

## Effect of Heat Treatment Conditions on the Catalytic Graphitization of Coal-Tar Pitch

G. P. Khokhlova<sup>a</sup>, Ch. N. Barnakov<sup>a</sup>, V. Yu. Malysheva<sup>a</sup>,  
A. N. Popova<sup>b</sup>, and Z. R. Ismagilov<sup>a</sup>

<sup>a</sup> *Institute of Coal Chemistry and Chemical Materials Science, Siberian Branch,  
Russian Academy of Sciences, Kemerovo, Russia*

<sup>b</sup> *Kemerovo Research Center, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia*  
*e-mail: gkhokhlova@yandex.ru*

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**Abstract**—The effect of heat treatment conditions on the properties of carbon materials obtained in the process of the low-temperature graphitization of coal-tar pitch in the presence of a cellular graphite catalyst was studied by X-ray diffraction and elemental analysis. It was found that materials whose X-ray structural characteristics are close to those of graphite were formed at 800–900°C. An increase in the process temperature to 1400°C, just as an isothermal exposure at 900°C, increased the degree of graphitization of carbon materials but decreased the amount of heteroatoms in their composition.

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Carbon materials are of considerable current interest because of their use as the anodes for lithium ion batteries [1, 2]. Graphites are the best anodic materials; however, the production of pure graphites is a highly power-intensive and time-consuming process. In the studies of others carbon materials as the anodes, it was established that the ability of all of the materials to intercalate lithium increases with the degree of their graphitization [3, 4]; moreover, the best specific capacity characteristics were obtained with the use of mesophase carbon prepared by the pyrolysis of pitch [3].

An increase in the degree of graphitization of carbon materials and a decrease in the process temperature can be achieved by the use of catalytic additives. The compounds of transition metals [5, 6], predominantly Fe, Co, and Ni [6–9], have been most frequently studied as catalysts. It was found that the graphitization of carbon precursors containing the compounds of these metals is accelerated due to the catalytic action of the resulting metal particles, and it can come into play even at 600°C [7, 8].

Earlier, we proposed a method of low-temperature catalytic graphitization with the use of Fe, Co, and Ni nanoparticles supported onto nanosized carbon material as catalysts [10, 11]. In this case, the temperature of the onset of graphitization is reduced to 400°C. Further research showed that carbon materials themselves can serve as the catalysts of low-temperature graphitization. Upon the carbonization of coal-tar pitch with the additives of cellular graphite (thermally

expanded graphite) or needle-shaped coke, carbon materials with a higher degree of graphitization and larger crystallite sizes than those upon the carbonization of individual pitch were obtained. Of the additives under consideration, cellular graphite exhibited the highest catalytic activity [12].

The aim of this work was to study the influence of heat treatment conditions on the low-temperature graphitization of pitch in the presence of cellular graphite.

### EXPERIMENTAL

Medium-temperature coal-tar pitch with the addition of 15% cellular graphite was used as a test material for this study. The cellular graphite obtained by the preliminary electrochemical oxidation of graphite in an aqueous solution of nitric acid with the subsequent thermal shock (thermal expansion) at a temperature of 1000°C [13, 14]. Tables 1 and 2 summarize the characteristics of the cellular graphite. The catalyst was introduced into the pitch via mechanical mixing. Carbonization was performed by heating to 800°C in a muffle furnace in stoppered crucibles under the two conditions: (1) with isothermal exposures for 1 h at 320, 400, 450, 500, and 600°C; (2) with isothermal exposures for 1 h at 320°C and for 3 h at 600°C; the temperature was increased at a rate of 10 K/min. The carbon material samples obtained at 800°C were subjected to additional thermal action in an inert atmosphere: heating

**Table 1.** Elemental composition of the carbon materials

Sample	$T, ^\circ\text{C}$	Isothermal exposure time, h	C, %	H, %	O + N + S (by difference), %	H/C atomic ratio
Pitch (conditions 1)	800	—	93.0	1.92	5.08	0.25
	900	—	96.2	0.78	3.02	0.10
	"	5	97.0	0.56	2.44	0.07
	"	10	97.1	0.56	2.34	0.07
	"	15	97.5	0.55	1.95	0.06
Pitch (conditions 2)	1400	—	98.1	0.34	1.56	0.04
	800	—	92.3	2.02	5.68	0.26
	900	—	96.0	0.51	3.49	0.06
	"	5	96.8	0.32	2.88	0.04
	Pitch + cellular graphite (conditions 1)	800	—	94.0	1.58	4.42
900		—	96.1	0.90	3.00	0.11
"		5	96.7	0.45	2.85	0.06
"		10	97.0	0.45	2.55	0.06
"		15	97.5	0.44	2.06	0.05
Pitch + cellular graphite (conditions 2)	1400	—	97.5	0.26	2.24	0.03
	800	—	93.3	1.61	5.09	0.21
	900	—	95.6	0.92	3.48	0.12
	"	5	97.2	0.38	2.42	0.05
	Cellular graphite	—	—	91.7	0.48	7.82

