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Study of the Morphology and Structure of Coal Vitrinites

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Abstract

Vitrinite concentrates of coal at different stages of metamorphism are studied by means of scanning electron microscopy and X-ray diffraction analysis. The results show that the cleaves and fractures on the surface of maceral particles have a structure characteristic of vitreous amorphous bodies for the whole metamosphism series. An increase in metamorphism degree is accompanied by an increase in the electrical conductivity of vitrinite particles and a decrease in the reflectivity with respect to electrons due to a decrease in the content of oxygen atoms. It is shown by means of X-ray diffraction that vitrinites have a turbostratic carbon structure, formed by polyarene layers with the interlayer spacing (d_{002}) decreasing from 3.64 to 3.50 Å with an increase in metamorphism stage, at the same time an increase in the dimensions of structured vitrinite fragments – height (L_c) andd width (L_a) of arene layer packets – is observed. A linear dependence is revealed between d_{002} and vitrinite reflectance.

Keywords: scanning electron microscopy, X-ray diffraction, X-ray structural parameters, coal vitrinites, arene layers

INTRODUCTION

Investigation of the micro- and nanosized characteristics of coal, shale rich in organics, and carbon-containing materials has been substantially improved by introducing various methods based on scanning electron microscopy (SEM). Scanning electron microscopy is usually applied to study strongly metamorphized organic matter, black coal, anthracite, coke and graphite [1]. Analysis of fracture surfaces during the destruction of various carbon materials, observed with the help of SEM, provides detailed information on their structure and allows better predictions of their behaviour during treatment [2].

An electron beam affecting the sample causes emission of the electrons with different energies and other kinds of radiation, which contain the information on sample surface morphology, composition, crystallographic structure and other physicochemical properties of an object. The recorded signals originate not only from sample surface but also at a definite depth, which depends on specific electron beam parameters and the properties of the material. The zone in which the signals arise from electron beam interaction with the sample is called excitation (interaction) region. The size and shape of this region are mainly due to sample composition and the accelerating voltage, which determines the amount of energy transferred by the electron beam to the sample: the higher is electron energy, the deeper is excitation region. Excitation volume is smaller in a sample with higher density, that is, containing elements with larger atomic number (Z), than in a sample composed of the elements with smaller Z. The excitation volume, as well as spot size (the diameter of electron beam on the sample) determine the resolution of microscopic image.

Secondary-electron image (SE) is one of the most frequently used image types to study sur-

face topography. An image in back-scattered electrons (BSE) is obtained by recording the electrons that leave the sample and possess the energy above 50 eV as a result of elastic collisions with the nuclei of atoms in the sample. Contrast in BSE image arises mainly from the differences in the average Z of excited atoms at different sites on the surface. So, analysis of contrast may give important information on sample composition and homogeneity.

X-Ray microanalysis, for example energy dispersive analysis (EDX), is carried out through recording characteristic X-rays that may be used to depict the qualitative, quantitative and spatial distribution of chemical elements in the sample.

A traditional method of maceral identification in the petrology of organic substances, based on the measurement of reflectivity, investigation of the shape and relief, as well as fluorescence, is optical microscopy. Coal metamorphism stages are usually determined relying on vitrinite reflectance ($R_{o,r}$) [3]. This method takes into account only one component of coal and is able to characterize the sample under investigation independently of its other characteristics.

One of the difficulties preventing the application of SEM in coal petrography is the problem of distinguishing between macerals [4]. SEM images of macerals exhibit contrast, which is connected with shape and relief (SE signal), atomic number (BSE), as well as chemical composition (EDX) of an object. The authors of [5] studied maceral groups (vitrinite, inertinite and liptinite) and showed that choosing the accelerating voltage one may form contrast in BSE images (in the grey colour rating scale), which would allow distinguishing between maceral subgroups (telovitrinite and detrovitrinite) or even macerals (sporinite and cutinite). At the same time, it turned out that identification based exclusively on the contrast between different inertinite macerals (semifusinite, fusinite, macrinite) is hindered unless a maceral possesses characteristic texture (fusinite and semifusinite). Differences in the contrast between inertinites and vitrinites were also practically unobservable.

