Study of coke by X-ray structural analysis and scanning electron microscopy

Z R Ismagilov, A N Popova and S A Sozinov

Federal Research Center of Coal and Coal Chemistry, Siberian Branch of Russian Academy of Science,
18 Sovetskiy Ave., 650000, Kemerovo, Russia
E-mail:h991@yandex.ru

Abstract. In this work, a number of industrial samples of needle cokes from various manufacturers were studied. The study of the samples was carried out by methods of X-ray diffractometry and analytical scanning electron microscopy. The parameters of their crystal structure were determined, and the features of their microstructure were investigated. The differences found in the crystal structure and morphology of coke particles made it possible to divide the studied samples into 2 groups: isotropic, with equal longitudinal and transverse crystallite sizes, and anisotropic, in which the longitudinal crystallite sizes exceed the transverse ones by 3-4 times. Particles of isotropic cokes have a fracture texture characteristic of a glassy amorphous body, in contrast to which particles of anisotropic cokes have a lamellar texture. The consistency of the conclusions obtained from the results of two independent methods makes it possible to consider X-ray diffraction analysis in combination with analytical electron microscopy as the necessary complementary tools for evaluating cokes with the aim of their possible application in various technological processes.

1. Introduction

Cokes are one of the main components in the production of anodes due to their unique properties, chemical purity and ability to acquire electrical conductivity during heat treatment [1-8]. The properties of anodes are largely determined by the properties of coke [9, 10].

The authors of [11] proposed to consider the amount and composition of impurities in coke, the perfection of the crystal structure and porosity as the main parameters of cokes that affect the properties of anodes.

In view of a number of specific requirements for the quality of coke for the production of anodes, it can be concluded that the assessment of the technological suitability of coke is a multifactorial task. There is no single indicator that would unambiguously determine the quality of coke. It is determined by a set of indicators that depend on the quality of the feedstock and the conditions for its processing [12-17].

One of the most important indicators is the degree of coke anisotropy [18], determined by the shape of coke particles using optical microscopy, and is estimated in points from 0 to 7, respectively, in the range from completely isotropic, so-called shot cokes, to anisotropic needle cokes (NCs). High scores belong to premium NCs, which have the most pronounced shape anisotropy. The structure of coke determines its physical and mechanical characteristics and the ability to graphitize. NCs have different
values of mechanical strength, electrical and thermal conductivity, coefficient of thermal expansion in different directions. Due to the fact that they are graphitized, they are used in the production of graphite electrodes [19, 20].

The forming structure of cokes is influenced by the molecular structure of the feedstock [8, 12, 21-24]. So, for example, in [23], differences are noted in the structure of cokes obtained from raw materials with a predominance of paraffinic structures and with a predominance of naphthenic and aromatic structures. Coke from oils with a predominance of paraffinic structures has an acicular structure, contains wide slit pores, consists mainly of elongated particles, which reflects the growth of carboid formations mainly in one direction; asphaltene coke has a fused isotropic structure and is the result of the growth of dense colloidal formations evenly in all directions; resin cokes occupy an intermediate position between oils and asphaltenes, have a spongy structure with a low degree of anisotropy with the inclusion of fibrous formations [8, 15, 21, 22]. According to the data [24, 25], the microstructure of the NC is represented by lamellar formations (lamellas) that form packets. Ordinary cokes can also have a lamellar structure, however, the plates of these cokes have a large thickness, they do not contain packet formations from thin plates [24]. In the author's opinion, the formation of lamellar forms can be associated with the structure of polycyclic aromatic hydrocarbon molecules contained in the feedstock. Initially, very defective mesogen molecules are associated with the formation of an aromatic, liquid crystalline phase. Subsequent heat treatment leads to an improvement in intramolecular perfection, improved packing of lamellas and leads to the formation of a structure, as in polycrystalline industrial graphites, and the reason for the difference in the structure of ordinary and NCs is the difference in the properties of mesophase formations and rheological properties. Thus, in all the studies considered, the influence of the molecular structure of the feedstock on the microstructure of the final product is noted. An important component of the structure of coke are pores, the size and shape of which change depending on the purity and nature of the feedstock, technological conditions of coking and calcination [19, 26-30]. Thus, a structure with small rounded pores is formed from a viscous raw material, while highly porous cokes with elongated large pores are formed from light raw materials [26]. The sulfur contained in them, which is in the form of thermally stable compounds with a thiophene bond, has a significant effect on the formation of a porous structure in cokes [30]. Removal of thiophenic sulfur occurs at 1400-1600 °C. An intense release of sulfur compounds occurs during coke calcination and leads to an increase in microporosity. The structure of the calcined petroleum coke consists of crystallites of various sizes and orientations. The packing of macromolecular formations, defects in their structure form cavities, micropores. According to [21], the average pore size of anisotropic cokes is almost an order of magnitude larger than that of isotropic ones.

