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X-Ray Diffraction Technique: Structure Determination of Carbonaceous Materials (Review)

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Abstract

X-ray powder diffraction is one of the most potential characterization tools and a nondestructive technique for characterizing carbon based materials and their composite properties. The method is used to measure phase identification, quantitative analysis and to determine structure imperfections of samples. The paper summarizes results of investigations of carbonaceous materials structure. X-ray diffraction is used as the technique for characterizing the structural order. As it turned out the carbonaceous materials obtained by the low-temperature graphitization of coal-tar pitch contain contemporaneously several phases of crystalline carbon and amorphous carbon with turbostratic structure. In the present report, to explain the heterogeneous structure of carbonaceous materials we compare data of X-ray diffraction analysis for the (001) reflection from the main crystal face. It was found that the (002) and (004) reflections are the superpositions of components, which correspond to the structural phases of crystalline carbon and amorphous carbon with different interplanar spacing. The ratio between the integrated intensities of separated reflection components accounts for the ratio between these phases; along with interplanar spacing, this ratio characterizes carbonaceous materials and makes it possible to detect difference between them. The degree of ordering, the interlayer spacing (d_{002}), and the crystalline sizes (L_a and L_c) are considered the key parameters for evaluating the stacking structure of carbonaceous materials.

Key words: coal pitch, graphite additives, carbonization, X-ray diffraction analysis

INTRODUCTION

The crystal structures of carbonaceous materials are commonly studied by the X-ray diffraction analysis (XRD), which produces a profile associated with the crystallite size and arrangement of atoms. Numerous investigations have estimated the sizes of carbon layers and the stacking structure of carbonaceous materials using XRD [1–6]. This review presents the results of the comparative studies of the one structure of carbonaceous materials (CM) by means of XRD analysis using the method of the asymmetric peak deconvolution. The carbonaceous materials obtained by the low-temperature graphitization of coal-tar pitch and some commercial graphite samples were used for study. The coal-tar pitch graphitization pro-

cess was carried out in the presence of the following catalytic $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$ and carbon-compounds of different structure and texture were used to catalyze.

EXPERIMENTAL

Structural studies were performed with a Bruker D8 ADVANCE A25 X-ray diffractometer, filtered FeK_α radiation ($\lambda = 1.93604 \text{ \AA}$, a Mn primary beam filter) at room temperature by the powder polycrystalline technique at the Center of Collective Use of the Federal Research Center of Coal and Coal Chemistry, SB RAS. Powdered samples were scanned from 20 to 80° in the 2 θ angle range with a step interval of 0.020° and a count time of 2 s/step.