It is known that the molecular structure of coal is represented by polyaromatic polynuclear macromolecules which may also include heteroatomic groups, and an increase in metamorphism stage is accompanied by an increase in the degrees of aromaticity and condensation. The fragments of polyaromatic molecules form layers, which possess a definite ordering degree and may be studied by means of X-ray diffraction (XRD). During XRD, reflections (002), (100), (110), characteristic of graphite, are detected in the diffraction patterns of fossil coal, which confirms the presence of crystallites (ordered regions) in coal structure. It is accepted that the structure of carbon matrix in coal is intermediate between graphite and amorphous disordered structure, so-called turbostratic structure. Disordered carbon phase dominates in coal, which is exhibited as an increase in background intensity in the diffraction patterns [6–11].

X-Ray diffraction allows determining interplane spacings (d_{002}) of turbostratic carbon structures and their dimensions: height (L_c) and width (L_a) of the packets of arene layers [6–8, 11].

In this work, investigation of vitrinite concentrates in coal samples of the metamorphism series is carried out by means of SEM and XRD [12]. The goal of the work is to study arene layer structuring on the basis of the obtained X-ray structural characteristics of vitrinites because vitrinite is one of the major components of fossil coals, responsible for their physicochemical properties.

EXPERIMENTAL

To carry out the investigation, we chose seven samples of vitrinite concentrates that have been extracted according to the procedure described in [13, 14] from different coal ranks. Results of the proximate analysis, chemical composition, petrographic parameters, as well as reflectance characteristics and metamorphism stages for the objects under investigation are presented in [12]. It has also been demonstrated in that work that the studied concentrates belong to four metamorphism stages. Some characteristics of vitrinite concentrates are listed in Table 1.

Electron microscopic analysis was carried out with the help of a scanning electron microscope JSM 6390 LV (JEOL, Japan). The images were obtained at the acceleration voltage of 20 kV in probe current 1 nA at a distance of 8 mm from the table in BSE mode, with detector configuration forming the contrast that depends on atomic number Z. Vitrinite samples prepared as analytical samples (particle size <0.2 mm) were placed on electrically conducting (carbon) scotch glues onto an aluminium objective table. To observe possible differences in the contrast connected

with maceral properties, at first we chose two extreme samples (Nos. 1 and 8) with the largest differences in characteristics, belonging to the I and IV stages of metamorphism, respectively. The samples were placed on the scotch separately but so that both samples were within the field of view, thus providing identical image taking conditions. Then, according to the same algorithm, the samples related to the II and III metamorphism stages were placed sequentially near sample 1. Among the samples related to one stage or to both stages at the same time, we chose the samples with the smallest O/C ratio and the largest $R_{o,r}$ value.

The XRD patterns of the samples were recorded with the help of a powder X-ray diffractometer D8 Advance A25 (Bruker, Germany) at room temperature in copper CuK_α-radiation (λ = 1.5406 Å, Ni-filter at the secondary beam) according to the polycrystal (powder) method. The diffraction patterns were recorded at long accumulation times (2 s), within angle range 5–100° over 2θ, scanning step 0.02°. The following characteristics were chosen for evaluation: interplanar distance d, the size of arene layer structured packets (the width and height of the packets – L_c and L_a, respectively) [13].

The phases were identified using the diffraction data of graphite (diffraction card PDF 01-089-7213 of ASTM database) [15]. X-Ray structural characteristics were calculated using the known equations [16]. The diffraction patterns of coal vitrinite samples are represented by broad asymmetric reflections, so decomposition of the reflections into components was carried out with the help TOPAS software for XRD patterns processing, according to the procedure described in [13].

The longitudinal size (width) of polyarene layers L_a and the height L_c of packets formed from these layers were calculated using equations:

$$L_a = 1.84\lambda/(\beta(10)\cdot\cos\theta(10)) \quad (1)$$

$$L_c = 0.9\lambda/(\beta(00l)\cdot\cos\theta(00l)) \quad (2)$$

where λ is the wavelength of X-ray radiation involved; $\beta(10)$ is the width of reflection (10) at the half of its height; $\theta(10)$ is the reflection angle from plane (10); $\theta(00l)$ is the angle of reflection from a family of planes (00l), (002) or (004); $\beta(00l)$ is the width of reflection (00l) at its half-height.