to 1400°C and heating to 900°C and an exposure of 0–15 h at this temperature.

The structure of carbon materials was studied by X-ray diffraction analysis on a Bruker D8 ADVANCE A25 powder X-ray diffractometer using  $\text{FeK}\alpha$  radiation ( $\lambda = 1.93604 \text{ \AA}$ ; Mn filter on a primary beam) at room temperature according to a polycrystal (powder) method at the Center of Collective Use of the Kemerovo Research Center, Siberian Branch, Russian Academy of Sciences. With the use of the TOPAS software for the processing of X-ray diffractograms, the main reflections in the diffraction patterns were best decomposed into two components, which characterize different carbon material phases, and their X-ray structural characteristics were calculated. Diffraction data for graphite [15] from the ASTM card file were used for the identification of phases.

The experimental X-ray diffraction patterns mainly exhibited the following reflections characteristic of carbon materials: reflections from the (002), (10), (004) and planes in the  $2\theta$  angle ranges of 22–40, 49–61, and 69–72°, respectively.

According to published data [15, 16], the interplanar spacing ( $d_{00l}$ ) for carbon materials was calculated from the formula

$$d_{00l} = \lambda / 2 \sin \theta_{00l},$$

where  $\lambda$  is the radiation wavelength, and  $\theta$  is the (00 $l$ ) reflection angle ((00 $l$ ) is (002) or (004)).

The polyarene layer stacking distance ( $L_c$ ) was evaluated according to the formula

$$L_c = 0.9 \cdot \lambda / (\beta_{00l} \cdot \cos \theta_{00l}),$$

where  $\beta_{00l}$  is the half-height width of the (00 $l$ ) reflection.

The longitudinal size of structural elements ( $L_a$ ) for carbon materials from pitch was calculated from the formula

$$L_a = 1.84 \cdot \lambda / (\beta_{10} \cdot \cos \theta_{10}),$$

where  $\beta_{10}$  is the half-height width of the (10) reflection, and  $\theta_{10}$  is the reflection angle of the (10) plane.

The longitudinal size of structural elements ( $L_a$ ) for carbon materials from pitch with cellular graphite was calculated from the formula

$$L_a = 0.9 \cdot \lambda / (\beta_{100} \cdot \cos \theta_{100}),$$

where  $\beta_{100}$  is the half-height width of the (100) reflection, and  $\theta_{100}$  is the reflection angle of the (100) plane.

The layer packing density was calculated from the formula

**Table 2.** X-ray structural characteristics of the carbon materials

Sample	$T, ^\circ\text{C}$	Isothermal exposure time, h	Phase	Phase fraction, %	Characteristic					
					$d_{00l}, \text{\AA}$	$L_c, \text{\AA}$	$L_a, \text{\AA}$	$\rho, \text{g/cm}^3$	$N, \text{items}$	$Y, \%$
Pitch (conditions 1*)	800	—	1	76	3.539	13	23	2.15	5	—
			2	24	3.397	27	34	2.24	9	48
	900	—	1	69	3.614	14	25	2.11	5	—
			2	31	3.414	23	50	2.23	8	29
	"	15	1	70	3.602	15	51	2.12	5	—
			2	30	3.425	25	51	2.22	8	17
	1400	—	1	63	3.527	18	88	2.16	6	—
			2	37	3.461	41	47	2.20	13	—
Pitch (conditions 2*)	800	—	1	74	3.563	12	20	2.14	4	—
			2	26	3.402	24	36	2.24	8	42
	900	—	1	61	3.647	15	46	2.09	5	—
			2	39	3.416	22	46	2.23	7	27
Pitch + cellular graphite (conditions 1**)	800	—	1	44	3.376	88	216	2.26	27	71
			2	56	3.362	196	882	2.27	59	86
	900	—	1	75	3.366	83	313	2.26	26	83
			2	25	3.360	273	299	2.27	82	89
	"	15	1	34	3.375	55	445	2.26	17	73
			2	66	3.359	130	192	2.27	40	90
	1400	—	1	81	3.367	58	165	2.26	18	81
			2	19	3.357	286	352	2.27	86	92
Pitch + cellular graphite (conditions 2**)	800	—	1	63	3.372	73	109	2.26	23	76
			2	37	3.360	230	233	2.27	70	89
	900	—	1	81	3.365	74	322	2.26	23	83
			2	19	3.355	300	622	2.27	90	94
Cellular graphite**	—	—	1	55	3.364	76	244	2.27	24	85
			2	45	3.361	305	441	2.27	92	87

