2 T(r,\tau)}{\partial r^2} + \frac{1}{r}\frac{\partial T(r,\tau)}{\partial r}\right]. \tag{2}$$

A sufficiently complete information on thermal properties of substances may be obtained when a quasi-stationary state is achieved, the analytical theory of which has been developed by A. V. Luikov [9]. In the present experiments up to temperatures of 1300 K, a quasi-steady regime set in several minutes after heating has begun; in other words, the heat flux was constant or the medium temperature changed linearly.

In the first case for the initial and boundary conditions of the form

$$T(r.0) = T_0, \tag{3}$$

$$-\frac{\partial T(R,\tau)}{\partial r} + \frac{q_s}{\lambda} = 0 \tag{4}$$

$$\frac{\partial T(0,\tau)}{\partial r} = 0, \tag{5}$$

$$T(0,\tau) \neq \infty \tag{6}$$

the solution of differential equation (2) reads

$$\Theta = \frac{T(r,\tau) - T_0}{T_s - T_0} = Ki\left[2Fo - \tfrac{1}{4}\left(1 - 2\frac{r^2}{R_2}\right) - \sum_{n=1}^{\infty}\frac{2J_0[\mu_n(r/R)]}{\mu_n^2 J_0(\mu_n)}\exp(-\mu_n^2 Fo).\right] \tag{7}$$

At $Fo \geqslant 0{\cdot}6$ the quasi-steady state occurs and the series may be neglected. For the case of a linear change of the medium temperature with the boundary conditions

$$T(r,0) = T_0 = \text{const.} \tag{8}$$

$$\frac{\partial T(0,\tau)}{\partial r} = 0, \quad T(0,\tau) \neq \infty, \tag{9}$$

$$-\frac{\partial T(R,\tau)}{\partial r} + H[T_0 + b\tau - T(R,\tau)] = 0 \tag{10}$$

the differential equation solution takes the form

$$\Theta = \frac{T(r,\tau) - T_0}{T_0} = Pd\left\{Fo - \tfrac{1}{4}\left[\left(1 + \frac{2}{B_i}\right) - \frac{r^2}{R^2}\right] + \sum_{n=1}^{\infty}\frac{A_n J_0[\mu_n(r/R)]}{\mu_n^2}\exp(-\mu_n^2 Fo)\right\}. \tag{11}$$

With $Fo \geqslant 0{\cdot}55$ the quasi-steady regime appears and the series may be neglected.

For the determination of thermal diffusivity it is advantageous to apply temperature retardation on the cylinder axis during heating as compared with temperature at radius r. Then, for the same temperature at two different points of the body, from simplified equation (7) the following equations are obtained

$$T(r_1, \tau_1) - T_0 = \frac{q_s R}{\lambda}\left[2\frac{a\tau_1}{R^2} - \frac{1}{4}\left(1 - 2\frac{r_1^2}{R^2}\right)\right], \tag{12}$$

$$T(0, \tau_2) - T_0 = \frac{q_s R}{\lambda}\left(2\frac{a\tau_2}{R^2} - \frac{1}{4}\right). \tag{13}$$

With the conditions $T(r_1, \tau_1) = T(0, \tau_2)$ and $\frac{q_s R}{\lambda} \neq \infty$, subtraction of (12) from (13) yields the expression for thermal diffusivity in terms of the retardation time $\Delta\tau$

$$a = \frac{r_1^2}{4\Delta\tau}. \tag{14}$$

The same formula may be obtained by solution (11).

If linear heating is difficult to be achieved particularly above 1300 K, use is made of the solution given in [5] (with allowance for dependence of coefficients upon temperature)

$$\gamma c(T)\frac{\partial T}{\partial \tau} = \lambda(T)\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \frac{\partial \lambda(T)}{\partial r}\frac{\partial T}{\partial r} \tag{15}$$

in a series form

$$T(r, \tau) = A_0(\tau) + \sum_{n=1}^{\infty} A_{2n}(\tau)\, r^{2n}. \tag{16}$$

Then with a monotonous temperature change the following expression is obtained for thermal dfffusivity

$$a = \frac{R^2}{4\Delta\tau}(1 + \varepsilon + \delta), \tag{17}$$

where

$$\varepsilon = -\frac{1}{4\Delta\tau} \cdot \frac{\mathrm{d}\Delta T}{\mathrm{d}\tau}\Delta\tau,$$

correction for variability of heating rate;

$$\delta = \frac{1}{4a}\frac{\mathrm{d}a}{\mathrm{d}T}\Delta T,$$

correction for dependence of thermophysical parameters upon temperature;

R, cylinder radius.