Interplanar distances d_{00l} for the samples were calculated using equation:

$$d_{00l} = \lambda/(2\sin\theta(00l)) \quad (3)$$

RESULTS AND DISCUSSION

The SEM images of powdered vitrinite samples with different carbon content and vitrinite reflectance parameters $R_{o,r}$ are shown in Fig. 1. The framed regions in the images correspond to the samples related to one of the stages II, III and IV with the lowest O/C ratio and the maximal $R_{o,r}$ value, while the regions without framing related to sample 1 (stage I). One can see that there are no observable differences in particle shapes and surface relief between vitrinite samples at different metamosphism stages, and for all concentrates the surface fracture structures on the particles were characteristic of vitreous amorphous species. However, vitrinite samples at I and IV stages of metamorphism, with maximal differences between each other in the vitrinite reflectance and O/C ratio, differ from each other in contrast (see Fig. 1, *a*). Thus, for vitrinites with high oxygen content, the presence of over-exposed regions on the surface of some particles is typical. The appearance of over-exposed regions in the

TABLE 1

Characteristics of the samples of vitrinite concentrates [12]

Sample	Elemental composition, % per daf (dry, ash-free)			Atomic ratio		$R_{o,r}$, %	Metamorphism stage
	C	H	(O + N + S)	H/C	O/C		
1	82.2	6.0	11.8	0.88	0.11	0.63	I
2	83.2	6.0	10.8	0.87	0.10	0.72	I-II
3	85.3	6.0	8.7	0.84	0.08	0.82	II
4	85.7	5.9	8.4	0.83	0.07	0.84	II
5	86.3	5.8	7.9	0.81	0.07	0.98	II-III
6	88.7	5.3	6.0	0.72	0.05	1.27	III-IV
7	88.6	5.3	6.1	0.72	0.05	1.31	IV
8	88.5	5.3	6.2	0.72	0.05	1.41	IV