\* The (002) reflection was used.

\*\* The (004) reflection was used.

$$\rho = 0.762/d_{00l}$$

The number of polyarene layers in a stack was evaluated using the formula

$$N = L_c/d_{00l} + 1.$$

The degree of graphitization of a phase was calculated from the formula

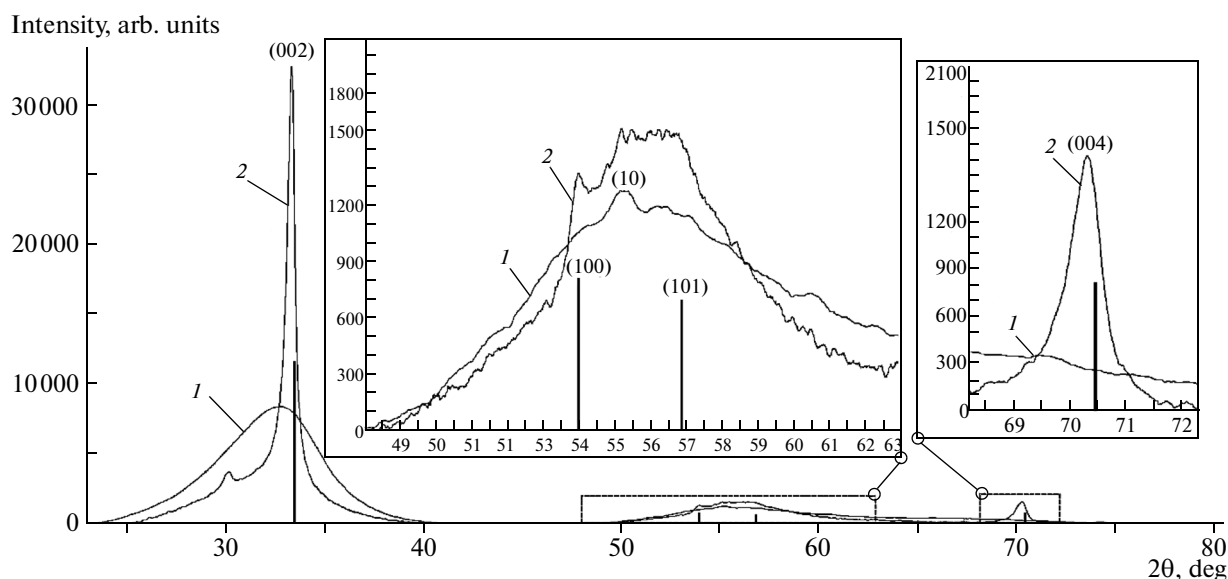
$$Y = (3.440 - d_{00l})/(3.440 - 3.354),$$

where 3.440 is interplanar spacing in carbon with a turbostratic structure, and 3.354 is interplanar spacing in a defect-free single crystal of graphite.

## RESULTS AND DISCUSSION

Table 1 summarizes data on the elemental analysis of the carbon materials from pitch and pitch with the additive of cellular graphite, which were obtained in a muffle furnace upon heating to a temperature of 800°C under conditions 1 and 2.

The carbon materials obtained from pitch in the presence of cellular graphite are characterized by a higher carbon content and a lower hydrogen content, as compared with those from individual pitch; this fact indicates that the processes of pitch condensation and aromatization in the presence of a catalyst occurred more deeply. In this case, the yield of carbon materials



**Fig. 1.** X-ray diffraction patterns of the carbon materials obtained from (1) pitch and (2) pitch with the addition of cellular graphite on heating to 800°C under conditions 1.

increased. The experimental results are consistent with data reported previously [12]. On slow heating (under conditions 1), in comparison with more rapid heating (under conditions 2), the yield of solid residue increased from 53 to 64% for pitch without additives and from 66 to 73% (on a pitch basis) for pitch with cellular graphite. It should be noted that a higher carbon content was achieved by slow heating regardless of the type carbon materials.

