AN EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITY OF HIGHLY POROUS GRAPHITIC CARBONS

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UDC 536.21

This paper gives the results of an investigation of the thermal conductivity of graphitic carbons of different porosity (up to 78%) by the static method involving a radial heat flux from an internal rod heater in the temperature range 500-2200°K.

Graphite and graphitic carbon are promising materials for high-temperature equipment. Little work has been done on the effect of porosity on the transport properties in graphites and such work relates to only a small range of porosity (up to 30%) at low temperatures [1-4].

We investigated the thermal conductivity of graphites with a total porosity of 19, 44.3, 54.3, 61, and 78%. All the specimens were fabricated by compression molding from the same initial material. Coal pitch was used as a filler. The parameters determining the porosity were the different amounts of burning-off additives and the molding pressure. The majority (90%) of pores had equivalent radii of $(10\text{-}100)\cdot 10^3$ Å. The porous structure of the materials was investigated by injection of mercury. The proportion of closed pores was 2%. The ash content of the porous graphites was not more than 0.6, and that of the dense graphites did not exceed 0.06%. The characteristics of the investigated graphites are given in Table 1.

The specimens were heat treated at 2700°K in an argon atmosphere for 12 h. This ensured adequate graphitization and stable properties in the investigated temperature range [5].

To measure the thermal conductivity we used the static method involving a radial flux of heat from an internal rod heater. The apparatus was described in [6]. The heater was a graphite rod (ℓ = 460 mm, d = 10 mm). The specimens were in the form of cylinders with external diameter 50 mm, internal diameter 18 mm, and height 380 mm. The measurements of heat flux and temperature were made on a test section in which the longitudinal temperature distribution was uniform (ℓ_t = 80 mm).

The method of determining the thermal conductivity is based on the solution of the equation for the case of a steady temperature field in a thick-walled tube of infinite length

$$\lambda = \frac{g_l \ln d_2/d_1}{2\pi (T_1 - T_2)}. \quad (1)$$

The heat flux was determined by measuring the current and voltage drop on the test section. The current was measured with a class 0.1 D-57 astatic ammeter connected through a class 0.2 UTT-6MI current transformer. The voltage drop was measured with a class 0.3 R-56 ac potentiometer. In the calculation of the specific heat flux we took into account the thermal expansion of the test section, using the measured heater temperature and tabulated data for the coefficient of linear expansion of graphite.

The temperature measurements were made with thermocouples and a pyrometer. Temperatures in the range 500-1400°K were measured with VR5/20 tungsten–rhenium thermocouples graduated to an accuracy of ±1%. The thermocouples were located in the test section of the specimen parallel to its axis, three at distance r_{int} = 10 mm and three at distances r_{ext} = 24 mm from the specimen axis. The thermocouples were made of 0.2 mm wire and were enclosed in a two-channel alundum sheath of diameter 1.8 mm. The temperatures at radii 10 mm and 24 mm were the arithmetic means of the readings of the three thermocouples.

Institute of High Temperatures, Academy of Sciences of the USSR, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 18, No. 4, pp. 696-701, April, 1970. Original article submitted October 17, 1969.

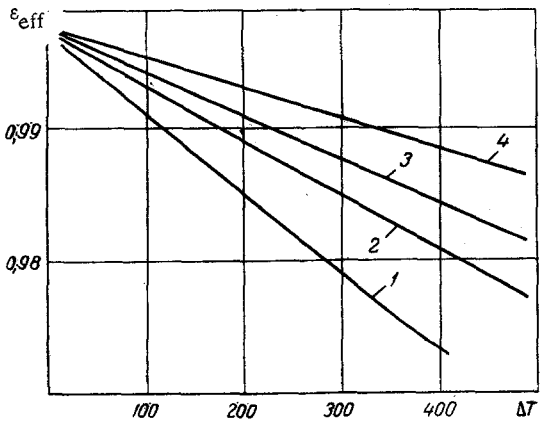

Fig. 1. Effective emissivity of bottom of nonisothermal pyrometric hole with bottom temperatures: 1) 1000; 2) 1500; 3) 2000; 4) 3000°C as functions of temperature drop over length of hole ($\ell/d = 7.5$; $\varepsilon = 0.85$), ΔT, deg.