Thus, it can be stated that carrying out complex studies by various physicochemical methods of the structural parameters and microstructure of cokes allows a more reasonable approach to the choice of raw materials and selection of thermal regimes for obtaining NCs.

2. Experimental
In the work, studies were carried out on 6 different samples of industrial cokes: O-1, O-2, O-3, O-4, O-5, O-6.

2.1. X-ray structural analysis technique
X-ray diffraction analysis was performed using a Bruker D8 ADVANCE A25 powder X-ray diffractometer (Germany) (CuKα radiation, Ni filter on secondary radiation) at room temperature by the polycrystal method. X-ray diffraction patterns were taken at long accumulation times (2 s) and a scanning step of 0.02°.

To perform X-ray diffraction analysis by powder X-ray diffraction, the initial samples were ground to a particle size of less than 0.02 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 indexing of the diffraction peaks present in the X-ray diffraction patterns was carried out using the powder databases ICDD and PDF2 [31]. The interplanar distances ($d_{00l}$), the sizes of the structural components ($L_c$ and $L_a$), as well as the packing density of the layers and the number of polyarene layers in the package of the studied samples were estimated according to the procedure described in [32-34].

2.2. Electron microscopic analysis technique

Electron microscopic studies were performed on a JEOL JSM-6390 LA analytical scanning electron microscope with a JED 2300 energy dispersive analyzer (Japan). To study the microstructure, samples of crushed coke with a particle size of about 3 mm were prepared. An electron microscopic image of the coke particles was obtained in secondary electrons. For X-ray microanalysis, analytical samples with a particle size of less than 0.2 mm were prepared. The registration of the spectra of characteristic X-ray radiation were taken from spots with an area of 1 mm$^2$ at an accelerating voltage of 20 kV and a probe current of 1 nA. The resolution of the energy dispersive detector is 133 eV. The calculation of the percentage of each element in the analyzed sample was carried out according to the obtained spectra using the Analysis Station software version 3.62.07 from JEOL Engineering using the standardless ZAF method.

3. Results and discussion

Figure 1 shows two typical types of X-ray patterns obtained for the studied coke samples.

![Figure 1. X-ray diffraction patterns of coke samples O-1 (1) and O-5 (2)](image)

The diffraction patterns of all the coke samples under study showed well-pronounced diffraction reflections 002 and 004, corresponding to structured carbon materials. On the diffraction patterns of a group of samples O-1, O-2, O-3, O-4, peaks corresponding to reflections 006 (type 00l) and (11) (type hk0) were observed. The appearance of reflection from plane (11) indicates a higher degree of crystallinity of these cokes and makes it possible to determine the sizes of crystallites along the basal plane (parameter $L_a$). The appearance of a pronounced reflection from the (006) plane in the group of samples O-1, O-2, O-3, O-4 is due to the stacking of graphene layers. The asymmetry in the shape of the profile of the 00l diffraction peaks indicates the presence in the samples under study of phases with different dispersion and with different interplanar spacing $d_{002}$. To assess the structural characteristics of the crystalline phases contained in the sample, the profiles of the (002) and (004) reflections were decomposed into their constituent components according to the technique [32–34]. Table 1 shows the data of X-ray structural analysis of samples.
Table 1. Structural parameters of cokes

| Sample | O-1 | O-2 | O-3 | O-4 | O-5 | O-6 |
|--------|-----|-----|-----|-----|-----|-----|
| Phase fraction, % | 40 | 60 | 40 | 60 | 40 | 60 | 30 | 70 | 40 | 60 |
| d₀₀₂, Å | 3.442 | 3.509 | 3.442 | 3.511 | 3.443 | 3.511 | 3.440 | 3.539 | 3.436 | 3.512 | 3.435 | 3.500 |
| Lc, Å | 31 | 13 | 32 | 13 | 32 | 13 | 28 | 11 | 31 | 16 | 34 | 20 |
| La, Å | 76 | 32 | 78 | 33 | 77 | 32 | 80 | 32 | 29 | 22 | 30 | 24 |
| N, шт. | 10 | 5 | 10 | 5 | 10 | 5 | 9 | 4 | 10 | 6 | 11 | 7 |

d₀₀₂ - interplanar distance.
Lc is the thickness of the pack of polyarene layers.
La 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.

