EXPERIMENTAL STUDIES CONCERNING THE ELECTRICAL CONDUCTIVITY OF HIGH-POROSITY CARBON – GRAPHITIC MATERIALS

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The electrical resistance of carbon–graphitic materials with different porosities (19-78%) was studied in the 300-1700°K temperature range, and the results are presented here. It is shown that, in generalized coordinates, the thermal and the electrical conductivity are analogous functions of porosity.

The electrical conductivity of porous carbon–graphitic materials was studied on specimens with an overall porosity of 19, 44.3, 54.3, 61, and 78%. All specimens were prepared from the same raw material by the same technology (extrusion, heat treatment at 2700°K). The porosity was regulated by varying the amount of coke additive and the extrusion pressure. The data on the structure of these materials were obtained (Fig. 1) by mercury porosimetry. Blind porosity amounted to 2% and the sol fraction was 0.6%. The characteristics of specimens tested earlier for thermal conductivity are given in [1]. The specimens were made from the same ingots here and, therefore, their dimensions had to be limited (ℓ = 120 mm, r_{out} = 15 mm). Specimens of high-density graphite (grades I, II, and III) were made in the shape of tubes (r_{in} = 8 mm) while the porous specimens (grades IV and V), because of their brittleness, were made in the shape of rods. The specimens were mounted across two current-conducting graphite beams, each l = 180 mm long and having an electrical resistance not much different from the resistance of the test pieces.

The electrical conductivity was measured by the potentiometric method. The specimens were heated directly by passing electric current through them. All measurements were performed on the active l = 35 mm long portion of each specimen with the temperature maintained constant there within 1%. The electrical resistivity was calculated according to the formula:

$$\rho = \frac{V}{I} \cdot \frac{S}{l} (1 + \alpha \bar{t}). \tag{1}$$

The measurements were performed over the 300-1700°K temperature range in an argon atmosphere at a 1.1 atm pressure. The voltage drop was measured with an R-56 Class 0.3 ac potentiometer through a UTT-6M Class 0.2 current transformer. The temperature was measured with WR5/20 tungsten–rhenium thermocouples. The latter were made up of 0.2 mm (diameter) wire in a two-strand alundum jacket d = 1.8 mm, which had been tightly inserted all the way into a 12-13 mm deep radial hole in the specimen. The temperature along a specimen was measured at four locations, one of the thermocouples was placed along the active portion of a specimen. Based on the four measured temperatures, first the mean-over-the-length temperatures at radius r_0 and then the mean-over-cross-section temperatures were found according to formulas

$$\bar{T} = \bar{T}_{r_0} + \frac{V'^2}{4l^2\lambda\rho}\left(r_0^2 - \frac{r_{out}^2}{2}\right) \tag{2}$$

for rods and

$$\bar{T} = \bar{T}_{r_0} + \frac{V^2}{4l^2\lambda\rho}\left(r_0^2 - \frac{r_{out}^2 + r_{in}^2}{2}\right) \tag{3}$$

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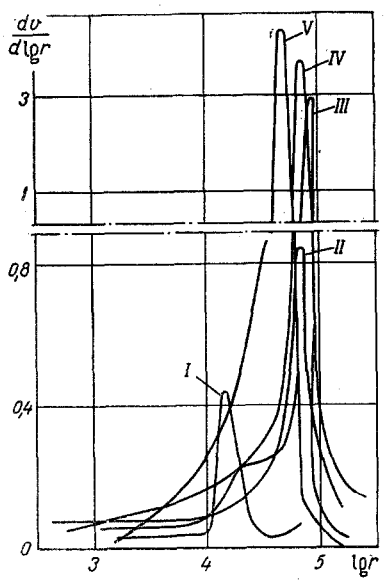

Fig. 1

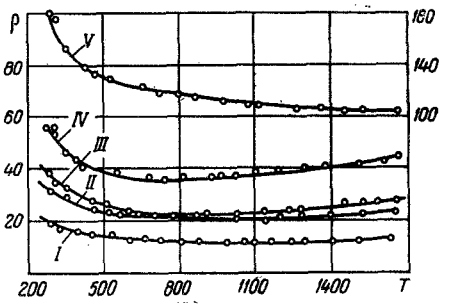

Fig. 2

Fig. 1. Differential structure curves for the test specimens, representing the distribution of porosity volumes with respect to the size of an equivalent pore radius: radius r (Å), volume v (cm^3/cm^3).