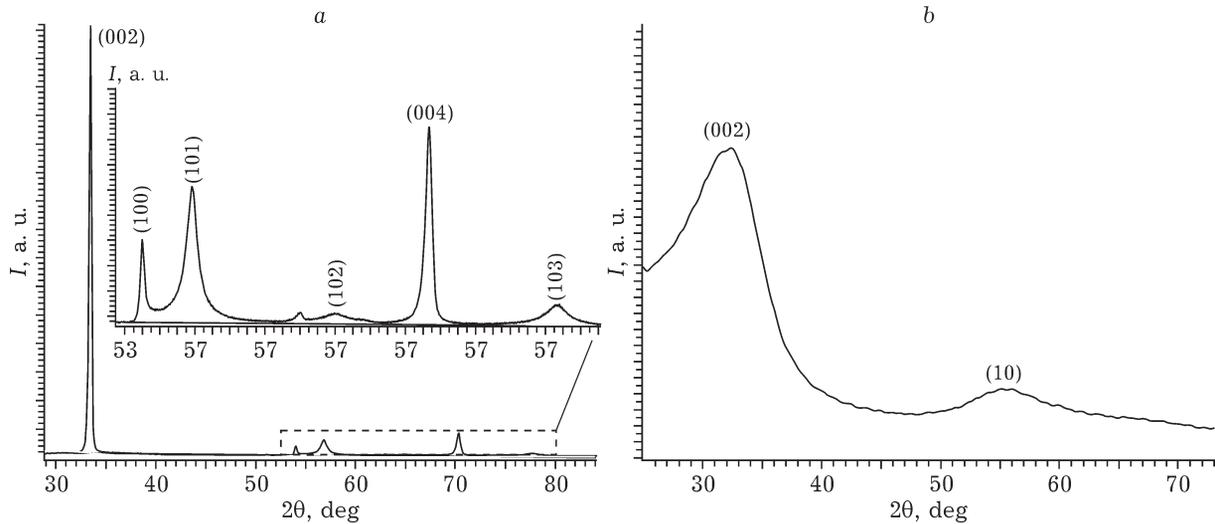


Fig. 1. X-ray diffraction patterns of graphite (a) and coal-tar pitch (b).

RESULTS AND DISCUSSION

The typical XRD patterns of graphite and amorphous carbon with the turbostratic structure are presented in the Fig. 1. The XRD patterns of graphite include (002), (100), (101), (102), (004), (103) reflexes: the (002) reflex ($2\theta \sim 33^\circ$) and (004) reflex ($2\theta \sim 70^\circ$) are reflections from polyarene layers; the long-range order is greater for the (004) reflex, reflections from the planes (100), (101), (102), and (103) determine the longitudinal dimensions of the structural elements and indicate the three-dimensional crystal structure of the samples. On the XRD patterns of pitch, there is the reflex (10), ($2\theta \sim 52\text{--}59^\circ$); this is typical of a two-dimensional turbostratic structure, determining the longitudinal dimensions of the structural elements.

XRD characteristics were calculated with the known formulas according to [7].

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

$$d_{00l} = \lambda / 2 \sin \theta_{00l} \quad (1)$$

where λ is the radiation wavelength, and θ 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

$$L_c = 0.9\lambda / (\beta_{00l} \cos \theta_{00l}) \quad (2)$$

where β_{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

$$L_a = 1.84\lambda / (\beta_{10} \cos \theta_{10}) \quad (3)$$

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

$$L_a = 0.9\lambda / (\beta_{100} \cos \theta_{100}) \quad (4)$$

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

$$c = 0.762 / d_{00l} \quad (5)$$

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

$$N = L_c / d_{00l} + 1 \quad (6)$$

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

$$Y = (3.440 - d_{00l}) / (3.440 - 3.354) \quad (7)$$

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.

In the paper [1], an attempt was made to estimate the crystalline structure of four samples of commercial graphites: synthetic graphite (G1) obtained by heating of a mixture of coal tar pitch and coke to $\sim 2800^\circ\text{C}$, pyrolytic graphite (G2) obtained by pyrolysis of gaseous hydrocarbons, thermally expanded graphite (G3) obtained from intercalation compounds with sulphuric acid, and natural graphite (G4)

