

EFFECT OF POROSITY ON THE EFFECTIVE THERMAL CONDUCTIVITY OF GRAPHITE

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An equation of the hyperbolic kind is proposed for describing the effective thermal conductivity of porous graphite over the 0.6 to 0.01 range of porosity.

Artificial graphites constitute cellular solid systems almost without cracks and with pores more or less uniformly distributed over the volume. One may assume, within a certain approximation, that the pores in graphite are regularly shaped. The effective thermal conductivity of porous graphite can apparently be described by the Maxwell equation, which is applicable to heterogeneous materials made up of spherical particles [1]. Calculations made by A. Eucken and based on a theoretical analysis of the Maxwell equation have led to the following expression [2]:

$$\lambda = \lambda_0 \frac{1-P}{1+P/2}. \quad (1)$$

This equation fits the test data in [3]. More precisely, however, the pores in graphite become anisometric under the pressure applied during molding. For this reason, it is permissible to use equations according to H. W. Russel [4] or A. L. Loeb [5]:

$$\lambda = \lambda_0(1 - KP_c). \quad (2)$$

Such an equation describes satisfactorily well the test results presented in [3, 6]. Although in [7, 8] the graphite was made porous by different techniques, the authors have concluded in each case that the thermal conductivity of porous graphite follows Eq. (2) at temperatures $T < 800^\circ\text{K}$. Only in one of the experimental studies enumerated here, namely in [8], was graphite made porous by drilling holes into compact specimens. In the other studies the porosity was varied either by adding different amounts of a foaming agent to the raw batch [3, 6] or by sealing the initial calcined batch through supplementary impregnation with coal-tar pitch [7]. In both cases the material was subsequently subjected to the usual high-temperature heat treatment (graphitization), always necessary for producing graphite.

On the basis of published test data pertaining to the effective conductivity of graphites, one may assume that the thermal conductivity of the solid graphite matrix is a function of its porosity, if the latter has been produced in the initial material (prior to graphitization).

According to [9], a decrease in porosity from 0.26 to 0.20 (such a decrease was attained there by an additional impregnation of calcined material in pitch) is followed by a 20% increase in thermal conductivity. It has been shown in [10] that, as the porosity decreases (there the porosity was produced by means of a foaming agent), the maximum on the thermal conductivity curve shifts toward lower temperatures, which indicates a higher thermal conductivity λ_0 of the solid graphite matrix. It is evident, then, that Eqs. (1) and (2) do not correctly describe the relation between the effective thermal conductivity and the porosity, inasmuch as the thermal conductivity of the solid graphite matrix λ_0 is also a function of the porosity.

The purpose of this study was to establish a relation between the effective thermal conductivity of graphite and the porosity of graphite over the 0.6 to 0.01 range of the latter. So far only graphites with a porosity from 0.2 to 0.8 have been investigated [3, 6, 7]. Within that range of porosity the thermal conductivity λ_0 varies still only slightly. A significant change is, apparently, to be expected when the porosity

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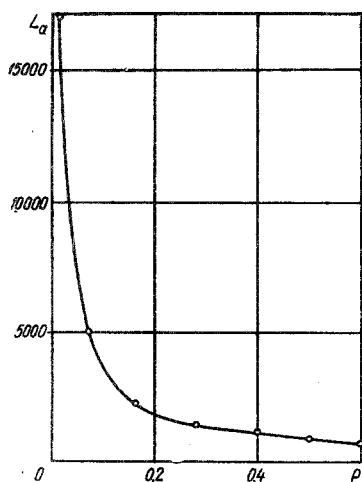


Fig. 1. Mean grain dimension of graphite L_a (Å) as a function of the porosity P .

of graphite approaches zero. The thermal conductivity of the solid graphite matrix is determined by the size of its nondefective regions (grains). The grain growth and, therefore, also the increase in the thermal conductivity of the solid graphite matrix are related to the parameters of the high-temperature treatment. Thin graphite grains grow in the direction of their dominant mutual orientation. During heat treatment there appear internal stresses, as a result of the large difference between the thermal expansivity of a graphite crystal along the a -axis and the c -axis respectively. A concurrent relaxation of internal stresses produces a complete orientation of crystallographic planes and, as a result, grain boundaries are annihilated so that the grains can grow. A more complete orientation of crystallographic planes corresponds, as a rule, to a lower porosity of polycrystalline graphite. When the grains are closely packed, then the relaxation of internal stresses spreads deeper into the bulk. Both factors contribute to a faster grain growth and raise the thermal conductivity of the solid graphite matrix. As zero porosity is approached, therefore, one may expect an extraordinarily fast increase in the effective thermal conductivity of graphite.