Fig. 2. Experimental data on electrical resistivity of materials with porosities: 19% (I), 44.3% (II), 54.3% (III), 61% (IV), and 78% (V); $\rho(\mu\Omega \cdot m)$, T, (°K).

for tubes. Axial heat flow was disregarded here. A temperature calculated according to (2) and (3) was taken to be the mean-over-the-volume temperature of the active portion. For dense specimens this temperature differed only slightly from $\overline{T}_{r_{out}}$ and $\overline{T}_{r_{in}}$, since the temperature drop along the radius was only less than 10°C. Specimens with a low thermal conductivity and, consequently, a high radial temperature gradient had (as mentioned earlier) the shape of rods. Therefore, the deviation of the mean-over-the-volume temperature from $\overline{T}_{r_{out}}$ and $\overline{T}_{r=0}$ may for some points have been as high as 3%.

According to [2], the macroporosity of carbon does not affect its thermal expansivity, which depends primarily on the microstructure. Test data on α are usually analyzed on the basis of two parameters: the degree of crystal anisotropy and the magnitude of the interstitial volume. Considering the technology used in the preparation of these specimens (extrusion, same raw material, same calcination temperature), the degree of anisotropy may be assumed to have been the same in all. The interstitial volume is usually measured by the volume P – P' of blind pores. For the specimens under study this volume varied between 1.5 and 2.5%, which could result in a variation of α not exceeding 3%. Based on all this, α was assumed to be equal to $5 \cdot 10^{-6}$ deg^{-1} and the same for all specimens over the entire range of test temperatures, and the error due to such approximation did not exceed 0.1% in the determination of ρ.

The maximum total experimental error fluctuated for the various specimens within a 2-5% range. The deviation of test points from the fitted curve did not exceed 2%.

As the graph in Fig. 2 indicates, the trend of the $\rho(T)$ curve is not exactly the same for all tested specimens, while the deviation from any one curve plotted in $\rho/\rho_{300} = f(T)$ coordinates is not more than 10%. There may be several reasons for this. First of all, the conditions of the crystal structure growth will vary somewhat – even when the specimens are prepared from the same raw material by the same technology – because of the variable ratio of graphite base to amorphous coke additive. A high coke content may retard further crystal growth in the tar pitch binder, which will result in shifting the temperature of minimum electrical resistivity ($T_{min\,\rho}$) upward [4]. Such a pattern is characteristic of specimen V, whose $T_{min\,\rho}$ is within 1600-1700°K.

Secondly, the specimens may contain macrodefects which are a source of an additional resistance variation with temperature. Such an additional resistance increasing with temperature should shift $T_{min\,\rho}$ downward, should increase the temperature coefficient of resistivity $d\rho/dT$ in the temperature range above $T_{min\,\rho}$, and should increase the absolute value of the electrical resistivity.