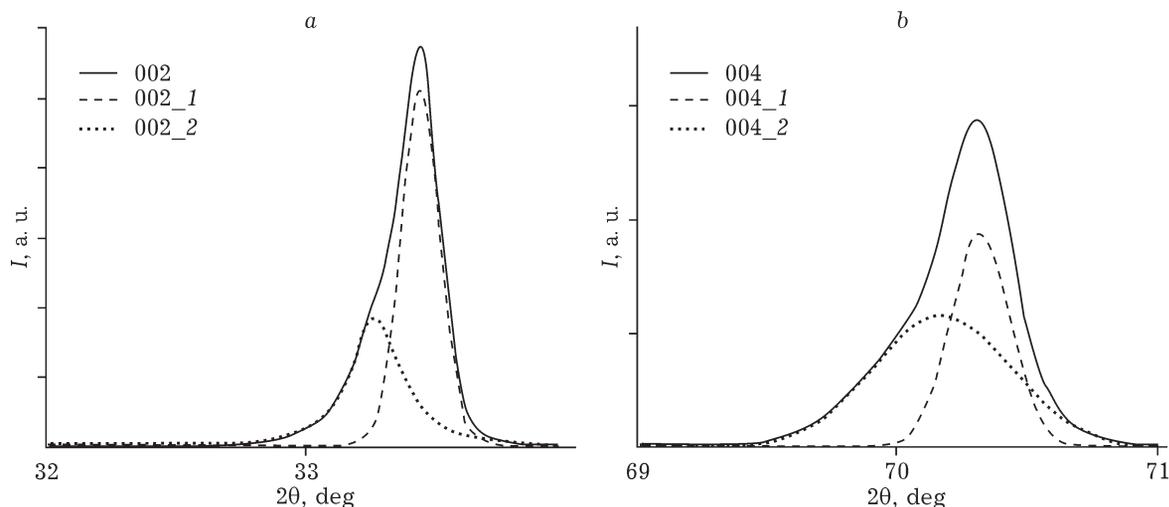


Fig. 2. Deconvolution of the (002) and (004) peaks of G1 graphite (dashed (1) and dotted (2) lines refer to more and less ordered phases, respectively).

(Kureisk deposit) calcined at ~ 2800 °C. It was found that all reflections in XRD patterns of the graphites exhibit asymmetry, which indicated the presence of several carbon phases with different structural characteristics (graphite sub-structure) in the graphites. The asymmetric XRD peaks were deconvoluted into the minimal number of symmetric peaks described by the Gaussian function with the 2θ position corresponding to certain phase using the TOPAS software for processing the X-ray diffraction patterns. For this purpose, we used as input data the d_{002} values of the suggested components, and the program calculated and optimized the intensity and integral width of the peaks and adjusted their positions. This allowed estimate the interplanar spacing of two components, which characterize different graphite sub-structures. Such analysis of the profiles of the asymmetric diffraction peaks was made for (002) and (004) peaks, the results, given in Fig. 2, exemplify the decomposition of the (002) and (004) reflections into two components for graphite G1.

The interplanar spacing estimated without the deconvolution of a reflection into the components with the use of both the (002) and (004) reflections was similar for all graphites. The sizes of crystallites (L_c) are different for all studied samples and they depend significantly on the reflection used for the calculation, and changes are not synchronous. Moreover, the value of L_c in G4 is 172 or 7 Å upon the calculations based

on the (002) and (004) reflections, respectively. It can be explained by the strong asymmetry and broadening of (004) peak, indicating the presence of structures with significantly different interplanar spacing. Therefore, it should be concluded that the formal calculation without deconvolution into components gives distorted results, yields little information, and it cannot be performed at all in some cases.

The treatment of X-ray diffraction patterns by the deconvolution of the asymmetric (002) and (004) XRD peaks into the minimal components number of symmetric peaks described by the Gaussian function with the 2θ position corresponding to certain phase makes it possible to more accurately characterize the structure of graphites and to estimate difference between them. Dedicated deconvoluted phases were characterized by different content and their different structural characteristics. The component ratio (proportional to the areas of the corresponding peaks) was one more additional characteristic of graphite, which allows to detect the difference between them. Structural phase with the interplanar spacing 3.370–3.385 Å characterizes a metastable state of the formation of the graphite-like structure, that is transition of turbostratic carbon into graphite. This structure, as the graphite structure (hexagonal, with the interplanar spacing of about 3.36 Å), is present in the natural and synthetic graphites. Table 1 shows the X-ray

TABLE 1
XRD characteristics of graphites

Graphite	Phase	Calculated							
		from the (002) reflection				from the (004) reflection			
		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
	2	62	3.366	755	82	41	3.364	522	85
	Without phase decomposition	3.366	441	82	100	3.364	300	85	
Natural	1	65	3.384	113	62	66	3.385	53	61
	2	35	3.365	322	84	34	3.362	185	86
	Without phase decomposition	3.367	172	81	100	3.363	7	85	

structural characteristics of synthetic (G1) and natural (G4) graphites calculated based on the deconvoluted (002) and (004) reflections, respectively. From Table 1, it is evident that XRD characteristics calculated according (002) and (004) peaks are not the same. Since the more precise determination on the long-range orders of reflection, in particular (004), is more precisely characterizes the crystal structure [8], we believe that (004) peak should be used to characterize graphite.

