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Note

HIGH-TEMPERATURE INVESTIGATION OF RAW MATERIAL FOR THERMALLY EXFOLIATED GRAPHITE (TEG) PRODUCTION AND STUDY OF THE THERMOPHYSICAL PROPERTIES OF TEG PRODUCTS

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Recently, products made of a new type of graphite, i.e., thermally exfoliated graphite (TEG), have been widely utilized. Due to this, problems associated with the optimizing conditions of TEG production and the exploitation of its products have been intensively investigated [1–3]. We, for the first time, conducted high-temperature physicochemical investigations of a product of graphite anodic oxidation (PGAO) in concentrated sulphuric acid, which is a raw material used to produce TEG. Similar results for compacted TEG products are also provided.

EXPERIMENTAL

Investigations were carried out using thermogravimetry (TG), differential thermal analysis (DTA), dilatometry, heat capacities set up, chemical analysis, electron microscopy, low-temperature absorption of nitrogen and mercury porometry methods, and X-ray techniques.

For PGAO preparation we used an ash-free graphite sample from Taiginsk deposit. As a result of its electrochemical oxidation in sulphuric acid, according to conditions proposed in ref. 3 for graphite bisulphate production, we synthesized a black coloured substance containing 2.05 mass% of sulphur, with a 3.37 Å interplanar distance in the *C*-axis direction. Its X-ray diffractogram is characterized by three reflections which practically coincide with a number of graphite main reflections and substantially differ from the data for graphite bisulphate [4]. We revealed exfoliation along the *C*-axis of

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initial graphite flakes on the packs with a small number of atomic planes and the formation of porous particles, but without any change in their initial morphology.

TEG was obtained by PGAO impulsive heating up to 2300 K. It has a bulk mass of ~ 1 g l^{-1}, specific surface ~ 17 m^2 g^{-1} and 2.2 cm^3 g^{-1} volume of open pores. TEG was characterized by the separation of initial graphite crystals along the *C*-axis into bands of a small number of thin planes and by a large deformation, leading to a folder structure formation.

Compacted TEG products were formed by pressing TEG powder. It was found that during the process of their preparation TEG particles were oriented, straightened and formed a laminated and greatly imperfect graphite.

RESULTS AND DISCUSSION

Under PGAO linear heating a material mass loss begins at temperatures above 350 K. By 725–730 K the substance decomposition degree (α) reaches 13 mass% and the mass loss rate ($d\alpha/dT$) is maximum (0.07–0.12% K^{-1}) at 670–675 K. Heating above 730 K in vacuum and in argon does not lead to a change in residual mass of the PGAO powder, but when the experiment is continued in air α increases and at temperatures above 820–830 K $d\alpha/dT$ abruptly increases and reaches a second maximum (0.75% K^{-1}) at 980 K and by 1040 K α equals 100%. The above peculiarities of $\alpha(T)$ and $d\alpha/dT(T)$ curves can be explained by PGAO decomposition and by carbon residue combustion at temperatures above 820–830 K in air.

PGAO DTA results coincide with TG data: above 370–380 K on the DTA curve there is an endothermic peak extended along the temperature scale with two maxima at 520 ± 5 and 620 ± 5 K which probably indicate a two-step character of the linear pyrolysis process.

The above characteristics of PGAO pyrolysis leave their mark on its thermal expansion. As is seen from Table 1, showing data on the relative

TABLE 1

Temperature dependence of relative elongations in axial ($\Delta l/l_0$) and radial ($\Delta d/d_0$) directions of compacted PGAO samples

Temperature (K)	325	350	375	400	415	425	450
$(\Delta l/l_0)\times10^3$ ($\pm5\%$)	2.35	3.21	1.91	−0.52	−1.42	−0.39	4.61
$(\Delta d/d_0)\times10^3$ ($\pm5\%$)	−0.05	−0.12	−0.22	−0.27	–	−0.25	−0.08

Temperature (K)	475	500	525	550	575	600
$(\Delta l/l_0)\times10^3$ ($\pm5\%$)	9.78	15.9	24.1	34.1	46.3	86.3
$(\Delta d/d_0)\times10^3$ ($\pm5\%$)	0.14	0.39	0.67	1.14	2.05	3.61

elongation of compacted PGAO samples in axial ($\Delta l/l_0$) and radial ($\Delta d/d_0$) directions, above 620 K PGAO thermodestruction leads to a complete destruction of the initial sample form. A sign-variable section of the $\Delta l/l_0 = f(T)$ graph and negative values of $\Delta d/d_0$ are explained by the removal of moisture and the intercalant component from PGAO crystal surface areas. Anisotropy of the thermal expansion of compacted PGAO samples is due to the samples' texturing when they are compacted.

A study of the heat capacity (C_p) temperature dependence for PGAO showed that the $C_p = f(T)$ dependence within the range 150–370 K is linear.

An analysis of the C_p temperature dependence for compacted TEG samples within the range 310–650 K showed that heat capacity had somewhat higher values in comparison with those for initial graphite. This confirms that pressed TEG samples have a less perfect structure than graphite from the Taiginsk deposit.

The values of a, b and c coefficients of the temperature dependence equation: $C_p = a + b \times 10^{-3}T + c \times 10^{-6}T^2$ (J g^{-1} K^{-1}) for PGAO and TEG are given below:

Substance	Sample density	*a*	*b*	*c*
PGAO	2.1	15.73×10^{-3}	3.35	–
TEG	0.8–2.16	–0.28	4.30	–2.66

Dilatometry results for compacted TEG products indicate an essential anisotropy of their thermal expansion and its considerable dependence on the sample density (Fig. 1). It was found that the samples having a density of

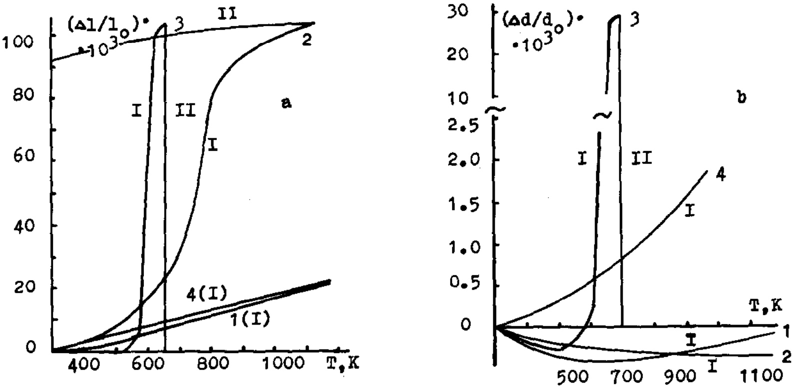

Fig. 1. Temperature dependence of relative elongations in axial (a) and radial (b) directions of compacted TEG samples with 0.8 (1), 1.25 (2), 2.16 (3) g cm^{-3} density and Taiginsk deposit graphite (4) when heated (I) and cooled (II).

1.1–1.5 g cm^{-3} were characterized by residual elongation, but in case of samples with higher density their thermomechanical destruction took place. The data of Fig. 1 also give an idea of permissible temperature conditions for the utilization of TEG products with different density and allow the conclusion that the TEG samples' thermal stability decreases with increasing density.

Thus, pyrolysis of the product of graphite anodic oxidation in concentrated sulphuric acid solution takes place within the range 350–730 K. The thermal stability limits and characteristics of pressed TEG products' behaviour under thermal effects essentially depend on their density.

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