

XRD Characterization of the Structure of Graphites and Carbon Materials Obtained by the Low-Temperature Graphitization of Coal Tar Pitch

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Abstract

The structure of some commercial graphites and carbon materials (CMs) obtained by the low-temperature catalytic graphitization of coal tar pitch with iron salt, needle coke, foamed graphite as the catalysts has been studied. The study was performed using the X-ray diffraction technique with reflections from base plane and their decomposition into two components corresponding to the structural phases of graphite which have different XRD characteristics. Various CMs were compared with respect to the structural phase ratio, distance between polyarene layers in these phases, and sizes of the coherent scattering regions. The (004) reflection provided a better fit of some properties of graphites to the calculated XRD characteristics as compared to calculation from the (002) reflection. In the case of carbonization of coal tar pitch with investigated catalyst additions, prepared carbon materials have a higher degree of graphitization and a crystallite size greater than in the other case of carbonization of the individual pitch. The highest catalytic activity is shown by foamed graphite. It was found that the use of foamed graphite as the catalyst at 800–900 °C produced carbon materials possessing a crystalline structure with interplanar spacing close to that in commercial graphites, while in the absence of catalyst the coal tar pitch material has an amorphous structure.

1. Introduction

Carbon materials (CMs) and particularly graphite are widely applied in various industries. The use of CMs as the anodes for lithium-ion cells is quite topical now. Graphites are the best materials for the anodes; however, their synthesis is a long-term process requiring high energy consumption. Investigation of other CMs as the anodes has shown that the ability to lithium intercalation for all the materials increases with the degree of their graphitization. The use of catalytic additives can increase the graphitization degree of CMs and decrease the process temperature. Such catalysts are usually represented by compounds of transition metals [1], mostly Fe, Co and Ni [1–3]. Graphitization of the carbon precursors containing compounds of these metals is accelerated by the catalytic action of metal particles formed in the process and can start at a temperature as low as 600 °C [2]. We have proposed a method of the

low-temperature catalytic graphitization catalyzed by Fe, Co and Ni nanoparticles that are deposited on a nanosized carbon material [4, 5]. In this case, the starting temperature of graphitization decreases to 400 °C. Further studies have revealed that carbon materials themselves can serve as the catalysts for low-temperature graphitization [6, 7].

Along with the development of advanced methods for the synthesis of graphite materials, it is necessary to select the most efficient criteria for estimating the quality of graphites and graphitization degree of CMs, and to relate these criteria with physicochemical properties of graphites. Studies of interrelations between structure and characteristics of carbon are based mainly on the model proposed by Franklin in 1951 [8], which assumes structural homogeneity of graphites. XRD characteristics calculated by this model are close to each other and do not explain differences in the properties of graphites. In recent works, the presence of several phases

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in the graphite structure has been discovered. The study of natural graphite [9] has shown that it is represented by two structural phases – graphite (the main phase) and turbostratic ones. The authors of [10] considered the (002) reflection in the diffraction pattern of graphite as superposition of two components corresponding to the graphite particles with different sizes of the coherent scattering regions (CSR). However, the phase ratio and its effect on the properties of graphites were not considered.

The goal of this work was to investigate the effect of the catalyst features on the structure of carbon material, which is synthesized by thermal conversion of coal tar pitch at relatively low temperatures (800-900 °C), and to estimate a potential of the X-ray diffraction method for comprehensive characterization of graphite materials and assessment of their properties.

2. Experimental

A carbon material was synthesized from commercial middle temperature coal tar pitch. The catalytic additives were represented by $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, structured carbon – petroleum needle coke (NC), and foamed graphite (FG), which was obtained by preliminary electrochemical oxidation of graphite in an aqueous solution of nitric acid followed by heat shock (thermal expansion) at a temperature of 1000 °C [11, 12]. The additives, in the amount of 15 wt.% in the case of structured carbon and 2.0 wt.% as referred to Fe in the case of $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, were introduced in the coal tar pitch by mechanical mixing. Carbonization was carried out in a muffle furnace using crucibles with ground stoppers by stepwise heating to 800 and 900 °C with holding for 1 h at 320, 400, 450, 500 and 600 °C. Temperature was raised at a rate of 10 °/min. Some CM samples obtained at 800 °C were subjected to additional thermal treatment in an inert atmosphere – heating to 1400 °C.