This approach of calculation was used to characterize the structure of carbonaceous materials obtained by low-temperature catalytic graphitization of coal-tar pitch with using as graphitization catalyst 2 % of iron salt, 15 %

of needle coke (NC) and a 15 % expanded graphite (G3) [2, 5, 6]. The (004) peak was decomposed into two components, as it was recommended in the study of graphite [1]. In the XRD-patterns of CM obtained from a pure pitch there is (10) reflection of two-dimensional turbostratic structure in CM, whereas the (004) reflection was almost not pronounced, so (002) peak is used for the calculations. XRD analysis shows (Table 2) that using catalysts such as transition metal salts, in particular, ferrum, and structured carbon, with varying degrees of crystallinity, facilitates the process of pitch graphitization and allows obtaining CM with a smaller interplanar spacing and a larger crystallite size.

TABLE 2
XRD characteristics of CMs (900 °C, calculations on (004) peak, except for pitch)

Samples	Phase	Phase fraction, %	Characteristics					
			d_{00l} , Å	L_c , Å	L_a , Å	ρ , g/cm ³	N, pieces	Y, %
Coal-tar pitch*	1	69	3.614	14	13	2.11	5	–
	2	31	3.414	23	25	2.23	8	29
Coal-tar pitch + 2 % Fe	1	90	3.456	34	33	2.20	11	–
	2	10	3.342	220	14	2.28	67	100
Coal-tar pitch + 15 % NC	1	81	3.457	35	14	2.20	11	–
	2	19	3.389	45	27	2.25	14	57
Coal-tar pitch + 15 % G3	1	75	3.366	83	313	2.26	26	83
	2	25	3.360	273	299	2.27	82	89
NC	1	41	3.477	22	53	2.19	7	–
	2	59	3.429	34	118	2.22	11	12
G3	1	55	3.364	76	244	2.27	24	85
	2	45	3.361	305	441	2.27	92	87

* Calculations on (002) peak.

In the case of Fe additives, in the CM it was formed graphite-like phase with a fraction of 10 % of the content. In the case of NC, graphite-like phase was not formed, but the degree of ordering of all the carbon is increased in comparison with the CM obtained from pitch without a catalyst. In the case of G3, with the high degree of ordering, it was obtained CM, which is characterized as almost completely crystalline carbon; its interplanar spacing was the same as that of graphite.

Data from electron microscopic studies of CM structure have confirmed that the CM obtained at the presence of Fe and G3 contains graphite-like phases, but if in the case of Fe, its part is small, that also it was determined by XRD, in the case of G3, part of graphite-like phases is not high, in contrast to the data of XRD, there is a significant amount of turbostratic carbon [5].

It should be mentioned that if in CM there are turbostratic and highly crystalline carbons together, deconvolution of weak (004) peak is difficult as the intensity of the (004) reflection of graphite-like phase is higher than one of turbostratic carbon. This approach of XRD characteristics calculations gives excessive results of crystallinity. That is to characterize the CM containing together graphite-like phase and carbon with a small degree of graphitization, it is better use of the (002) reflection of carbon. In case of more complex composition of CM, *i. e.* coexistence of amorphous (turbostratic), crystalline phase and metastable states of the formation of the graphite-like phase, that leads to high asymmetry of diffraction peaks, to get more accurate results asymmetric peaks should be deconvoluted into four symmetric peaks described by the Gaussian function.

This approach of calculation was used in [3], in studying the effect of different carbon additives with varied textural characteristics on the thermal transformations of coal-tar pitch. The additives were nanostructured carbon matter (NCM) "Kemerit", carbon nanotubes (CNT) "Taunit", activated carbon AG-3 and G3 (the amount of additive is 5 %). The XRD patterns of obtained CM and individual additives are presented in Fig. 3.

