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Modern Ideas About the Mechanism of the Formation of the Structure of Graphitising Coke

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The review considers studies on the mechanism of low-temperature carbonisation, which determines the fundamental structural characteristics of carbonaceous materials. Particular attention has been devoted to the mesophase transformation as the principal factor responsible for the formation of the structure of graphitising coke. The structural features of various types of coke, whose formation proceeds via the mesophase transformation stage, are described.
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I. INTRODUCTION

The unique properties of carbon-graphite materials have ensured their wide-scale application in various branches of modern engineering. The development of the technology of their manufacture has required the solution of many complex problems associated with the preparation of materials having specified properties. The principal raw materials in the technology of carbon-graphite materials are petroleum, pitch, and shale coke, which are converted into graphite on heat treatment at 2300°C and above. The raw materials for the preparation of such coke consist of heavy hydrocarbon residues from the processing of petroleum, coal, and bituminous shale.

It has been established by microscopy in polarised light that the above types of coke have complex and varied structures, but the mechanism of their formation remained unknown for a long time. The most realistic hypothesis [1] concerned the relation between the structure of coke and the complex chemical composition of the raw coking material, and the formation of particular regions in the microstructure was believed to be genetically linked to a particular group component of the raw material.

The ideas about the mechanism of structure formation in coke, which developed mainly on the basis of chemical research techniques, have been described most fully in the monographs of Krasyukov [1] and Onusaitis [2]. The inadequacy of these concepts became evident after Brooks and Taylor [3,4] and later a number of other workers [5,6] investigated by microscopy in polarised light the products of the low-temperature carbonisation of substances from which graphitising coke is obtained. Even before this, it was observed that the graphitising coke obtained at 450°C already had a textured layer structure [7,8]. It was also firmly established that graphitising coke may be obtained solely from substances melting at 350-500°C [9,10]; a characteristic feature of low-temperature types of coke, which makes it possible to infer unambiguously their capacity for graphitisation, is the presence of regions of optical anisotropy [11]. However, the most important stage in the understanding of the mechanism of structure formation in graphitising coke was the so called mesophase transformation discovered by Brooks and Taylor [3,4].

II. THE MESOPHASE TRANSFORMATION—THE MAIN STAGE IN THE FORMATION OF THE STRUCTURE OF COKE

1. General Description of the Phenomenon

The formation of the structures of all types of graphitising coke proceeds via the mesophase transformation. The latter occurs in the temperature range 390-520°C and consists of a phase transition in the liquid state during which large polymerised aromatic molecules in the isotropic mass of the pitch are arranged in parallel and form anisotropic liquid crystals of the mesophase [4]. The temperature range of the mesophase transformation varies somewhat for different substances and its extent depends significantly on many factors, which will be discussed below.

The liquid crystals of the mesophase arise in the isotropic liquid mass of the pitch, following an increase of temperature to 390-400°C, in the form of approximately 0.1 μm particles observed on ultrathin sections with the aid of an electron microscope, but Brooks and Taylor have no doubts about the existence at this stage of spherical formations of even smaller size. With increase of the temperature and the duration of treatment, the spherical formations grow in size and the proportions of the pitch and the mesophase change in favour of the latter. As long as the ratio of the phases in specified volumes does not exceed 1:1, the growth of the spherical formations takes place at the expense of the surrounding pitch; their shape remains rigorously spherical and their diameter may reach tens of micrometres. When the proportion of the mesophase is high, the coalescence of the individual spherical particles begins with formation of larger particles of different shapes (Fig. 1). At the instant of the complete conversion of the pitch into the mesophase, the multiple coalescence of the spherical particles results in the formation of a complex structure, which Brooks and Taylor [4] called the mosaic structure although it does not in fact consist of sharply delimited regions.

The structure of the mesophase spheres at the instant of their formation and during their initial growth was investigated by microscopy in polarised light [3,4,12], by electron diffraction [4], and by X-ray diffraction [13]. It was established that the mesophase spheres are optically monoaxial positive liquid crystals with straight extinction belonging to the hexagonal system. The planar aromatic layers are arranged at right angles to one diameter of the sphere becoming bent at its edges in such a way that they become perpendicular to its surface (Fig. 2). The distance between the layers is 3.43–3.49 Å. The fact that the planar molecules forming the sphere have a radial arrangement near the surface promotes the initial coalescence of the spheres. The coalescence results in the formation of mesophase regions with a more complex structure than that of the initial spheres.



Figure 1. Particles of the mesophase in coal tar pitch. Coalesced formations observed together with individual spheres. Polarised light; magnification × 350.



Figure 2. Sphere in which the lamellar layers are distributed at right angles to the surface of the polished section passing through the centre of the sphere. The "poles" refer to the ends of the principal axis of symmetry of the sphere. Polarised light [3].

At the instant of complete conversion of the pitch into the coalesced mesophase, the coking material consists of a very viscous liquid. At a somewhat higher temperature, the mesophase swells under the influence of the evolved gases and is converted into solid semicoke. During swelling, the mesophase is markedly deformed and the microstructure produced at this time hardly changes on subsequent heat treatment and on conversion into coke.

