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Study of Coal Tar Pitch Morphology and Structure

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Abstract

The morphology and structure of the mesophase in the series: coal tar pitch (CTP) – α-fraction of CTP – carbonised α-fraction after heating to 1200 °C, were studied by scanning electron microscopy, X-ray phase and X-ray structural analysis. The X-ray structural parameters were determined: longitudinal and transverse dimensions of the lamellae and the thickness of packages, the distance between the lamellae and the number of lamellae in the formed packages. It is shown that the two-dimensional structures of carbon mesophase are ordered into three-dimensional packages during the formation of semi-coke under CTP heating. It is established that the carbon structure of CTP and its α-fraction is represented by the turbostratic and graphite-like phases. The sizes of the packages formed by the lamellae during structuring in the transverse direction in the studied samples are of the order of 18–25 Å, in the longitudinal direction 46–63 Å, the average distance between the lamellae in the studied samples is 3.46–3.52 Å.

Keywords: coal tar pitch, α-fraction, mesophase, semi-coke, scanning electron microscopy, X-ray phase analysis, X-ray structural analysis

INTRODUCTION

The permanent essential attention to the studies of the physicochemical properties of coal tar pitch (CTP) is due to its application as the starting material in the production of a broad range of various functional carbon materials [1–9]. The physicochemical properties of the obtained materials depend on the structure of mesophase formed during CTP carbonization. The perfection of the formed structure is determined by the mesophase processes. The mesophase formation starts during the distillation of coal tar (CT), resulting in the formation of CTP [2, 3, 10]. Mesophase formation and its subsequent growth during pitch carbonisation are affected by the group composition of the pitch, as well as by carbonisation conditions [2, 3, 10–13]. To control mesophase formation, growth, and structural improvement during pitch carbonisation, additional treatment of the pitch with precursors is applied, as well as carbonisation with various additives [14–18]. Another method is the physical separation of CTP with the isolation of its components with different mean molecular masses [19–21]. Pitch is divided into four components with respect to the group chemical composition: maltenes (γ-fraction), asphaltenes (β-fraction), carbenes (α_2-fraction), and carboides (α_1-fraction). Each of the listed fractions affects the processes involved in the mesophase formation. Thus, the most low-molecular γ-fraction (maltenes) affects the mobility and stability of the mesophase; aromatic components that are present in asphaltenes determine the formation of highly anisotropic carbon mesophase and finally lead to a more perfect structure of the carbon material; fractions that are insoluble in organic solvents (containing carboides) carry mesophase nuclei [11]. In other words, an optimal ratio of the listed components in the pitch and optimal conditions during carbonisation are necessary to form a perfect graphitised carbon structure. For

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instance, the authors of [22–29] described the formation of carbonisate particles of various shapes and microstructures, depending on the molecular group composition of the compounds that are present in the initial feedstock. Observable inhomogeneity of the carbon body, so-called texture (microstructure), is connected with the regions of mutually oriented crystallites comprising it, for example, shape anisotropy and layered texture of needle-like coke are consequences of the anisotropy of structural fragments (crystallites) that form the resulting material [30]. The texture may be detected sometimes even with the unaided eye and is investigated by means of optical and electron microscopy. The structure is characterised quantitatively by X-ray structural analysis (XSA). This method allows one to determine the size of polyarene layer (L_a), the height (L_c) of packages that form these layers (lamellae), the distance between the layers (d_{002}), and to evaluate graphitisation degree, which may be measured if package height is known [31].

It should be noted that CTP from different manufacturers, exhibiting insignificant differences from each other in chemical elemental composition, contain substantially different amounts of toluene-soluble components (these are γ- and β-fractions), varying within broad ranges (45.79–79.20 %) [32]. This fact is of decisive importance in choosing the raw material for obtaining highly structured carbon materials. For instance, it has been demonstrated by means of XSA that pitch components with large mean molecular masses produce a higher yield of the crystallisable carbon phase during carbonisation [8, 33].

In the present work, the mesophase origin in the series: coal tar pitch (CTP) – α-fraction of CTP – carbonised α-fraction of CTP after heating to 1200 °C was investigated by scanning electron microscopy (SEM) and XSA.