The technological means of reducing the porosity of artificial graphite below 0.2 are very limited. By many repeated impregnations with pitch, it is possible to reduce the porosity of graphite to 0.16 approximately. In order to attain a porosity of about 0.07, one subjects graphite to a high-temperature treatment under pressure. Note must be taken of the considerable anisotropy of properties of such a graphite: the thermal conductivity is 3-4 times higher perpendicular than parallel to the direction of molding. Finally, pyrolytic carbon is obtained while the products of methane pyrolysis precipitate on the hot graphite surface. The pores vanish almost completely (the porosity decreases to below 0.01) after an additional high-temperature anneal in pyrolytic carbon. In terms of structure and properties, this material is similar to a single crystal of graphite. The properties of annealed pyrolytic carbon are highly anisotropic: its thermal conductivity is 200-250 times higher along the precipitation surface than normally to it. Results of thermal conductivity measurements made on high-density graphites are given in [11]. The anisotropy of properties of high-density graphites casts some doubt on the validity of the established relation between their thermal conductivity and porosity. Graphite with a 0.3 or higher porosity is almost isotropic. This isotropy is a consequence of an equiprobable distribution of crystallographic a -axes within a grain volume. Heat travels through polycrystalline graphite essentially along the a -axes in grains, because the thermal conductivity along the c -axes is very low. Therefore, the path of phonons in polycrystalline graphites is longer than the dimension of a specimen. The difference between these two lengths is maximum in isotropic graphites. Because of a dominant orientation of crystals in high-density graphites, this difference decreases here and becomes minimum in annealed pyrolytic carbon. In an analysis of the relation between thermal conductivity and porosity, therefore, the former must be based on the length of the phonon path. It is also desirable to eliminate phonon-phonon interaction, which seems different in different grades of graphite at the same temperature. This requirement is met by a thermal resistance solely due to a scatter of phonons at the grain boundaries. It has been established that the mean free path of phonons in graphite retains a constant length up to a temperature $T = 120-130^\circ\text{K}$. This path length has been adopted as the a -dimension (L_a) of graphite grains. With the aid of temperature characteristics of the thermal conductivity established experimentally in [10, 11] for various grades of graphite, the mean L_a dimensions of grains have been calculated according to the modified Debye equation

$$\lambda = 1/4\gamma C_p \bar{V}_a \cdot \overline{\cos \varphi} \cdot L_a \quad (3)$$

In directions parallel and perpendicular to the direction of molding, $\cos \varphi$ for graphite is calculated as follows:

$$\overline{\cos \varphi_{\parallel}} = 1 - \frac{1}{2} \frac{\int_0^{\pi/2} I(\varphi) \sin^3 \varphi d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi d\varphi}; \quad \overline{\cos \varphi_{\perp}} = \frac{\int_0^{\pi/2} I(\varphi) \sin^3 \varphi d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi d\varphi} \quad (4)$$

For the graphites tested this mean value $\cos \varphi$ varies from 0.6 to 0.95 [11].

The mean grain dimension L_a as a function of the porosity is shown in Fig. 1 for graphite with porosities 0.6, 0.5, 0.4, 0.28, 0.16, 0.07, and 0.01. This relation is distinctly of the hyperbolic kind. Within an accuracy of $\pm 3\%$, the curve can be described by the equation

$$L_a = \frac{945}{P^{0.643}} - 690 \text{ [}\mu\text{]}. \quad (5)$$

At $P = 0$ this semiempirical relation becomes physically meaningless. This relation is valid for graphites with a porous structure. Even in annealed pyrolytic carbon, which comes close to a single crystal in terms of properties, there exist defects which produce some slight porosity. Within the 0.6–0.3 range of porosity Eqs. (1) and (5) yield the same relative increase in thermal conductivity. This means that the thermal conductivity of the solid graphite varies very little within this range of porosity.

At a less than 0.3 porosity the thermal conductivity of the solid graphite matrix begins to increase appreciably, which leads to a large difference between values calculated by Eqs. (1) and (5) respectively.

Thus, with the porosity decreasing from 0.3 to 0.05, the thermal conductivity increases relatively 4.6 times according to Eq. (5) and 1.53 times according to Eq. (1). The thermal conductivity of graphite as a function of its porosity is described by the Maxwell equation with sufficient accuracy, therefore, as long as the thermal conductivity of the solid graphite matrix remains constant. However, technological processes by which a reduction in porosity is attained also increase the thermal conductivity of the solid graphite matrix, especially at a below 0.3 porosity. For this reason, the effective thermal conductivity of artificial graphites must be calculated according to Eq. (5) applicable within the 0.6 to 0.01 range of porosity.

NOTATION

λ	is the effective thermal conductivity;
λ_0	is the thermal conductivity of the solid matrix;
P	is the porosity;
P_c	is the porosity referred to a cross section;
γ	is the specific gravity;
C_p	is the specific heat;
φ	is the angle between the crystallographic c-axis and the direction of the molding pressure;
$\overline{\cos \varphi}$	is the mean cosine of angles φ ;
$I(\varphi)$	is the distribution function of c-axes in grains of a specimen;
$\overline{V_a}$	is the mean velocity of phonons along a-axes in graphite crystals, $1.23 \cdot 10^6$ cm/sec [12];
L_a	is the mean free path of phonons, equal to the mean grain dimension.

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