TABLE 1. Characteristics of Investigated Materials

Material	Density, g/cm³		Specific volume of pores, cm³/g	Bulk porosity, %
	apparent	true		
I (N)	1,82	2,18	0,091	19
II (PÉ-15)	1,22	2,19	0,366	44,3
III (VS-25)	1,01	2,23	0,536	54,3
IV (PÉ-60)	0,85	2,18	0,72	61
V (PÉ-60)	0,52	2,23	1,49	78

Temperature measurements in the range 1200-2200°K were made with a class 0.2 OP-48 pyrometer. The temperature was measured at three points along the test section. The surface temperature was determined from the measured brightness temperature and the calculated effective emissivity of the surface, for which we used the calculations carried out in [6].

The temperature of the inside surface of the specimen was measured on the flat bottom of a radial hole drilled to a depth close to the diameter of the inside surface of the specimen. The drill hole was 15 mm deep and 2 mm in diameter. With a pyrometric hole of these geometric dimensions ($\ell/d = 7.5$) and the high emissivity of the investigated material ($\varepsilon_\lambda = 0.8$-0.9) the effective emissivity of the bottom of an isothermal hole is close to unity (~0.99). In our experiments, however, the change in temperature over the length of the hole was 50-500°C and, hence, we had to calculate $\varepsilon_{\lambda eff}$ of a nonisothermal hole with these temperature differences. To do this we used [7].

The formula for the calculation of $\varepsilon_{\lambda eff}$ in the case of diffusely reflecting bodies takes the form

$$\varepsilon_{\lambda_{eff}}(\xi_0) = \varepsilon_\lambda + 8(1-\varepsilon_\lambda)\int_0^{L/d} \frac{E_c(\eta)}{E_c(\xi)} \frac{\varepsilon_{\lambda eff}(\eta)\,\eta}{(4\eta^2+1)^2}\, d\eta. \qquad (2)$$

The emissivity of the material was assumed to be constant within the calculated temperature drop. For simplicity we calculated the integral emissitivity, which is quite valid in the case of gray bodies like graphites. The calculation was made for the case of linear variation of $T(\eta)$ and $\varepsilon_{eff}(\eta)$ over the lateral surface of the pyrometric hole. Figure 1 shows the results of calculation of $\varepsilon_{eff}(\xi_0)$ for a hole with $l/d = 7.5$ and $\varepsilon = 0.85$.

In all our experiments ε_{eff} of the bottom of the pyrometric hole was equal to or exceeded 0.98 and, hence, the use of the obtained data was valid in our case, even though the variations of $T(\eta)$ and $\varepsilon_{eff}(\eta)$ of the lateral surface were nonlinear.

Calculation of the effective emissivities of the surface and bottom of the pyrometric hole requires a knowledge of the spectral emissivities of the investigated materials. We determined them by the following relative method. Material I was investigated on a special apparatus for the determination of spectral emissivities. We found that ε_λ could be regarded as constant, equal to 0.85 in the range 1300-2300°K. We calculated the value of $\varepsilon_{\lambda eff}$ of the external surface of this specimen.