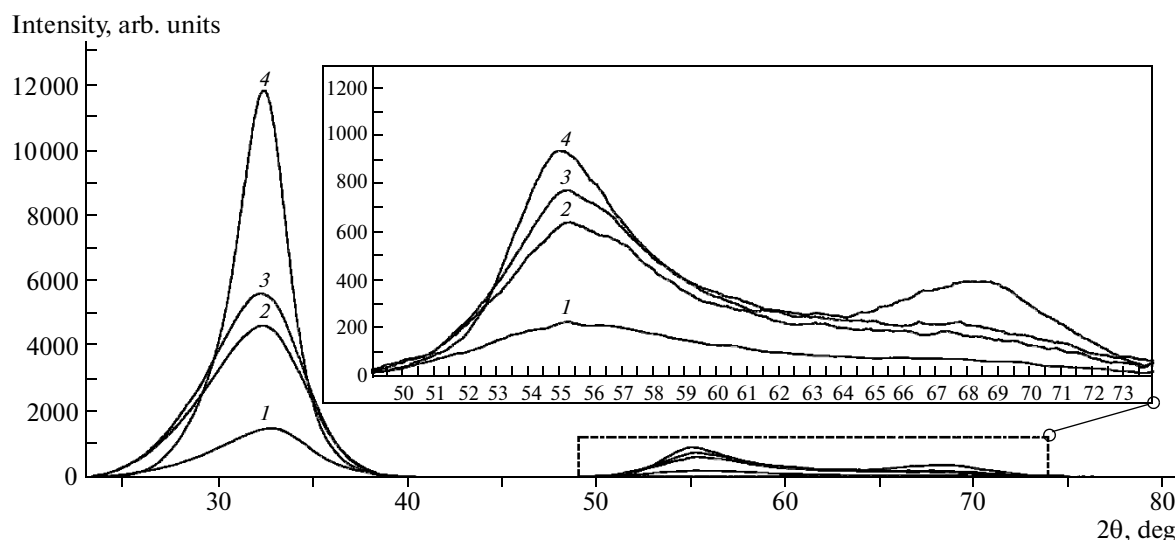
The X-ray diffraction patterns of carbon materials obtained under different heating conditions have identical shapes. As an example, Fig. 1 shows the X-ray diffraction patterns of carbon materials prepared from pitch and pitch with the addition of cellular graphite under conditions 1. Table 2 summarizes the calculated X-ray structural characteristics of carbon materials obtained from pitch and pitch with the additive of cellular graphite upon heating to 800°C under conditions 1 and 2.

In the spectra of the carbon materials obtained from pitch, the (10) reflection, which characterizes a two-dimensional turbostratic structure, was detected, whereas the (004) reflection was almost not pronounced. The (002) reflection was decomposed into the following two components: (1) almost amorphous phase 1 and (2) and phase 2 with a small degree of ordering. Table 2 indicates that the carbon materials obtained upon slower heating (under conditions 1) are characterized by a somewhat higher degree of graphitization and greater crystallite sizes.

In contrast to the carbon materials prepared from pitch without a catalyst, the X-ray diffraction patterns of the carbon materials obtained from pitch with cellular graphite exhibited reflections from the planes (100) and (101); this fact is indicative of the three-dimensional crystal structure of the samples. The (004) reflection is the superposition of two reflections from two phases, whose interplanar spacing is close to that of graphite. For comparison, Table 3 gives analo-

**Table 3.** X-ray structural characteristics and the elemental composition of commercial graphites (the (004) reflection was used)

Sample	Phase	Phase fraction, %	$d_{00l}$	$L_c$	$L_a$	$\rho$ , g/cm <sup>3</sup>	$N$ , items	$Y$	$C$	$H$	H/C atomic ratio
			Å					%			
Pyrolytic graphite	1	56	3.372	129	173	2.26	39	75	99.7	0.28	0.03
	2	44	3.365	347	561	2.25	104	83			
Anodic graphite	1	59	3.370	197	206	2.26	59	78	99.9	0.06	0.01
	2	41	3.364	522	931	2.27	156	85			