With $\varepsilon = \delta = 0$, which occurs at the relevant low heating rate and with $\Delta T \leqslant 40$ K, the derived equation (17) fully coincides with that for the quasi-steady regime of heating (14). E. S. Platunov [10] has suggested another method for a solution of the nonlinear heat-conduction equation. For the materials investigated his solution coincides with solution (17).

Relations (14) and (17) hold for an infinite isotropic cylinder. In the present paper a one-dimensional temperature field over the sample length of finite dimensions ($1/d = 3$) was maintained by a graduated heater and end screens. In practice, external heat transfer does not influence the retardation time if the mean volumetric temperature of the body is taken as the reference temperature. For a cylinder the coordinate of such a temperature is at $r_1 = 0{\cdot}707\,R$ [11].

Though the plastics investigated are of anisotropic nature and of laminated structure, nevertheless at temperatures above 900 K they turn out to be thermally isotropic. Often the most refractory, coking phenolic resins are used as binders [12]. From infrared spectroscopy data at heat treatment up to 773 K, hydrogen bonds and methylene bridges are still detected in the resin, i.e. initial space structure and anisotropy in plastics are still retained. Finally, at heat treatment at 873–973 K, hydrogen bonds are broken and hydrogen is split off the benzene ring leading to the formation of carbon lattices and cross bonds between them [12]. As a result of coking of the resin, a secondary carbon framework appears in the bulk of the material, the thermal conductivity of which is much higher than that of the filler, i.e. fibre. This qualitative change of the binder structure all over the volume of plastic considerably diminishes its anisotropy with respect to thermal properties.

In a heating process while measuring directly temperature fields on r_1 by thermocouple and photoelectric methods along and across the layers, the temperatures appeared to be practically equal.

Thus, application of equations (14) and (17) for thermal diffusivity is reasonable.

EXPERIMENTAL PROCEDURE

Plastics were tested in the apparatus [13] shown in Fig. 1. To achieve temperature of 2800 K the power required was 14 kVA (40 kVA was available) and smooth temperature control or slow power input was obtained with the help of an autotransformer.

Inside a tubular graphite heater 3, 330 mm long and 30 mm i.d., end-face graphite screens 10 and 12 were aligned from above and below. Sample 9 was fixed to screen 10 with holes 5 mm dia. drilled inside along its axis; the holes were provided as outlets for thermocouples or radiation. The sample proper was a cylinder, 76·5 mm long and 25·5 mm dia., fibre layers being parallel to the sample axis.

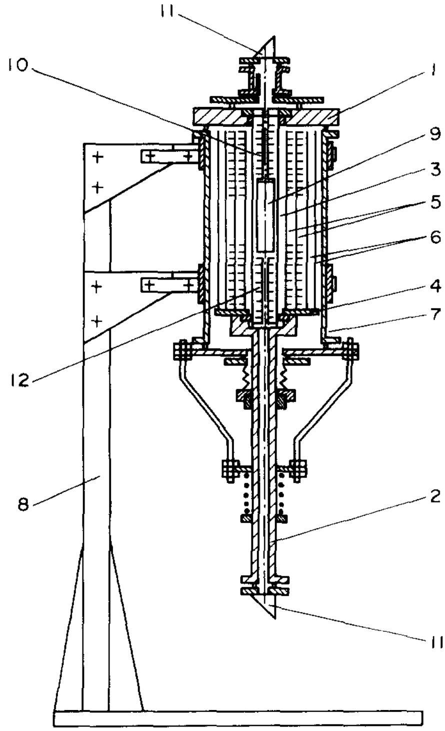

FIG. 1. Schematic drawing of experimental installation for thermal diffusivity of poor heat conductors at temperatures up to 3300 K.

1, upper current supply; 2, lower current supply with flange; 3, graphite heater; 4, graphite flange; 5, four graphite screens with fins; 6, tantalum screens; 7, furnace body; 8, stand; 9, sample; 10, upper graphite screen; 11, reflecting prism; 12, lower graphite screen.