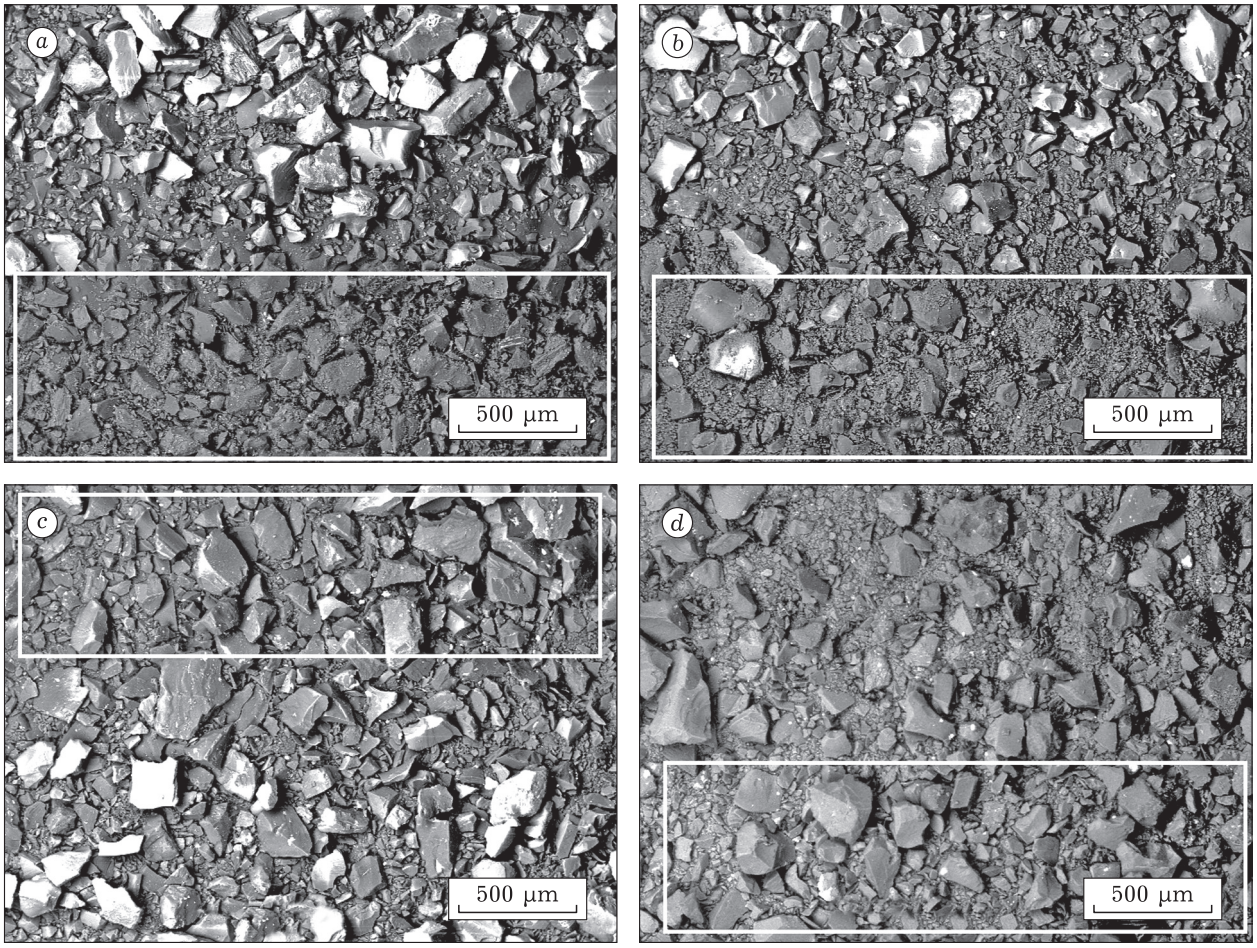

Fig. 1. SEM images of vitrinite concentrates. The framed area marks samples at one of metamorphism stages (indicated in brackets) with the maximal vitrinite reflectance and minimal O/C ratio in comparison with sample 1 (I) (non-framed area): *a* – samples 1 (I) and 8 (IV); *b* – samples 1 (I) and 6 (III); *c* – samples 1 (I) and 5 (II); *d* – samples 1 (I) and 8 (IV). Image (*d*) is obtained under the conditions of low vacuum.

image may be caused by charging of vitrinite particles under the action of electron beam. The presence of contrast connected with the effects of particle charging was observed for samples 1–5. Effects of this kind were not detected for samples 6–8. It is known that with an increase in metamorphism stage the electric conductance of coal increases because coal samples are an intermediate step from condensed polycyclic compounds to graphite, and their conductivity depends on graphitization extent, which increases with an increase in carbon content. The absence of vitrinite sample charging effects was observed for carbon content in them more than 88 %. To reduce the effects connected with sample charging in image contrast, recording was carried out under the conditions of low vacuum, with the residual pressure 100 Pa in the microscope column. Under the chosen conditions, the indicated effect was not observed, however, in this case distinguishable contrast was successfully observed only for sample pairs 1 and 6, 1 and 7, 1 and 8 (see Fig. 1, *c*). It should be stressed that the difference between the values of O/C atomic ratio for sample 1 and samples 6, 7, 8 (see Table 1) has the same value, which is maximal over the whole series under comparison, so the observed difference in vitrinite image contrast may be connected with different contents of heteroatoms. The higher is heteroatom content, the most significant is the contrast. So, only the differences between vitrinites of I and IV stages of metamorphism have been revealed by means of SEM.