**Fig. 2.** X-ray diffraction patterns of the carbon materials obtained from pitch under conditions 1 depending on heat treatment: (1) the heating of pitch to 800°C, (2) the heating of carbon materials to 900°C, (3) the heating of carbon materials to 900°C and an exposure for 15 h, and (4) the heating of carbon materials to 1400°C.

gously calculated data for the X-ray diffraction of two industrial graphites. On slower heating, the fraction of a more structured phase and the longitudinal sizes of crystallites in the carbon materials increased (Table 2). Note that the results obtained cannot be explained only by the presence of cellular graphite itself, which possesses a crystal structure and gives corresponding reflections, in the carbon materials because its concentration in the test carbon materials does not exceed 20–23%, whereas the entire sample is characterized by a high degree of ordering.

The stage of a thermoplastic state (about 350°C) is responsible for the two-phase structure of the carbon materials from pitch. On heating optically isotropic pitch in the process of thermal polycondensation in a plastic state, the differentiation of structural fragments always occurs with the formation of regularly structured condensed aromatic layers, which are ordered in stacks with an interlayer distance of  $\sim 3.5$  Å (turbotratic crystallites); that is, a transition of the amorphous structure of pitch to a two-phase mesomorphic structure occurs. The average sizes of crystallites increase because of the addition of molecules from the isotropic part of pitch to them and due to their association. The sizes of crystallites in a mesophase are considerably higher than those in an optically isotropic matrix [17].

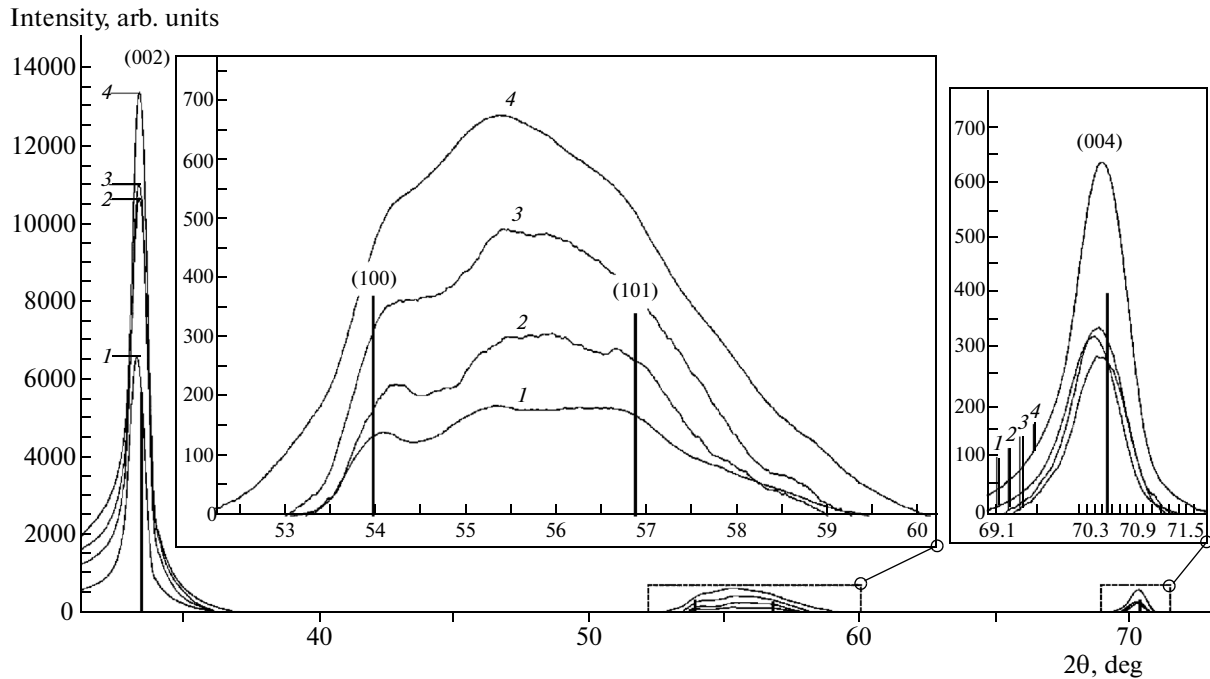
On the thermal conversion of pitch in the presence of cellular graphite, the molecules of pitch and crystallites formed in the bulk are located on catalyst particles to increase them. Because of the crystal structure of the catalyst and the interaction of the electrons of graphite structures with the aromatic molecules of

pitch, adsorption and condensational processes on its surface are oriented (predominantly in parallel to the surface of catalyst particles) to cause the formation of the crystal structure of carbon materials, where the catalyst serves as a crystallization center (nucleus).