EXPERIMENTAL

Commercial samples of CT and CTP obtained through CY distillation were studied. The α-fraction of CTP was isolated by selective dissolution according to GOST 10200-2017, and thermolysis was carried out up to 1200 °C.

The morphology of CT microdrops, CTP and its α-fraction was studied by SEM with a JEOL JSM-6390 LA scanning electron microscope (Japan). For electron microscopic analysis, a sample of tar was deposited with a glass microcapillary onto an aluminium objective table or on carbon scotch for electron microscopy glued on the aluminium table. The images of the deposited tar drops were recorded at an accelerating voltage of 20 kV and a probe current of 1 nA in the back-scattered electron mode at room temperature of the objective table. The residual pressure in the microscope column was not more than 10^{-3} Pa.

To study the pitch and its α-fraction by means of XSA and SEM, analytical sample with particle size not more than 0.25 mm was prepared.

To describe the structure of the samples under investigation, XSA was carried out with the help of a Bruker D8 ADVANCE A25 powder X-ray diffractometer (Germany) (CuK_α-radiation, Ni-filter at the secondary radiation) at room temperature according to the polycrystal method. The X-ray diffraction patterns were recorded with a long integration time (2 s) at a scanning step of 0.02° over 2θ. Diffraction peaks in the recorded patterns were identified using the powder databases ICDD and PDF2 [34].

The distances between lamellae d_{002}, the longitudinal dimensions of the lamellae L_a, the thickness of lamellae packages L_c, and the number of lamellae (N) comprising the package were calculated according to the procedure described in [35].

RESULTS AND DISCUSSION

To obtain SEM images, the microdrops of CT, which is a viscous liquid, are subjected to a high-energy electron beam in vacuum. So, it should be taken into account that sublimation, thermolysis, polymerisation and other chemical reactions may proceed simultaneously under these conditions.

The images of drop surface on an aluminium substrate, recorded almost immediately after pumping the microscope column, that is, under the minimal action of electron beam, are presented in Fig. 1, *a*. Tar drops in direct contact with the aluminium table spread over the surface to form a thin, almost uniform layer. In the case of CT deposition onto carbon scotch, the microdrops conserved almost spherical shape (see Fig. 1, *b*). The observed differences may be explained by different wettabilities of aluminium and carbon surfaces with respect to CT. It should be noted that CT spreading over the surface of the aluminium table caused an increase in contact surface, which, in turn, provided more intense heat

exchange between the table and CT heated under the action of electron beam. To estimate the extent of the electron beam effect on CT, the images were recorded sequentially in definite action time intervals. From the very first minutes under the electron beam, micro-inclusions of a new phase were observed on the surface of drops. This new phase differs in contrast from the amorphous liquid phase. The particles of the new phase were spherical and uniformly distributed over the surface under observation. With an increase in the time of electron beam action, in the case of drops in contact with the carbon substrate, we observed an increase in the number of new phase particles and their size (see Fig. 1, *f*) in comparison with the surface of drops in con-