Typical diffraction patterns of the samples of vitrinite concentrates of fossil coals are presented in Fig. 2. One can see that a broad halo is observed in the diffraction patterns within the angle range $2\theta \approx 18–34°$ and reflections at 41–46 and 51–55°. A broad halo with asymmetry from the small angle side relates to reflection from the

TABLE 2

Structural parameters of vitrinite concentrates

Parameter	Sample						
	1	2	3	4	5	6	7
d_{002}, Å	3.64	3.64	3.61	3.58	3.52	3.52	3.50
L_c, Å	11	12	14	15	19	19	20
L_a, Å	17	19	21	23	24	25	25

plane (002); asymmetry of this reflection is an evidence of the existence of additional reflection (γ-band). The authors of [6–9] explain the appearance of γ-band, with the maximum within angle range $2\theta \approx 20–22°$, by the presence of saturated structures in coal composition (for example, aliphatic side chains), attached to coal crystallites. Reflection (002) determines the distance between polyarene layers, while the γ-band depicts the distance between saturated structures. After subtraction of γ-band, the reflection from plane (002) manifested itself, with the maximum within angle range $2\theta \approx 24.5–25.5°$, which points to the presence of graphite-like structures. The diffraction patterns also contain weak reflections from planes (10) and (004) within angle ranges $2\theta \approx 41.4–43$ and $50–52°$, respectively. The profile shape of reflection from (002) plane of coal vitrinite samples becomes more clearly pronounced with an increase in the degree of metamorphism, and the interplanar spacing d_{002}, determined from this reflection, decreases. Interplanar spacings obtained after separation of reflections from (002) plane and γ-band, as well as other structural parameters calculated according to equations (1)–(3) for all samples, are presented in Table 2.

One can see that an increase in carbon content and coal metamorphism degree is accompanied by an increase of the average longitudinal lamella side (L_a) and the height of their packing (L_c) in vitrinite samples, calculated using Scherrer equation, from 17 to 25 and from 11 to 20 Å, respectively, while d_{002} decreases from 3.64 to 3.50 Å (see Table 2). Thus, it has been discovered that L_a and L_c values increase with a decrease in d_{002} value with an increase in vitrinite reflectance $R_{o,r}$ and coal metamorphism stage, while there is a linear dependence between structural parameters L_a, L_c and $R_{o,r}$, with a high correlation coefficient (Fig. 3, *a*). A similar dependence is also observed between d_{002} and $R_{o,r}$ (see Fig. 3, *b*).

It has been demonstrated previously in [17] that the size L_c increases with simultaneous decrease in interplanar spacing d_{002} with a decrease in the yield of volatile substances from coal. This interrelation is evident because the yield of volatile substances is due to the presence of saturated hydrocarbons, and the degree of coal aromaticity increases with a decrease in the content of side aliphatic chains. Thus, interplanar spacing d_{002} may be related to the parameters that characterize the degree of perfection in the periodicity of polyarene layer packing; a decrease in d_{002} with