In a solid state (starting from approximately 500°C), the processes of crystallite growth and structure ordering continue but less intensely; therefore, slow heating, which increases the lifetime of a thermoplastic state, ensures a more significant increase in the mesophase crystals and an improvement in their structure.

The additional heating of the carbon materials from pitch and pitch with cellular graphite, which were obtained by heating to 800°C under conditions 1 and 2, to 900 and 1400° in an inert atmosphere, as well as an isothermal exposure at 900°C, increased the carbon content of the samples (Table 1). At an exposure of 15 h at 900°C or heating to 1400°C, the carbon content increased to 97.5–98.1%, and the H/C ratio decreased to 0.03–0.06.

The structure of carbon materials from pitch remained amorphous after additional heat treatment; a certain ordering was observed only upon the heating of a sample to 1400°C: the X-ray diffraction patterns exhibited a weak (004) reflection (Fig. 2). The X-ray structural characteristics given in Table 2 show that, in comparison with the initial carbon materials (obtained at 800°C), fraction of a more structured phase increased and the longitudinal size of crystallite stacks somewhat increased in both of the phases. In this case, an increase in the interlayer distance can be caused by structure loosening upon the release of the gaseous



**Fig. 3.** X-ray diffraction patterns of the carbon materials obtained from pitch with the addition of cellular graphite under conditions 1 depending on heat treatment: (1) the heating of pitch with cellular graphite to 800°C, (2) the heating of carbon materials to 900°C, (3) the heating of carbon materials to 900°C and an exposure for 15 h, and (4) the heating of carbon materials to 1400°C.

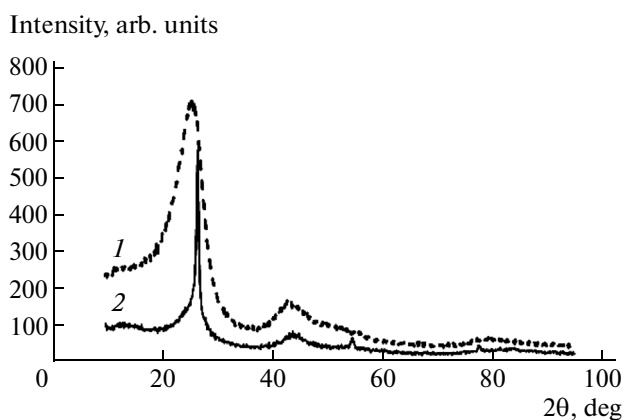
products of high-temperature destruction and by the bending of graphene sheets on their growth as a result of the removal of heteroatoms and side substituents followed by dangling bond saturation.

In contrast to the carbon materials from pitch, in the case of the carbon materials from pitch with the addition of cellular graphite, additional thermal action produced diverse changes in the ratio between different phases and the size of crystallites; however, the degree of graphitization increased (Fig. 3, Table 2). The distance between graphene sheets in crystallites is almost equal to the distance of ideal graphite (3.354 Å), and the degree of graphitization increases to 83–94%, which is higher than these characteristics of graphites obtained in the usual way (Table 3). Obviously, the orienting effect of the catalyst surface area hampers this interaction of dangling bonds formed upon the thermal destruction with the bending of graphene layer and their saturation within a flat fragment. Ultimately, the crystallite can be divided into smaller parts with smaller thickness and diameter; however, in this case, the imperfection of layers decreased and the degree of their ordering increased. The amount of gaseous degradation products, which loosened the structure, was much smaller in this case as a result of deeper condensation and aromatization processes at the earlier stages of the thermal transformation of pitch in the presence of the catalyst. The

most important changes in the structural ordering of the carbon materials obtained at 800°C occurred upon their heating to 900°C. The subsequent isothermal exposure at 900°C or heating to 1400°C less considerably increased the degree of graphitization of the carbon materials from pitch with the catalyst.