TABLE 1. Results of Electrical Resistance Measurements Performed on the Various Materials (t = 18°C)

Specimens	P, %	ρ, μΩ·m: ρ^0_{dc} (with direct current before tests)	ρ^0 (with alternating current before tests)	$\rho^{0'}$ (with alternating current after tests)	$\rho^{0''}$ (with alternating current after tests and under tension)	$(\rho^0_{dc}-\rho^0)/\rho^0_{dc}$, %	$\frac{\rho^{0'}-\rho^0}{\rho^{0'}}$, %	$\frac{\rho^{0''}-\rho^{0'}}{\rho^{0''}}$, %	$T_{min\,\rho}$, °K	dρ/dT, μΩ·m/deg
I	19	18,21	17,69	17,84	17,9	2,85	0,84	0,335	1100	$+1{,}0\cdot10^{-3}$
II	44	28,52	28,48	30,90	32,0	0,14	7,83	3,44	900	$+8{,}5\cdot10^{-3}$
III	54	34,47	34,45	36,00	37,0	0,06	4,3	2,70	1050	$+1{,}87\cdot10^{-3}$
IV	61	44,22	42,25	47,95	55,5	4,25	11,9	13,6	850	$+11{,}0\cdot10^{-3}$
V	78	135,2	133,5	154,5	177,0	1,27	13,6	12,7	1650	—

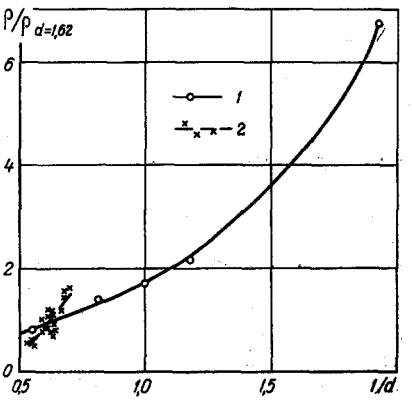

Fig. 3

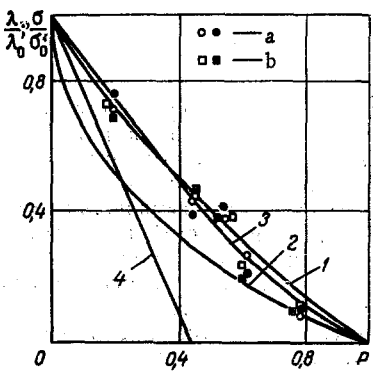

Fig. 4

Fig. 3. Reduced electrical resistivity $\rho/\rho_{d=1.62}$ as a function of the bulk weight: data from this study (1), data from [3] (2); 1/d (cm^3/g).

Fig. 4. Thermal and electrical conductivity as functions of porosity, in generalized coordinates: based on the data in [5] (1), in [9] (2), in [8] (3), and in [3] (4); $a = \sigma/\sigma_0$, $b = \lambda/\lambda_0$, blank dots refer to 500°K, black dots refer to 1500°K.

The authors have measured the electrical resistivity of the materials for this study at room temperature with direct and with alternating current before the tests and with alternating current after the tests. The measurements were made on specimens which had been slightly compressed. During high-temperature measurements, however, the specimens were placed under tension (to compensate for linear elongations). The data obtained in all these tests are shown in Table 1. Their analysis shows that during the process some material burned out $[(\rho^{0'}-\rho)/\rho^{0'}]$ and an additional resistance appeared in the specimens as a result of cracks and poor contact between grains $[(\rho^{0''}-\rho^{0'})/\rho^{0''}]$, this resistance having possibly increased under tension at high temperatures. This should cause a downward shift of $T_{min\,\rho}$ and an increase of the temperature coefficient $d\rho/dT$ which, as can be seen in Table 1, indeed occurred in correspondence with an increased defectiveness of the material. It ought to be noted that some differences in the $\rho(T)$ curves are not indicative of a general trend concerning the effect of porosity on the thermal and the electrical conductivity of carbon–graphitic materials.

The authors' experimental data are compared with the data in [3]. According to Fig. 3, the curve proposed here is much less steep than the one proposed in [3] and plotted for a narrow range of porosities. Those specimens were impregnated to different degrees, contained different amounts of tar pitch binder, and were prepared under different extruding conditions. In [3] the relation $\lambda/\lambda_0 = f(P)$ is seen to be different in character than the relation $\sigma/\sigma_0 = f(P)$ plotted from experimental data for a 17-30% porosity range at constant room temperature. As can be seen in Fig. 4, this relation differs considerably from the relation proposed on the basis of various theories and would lead to absurd conclusions already at P = 40%. In the authors' opinion, the porosity range 17-30% covered in [3] is too narrow to serve as a basis for defining the $\lambda/\lambda_0 = f(P)$ and the $\sigma/\sigma_0 = f(P)$ relations, and the data presented there must be used with great caution.