Argon was taken as an experimental gas, a special hydraulic valve maintaining a constant internal pressure of 1·03 × 10^5 N/m^2. Prior to filling, the apparatus was evacuated down to a residual pressure of 1·333 to 1·333 × 10^{-2} N/m^2. Measurement of temperature and retardation time for any of the temperatures is carried out as shown in Fig. 2. Up to 1300 K measurements were made by means of chromel–alumel thermocouples [3] in porcelain insulation with an outer diameter of 2 mm tightly mounted into holes 35 mm in depth along the axis and on the radius $r_1 = 9$ mm. A low-ohmic potentiometer (7) was set at some magnitude of e.m.f., corresponding to a definite temperature. As soon as the temperature front from the surface reached the point on r_1, full compensation occurred and an electric timing device was switched on by photoelectric relay 11. The potentiometer was switched over to the central thermocouple without changing the set e.m.f.; at the moment of the second compensation the timing device was switched off. The accuracy of the time reading was 1 × 10^{-2} s.

In a similar manner the retardation time was measured by the contactless method. After critical consideration of photocells produced in this country [14] from the point of view of

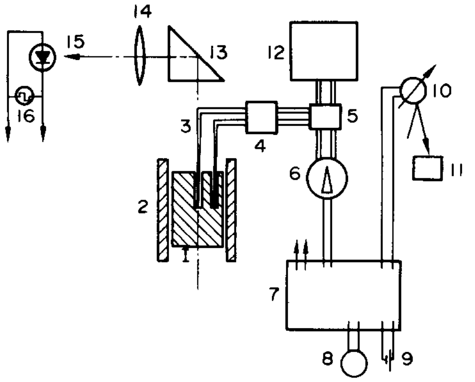

FIG. 2. Electrical and optical measuring circuits.
1, sample; 2, heater; 3, chromel–alumel thermocouples; 4, thermostat of cold junctions; 5 and 6, change-over switches; 7, low-ohmic potentiometer; 8, standard cell; 9, storage battery; 10, mirror galvanometer; 11, photo-relay for switching off and on of the timing device; 12, electronic potentiometer; 13, total reflection prism; 14, quartz lens; 15, germanium photodiode ФД-3; 16, controlled resistance.

spectral and total sensitivity and simplicity of design, the barrier-layer photocells, photodiodes, have been chosen as temperature sensors. They possess the property that due to radiation there occurs the n–p transition generating photo-electromotive force sufficient for measurements. If the absence of inertia (time constant is equal to 1×10^{-5} s), stability and durability are taken into account, it will be clear that germanium photodiodes ФД are useful for contactless temperature measurements.

The operational principle of the present device is shown in Fig. 2. A bottom image of the black body model on r_1 in the sample, magnified 2·7 times with the help of lens 14, is focused in plane of photocell 15. Generated photoelectromotive force produces photocurrent in the load circuit 16 which results in a potential difference u_2 across the resistance 16 measured by the potentiometer 7. The arising signal u_2 may be quite accurately measured and recorded without amplification because at 2800 K it is 7·5 mV and as temperature increases further it outruns the temperature growth. After measurements on r_1, i.e. the first compensation, the stand with photodiode 15 is replaced along the leading lines at a distance, equal to that between the centers of optical channels of the sample in the image plane.

Calibration procedure of this photoelectric unit is described elsewhere [13]. The error of the absolute temperature measurement depends on the instrument precision; when the optical pyrometer ЭОП–51 is used the error may be within ±0·2 per cent at 3300 K. In the present experiments it was more important to establish identity of temperature at two points of the sample rather than its absolute value, and an error of the temperature measurement of 1–1·5 per cent will affect the error of the results based on thermal diffusivity.

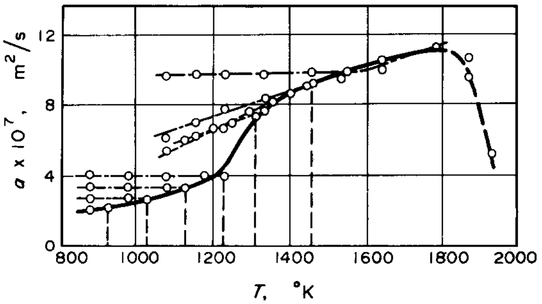

FIG. 3. Thermal diffusivity of stabilized plastic as a function of temperature.

Experimental data obtained in this paper on retardation time and dependence of temperature at the sample axis on time are used for calculation of thermal diffusivity by equations (14) and (17), the results of which are given in Figs. 3, 5 and 6. The present authors estimate for plastics the instrumental error of thermal diffusivity determination to be ±7 per cent at temperatures up to 1300 K and 5–6 per cent at higher temperatures.