We then carried out experiments in vacuum for all the specimens and obtained plots of the specific heat fluxes against the surface brightness temperature. The plots of specimens I, II, and III coincided, while those of specimens IV and V differed slightly. In addition, since the specimens were composed of the same initial material, which could be regarded as gray and diffusely reflecting and differed only in porosity, had the same geometry, and were investigated in similar conditions, and the temperatures at different g_l differed by not more than 2-3%, we can assume with sufficient accuracy that if $g_{l\,I} = g_{l\,II}$

$$\left.\begin{aligned} T_I &= T_{II} \\ b^0_{\lambda I} &= b^0_{\lambda II} \end{aligned}\right\} \varepsilon_{\lambda eff} \exp(C_2/\lambda T_{SI}) = \varepsilon_{\lambda_{eff\,II}} \exp(C_2/\lambda T_{SII}). \qquad (3)$$

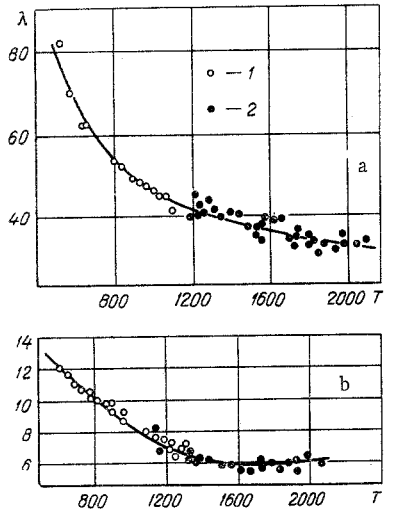

Fig. 2

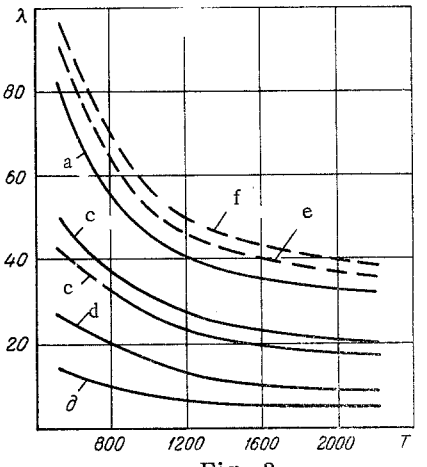

Fig. 3

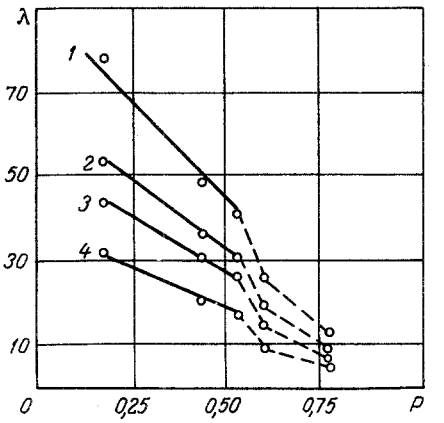

Fig. 4

Fig. 2. Thermal conductivity, W/m · deg, as function of temperature, °K, for specimens: a) I; b) V [1) temperature measured with thermocouples; 2) with pyrometer].

Fig. 3. Relationship λ(T) for materials: a) I (N); b) II (PE-15); c) III (VS-25); d) IV (PE-60); e) V (PE-65); f) λ_0 [14]; g) λ_0 [11]. λ, W m · deg; T, °K.

Fig. 4. Isotherms of conductivity–porosity relationship for carbon materials: 1) 500; 2) 800; 3) 1000; 4) 2000°K.

Whence

$$\varepsilon_{\lambda_{\text{eff II}}} = \varepsilon_{\lambda_{\text{eff I}}} \exp\left[C_2/(\lambda(1/T_{SI} - 1/T_{SII}))\right].$$

From the data obtained for $\varepsilon_{\lambda\text{eff}}$ we could calculate ε_λ of each specimen. Since the relationships $g_l(T_S)$ were the same for specimens I, II, and III, we assumed $\varepsilon_{\lambda I} = \varepsilon_{\lambda II} = \varepsilon_{\lambda III} = 0.85$. For specimens IV and V we obtained $\varepsilon_{\lambda IV} = 0.87$ and $\varepsilon_{\lambda V} = 0.89$, respectively.

