ON ANISOTROPY OF APPARENT DENSITY AND POROSITY OF FINE-GRAIN GRAPHITES

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Introduction

It is well known [1-3] that artificial graphites obtained by the electrode technology [1] are characterized by anisotropy of a number of physical properties conditioned by a specific disposition of coke filler particles under the action of molding force (***MF***) to obtain green blanks. And whereas for such properties as mechanical strength, electrical and thermal conductivities, permeability, the anisotropy has been throughly enough investigated, which fact is reflected in literature [1-5], no such investigations with respect to the pore structure anisotropy are known to us.

Moreover, an erroneous opinion was unfoundedly alleged in [6] that "graphite produced by extrusion is an anisotropic material, however attempts to ascertain the anisotropy effect on the pore size distribution by the mercury porosimenry technique fail. The pore size distribution is independent of the sample cutting out direction (with respect to the molding axis) from a starting graphite block, however samples cut out of different places along the block cross section differ from each other by the pore size distribution" (in small parts only, to be added from ourselves !).

Previously [7], when studying characteristics of a pore structure of fine-grain (>90 % of particles being <90 *μm*) MPG-6 graphite (uncalcined petroleum coke +medium-temperature coal-tar pitch) obtained in a mold using a complex of various techniques, it was found that a number of samples the principal axis of symmetry whereof is normal to the blank ***MF***, had increased values of apparent density (ρ_a) as compared to samples cut out of the same blank part but parellel to the ***MF***, i.e. $\rho^{\perp}_a > \rho^{\parallel}_a$.

Experimental

To check and substantiate this fact, by random sampling several blanks of MPG-6 (⌀ 100, H 180 *mm*) and MPG-8 graphites (calcined coke + high-temperature pitch) with different ρ_a values were selected. Some of the blanks were cut into 3 equal parts (top, middle, bottom) and out of each part there were cut out 10 cylindrical samples (⌀10, H 20 *mm*) parallel (||) and normal (⊥) to the ***MF*** and 3 tubes (|| and ⊥: ⌀10*4; H 40 *mm*).On all the samples there were determined values of ρ_a and ρ_p (pycnometric) densities by a hydrostatic weighing method according to the procedure of GOST 2409-80 with the use of a *2004 MP6* type balance (*Sartorius*, Germany) and *isooctane* as a substituting medium [8]. On the tubes gas permeability (K_g) was determined by a simplified "*flow in vacuum*" method [5] via measuring pressure increase speed in a preevacuated vessel of known capacity separated from the atmosphere by the test material sample of known dimensions.Preliminarily, when effecting the metrological certification of the procedure for determining ρ_a/ρ_p and open porosity (P_o), it was found that the absolute measurement error $\Delta\rho_a$ is 0.007 g/cm^3, $\Delta\rho_p$ is 0.002 g/cm^3, and ΔP_o is 0.11 %. The metrological certification of the procedure and instrument for determining K_g has revealed that the absolute error of K_g measurement for the values $12*10^{-5}$; $12.1*10^{-2}$; 1.85, and 13.3 cm^2/s is $4*10^{-5}$; $0.8*10^{-2}$; 0.13, and 1.6 cm^2/s, respectively. The measurement error for K_g values being between the above-mentioned indices is calculated via linear interpolation of 2 closest ΔK_g values. The data obtained are presented in the Table in a statistically treated form.

Results and Discussion

As follows from the data given in the Table, for samples of MPG-6 graphite cut || (n=49) and ⊥ (n=45) to the ***MF*** $\bar{\rho}^{\parallel}_a$=1.58 and $\bar{\rho}^{\perp}_a$=1.60 g/cm^3, respectively. These differences is also supported by lower values of $\bar{P}^{\perp}_o$ and $\bar{K}^{\perp}_g$ as compared to $\bar{P}^{\parallel}_o$ and $\bar{K}^{\parallel}_g$. And in view of the fact that ρ_p remains actually unchanged and is independent of the samples cutting out direction, a direct relation exists between P_o and ρ_a with r=–1.0 for the case of $P^{\perp}_o = f(\rho^{\perp}_a)$ and r=–0.97 for $P^{\parallel}_o = f(\rho^{\parallel}_a)$. For the MPG-8 graphite samples from 5 blanks (ρ_a = 1.68 ÷ 1.84 g/cm^3) cut || to the ***MF*** (n = 193) $\bar{\rho}^{\parallel}_a$ = 1.723±0.066 g/cm^3 and ⊥ to the ***MF*** (n = 195) $\bar{\rho}^{\perp}_a$ = 1.748±0.052 g/cm^3. And samples cut ⊥ to the ***MF*** are characterized by lower values of $\bar{P}^{\perp}_o$ and $\bar{K}^{\perp}_g$ ($\bar{P}^{\perp}_o$ =19.56±2.33 %; $\bar{K}^{\perp}_g$=0.324±0.116 cm^2/s) as compared to those cut || to the ***MF***. The relation between P_o and ρ_a for the MPG-8 graphite samples,same as for MPG-6,has a clearly pronounced character and is described by the equations: $P^{\parallel}_o$= 98.60 – 45.16*$\rho^{\parallel}_a$ (r = –1.00) and $P^{\perp}_o$ = 95.33 – 43.32*$\rho^{\perp}_a$ (r = –0.98). There is actually no correlation between K_g and P_o values [for samples cut || (n=45) and