Prior to the experiments, the samples were annealed (stabilized) at temperatures denoted by vertical dotted lines in Figs. 3, 5 and 6 until weight losses and physical and chemical changes ceased completely. After cooling and ageing measurements were carried out while heating-up, in this case the thermal diffusivity value

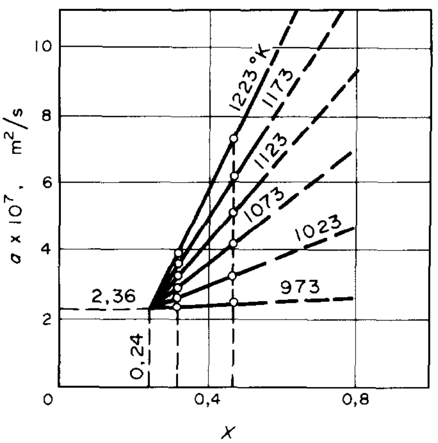

FIG. 4. Thermal diffusivity of asbestos plastic as a function of composition.

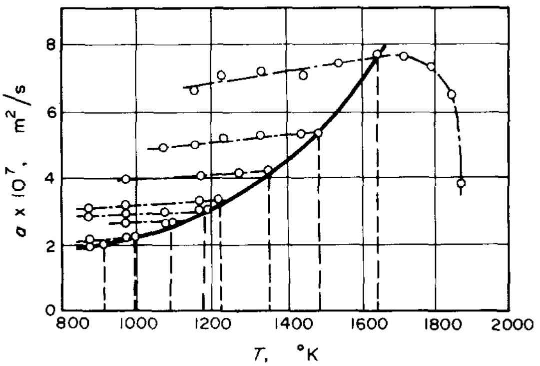

FIG. 5. Thermal diffusivity of stabilized glass plastics as a function of temperature.

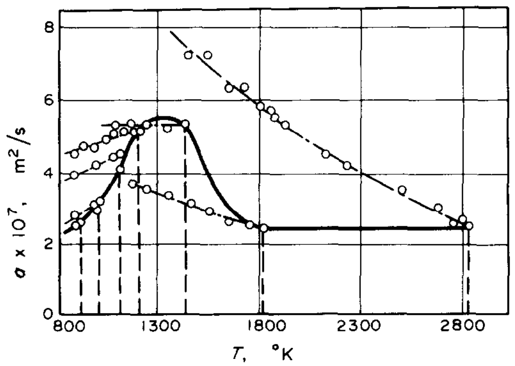

FIG. 6. Thermal diffusivity of stabilized carbon plastics as a function of temperature.

corresponding to the annealing temperature was found by extrapolation (sometimes interpolation) of temperature dependence of thermal diffusivity up to the annealing temperature.

ANALYSIS OF RESULTS

At 900–1000 K thermal diffusivities of investigated composite materials slightly differ from each other. Carburizing of solid residue bulk and formation of the secondary carbon skeleton are of influence at temperatures above 1000 K.

Preliminary annealings of armoured plastics lead to formation of materials whose conductivity is independent of the heating rate i.e. to formation of "ordinary" materials. In Figs. 3, 5 and 6 smooth dash-dotted lines are drawn through the experimental points with a corresponding stabilization temperature as a parameter.

(a) *Asbestos plastics*

A material with an initial content of resin of 32 per cent by weight was investigated. The thermal diffusivity data are presented in Fig. 3.

The first heating in the optical range of temperatures was conducted after stabilization at 1310 K, the second one—after stabilization at 1460 K, both values of thermal diffusivity being however quite close to each other. The third heating was significant particularly at temperatures above the stabilization value (1473 K). As seen from Fig. 3, thermal diffusivity from 1153 to 1773 K increases linearly and only at 1823 K there occurs a rapid fall due to the reduction reaction of magnesium and fusion of $\alpha\,MgOSiO_2$.

The asbestos plastic was then immediately annealed at 2060 K. Finally, the fourth heating has displayed constant thermal diffusivity ($a = 9{\cdot}84.10^{-7}$ m^2/s) within 1073–1573 K, and at higher temperatures relations of the third heating are repeated due to $\alpha\,MgOSiO_2$ fusion.

Thus, for the asbestos plastic investigated, the differential heat-conduction equation without heat sources (sinks) (1) is valid only for temperatures up to 1823 K. At higher temperatures it requires the flux term of the internal heat source (sink) q_v or it may give only effective characteristics including physical and chemical conversions as effective heat capacity.