Different versions of the coalescence of the mesophase spheres and the resulting structures as well as the structures formed on deformation of the coalesced mesophase have been investigated in detail [12,14,15]. The relation between the microstructure of coke and the structure of the coalesced mesophase and its deformation has been described [16]. Owing to the high viscosity of the mesophase and the insufficient time during which it exists in the fused state, there is insufficient time during the coalescence of two and more spheres for the formation of a regular arrangement of their layers and a simple layer structure. Furthermore, the structural result of the coalescence depends on the mutual orientation of the *C*-axes of the coalescing spheres [12]. In the multiple coalescence of spheres, the above factors lead to the formation of a complex structure of the coalesced mesophase, including linear defects in the packing of the planar layers, discontinuities, and pronounced bending. The extensive deformation of the mesophase on swelling increases by several orders of magnitude the number of defect structures [12]. Linear defects are the preferred site of the generation of contraction cracks on subsequent heat treatment [15].

2. The Chemistry of Carbonisation Processes

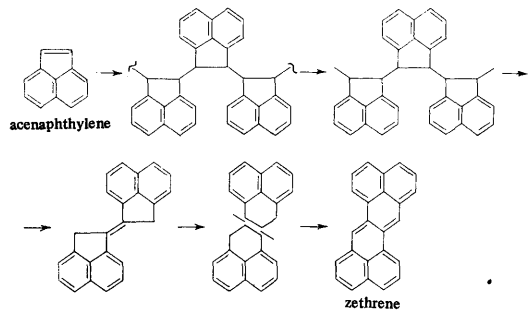
The chemical composition of isotropic pitch in which the mesophase spheres are formed and grow is extremely complex. In broad outline, the chemistry of the processes occurring during coking in the temperature range 380 to 460°C is described as a sequence of thermal dehydropolycondensation reactions. Detailed studies on these processes involve considerable difficulties associated with the complexity of the chemical composition of the coking raw material and with secondary interactions—the recombination of radicals, mutual influence and interaction of various hydrocarbons with different activities, and polycondensation processes.

The mechanisms of coking reactions have been inferred [1,3] from the results of a detailed analysis of the volatile products and simple measurements of certain properties of the condensed phase, such as density, the C/H ratio, group composition, etc. In recent years vigorous research has been undertaken on the intermediate stages in the carbonisation process using ESR, ultraviolet and infrared spectroscopic, mass-spectrometric, and NMR methods. In combination with special methodological procedures, it was possible to obtain certain data on the mechanisms of the reactions occurring in the condensed phase.

Certain fundamentally important results were secured in the study of the carbonisation of individual hydrocarbons, including those forming graphitising coke, such as acenaphthylene, anthracene, phenanthrene, naphthacene, dibenzanthrene, etc. [17–20]. Acenaphthylene has been most thoroughly investigated. Its carbonisation was initially achieved via low-temperature polymerisation with subsequent thermal depolymerisation above 350°C, resulting in the formation of fragments which react, giving rise to larger condensed aromatic molecules [20]. The mesophase transformation in the carbonisation of acenaphthylene begins at 405°C.

Ruland [17] established by X-ray diffraction that the formation of carbon in the carbonisation of acenaphthylene proceeds via the formation of zethrene followed by condensation of the zethrene elements into extended polycyclic aromatic systems. This rearrangement is accompanied

by the dissociation of carbon–carbon bonds in the five-membered ring and the formation of the perinaphthenyl radical in the intermediate stage via the following mechanism:



Singer and Lewis [18,19] studied the carbonisation of acenaphthylene and other aromatic hydrocarbons by ESR in order to identify the intermediate radicals generated and refine the mechanism of the chemical reactions occurring at various stages of the process. The ESR spectra of various types of semicoke usually observed consist of a single line without hyperfine structure, the width and intensity of which depend on the treatment temperature. Such spectra do not yield information about the free radical structures present in the carbonised system. In order to overcome this difficulty, the authors [17,18] carried out the carbonisation in an inert solvent—*m*-pentaphenyl. Dissolution decreased the probability of the combination of free radicals and thereby permitted their detection and identification by ESR. It was established [17] that the carbonisation of acenaphthylene proceeds via the scheme described by Ruland with the intermediate formation of the perinaphthenyl or dimethylperinaphthenyl radicals [17].

The results of the study of six different compounds led to the conclusion that the intermediates in the formation of large condensed molecules are free radicals arising as a result of the thermal dissociation of the bond at the most active site of the molecule. Depending on their reactivity, these aromatic free radicals can either condense with loss of hydrogen into large aromatic fragments or can undergo an internal rearrangement. If the intermediate free radical products have a planar configuration, then the carbonisation of the compound proceeds via the mesophase transformation and high-temperature treatment yields ordered graphite; on the other hand, when non-planar radicals are formed, the formation of the mesophase is not observed and the subsequent graphitisation is unsatisfactory.