The experiments to determine the thermal conductivity of the investigated materials were carried out in an argon atmosphere at a pressure a little above atmospheric. The measurements were made as the average temperature increased and decreased. The agreement between the data obtained by temperature measurement with the pyrometer and thermocouples was good.

As an example, Fig. 2 shows the experimental points and smoothed curves for the most dense and most porous specimens.

The scatter of points does not exceed ±10% in the high-temperature region, and ±3% in the low-temperature region. The accuracy of the smoothed curves is 3%. Figure 3 shows the smoothed curves of thermal conductivity against temperature for the investigated materials. To analyze the obtained data we constructed isotherms of the conductivity–porosity relationship; these are shown in Fig. 4. In the given case the thermal conductivity of a bound porous structure will be a function only of the porosity and thermal conductivity of the solid phase. The thermal conductivity of the gas phase in the pores and the radiant heat transfer in the case of pores with diameter $(10\text{-}100) \cdot 10^3$ Å will at worst be 0.06 kcal/m · h · deg [8-10], which is three or four orders below the thermal conductivity of the solid phase.

We checked the agreement between the obtained experimental data and the formulas proposed by various authors. The investigated materials are porous systems with a statistically uniform distribution of irregular pores connected by fine channels. In the case of low porosity (less than 50%), however, we can assume in a first approximation that the material is a regular porous system with closed pores of regular form. Among the papers dealing with such systems our experimental data agree best with the Loeb [11] and Russel [12] formulas, and the Odelevskii formula for a matrix mixture [13], which is essentially the Maxwell formula [14].

The Loeb formula for the case of absence of heat transfer in the pores takes the form

$$\lambda = \lambda_0 (1 - P). \tag{5}$$

The obtained experimental data for specimens I, II, and III fit this relationship to an accuracy of better than 3%. This applies to the whole measured temperature range and we can recommend the Loeb formula for calculation of the thermal conductivity of porous graphites in the range P = 15-50%.

However, although the Loeb formula describes the relationship $\lambda = \lambda(P)$ better in the porosity range 15-50%, while the deviation of the experimental data from the Russel and Odelevskii relationships is ±10%, we think it is sounder to use the latter relationships for extrapolation to zero porosity, since the model of a porous material considered by Russel and Odelevskii was more real. The value of the thermal conductivity λ_0 obtained from the Odelevskii (Maxwell) formula and the average of the two solutions obtained from the Russel formulas agreed. The thermal conductivity λ_0 calculated from the Loeb formula was 7% lower (Fig. 3).

It should be noted that there is a much more rapid reduction of thermal conductivity in the porosity range 50-60%. We think that this is due to cracking of the material and destruction of the initial system. The quantitative change in λ and the porosity value at which the deviation from the initial relationship occurs will depend on the viscosity of the material, the nature of the contact of the solid particles, the size and shape of the pores, and the method of manufacture.

NOTATION

λ	is the thermal conductivity of porous material;
g_l	is the specific heat flux;
T_1, T_2	are the temperatures on diameters d_1 and d_2;
$\varepsilon_{\lambda eff}(\xi_0)$	is the effective monochromatic emissivity of element at center of bottom of pyrometric drill hole;
ε_λ	is the emissivity of material at T_{ξ_0};
$\varepsilon_{\lambda eff}(\eta)$	is the effective emissivity of element on lateral surface;
$\xi = r/R$	is the generalized coordinate of bottom of pyrometric hole;
$\eta = l/L$	is the generalized coordinate of lateral surface;
L	is the length of hole;
$d = 2R$	is the diameter of hole;
E_s	is the energy of self-emission of surface element;
b^0_λ	is the black-body emission;
T_I, T_{II}	are true temperatures of specimens I and II with same heat flux;
T_{SI}, T_{SII}	are the brightness temperatures of specimens I and II with same heat flux;
$\varepsilon_{\lambda effI}$, $\varepsilon_{\lambda effII}$	are the monochromatic emissivities of specimens I and II;
λ_0	is the thermal conductivity of nonporous material;
P	is the porosity.

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