As a result of the decomposition of the diffraction peaks of reflections from planes of the 00l type, two crystalline phases were isolated for all the studied samples, one of which had a graphite-like structure and an interplanar distance d₀₀₂ close in value to the graphite value, the other phase was a phase with a turbostratic structure. As follows from the data of our X-ray structural analysis of coke samples (Figure 2), the group of cokes O-1, O-2, O-3 and O-4 is characterized by anisotropy of the crystallite shape. For these cokes, the La parameter exceeds Lc by a factor of 3, while the crystallites of the O-5 and O-6 cokes are isotropic (the ratio of the parameters Lc and La for these cokes is close to unity). The O-5 and O-6 cokes, although they have smaller crystallite sizes along the basal plane, practically do not differ in the Lc parameter from the group of "anisotropic" cokes; in addition, the interplanar distance d₀₀₂ of these cokes is closer in magnitude to the interplanar distance of graphite.

It is assumed that low-temperature cokes (semi-cokes) have the structure of a spatial polymer consisting of condensed aromatic rings ordered in a two-dimensional plane [35-37]. The rings are linked in the polymer by side carbon chains that make up the disordered part. When coke is calcined, simultaneously with the processes of side chain destruction, accompanied by the release of volatile products, two-dimensional polyarene planes are ordered, which form packs of parallel layers (crystallites). At temperatures above 1100 °C, the process of graphitization of coke occurs, and in the range of 1500-2000 °C, crystallites are formed with longitudinal dimensions (La) significantly larger than those in the transverse direction (Lc), which causes the anisotropy of cokes. The described genesis of the coke structure upon heating will manifest itself in a change in the shape of the diffraction peak profile, which should become narrower, with a simultaneous shift of the peak maximum towards larger angles, which may be associated with an increase in the number of polyarene layers in a pack and an “improvement” in the quality of their packing. According to [38–43], as the calcination temperature increases, the crystallite size (parameter Lc) increases in the direction of the axis perpendicular to the arene planes; the number of layers in the pack increases.
According to the data of scanning electron microscopy, samples of cokes O-1, O-2, O-3, O-4 have a pronounced anisotropy of the particle shape and have a lamellar texture (Figure 3 a, b), formed by thin extended packaged lamellas oriented along pore spaces. The shape of the particles of O-5 and O-6 cokes is close to isotropic (Figure 3 c, d). The texture of the particles of these cokes is determined by the absence or low content of the lamellar component and has practically the same texture characteristics in all directions, while the fracture surface of the particles has a form characteristic of a glassy amorphous body.

According to X-ray microanalysis data, the identified groups of cokes differ in sulfur content (Figure 2 c). Anisotropic images of O-1, O-2, O-3, and O-4 cokes differ from isotropic O-1 and O-2 in a higher sulfur content, which can be both a consequence of the use of feedstock of different composition, as well as a consequence of the temperature treatment of cokes in the temperature range insufficient for the destruction of the thiophene bond, which leads to the accumulation of sulfur in the coke.
Figure 3. Electron microscopic images of coke particles: anisotropic (elongated) particle shape (a); characteristic lamellar texture (b) isotropic shape of coke particles (c); typical fracture structure of an amorphous body (d).

4. Conclusion
The results of X-ray diffraction and electron microscopic analysis made it possible to divide the studied cokes into two types: anisotropic (L_a >> L_c) with a lamellar microstructure and isotropic with comparable L_a and L_c parameters and the microstructure of an amorphous body. Thus, the relationship between the structural parameters and the morphology of coke particles is shown, and the correlation between the data obtained by two independent methods makes it possible to consider such a set of methods as a necessary complementary toolkit for determining the basic properties of coke, depending on the choice of feedstock and heat treatment modes in order to obtain anisotropic acicular high quality coke.

Acknowledgments
The work was carried out using the equipment of the Center for Collective Use of the Federal Research Center of Coal and Coal Chemistry SB RAS within the framework of the state assignment of the Federal Research Center of Coal and Coal Chemistry SB RAS (project AAAA-A17-117041910151-9).

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