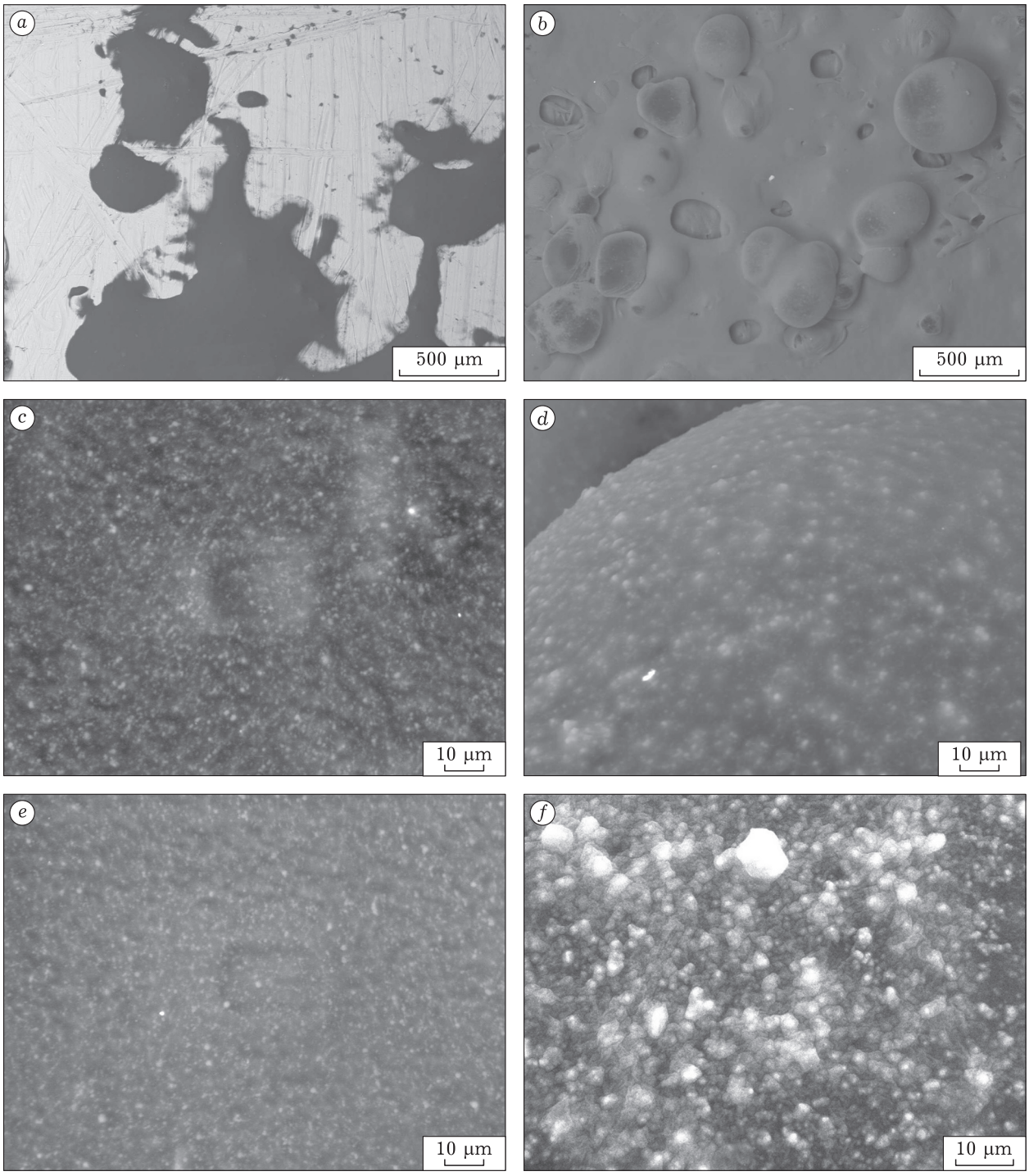

Fig. 1 (Beginning).