Our test data were checked against calculations by formulas which had been proposed by various authors. The materials in this study comprised cellular structures with a statistically uniform distribution of pores irregularly shaped and interconnected through fine channels. At low porosity levels (under 50%) one may – to a first approximation – treat the material as a regular cellular system with regularly shaped blind pores. It appears from studies of such systems that the experimental data fit best into the Maxwell formula [5] and into the closely approaching it in this porosity range Rayleigh formula for spheres stacked into a cube [6]. With zero conductivity through the pores, the Maxwell formula becomes

$$\frac{\sigma}{\sigma_0}\left(\frac{\lambda}{\lambda_0}\right)=\frac{2-2P}{2+P}. \tag{4}$$

For porosities in the 20-50% range it is entirely permissible to apply the superposition rule [7], but σ_0 and λ_0 must also be calculated accordingly:

$$\frac{\sigma}{\sigma_0}\left(\frac{\lambda}{\lambda_0}\right)=1-P. \tag{5}$$

The test points (specimens I, II, and III) for σ and λ do not deviate from the relation (4) by more than 10% over the entire temperature range. Relation (5) describes this range within a 5% accuracy, but yields values for σ_0 and λ_0 which are 7-10% lower than according to Maxwell.

Among the various relations which may be considered for describing high-porosity systems, the one given in [8] has been found most applicable. The largest deviation from it is 35% for some points. Our test values for σ and λ [1] are shown in Fig. 4 in generalized coordinates. The isotherms have been constructed on the basis of smooth $\sigma(T)$ and $\lambda(T)$ curves. Both σ_0 and λ_0 were calculated according to Maxwell.

NOTATION

ρ	is the electrical resistivity;
V	is the voltage drop;
I	is the current;
S	is the specimen cross section at room temperature;
l	is the active specimen length at room temperature;
α	is the thermal expansivity;
$\overline{t}(\overline{T})$	is the mean-over-the-volume temperature of specimen;
$\overline{T}_{r_0}$	is the mean-over-isothermal-length temperature of specimen at radius r_0;
λ	is the thermal conductivity of specimen;
r_{out}	is the outside radius of specimen;
r_{in}	is the inside radius of specimen;
P	is the total volume of pores;
P'	is the volume of open pores;
ρ^0	is the electrical resistivity at room temperature;
λ_0	is the thermal conductivity of dense material;
σ_0	is the electrical conductivity of dense material;
ρ_0	is the electrical resistivity of dense material.

LITERATURE CITED

1. É. A. Bel'skaya and A. S. Tarabanov, Inzh. Fiz. Zh., 18, No. 4 (1970).
2. Okada, in: Graphite as a Refractory Material [Russian translation], Vol. 1, Mir, Moscow (1964), p. 65.
3. Hutcheon and Price, in: Graphite as a Refractory Material [Russian translation], Vol. 1, Mir, Moscow (1964), p. 320.
4. A. I. Lutkov, in: Design Materials Based on Graphite [in Russian], Vol. 4, Metallurgiya (1968), p. 67.
5. J. C. Maxwell, Treatise on Electricity and Magnetism, Oxford (1873).
6. Lord Rayleigh, Phil. Mag., 34, 481 (1892).
7. A. L. Loeb, J. Appl. Phys., 22, 252-285 (1951).
8. G. S. Son Frei, Z. Elektrochem., 38, 260 (1932).
9. G. N. Dul'nev, Inzh. Fiz. Zh., 9, No. 3, 399 (1965).