At calculations of structural characteristics of the CM with additives of CNT "Taunit",

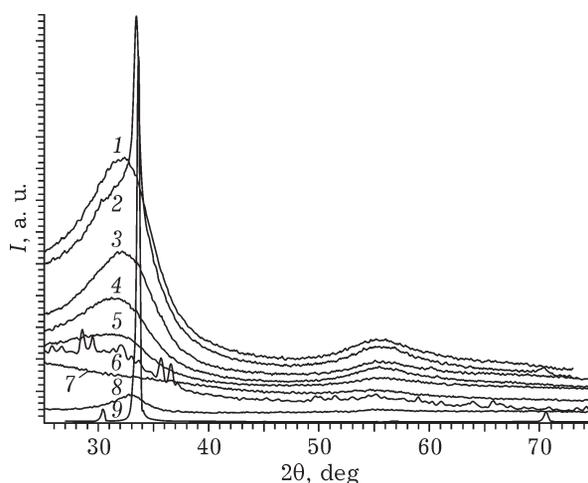


Fig. 3. XRD patterns of CM synthesized from coal-tar pitch (1) and coal-tar pitch supplemented with foamed graphite G3 (2), activated carbon AG-3 (3), NCM "Kemerit" (4), CNT "Taunit" (5), and XRD patterns of AG-3 (6), NCM "Kemerit" (7), CNT "Taunit" (8) and G3 (9).

AG-3 and NCM "Kemerit" we use deconvolution into two components described by the Gaussian function. In the case of CM obtained from pitch with G3 it is observed significant asymmetry of diffraction peak, and the best way of deconvolution is to decompose it into four components (Fig. 4).

The calculated XRD characteristics of the CM samples are shown in Table 3.

According to the results, the addition of crystalline carbon (G3) supports catalysis, *i. e.* graphite-like structures are formed at thermal transformations pitch, but their content in the pitch, carbonized at 900 °C, is 30 % (with tak-

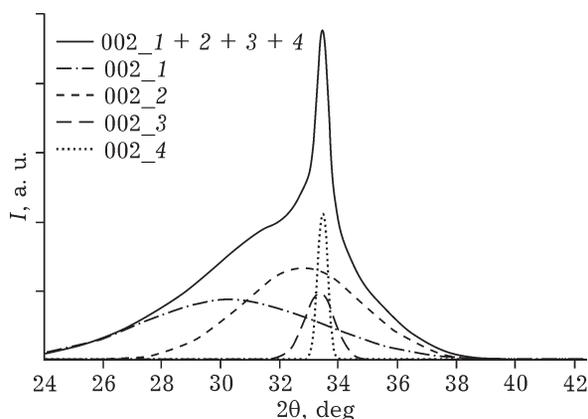


Fig. 4. Deconvolution of the (002) peak of CM synthesized from coal-tar pitch supplemented with foamed graphite.

TABLE 3
XRD characteristics of CMs (calculations on (002) peak)

Samples	Phase	Phase fraction, %	d_{002} , Å	L_c , Å	L_a , Å	ρ , g/cm ³	N , pieces	Y , %
CM (coal-tar pitch + 5 % AG-3)	1	37	3.87	14	23	1.97	4	–
	2	63	3.44	19	44	2.22	6	–
CM (coal-tar pitch + 5 % Kemerit)	1	49	3.86	13	21	1.98	4	–
	2	51	3.47	19	37	2.20	6	–
CM (coal-tar pitch + 5 % CNT)	1	80	3.63	14	27	2.10	5	–
	2	20	3.42	27	50	2.23	9	19
CM (coal-tar pitch + 5 % G3)	1	70	3.54	16	31	2.15	5	–
	2	10	3.36	35	70	2.26	11	84
	3	10	3.36	214	53	2.26	64	84
	4	10	3.36	527	248	2.27	158	94

ing into account the content of the added PG). That is, structured carbon additive promotes oriented pitch carbonization, but it does not allow obtaining completely crystalline carbon at the experimental conditions. Additives of amorphous and, in particular, nanostructured carbon cause disordering carbon structure in the pitch during its carbonization. The presence of oriented structures in nanostructured carbon additive, that is in the case of CNT, has slight influence on pitch structure, there is dominated a disintegrating effect of nanosized particles.