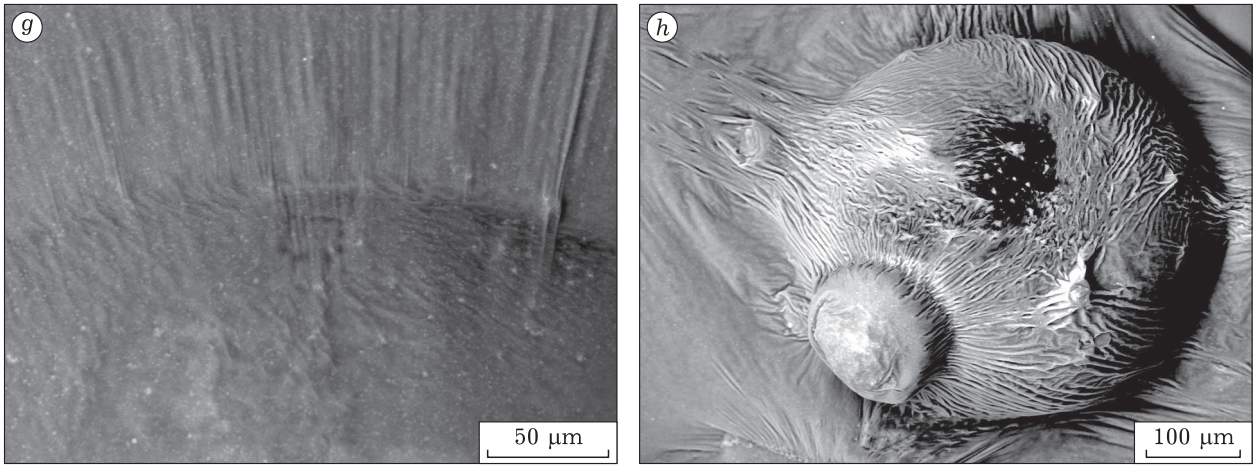

Fig. 1 (Ending). Electron microscopic images of the surface of coal tar drops deposited on the aluminium objective table (*a*, *c*, *e*, *g*) and on carbon scotch (*b*, *d*, *f*, *h*): immediately after pumping the microscope column to a pressure of 10^{-3} Pa (*a*, *b*); after scanning with the electron beam for 2 (*c*, *d*) and 60 min (*e*, *f*); after exposure at a pressure of 10^{-3} Pa for 4 h and scanning for 30 min (*g*, *h*).

tact with the aluminium substrate, for which no changes of the number and size of the particles of this phase could be revealed in the course of action (see Fig. 1, *c*, *e*). These differences in behaviour may be due to differences in CT heating temperature With the same electron beam parameters (beam current and the kinetic energy of electrons), identical vacuum conditions and the time of beam action, larger area of CT contact with the aluminium table and its high thermal conductivity lead to more efficient heat removal and a decrease in CT heating temperature in comparison with the tar sample deposited onto the carbon substrate, which provides less intensive formation and growth of the new phase. After long-term CT residence under vacuum, the surface of drops was observed to deform, with the formation of folds (see Fig. 1, *g*, *h*). This may be due to tar sublimation and evaporation of light components, which results in shrinkage and formation of folds on the surface.

The SEM images of pitch particles are shown in Fig. 2. According to the obtained data, particle shape and the morphology of particle surface are characteristic of amorphous bodies: the particles do not have any definite shape, and their surface has a structure of fused body (there are no sharp boundaries, and protuberances are present on the surface). According to Fig. 2, *c*, pitch particles are a two-phase system composed of an amorphous matrix, in which the inclusions of another phase are dispersed. This latter phase is likely a mesophase, in the form of agglomerations of spherical particles with a size from several tenths of a micrometre to several micrometres. Higher reflectance of these particles with respect to electrons may be caused by a higher degree of their ordering in comparison with the matrix. So, along with polarisation optical microscopy, SEM may be used to study the mesophase in pitch.

As mentioned previously, the α_1-fraction of CTP is one of the sources of nuclei for the isotropic mesophase. Thus, we studied the α-fraction isolated from the pitch. A SEM microphotograph of the α-fraction of CTP, which is fine powder with particle size from several tenths of a micrometre to several micrometres, is shown in Fig. 3, *a*. The shape of particles is mainly spherical. It is necessary to mention that the size and shape of the particles of α-fraction are comparable with the size and shape of mesophase particles observed in the pitch. Thus, it may be accepted that α-fraction serves as the nuclei of the isotropic mesophase to be formed in the pitch.

The studies of the carbonisate of CTP α-fraction after heating in the inert atmosphere to 1200 °C show that partial agglomeration of the particles occur, along with insignificant increase in particle size. The particle shape remains practically unchanged (see Fig. 3, *b*). These insignificant changes in the morphology of particles of α-fraction during thermolysis may be explained as follows. It is known that α-fraction is composed of α_1-fraction, which is insoluble in organic solvents, and α_2-fraction, which is soluble in quinoline. The α_1-fraction is composed of high-molecular substances with a high content of condensed aromatic rings associated into crystallite-

like structures. As mentioned previously, the latter act as the nuclei of mesophase, which needs the construction material (asphaltenes) for its growth and a liquid phase (low-molecular fraction) to deliver the construction material. It is known that ordering of a solid structure is substantially hindered in comparison with a liquid-phase system, but insignificant changes that occur anyway become possible due to the α_2-fraction, incorporated into α-fraction. For instance, it has been demonstrated in [11] that the emergence of mesophase in the course of obtaining the pitch proceeds with the accumulation of α_2-fraction.