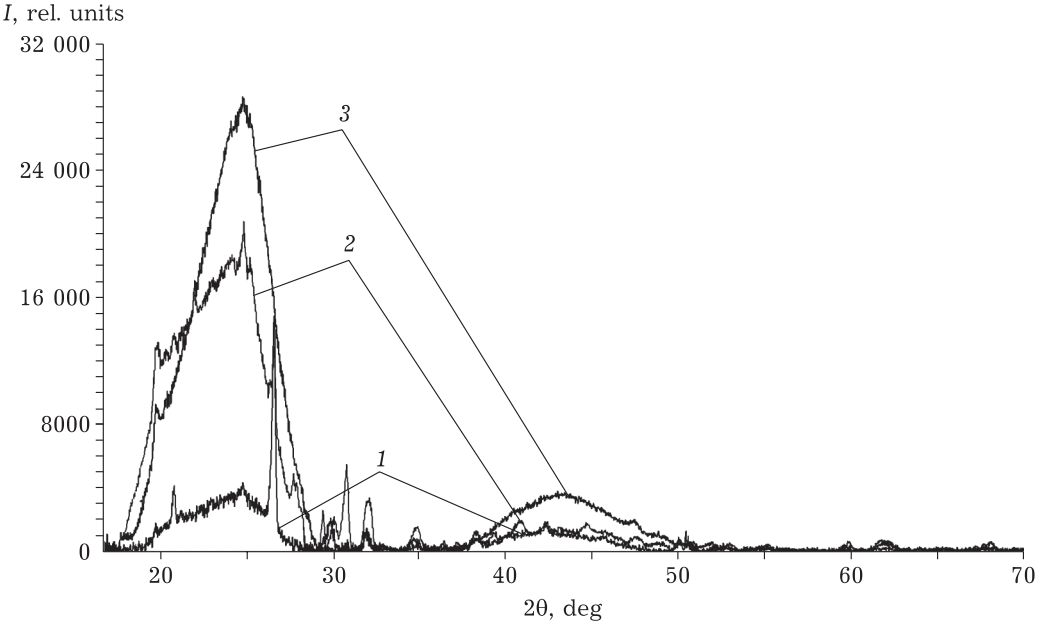

Fig. 2. Typical diffraction patterns of vitrinite concentrate samples from fossil coal: *1* – sample 1; *2* – sample 4; *3* – sample 7.

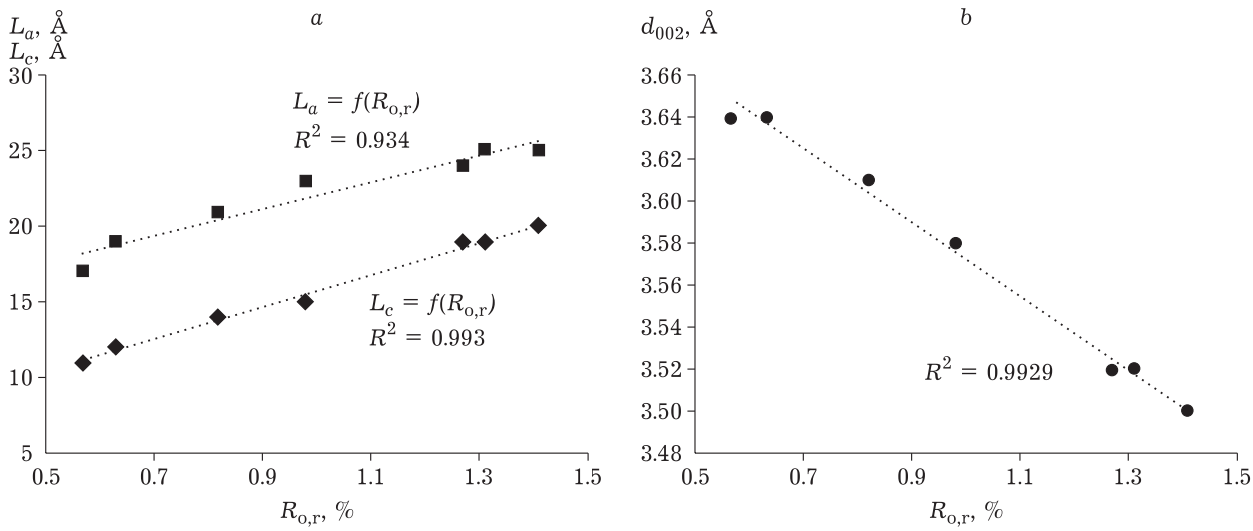

Fig. 3. Dependence of the latitudinal and longitudinal sizes of packets (L_c and L_a, respectively) (*a*) and interplanar spacing (d_{002}) (*b*) on vitrinite reflectance ($R_{o,r}$).

an increase in carbon content and an increase in the degree of aromaticity is connected with denser packing of polyarene layers with a decrease in the content of side aliphatic chains and a trend of this parameter to the value characterizing the crystal structure of graphite [6–9]. An increase in the degree of polyarene layer ordering with an increase in metamorphism stage is also exhibited as an increase in parameter L_c.

CONCLUSION

Integrated investigation of a series of vitrinite concentrate samples from coals at different degrees of metamorphism has been carried out by means of SEM and XRD. It is discovered that electric conductance increases within the series of the studied vitrinite samples with an increase in metamorphism stage, and reflectance with respect to electrons decreases as a consequence of a decrease in oxygen atom content. It is demonstrated that the structure of maceral particle surface is similar to that of vitreous amorphous bodies for the entire metamorphism series. It is shown by XRD that the carbon structure of vitrinites is formed by polyarene layers, and interplanar spacing between the layers increases with an increase in metamorphism stage, while the sizes of structured packets increase.

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