Four samples of commercial graphites were used in the study: synthetic graphite obtained by heating of a mixture of coal tar pitch and coke to ~ 2800 °C, pyrolytic graphite obtained by pyrolysis of gaseous hydrocarbons, thermally expanded graphite obtained from intercalation compounds with sulfuric acid, and natural graphite (Kureisk deposit) calcined at ~ 2800 °C.

Carbon structure was examined using X-ray diffraction on a Bruker D8 ADVANCE A25 powder X-ray diffractometer with FeK_α radiation ($\lambda = 1.93604 \text{ \AA}$, a Mn primary beam filter) at room temperature by the powder polycrystal technique at the Center of Collective Use of Kemerovo Scientific Center SB RAS. Reflections were decomposed into components using the TOPAS software for pro-

cessing the X-ray diffraction patterns. XRD characteristics were calculated with the known formulas according to [13].

The interplanar spacing (d_{00l}) for carbon materials was calculated from the formula

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

where λ is the radiation wavelength, and θ is the (00l) reflection angle ((00l) 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 β_{00l} is the half-height width of the (00l) 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 β_{10} is the half-height width of the (10) reflection, and θ_{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 β_{100} is the half-height width of the (100) reflection, and θ_{100} is the reflection angle of the (100) plane.

The layer packing density was calculated from the formula

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

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.

Micrographs were obtained on a JEOL JEM 2100 transmission electron microscope at accelerating voltage 200 kV at the Analytical Center of Kemerovo State University.

3. Results and Discussion

3.1. Assessment of the structural features of various graphites by X-ray diffraction method

To determine the possibilities of X-ray diffraction for comprehensive characterization of graphite materials and assessment of their properties, structural features of graphites were estimated by calculation using the (002) and (004) reflections. X-ray diffraction patterns of the graphites under examination are displayed in Fig. 1. The (002) and (004) reflections in the diffraction patterns are asymmetric; they can be considered as a superposition of two components corresponding to the structural phases of graphite with different interplanar spacing. Figure 2 illustrates the decomposition of a reflection into two components. A ratio of integrated intensities of the reflection components corresponds to the phase ratio, which can be used to characterize graphites along with interplanar spacing and size of the coherent scattering region. Table 1 lists the XRD characteristics of graphites calculated from the isolated components of reflections and from the initial (not decomposed) (002) and (004) reflections.

A comparison of the structural characteristics of graphites, which were obtained by calculation without decomposition of the (002) and (004) reflections into components, gave a smaller interplanar spacing

for thermally expanded graphite, but did not reveal a significant difference between other graphites. The CSR sizes (L_c) differ for different graphites and depend quite strongly on a reflection used for the calculation (for example, L_c is equal to 172 and 7 Å for the (002) and (004) reflections in the case of natural graphite), which can be attributed to strong asymmetry and broadening of the (004) reflection caused by the presence of structures with substantially different interplanar spacing (Fig. 1). As a result, formal calculation without decomposition into components produces distorted results. Thus, a comparison of the crystal structures of different graphites using the calculation from the initial (002) or (004) reflection is low informative and even impossible in some cases.

On the contrary, processing of XRD patterns by decomposition of the asymmetric (002) and (004) reflections into components makes it possible to characterize more accurately the structure of graphites and estimate the difference between them. One can see from Table 1 that the isolated graphite phases (1 – less structured, 2 – more structured) have different contents and structural characteristics for different graphites. For all the graphites studied, interplanar spacings are substantially smaller and crystallite sizes (L_c) are greater by a factor of 2-3 in structure 2 as compared to structure 1. The smallest L_c values were obtained for the natural graphite structures.

Table 1
XRD characteristics* of graphites and discharge capacity ($Q_{d,av}$) of lithium-ion cells with the anodes made from these graphites

Graphite	Phase	Calculated from the (002) reflection				Calculated from the (004) reflection				$Q_{d,av}$, mA·h/g [14]
		Phase fraction, %	d_{00l} , Å	L_c , Å	Y, %	Phase fraction, %	d_{00l} , Å	L_c , Å	Y, %	
Synthetic	1	38	3.383	375	63	59	3.370	197	78	353
	2	62	3.366	755	82	41	3.364	522	85	
	Without phase separation		3.366	441	82	100	3.364	300	85	
Pyrolytic	1	62	3.377	277	70	56	3.372	129	75	340
	2	38	3.366	540	84	44	3.365	347	83	
	Without phase separation		3.366	307	82	100	3.365	213	83	
Natural	1	65	3.384	113	62	66	3.385	53	61	240
	2	35	3.365	322	84	34	3.362	185	86	
	Without phase separation		3.367	172	81	100	3.363	7	85	
Thermally expanded	1	49	3.366	224	82	66	3.359	195	90	-
	2	51	3.347	727	100	34	3.354	616	96	
	Without phase separation		3.346	147	100	100	3.354	280	95	

* d_{00l} – interlayer spacing, L_c – stack height, Y – degree of graphitization.

