Investigation of the structural characteristics of vitrinites of some coals of the Kuznetsk Basin

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Abstract. In this work, the structural parameters of vitrinites of coal of various degrees of metamorphism were investigated by X-ray diffraction methods. Vitrinite concentrates were obtained from coal of the Kuznetsk Basin by the method of fractional analysis of coals, according to which the studied fuel is stratified into fractions in liquids of different densities. The following X-ray structural parameters were analyzed: the number of carbon atoms in the lamellae (natC), the longitudinal size of the lamellae, the height of their stacking (La and Lc), the number of polyaromatic layers in the stack (N), and the packing density of the lamellae (ρ). It was shown that in vitrinite concentrates, an increase in all analyzed structural parameters (Lc, La, natC, N, ρ) is observed with an increase in the degree of metamorphism, at the same time, a decrease in the value of the interplanar distance (d002) is observed. The performed X-ray diffraction studies showed that the average number of layers in a package and carbon atoms per monolayer in the samples of vitrinite concentrates of bituminous coals of high stages of metamorphism (Ro, r = 1.41%) varies from 7 to 8 and 14-15, respectively. A correlation was found between the linear nature of the number of arene layers and the height of their packing. The results obtained are in good agreement with the literature data given for coals of various deposits.

1. Introduction
The study of the structural characteristics of coals attracts much attention of researchers due to the fact that they affect the reactivity of coals in all coal processing processes: combustion, pyrolysis, liquefaction and gasification [1-8]. Due to natural heterogeneity, the structure of coals is also of particular interest to chemists. At the primary (molecular) level, the structure of coal can be described by macromolecules of condensed polynuclear structures with the inclusion of groups with heteroatoms, while the macromolecules do not contain repeating fragments. At the secondary level, the structure of coal consists of stacked planes of aromatic rings, aliphatic interweaving of side chains, hydrogen bonds, and cation bridges. Various instrumental methods are used to study the chemical structure of coal, such as IR-Fourier spectroscopy, Raman spectroscopy, X-ray structural and X-ray phase analysis, various methods of microscopy (scanning, transmission, atomic force) [1-3, 9-10].

X-ray diffraction analysis based on the X-ray diffraction method is the main method for describing the structure of a solid, which is widely used to assess the structural parameters of carbon materials and coal [2, 6]. To characterize the degree of ordering of structural components in carbon materials,
the following structural parameters are used: aromaticity (\(fa\)), interplanar distance (\(d_{002}\)) and sizes of ordered structures (\(L_c, L_a\)), as well as the number of polyarene layers (\(n\)) stacked in packs [11-13]. All these parameters can be determined using the method of X-ray diffraction on charcoal.

The Kuznetsk coal basin is one of the largest in terms of coal deposits. For the efficient use of these resources, it is necessary to actively carry out scientific studies of the chemical structure of coals, which are very rare today [14-16]. In this work, samples of vitrinite from coal of different stages of metamorphism were studied by X-ray diffraction analysis.

2. Experimental

In this work, a series of samples of vitrinite from coal of low, middle and high stage of metamorphism were studied.

To isolate the vitrinite component from coal, we used the method of fractional analysis of coals (GOST 4790-80), the essence of which is the stratification of the fuel under study into fractions in liquids of different densities. The separation was carried out in a mixture of carbon tetrachloride and benzene at a decreasing density of solutions: 1.40 and 1.30 g/cm\(^3\). The choice of solution densities was determined by the fact that the maximum content of vitrinated inclusions is concentrated in fractions floating up in liquids with a density less than 1.30 g/cm\(^3\) [17].

X-ray phase and X-ray structural analysis technique. X-ray phase and X-ray diffraction analysis was performed by analyzing the data obtained on a Bruker D8 ADVANCE A25 powder X-ray diffractometer (CuK\(\alpha\) radiation, Ni filter on secondary radiation) at room temperature by the polycrystal method.

To perform X-ray diffraction analysis by powder X-ray diffraction, the initial samples were ground to a particle size of less than 0.2 mm. The resulting powder was poured into a cuvette and compacted. To avoid, after pressing, the appearance of undesirable texture along the crystallite faces, which is a hindrance in measuring the position of the peaks, a matte glass slide was used for pressing. Then the cuvette with the sample was placed on the stage, aligning the sample surface with the focusing plane of the X-ray tube. Then X-ray diffraction patterns were recorded. The X-ray diffraction patterns of powder samples were taken in the range of angles of 5–70° at long accumulation times (2s) and a scanning step of 0.02°. The indexing of the diffraction peaks present in the X-ray diffraction patterns was carried out using the powder databases ICDD and PDF2 [18].

X-ray structural analysis was carried out using the method of full-profile analysis [19]. The main structural parameters of the components were estimated according to the methods described in [11, 13, 19, 20].

3. Results and discussion

To carry out X-ray diffraction analysis, characterized low-ash samples (\(A_d <5\%\)) of vitrinite concentrates of coal of the I, II, III and IV stages of metamorphism were selected, the reflection indices (\(R_{002}\)) vary in the range 0.58-1.41% (see Table 1). According to the technical analysis of the studied samples, an increase in the vitrinite reflectance in coal samples is observed with a decrease in the yield of volatile substances (\(V_{daf}\)), while the carbon content increases from 79.9 to 88.5% and the amount of oxygen and heteroatoms in the organic mass decreases from 14.3 to 6.2%.