The X-ray diffraction patterns of CTP under investigation, obtained by CT distillation, the α-fraction of CTP and carbonisate of α-fraction, obtained at 1200 °C, are presented in Fig. 4. These diffraction patterns are typical for carbon materials with the turbostratic graphitised carbon structure. Clearly pronounced reflections from (002) planes were recorded in all samples, with broad maxima at angles about 26° over 2θ, and two-dimensional reflections (10) within the angle range 42–47° over 2θ. It should be stressed that a reflection from (101) plane, which is characteristic of graphite, is not observed in the diffraction patterns, which is an evidence of the now degree of graphene layer orientation in the samples under investigation, in comparison with graphite structure.

The asymmetric profile shapes of the diffraction peaks related to reflections from (002) planes, observed for all samples, are a consequence of the presence of several carbon phases at the same time (in the form of weakly ordered naphthene-aromatic and aromatic structures, as well as lamellae packages composed of flat polyaromatic molecules) with different distances between the lamellae (d_{002}) and differing from each other in dispersity.

Results of the evaluation of structural parameters of the samples under study are presented in Table 1. The dimensions of packages formed by the lamellae during structuring are larger by ~25 % in the transverse direction (L_c) in the samples of α-fraction than in CTP samples. In the longitudinal direction, the size of these packages (L_a) changes more substantially: it increases by ~50 % when passing from CTP to the α-fraction. The average distance between the lamellae d_{002} in CTP samples under investigation is much longer than that for graphite (3.35 Å) [33]; the presence of an intermediate graphite-like phase [36] with a distance of ~3.49 Å between the lamellae was revealed in the samples of α-fraction.