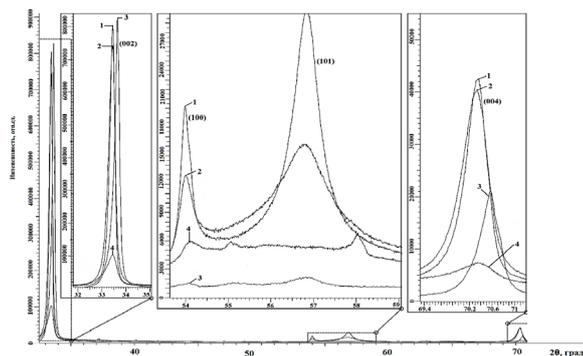


Fig. 1. XRD patterns of graphites: 1 – synthetic, 2 – pyrolytic, 3 – thermally expanded, 4 – natural.

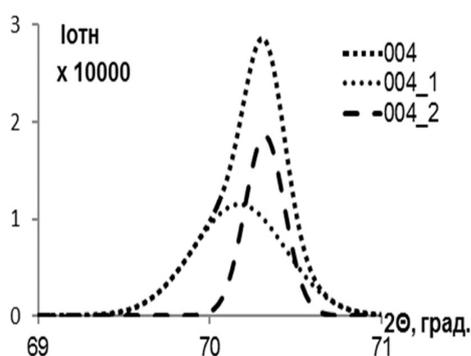


Fig. 2. An example of decomposition of the (004) reflection in the diffraction pattern of synthetic graphite: dash line – a more ordered phase, dot line – a less ordered phase.

The structural phase with the interlayer spacing 3.370, 3.385 Å characterizes an intermediate step in the graphite structure formation – a transition of turbostratic phase into graphite. This structure, along with the graphite one (hexagonal, with interlayer spacing of ~3.36 Å), is present in both the natural and artificial graphites, but is not observed in thermally expanded graphite. A ratio of these two structures is an additional characteristic of graphites, which can reveal their distinctions.

Graphites have different ratios of structural phases and CSR sizes when calculated from the (002) and (004) reflections. A comparison of XRD data with electrophysical properties of graphites, in particular with discharge capacity of lithium-ion cells having the anodes made from such graphites, as well as with irreversible capacity and cyclability [14] allowed us to elucidate a relation between them, the best fit being obtained for the structural characteristics calculated from the (004) reflection. As seen from Table 1, when calculated from the (002) reflection, the ratio of structural phases and the L_c value are close for

natural and pyrolytic graphites, while according to calculation from the (004) reflection, these values are close for synthetic and pyrolytic graphites. Capacity characteristics are close for the anodes made of synthetic and pyrolytic graphites; this corresponds to the structural data obtained by calculation from the (004) reflection. A possible reason is that the long-range orders of reflection from base plane give more accurate data on interplanar spacing of graphites [15]. The highest capacity characteristics are observed for the graphites with a higher crystallinity and greater crystallite sizes – synthetic and pyrolytic graphites; these graphites have close characteristics. Natural graphite, similar to high-crystalline ones, is capable of repeated cycling; however, its reversible capacity is lower. The values of irreversible capacity for natural graphite are higher (164 mA·h/g) than for more crystalline artificial graphites (50-60 mA·h/g) [14].

Thus, the analysis of graphites with respect to isolated structural components reveals their distinctions, although calculation from the initial (not decomposed) reflections gives close characteristics of the graphites. The ratio of structural phases is an additional characteristic of graphites. Analysis from the (004) reflection shows a better fit to the graphite properties. Capacity characteristics of graphitic anode material depend on crystallinity of the graphite structural phases and on the crystallite sizes. Thus, XRD data on the structural features can be used to estimate the capacity parameters of graphite when it is used as the anode material.

3.2. Assessment of the structural features of CMs synthesized by the low-temperature catalytic graphitization

Taking into account the above results, CMs obtained by the low-temperature catalytic graphitization were characterized using the (004) reflection. In the case of CM synthesized from coal tar pitch in the absence of catalyst, the (002) reflection was employed.