In order to confirm the crystal structure of the carbon materials based on pitch with cellular graphite, we additionally obtained X-ray diffraction patterns on an HZG 4 instrument with copper radiation. Figure 4 shows the X-ray diffraction patterns of carbon materials from pitch and pitch with cellular graphite prepared upon heating to 900°C. It is evident that the spectrum of the carbon material from pitch with cellular graphite exhibits the (110) and (112) reflections (about 78 and 84°, respectively), which are characteristic of the crystal structure of graphite. These reflections are absent from the spectrum of the carbon material from pitch without the addition of cellular graphite.

Thus, upon the catalytic graphitization of coal-tar pitch with the use of cellular graphite as a catalyst, carbon materials characterized by the presence of a crystal structure with interplanar spacing close to that of graphites were obtained even at 800°C, whereas the carbon material from pitch in the absence of a catalyst had an amorphous structure. As the temperature was increased to 900°C, the structure of the carbon mate-



**Fig. 4.** X-ray diffraction patterns of the carbon materials obtained from (1) pitch and (2) pitch with the addition of cellular graphite on heating to 900°C (measured on an HZG 4 instrument with copper radiation).

rials of pitch with cellular graphite was even more ordered. Although the resulting carbon materials were inferior to commercial graphites in terms of the carbon content and the size of crystallite stacks; however, they were superior to the commercial graphites in terms of the degree of graphitization and the similarity of interplanar spacing to the interplanar spacing of defectless single-crystal graphite. A decrease in the rate of heating resulted in the production of carbon materials with a more ordered structure. The increase in the final process temperature to 1400°C or the isothermal exposure at 900°C somewhat increased the degree of graphitization of carbon materials, but it mainly decreased the amount of heteroatoms in their composition.

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#### REFERENCES

- Iijima, T., Suzuki, K., and Matsuda, Y., *Synth. Met.*, 1995, vol. 73, p. 9.
- Wu, Y.P., Rahm, E., and Holze, R., *J. Power Sources*, 2003, vol. 114, p. 228.
- Yamaura, J., Ozaki, Y., Morita, A., and Ohta, A., *Abstracts of Papers, 6th Int. Meet. Lithium Batteries*, Munster, 1992, p. 103.
- Fialkov, A.S., Dubasova, V.S., Nikolenko, A.F., et al., in *Fundamental'nye problemy elektrokhimicheskoi energetiki* (Fundamental Problems of Electrochemical Power Engineering), Saratov: Izd. Saratov. Gos. Univ., 1999, p. 134.
- Yasuda, E., Park, S.-M., Tanabe, Y., et al., *Tokyo Inst. Technol., Rept. Res. Lab. Eng. Mater.*, 1992, no. 17, p. 145.
- Taegwhan, H. and Sangjin, H., US Patent 2005/0008562, 2005.
- Kodama, Y., Sato, K., and Suzuki, K., et al, *Carbon*, 2012, vol. 50, no. 10, p. 3486.
- Yasuda, H., Miyanaga, S., Nakamura, A., and Sakai, H., *J. Inorg. Organomet. Polym.*, 1991, vol. 1, no. 1, p. 135.
- Zhang, C., Fransson, M., Liu, C., and Zhou, B., US Patent 2007/0265162, 2007.
- Barnakov, Ch.N., Seit-Ablaeva, S.K., Ismagilov, Z.R., et al., RF Patent No. 2429194, *Byull. Izobret.*, 2011, no. 26.
- Barnakov, Ch.N., Seit-Ablaeva, S.K., and Ismagilov, Z.R., RF Patent No. 2476374, *Byull. Izobret.*, 2013, no. 6.
- Khokhlova, G.P., Malysheva, V.Yu., Barnakov, Ch.N., et al., *Vestn. Kuzbass. Gos. Tekhn. Univ.*, 2013, no. 5, p. 21.
- Avdeev V.V., Finaenov A.I., Yakovlev A.V., et al., RF Patent No. 2233794, *Byull. Izobret.*, 2004, no. 22.
- Sorokina, N.E., Khaskov, M.A., Avdeev, V.V., and Nikol'skaya, I.V., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 2, p. 184.
- Trucano, P. and Chen, R., *Nature*, 1975, vol. 258, p. 136.
- West, A. R., *Solid State Chemistry and Its Applications*, New York: John Wiley & Sons, 1984, part. 1, ch. 5.
- Sherryuble, V.G. and Seleznev, A.N., *Pekovyyi koks v uglerodnoi promyshlennosti* (Pitch Coke in the Carbon Industry), Chelyabinsk: Chelyabinskii Dom Pechati, 2003.

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