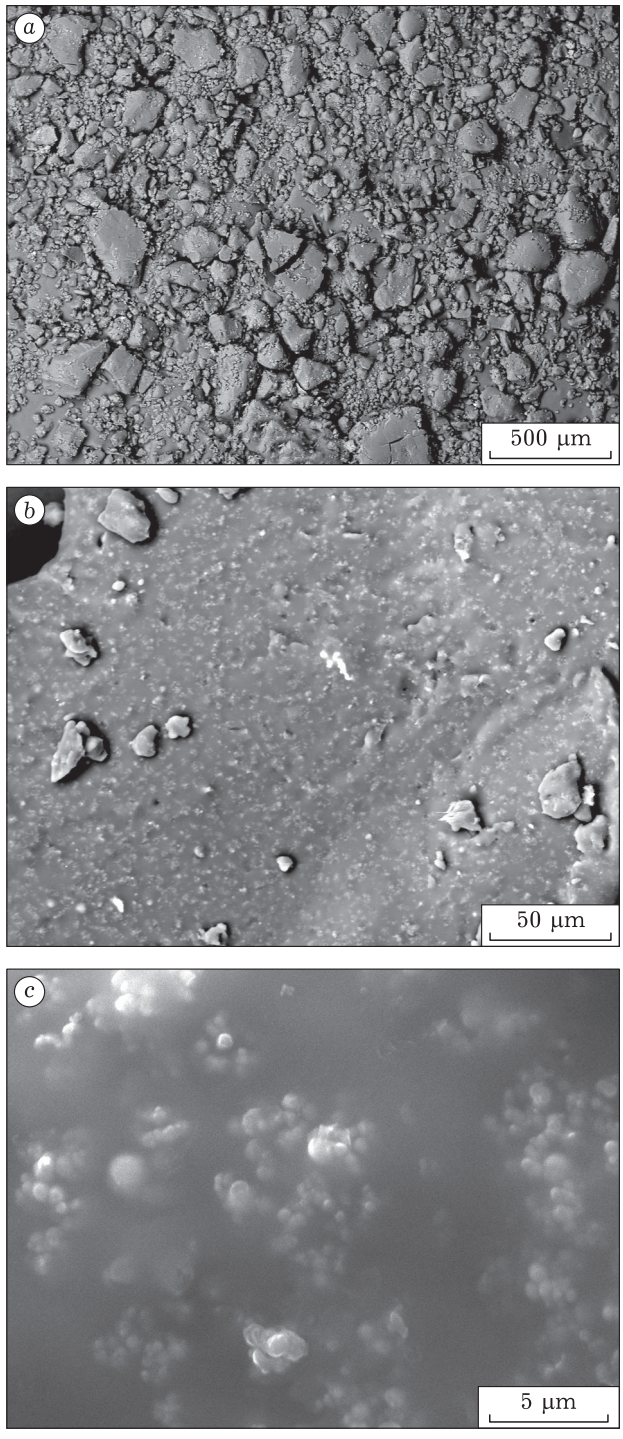

Fig. 2. Electron microscopic images of coal tar pitch particles in backscattered electrons at different magnifications.

One can see in Fig. 4 that a shift of the (002) maximum to larger angles is observed for the carbonisate of the α-fraction of CTP after heating to 1200 °C, while the half-width of the recorded profiles of reflections from the corre-

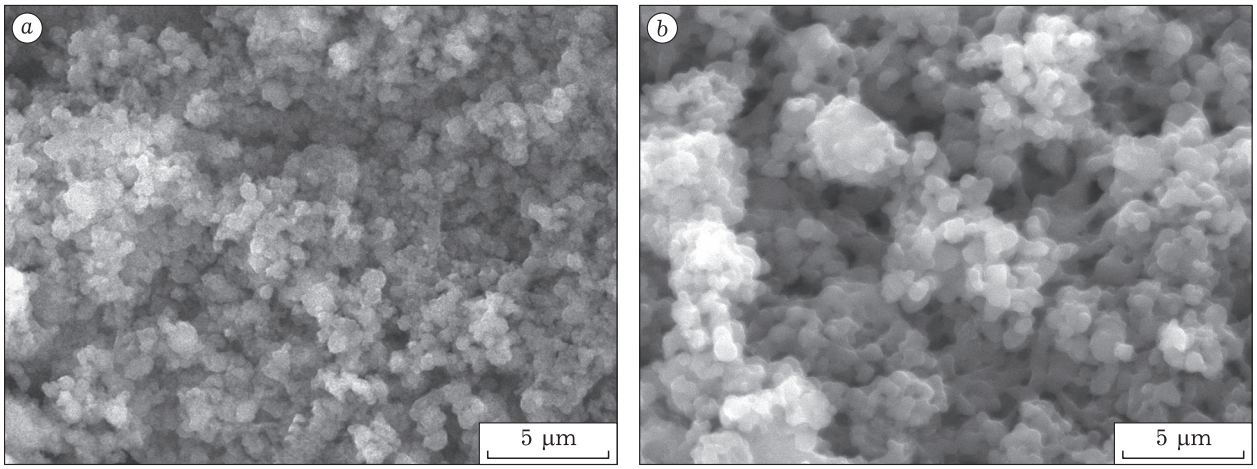

Fig. 3. Electron microscopic images of the α-fraction of coal tar pitch: initial powder (*a*); after heating to 1200 °C (*b*).