The calculated XRD characteristics of CMs are listed in Table 2. By way of example, Fig. 3 shows the diffraction patterns of CMs synthesized from pure coal tar pitch and coal tar pitch supplemented with catalysts.

In the spectra of CM synthesized from coal tar pitch, the (10) reflection was recorded, which characterizes a 2D turbostratic structure, whereas the (004) reflection is virtually not pronounced. The (002) reflection is decomposed into two components: a virtually amorphous phase 1 and a weakly ordered phase 2. The both phases have big interplanar spacing (d_{001}) and small CSR sizes (L_c and L_a).

Table 2
XRD characteristics of CMs

Sample	T, °C	C, %	Phase	Phase fraction, %	Characteristic*					
					d_{00l} , Å	L_c , Å	L_a , Å	ρ , g/cm ³	N, pieces	Y, %
Coal tar pitch	900	96.2	1	69	3.614	14	13	2.11	5	-
			2	31	3.414	23	25	2.23	8	29
	1400	98.1	1	63	3.527	18	44	2.16	6	-
			2	37	3.461	41	24	2.20	13	-
Coal tar pitch + Fe	900	93.6	1	90	3.456	34	33	2.20	11	-
			2	10	3.342	220	14	2.28	67	100
Coal tar pitch + NC	900	95.2	1	81	3.457	35	14	2.20	11	-
			2	19	3.389	45	27	2.25	14	57
Coal tar pitch + FG	80	94.0	1	44	3.376	88	216	2.26	27	71
			2	56	3.362	196	882	2.27	59	86
	900	96.1	1	75	3.366	83	313	2.26	26	83
			2	25	3.360	273	299	2.27	82	89
	1400	97.5	1	81	3.367	58	165	2.26	18	81
			2	19	3.357	286	352	2.27	86	92

* d_{00l} – interlayer spacing, L_c – stack height, L_a – longitudinal dimension of a stack, ρ – XRD density, N – number of layer in a stack, Y – degree of graphitization.

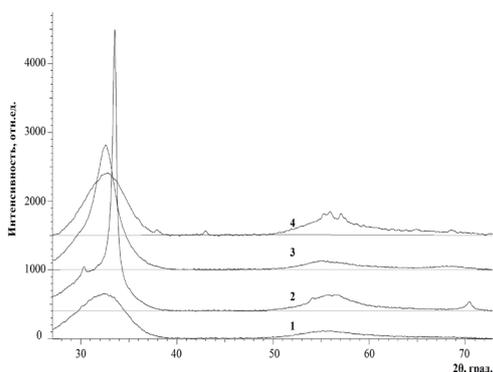


Fig. 3. XRD patterns of carbon materials synthesized from coal tar pitch (1) and coal tar pitch supplemented with foamed graphite (2), petroleum needle coke (3) and Fe (4) upon heating to 900 °C.

The introduction of the indicated additives in coal tar pitch catalyzes its graphitization to produce CMs with a smaller interplanar spacing and an increased CSR size. However, efficiency of the catalytic effect of the additives under consideration strongly varies. The weakest effect on the CM structuring is exerted by Fe. The efficiency of NC is somewhat higher. In CM synthesized in the presence of Fe and NC, characteristics of a less structured phase (phase 1) are close to those of a more structured phase (phase 2) of CM synthesized in the absence of catalyst. Phase 2 in CM with NC is close to a less structured phase that was isolated from the graphites. In the case of

Fe, a small part of the structure (10%, phase 2) has a smaller interplanar spacing as compared to graphites. Such a structure occurs in artificial graphites [16] and was predicted by A.I. Kitaigorodsky [17]. It has a substantial shift of the second layer atoms; so, it cannot be considered as a graphitic structure.

The most pronounced catalytic effect on graphitization of coal tar pitch is produced by FG. Unless other catalysts under consideration, the diffraction patterns of CMs synthesized from coal tar pitch with FG show reflections from the (100) and (101) planes, which indicate a 3D crystal structure of the samples. The both structural phases of CM obtained at 800 °C have interplanar spacing corresponding to that in the structural phases of artificial graphites; at 900 °C the spacing is even smaller. The CSR sizes in both phases do not reach those of artificial graphites, but exceed the CSR sizes of natural graphite (see Table 1). Heating to 1400 °C leads to a further increase in the ordering of CM structure: interlayer spacing decreases, crystallinity increases, carbon content also increases, thus decreasing the number of heteroatoms. (In the absence of catalyst, heating to 1400 °C does not change the amorphous structure of CM, but slightly increases the carbon content and CSR size).