The influence of crystalline carbon additives with developed surfaces (in other words, graphite additives) on the formation of carbon structures during pitch carbonization was considered in [4]. To study, industrial pyrolysis graphite (IG) and thermally expanded graphites (graphite foam) with different specific surface were selected. In calculations the (004) XRD peaks were deconvoluted into the four components of symmetric peaks described by the Gaussian function with the 2 θ position corresponding to certain phase. It was observed (Table 4) that all the above-mentioned additives catalyzed the formation of the graphite structures during pitch carbonization, but direct dependence of the structure ordering degree of the carbon additives or development of its surface on the efficiency of the catalytic effect was not found.

If the specific surface of graphite additives was 4–12 m²/g (G-4, PG-12), during pitch carbonization it was formed more than 20 % crystalline fraction with a high degree of structure

ordering and large size of crystallites. In the case of graphite foam additive (PG-110) with high specific surface (110 m²/g) and a low bulk density (4 g/L), the process of forming graphite structures passes less efficiently during pitch carbonization.

In this way, it was shown that the main diffraction peaks on the XRD patterns of graphite and carbonaceous materials, obtained from coal-tar pitch with catalytic additives, are not symmetric and can be decomposed into two components, which characterize the carbon structure with varying degrees of ordering.

The fulfilment of calculations for the original asymmetric peaks without taking into account their deconvolution can lead to highly distorted results, especially if peak has high asymmetry due to existence of structures with significantly different characteristics. At the same time, the decomposition of the carbonaceous material on the different structural phases al-

TABLE 4
Content of the graphite fraction in the carbonaceous material (on (002) peak)

Samples	Content of graphite fraction, %	
	Total	After subtracting the additive
Coal-tar pitch + 10 % PG-12	38	22
Coal-tar pitch + 10 % PG-110	19 (+24*)	4 (+24*)
Coal-tar pitch + 10 % G-4	35	19

*Content with a low degree of graphitization (~60 %).

allows entering an additional characteristic of the sample that is the phase ratio that allows better to characterize CM and to compare it with others that have similar overall structural characteristics. However, in the case of (004) peaks treatment in the presence of carbon with low crystallinity together with graphite, identification components belonging to a less structured carbon is difficult due to their very low intensity and shielding of much more intense graphite peak. In this regard, to characterize carbonaceous materials, containing both graphite-like structures and carbon with a low degree of graphitization, it should be better to use the (002) diffraction peak whose intensity is sufficiently high and for low crystalline carbon. In case of a complex composition of the CM, *i. e.* there is of amorphous (turbostratic), crystalline phase and metastable states of the formation of the graphite-like phase, asymmetric peaks should be deconvoluted into four components to get results that are more accurate in comparison with two-component decomposition.

CONCLUSION

The approach of diffraction peaks deconvolution is used to show the difference of the

structure of graphites of varying nature. It was found that crystalline carbon additives facilitate oriented carbonization of pitch, which results in the formation of up to 30 % graphite-like structure of CM composition, obtained by carbonization of coal-tar pitch to a final temperature of 900 °C. Additives of amorphous and, in particular, nanostructured carbon cause to disordering carbon structure of pitch during its carbonization.

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Определение структуры углеродных материалов методом рентгенофазового анализа

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Аннотация

В данной работе представлены результаты исследования структурной упорядоченности углеродных материалов методом рентгенофазового анализа с использованием метода разложения рефлексов. Исследованы графиты разной природы и УМ, полученные карбонизацией каменноугольного пека до конечной температуры 900 °С по методу низкотемпературной каталитической графитации. В качестве катализаторов использованы углерод разной структуры и текстуры. В результате работы показано различие в структуре графитов разной природы. Установлено, что добавка структурированного углерода способствует ориентированной карбонизации пека и формированию до 30 % графитовой структуры в составе УМ, полученного карбонизацией каменноугольного пека до конечной температуры 900 °С. Добавки аморфного и особенно наноразмерного углерода приводят к разупорядочению углеродной структуры пека при его карбонизации.

Ключевые слова: пек, графит, углеродистые материалы, рентгенофазовый анализ