For the material of asbestos plastic type there is found in the first approximation the dependence of the thermal diffusivity on the composition, the initial content of resin, within 973–1223 K. In Fig. 4 on the constant composition lines $x_1 = 0{\cdot}32$ and $x_2 = 0{\cdot}48$ there are plotted experimental values of thermal diffusivity for the temperatures of 973, 1023, 1073, 1123, 1173 and 1223 K. If isotherms are approximated by straight lines, they will cross at a point whose coordinates are $a = 2{\cdot}36 \,.\, 10^{-7}$ m^2/s and $X = 0{\cdot}24$. From Fig. 4 it follows that thermal diffusivity of a plastic with 24 per cent content of resin is independent of temperature. The chart obtained permits to determine thermal diffusivity without experiments.

(b) *Glass plastic*

The results on thermal diffusivity of glass plastic with initial content of resin of 40 per cent are presented in Fig. 5. For this plastic, measurements have been carried out by thermocouples up to 1353 K and they are in quite a satisfactory agreement with photoelectric measurements of thermal diffusivity at higher temperatures. As is seen from Fig. 5, the differential heat conduction equation without heat sources (sinks) holds for the cases when the temperature is up to 1643 K. Above this temperature the heterogeneous chemical reaction of the type

$$SiO_2 + C \xrightarrow{1643K} SiO\uparrow + CO\uparrow \qquad (18)$$

starts to occur at a measurable rate which agrees well with [15].

(c) *Carbon plastic*

Plot of thermal diffusivity of carbon plastic vs. the annealing temperature is shown in Fig. 6. It may be noted that after proper annealing (stabilization) from 900 to 1300 K, the slope of the thermal diffusivity versus temperature curves falls constantly until at 1323 K it becomes equal to zero with subsequent change of direction, i.e. maximum thermal diffusivity occurs at 1323 K. The decrease of thermal diffusivity proceeds up to 1773 K, after which its value remains constant up to the limiting temperature of the investigation, namely 2823 K. Such a mode of thermal diffusivity change may be explained as follows. Within 900–1300 K the increase in thermal diffusivity is due to the coking processes of the binder and the formation of the secondary carbon skeleton in the bulk of the carbon laminate, leading to increase of conductivity of the solid residue; a sharp fall of thermal diffusivity within 1400–1800 K can very likely be attributed to growth of porosity, which was confirmed by a rapid decrease in density.

On the whole, the shape of the thermal diffusivity curve above 1300 K qualitatively agrees with the predicted values of thermal diffusivity of carbon-graphite materials for which a monotonous fall of thermal diffusivity is generally observed with temperature increase up to 1900 K after which the thermal diffusivity remains almost constant. Absolute values, of course, differ by an order of magnitude.

In experiments with carbon plastics heterogeneous chemical reactions were not found to proceed in accordance with its composition.

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Abstract—Theoretical basis is considered of the experimental determination of thermal diffusivity by the quasi-stationary and monotonous methods.

Experimental technique in a recovery medium with temperatures up to 3300 K is presented and, a specially contructed photo-electric unit described.

The results on thermal diffusivity of phenolic plastics are analysed and the dependence of thermal diffusivity of asbestos plastics on their composition is established. The domain of validity of the differential heat-conduction equation without heat sources (sinks) is determined.

DIFFUSIVITÉ THERMIQUE DES MATÉRIAUX COMPOSITES AUX HAUTES TEMPÉRATURES

Résumé—On considère les fondements théoriques de la détermination expérimentale de la diffusivité thermique par les méthodes quasi-stationnaires et monotones.

L'article présente la technique expérimentale utilisée pour un milieu récepteur à des températures jusqu'à 3300°K et décrit un ensemble photoélectrique spécialement construit.

On analyse les résultats sur la diffusivité thermique des plastiques phénoliques et on établit la dépendance entre la diffusivité thermique des plastiques fibreux et leur composition. On détermine le domaine de validité de l'équation aux dérivées partielles de la conduction sans sources de chaleur (puits).

TEMPERATURLEITZAHL VON ZUSAMMENGESETZTEN MATERIALIEN BEI HOHEN TEMPERATUREN

Zusammenfassung—In der Arbeit sind die theoretischen Grundlagen für die experimentelle Bestimmung von Temperaturleitzahlen durch quasistationäre und stetige Verfahren betrachtet.

Die Arbeit beschreibt das Versuchsverfahren in einem Wiedereintrittsmedium bei Temperaturen bis zu 3300 K und eine besonders konstruierte photoelektrische Einheit.

Die Ergebnisse der Temperaturleitzahlen von Phenol-Pressstoffen wurden genau untersucht, die Abhängigkeit der Temperaturleitfähigkeit von Asbest-Pressstoffen von deren Zusammensetzung ist begründet. Der Gültigkeitsbereich der Differentialgleichung für Wärmeleitung ohne Wärmequellen (-Senken) ist bestimmt.