⊥ (n=43) to the *MF*, r = 0.67 and 0.51, respectively]. Thus, we have revealed the availability of anisotropy in values of ρ_a, P_o and K_g for the fine-grain graphites. Previously on MPG-6 graphite samples it was shown [7] that generally with the graphite density increase, the size of prevailing pores in the material (R_{max}) and the effective diffusion coefficient D^* decrease. The same phenomenon was also observed by one of the authors of [9] for MPG-7 graphite samples with different ρ_a (1.70 ÷1.90 g/cm^3). And in terms of the Hg-porosimetry data, from 80 to 90 % P_o fell on "*traps*" pores wherein Hg remained after pressure drop from 414 *MPa* to the atmosphere one. This suggests a *spherical* or *disk-like* shape of the pores positioned close to each other (*capillary* pores, through which the "*trap*" pores are connected therebetween and with the sample external surface, constitute from 14 to 20 % P_o). Such shape of the pores (microcracks) was suggested in [10], when analyzing the effect of compressive prestress on elastic modulus, bending strength, and pore structure of fine-grain isotropic graphite. The conclusion as to the *oblate* (*disk-like*) shape of the pores was also made in [12] when investigating the interrelation between electric conductivity and porosity of samples of quasi-isotropic fine-grain MPG-7 graphite with different ρ_a heat treated in the temperature range of 1200-3000 ^oC.

Conclusion

On statistical data there has been shown the availability of anisotropy of apparent density and open porosity for the fine-grain graphites obtained by molding in a blind die. Thus, for MPG-6 graphite $\bar{\rho}^{\perp}_a > \bar{\rho}^{\parallel}_a$ and $\bar{P}^{\perp}_o < \bar{P}^{\parallel}_o$, by 0.020 g/cm^3 and 0.9 %, respectively; and for MPG-8 graphite $\bar{\rho}^{\perp}_a > \bar{\rho}^{\parallel}_a$ and $\bar{P}^{\perp}_o < \bar{P}^{\parallel}_o$ by 0.025 g/cm^3 and 1.26 %, respectively, which is conditioned by the formation in the graphite structure of pores of *lentil-like* shape the principal axis of symmetry whereof is parallel to the blank molding force.

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Table — The main indicies of pore structure of fine-grain graphites

Type of graphite, code of blank and its parts, quantity of samples, and direction of cutting out		Average values of density, g/cm^3, open porosity, %, and permeability, cm^2/s and root mean square deviation (s)				
		$\rho_a \pm s$	$\rho_p \pm s$	$P_o \pm s$		$K_g \pm s$
All MPG-6	n= 49 ∥	1.580±0.023	2.173±0.004	27.31±1.11	n=18	1.984±0.431
	n= 45 ⊥	1.600±0.021	2.173±0.002	26.40±0.97	19	1.820±0.320
MPG-8, No.A; top,	n= 13 ∥	1.679±0.027	2.170±0.013	22.62±1.21	3	0.305±0.020
⌀ 150 *mm*	n= 13 ⊥	1.717±0.011	2.171±0.006	20.91±0.48	3	0.260±0.014
H 180 *mm* middle,	n= 12 ∥	1.707±0.026	2.170±0.018	21.34±1.16	3	0.262±0.041
	n= 13 ⊥	1.734±0.029	2.171±0.012	20.11±1.32	3	0.235±0.043
bottom,	n= 13 ∥	1.744±0.037	2.170±0.019	19.64±1.67	3	0.213±0.036
	n= 13 ⊥	1.747±0.026	2.171±0.051	19.53±1.19	3	0.211±0.018
All MPG-8	n=193 ∥	1.723±0.066	2.176±0.061	20.82±2.99	45	0.356±0.119
	n=195 ⊥	1.748±0.052	2.175±0.052	19.56±2.33	44	0.324±0.116