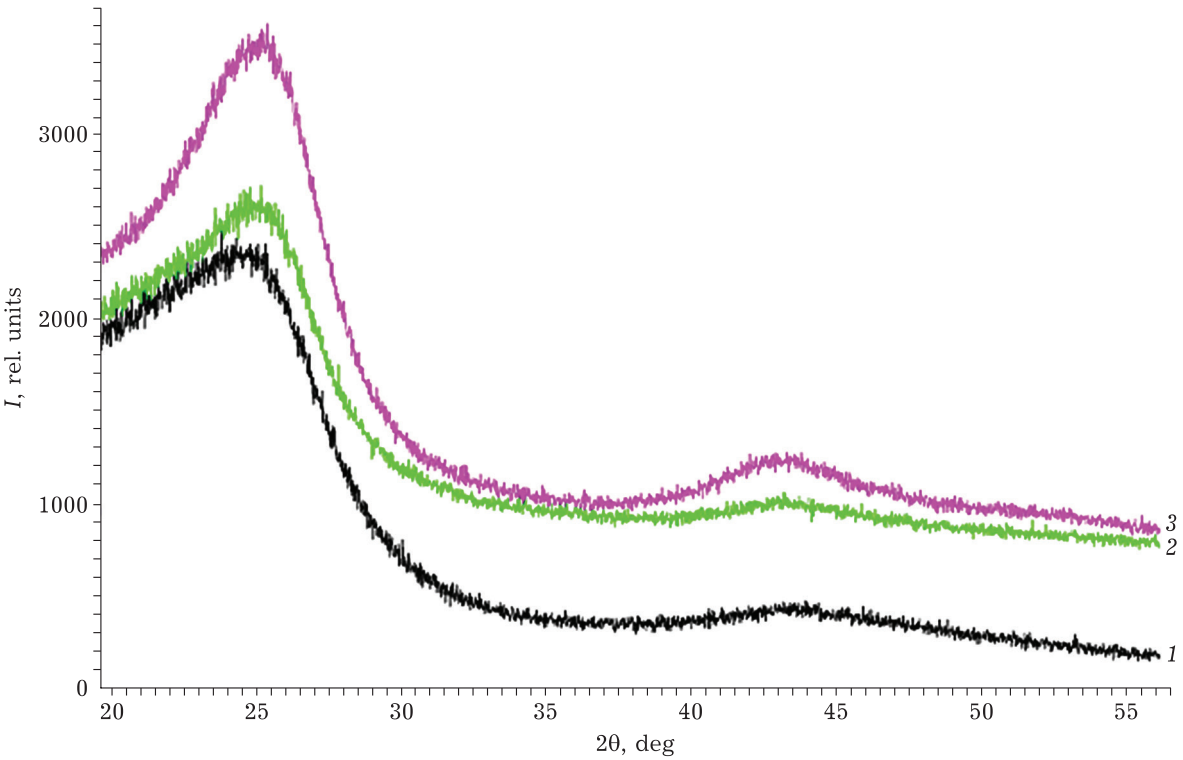

Fig. 4. X-ray diffraction patterns of the samples under investigation: *1* – coal tar pitch (CTP); *2* – α-fraction of CTP, initial; *3* – α-fraction of CTP after high-temperature treatment at 1200 °C.

sponding planes does not change. Therefore, as a result of the high-temperature treatment of CTP α-fraction, the packages of α-fraction get compacted (3.46 Å), while the average number N of the lamellae forming one package remains practically unchanged. So, turbostratic carbon structure is formed in the CTP samples under investigation, while an intermediate graphite-like phase represented by the packages of flat polyaromatic molecules is formed in α-fraction.

CONCLUSION

By means of SEM, X-ray phase and X-ray structural analysis, the morphology and structure of the mesophase were investigated in the series: CTP – α-fraction of CTP – carbonised α-fraction of CTP after heating to 1200 °C. Relying on the data obtained in the work, we may describe the process of mesophase formation as follows. Two-dimensional structures of the carbon isotropic

TABLE 1

X-ray structural parameters of the samples under investigation

Structural parameter	CTP		α-Fraction of CTP (initial)		α-Fraction of CTP (1200 °C)	
	Phase 1	Phase 2	Phase 1	Phase 2	Phase 1	Phase 2
d_{002}, Å	4.01	3.52	3.86	3.49	3.62	3.46
L_c, Å	10	18	12	23	11	25
Relative content of phase, %	64	36	65	35	63	37
N, pcs.	4	6	4	8	4	8
L_a, Å	20	46	21	63	20	61

Note. d_{002} – interplanar distance; L_c – thickness of lamellae package; L_a – lamellae size; N – number of lamellae in a package; CTP – coal-tar pitch.

mesophase of CTP become more mobile during distillation, as a result of the loss of side chains, and start to get ordered into three-dimensional packages (crystallites). It is possible that the structure of mesophase is similar to the structure of spatial polymer composed of condensed aromatic rings ordered in the two-dimensional plane. The rings are bound in the polymer through the side carbon chains comprising unordered part. Excess of the free energy provides spontaneous transition into a more stable state of two- and three-dimensional ordering. Subsequent heating accelerates ordering processes. The products of side chain destruction are released into the gas phase in the form of volatile substances. Two-dimensional planes form the packages of parallel layers, and then the systems of packages attain the shape that is most favourable from the viewpoint of energy, forming microspheres.

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