X-ray diffraction patterns of all studied vitrinite concentrates of bituminous coals are typical for coal samples: broad diffraction maxima with indices (002) (10-30 degrees), characteristic reflections from polyarene layers, and (10) (38-48 degrees), typical for two-dimensional turbostratic structures, which determine the longitudinal size of structural elements. It should be noted that an intense background is recorded in the X-ray diffraction patterns, possibly due to the presence of poorly ordered phases of amorphous carbon [1, 2, 6, 7, 20-22]. Figure 1 shows a typical example of an X-ray diffraction pattern of vitrinite from grade IV coal metamorphism.
As can be seen, the (002) reflection has a pronounced asymmetry in the low-angle region because of g-bands arising due to the ordering in the peripheral part of the graphite-like phase of the organic mass of coals. The appearance of g-bands, with a maximum in the range of angles $2\theta \approx 20-22^\circ$, is described in the literature [1, 2, 6, 7, 21, 22], the authors suggest that due to the presence of saturated structures in the coals, such chains attached to the edge of carbon crystallites. Reflection from the (002) plane characterizes the distance between the polyarene layers, and the g-band characterizes the packing distance of saturated structures. As a result of the deconvolution of a complex profile with the separation of the g-band, a “true” reflection of the reflection from the (002) plane appeared, the maximum of which is in the range of angles $2\theta \approx 24.5-25.5^\circ$; it is this reflection that is characteristic of graphite-like ordered structures. It should be noted that the profile of the (002) reflection of vitrinite concentrate samples becomes narrower with an increase in the degree of metamorphism of coal, while the value of the interplanar distance ($d_{002}$) decreases. Also, an assessment of other structural parameters was carried out using the method described in [11, 13, 19, 20]. The values of the longitudinal and transverse dimensions of the bundles of lamellas, namely $L_a$ and $L_c$, lie in the range 1.6-2.2 nm and 1.0-2.3 nm, respectively. The degree of ordering of the carbon phase, which characterizes the degree of parallel packing of polyarene layers in the packs, increases in the series of metamorphism of the studied samples. The interplanar distance ($d_{002}$) of the turbostratic carbon phase ranges from 0.355 ± 0.010 nm. The calculated structural parameters of the studied vitrinite samples are presented in Table 1.

A relationship was established between the structural parameters of the studied vitrinite coal concentrates with the degree of their metamorphism, so with an increase in the stage of vitrinite metamorphism, the dimensional values of the lamellae, that is, $L_a$ and $L_c$, increase, and the interplanar distance $d_{002}$ decreases. Such dependences are partially described in works [8, 22], the authors explain the process of ordering of the turbostratic phase of coal by reducing the aliphatic side chains. In this regard, we can say that the interplanar distance is a necessary characteristic of the degree of perfection in the periodicity of the structure of the packing of polyarene layers in packets [2-8]. In addition, the work evaluates the thickness of the stacking structure along the $a$ and $c$ axes. It was found that with an increase in the vitrinite reflection index, the $L_c$ and $L_a$ values also increase, and the interplanar distance decreases again.
Table 1. Basic parameters of the studied samples.

| Parameter | 1  | 2  | 3  | 4  | 5  |
|-----------|----|----|----|----|----|
| R<sub>o,r</sub>, % | 1.41 | 1.27 | 0.98 | 0.82 | 0.58 |
| d<sub>002</sub>, nm | 0.350 | 0.352 | 0.358 | 0.361 | 0.364 |
| L<sub>c</sub>, nm | 2.0 | 1.9 | 1.5 | 1.4 | 1.1 |
| L<sub>a</sub>, nm | 2.5 | 2.4 | 2.3 | 2.1 | 1.7 |
| ρ, g/cm³ | 2.18 | 2.16 | 2.13 | 2.11 | 2.09 |
| N<sub>a</sub>, pcs. | 7 | 6 | 5 | 5 | 4 |
| natC, pcs. | 14 | 13 | 9 | 8 | 5 |

R<sub>o,r</sub> - vitrinite reflectance index.
d<sub>002</sub> - interplanar distance.
L<sub>c</sub> is the thickness of the pack of polyarene layers.
L<sub>a</sub> is the size of the flat aromatic network.
ρ is the packing density of the layers.
N is the number of polyarene layers in the package.
natC is the number of carbon atoms per polyarene layer.

The authors of the work calculated the specific number of carbon atoms (natC) per one polyaromatic layer [11, 13, 19, 20]. Since the number of natC is in the range of 5-15, it should be noted that the number of carbon atoms in the polyaromatic layer is confirmed by an increase in the carbon content in vitrinite samples [23]. This result is in good agreement with studies carried out by other authors [1, 4, 6-8, 24] on coals of various deposits.

According to the analysis of the data obtained in this work, the stacking height of polyaromatic layers (L<sub>c</sub>) and their amount (N) in the studied samples of coal vitrinites increase with an increase in the degree of their metamorphism. A linear dependence of the packing density of polyarene layers on the value of the vitrinite reflectance was also revealed.

4. Conclusion

An X-ray diffraction analysis of a series of vitrinite coal concentrates of various stages of metamorphism was carried out, according to which there is a directly proportional linear dependence of the main structural parameters of the samples under study (L<sub>c</sub> and L<sub>a</sub>) on the stage of coal metamorphism, and the opposite one for the distance between structured layers (d<sub>002</sub>). It was found that the smallest distance between polyaromatic layers in the samples under study varies from 0.345 to 0.365 nm. With an increase in the stage of metamorphism, that is, with an increase in the value of the vitrinite reflectance (R<sub>o,r</sub>), the distance between the polyaromatic layers decreases, and the structuring of the organic mass of the samples occurs. The calculated average number of carbon atoms per aromatic layer was 5-15, and the number of layers in packs was in the range from 4 to 7. A linear dependence of the number of polyaromatic layers on the height of their stacking in the studied coals was established.

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