The XRD data were supported by the electron microscopy studies. According to Fig. 4, the structure of CM that was synthesized at 900 °C from coal tar pitch in the absence of catalyst is turbostratic. Fe-addition, as catalyst, shows graphite structure with

the average value of L_a (Fig. 5). In the case of FG additives at the same temperature, well-crystallized graphite structure is observed (Fig. 6).

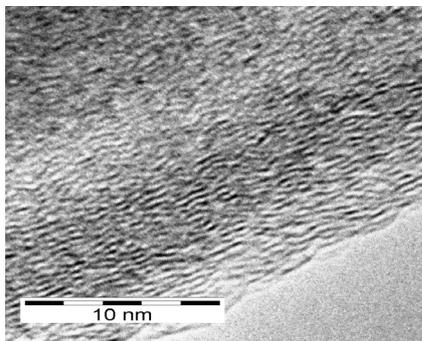


Fig. 4. TEM images of carbon material synthesized from coal tar pitch by heating to 900 °C in the absence of catalyst.

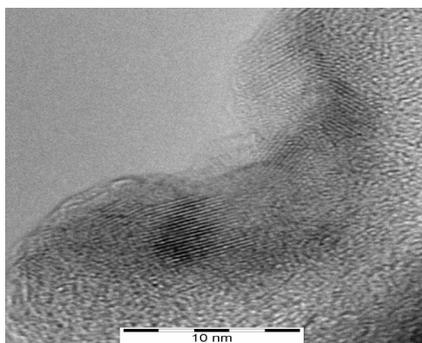


Fig. 5. TEM images of carbon material synthesized from coal tar pitch with Fe-additives by heating to 900 °C.

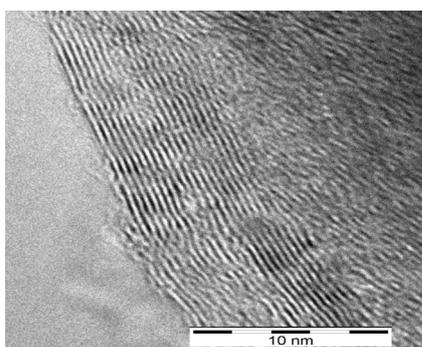


Fig. 6. TEM images of carbon material synthesized from coal tar pitch with foamed graphite by heating to 900 °C.

A possible explanation of the FG effect on the formation of graphite structures is that during the thermal conversion of coal tar pitch in the presence of FG, the coal tar pitch molecules and the coal tar pitch crystallites that formed in the bulk are located on the catalyst particles, thus building them up. Due to the crystalline structure of the catalyst and interaction of electrons of the graphite structures

with aromatic molecules of coal tar pitch, the adsorption and condensation processes on its surface occur in the oriented manner (mainly parallel to the surface of the catalyst particles), which leads to the formation of the CM crystal structure where catalyst serves as the crystallization center (“seed”). The less structured NC carbon exerts a weaker orienting effect on the crystallite growth. A mechanism underlying the action of d-metal salts, particularly Fe salts, may consist in the formation of donor-acceptor complexes with the electrons of condensed aromatic structures of coal tar pitch. This results in orientation of the growing condensed layers that are formed during thermal conversion of coal tar pitch; however, this effect is not pronounced.

Thus, it has been shown that FG, needle coke and Fe are the catalysts of the low-temperature graphitization of coal tar pitch. Among the additives examined in the study, the highest catalytic activity was observed in the case of foamed graphite. Even at 800 °C, the catalytic graphitization of coal tar pitch with foamed graphite as the catalyst leads to carbon materials that possess a crystal structure with interplanar spacing close to that of graphites, whereas in the absence of catalyst, CMs synthesized from coal tar pitch have an amorphous structure. Raising the temperature to 900 °C increases the structural ordering of CM produced from coal tar pitch with FG; the resulting CMs, although being inferior to commercial graphites with respect to carbon content and size of crystallite stacks, surpass them in graphitization degree and close similarity of their interplanar spacing to that of defectless single-crystal graphite. An increase in the final temperature of the process to 1400 °C slightly enhances the degree of CM graphitization and strongly decreases the number of heteroatoms in CM.

The XRD analysis and calculation from the (002) or (004) reflections without their decomposition cannot reveal structural distinctions of various graphites, while decomposition of the reflections into components makes it possible to isolate structural phases of carbon and estimate differences between graphites from the content and structural characteristics of such phases. More reliable results are provided by calculation using the (004) reflection.

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