Evans and Marsh [20] observed by mass-spectrometric measurements that the principal component of the carbonisation products at 405–500°C (the region of the mesophase transformation) is decacyclene, while at higher temperatures molecules with zethrene configuration begin to predominate. The molecules of both types are planar (in the decacyclene molecule the acenaphthylene units are inclined at an angle of 3° with respect to the plane) and their further condensation leads to the formation of large planar structures capable of an ordered arrangement to give the liquid crystals of the mesophase.

The mechanism of the carbonisation of anthracene, phenanthrene, and naphthacene is simpler and consists in the formation of dimers and trimers, which are capable, by virtue of their configuration, of giving rise to large planar structures, ensuring the formation of ordered graphite.

Extremely interesting results were obtained in a study of the products of the carbonisation of acenaphthylene at 625°C, i.e. after the completion of the mesophase transformation [20]. In order to investigate spectrometrically this high-molecular-weight involatile compound, it was subjected to hydrogenolysis by atomic hydrogen. The material treated in this way gave rise to a mass spectrum which contained peaks due to acenaphthylene, zethrene, decacyclene, acenaphthene, and zethrene dimers, whose intensities corresponded to their abundance. These results show that the carbonisation of acenaphthylene proceeds via identical condensation reactions over the entire region of the mesophase transformation.

The mass-spectrometric and elemental analytical data demonstrated only a slight difference between the compositions of the mesophase and the isotropic material from which it arises. On the basis of the results, the authors [20] concluded that the formation of the mesophase consists in the ordering of the molecules of the isotropic phase and not in the formation of other chemical structures.

In the coking of hydrocarbon raw materials of complex composition (pitches and resins) from which industrial coke is obtained, the chemistry of the processes is complicated by the factors mentioned above, but in the region of the mesophase transformation the fundamental nature of the chemical reactions and the physicochemical processes is the same as in the carbonisation of the individual hydrocarbons.

At the beginning of the mesophase transformation, the substances present in pitches largely consist of polynuclear hydrocarbons and certain nitrogen and oxygen compounds. The ^1H NMR spectrum of the soluble fractions from which the mesophase is formed shows that more than 90% of the protons are linked to aromatic rings [14,18]. The average molecular weight of these fractions is 390–450; a stronger absorption is observed in the ultraviolet spectrum in the range between 370 and 450 nm.

Under carbonisation conditions, these compounds decompose via a radical mechanism with evolution of an insignificant amount of hydrogen and subsequent formation of more complex coplanar regions.

The results of elemental analysis of the partly carbonised pitch ($C_{100}H_{53}O$) differ little from the results of the analysis of the insoluble mesophase residue ($C_{100}H_{49}O_{1.4}$), but their average molecular weights differ significantly, amounting respectively to 790 and 1700. [4,5]

Ihnatowicz et al. [5] believe that the insolubility of the mesophase and its higher density compared with the pitch (1.48 and 1.25 g cm^{-3} respectively) are a direct consequence of the fact that the mesophase consists of more highly polycondensed molecules.

Honda et al. [12] found by X-ray diffraction analysis and by measuring a number of physical properties of pitch specimens as a function of the carbonisation temperature and time that the activation energy for the processes occurring in the region of the mesophase transformation is 35–45 kcal $mole^{-1}$. According to the authors, the growth of the spherical particles of the mesophase is due to a rearrangement of the C–C bonds and the evaporisation of low-molecular-weight substances.

Magaril and coworkers [21,22] obtained similar results. They investigated by infrared spectroscopy, ESR, elemental analysis, and measurements of the molecular weights and densities the intermediates in the carbonisation of petroleum tars and asphaltenes at 350°, 390°, and 410°C in solution

in transformer oil. The molecular weight of the asphaltenes (the benzene-soluble fraction), determined cryoscopically in naphthalene, was 940 and the molecular weights of carbenes (the fraction evolved from coke on extraction with carbon disulphide after the removal of benzene-soluble substances), determined osmometrically in carbon disulphide, were 135 600, 122 100, and 117 000 respectively at 360°, 390°, and 410°C. The authors concluded on the basis of ESR and infrared spectroscopic data that asphaltenes, carbenes, and carboids are substances of the same type. The fundamental difference between carbenes and asphaltenes is only a much higher (by two orders of magnitude) average molecular weight of carbenes and the difference between carboids and carbenes is insolubility of the former. The carboids may be insoluble, according to the authors, because their molecular weight is still higher than that of carbenes or because (and this appears much more likely) carboids are cross-linked three-dimensional polymers. It is noteworthy that the above study quotes molecular weights of substances soluble in carbon disulphide higher by almost two orders of magnitudes than the values given elsewhere [3-5,13].

The formation of coke in the thermal decomposition of asphaltenes is represented [22] as a chain process leading simultaneously to the formation of relatively low-molecular-weight products, carbenes, and carboids. The process activation energy obtained from experimental data is 58–60 kcal mole^{-1}, which corresponds to the dissociation energy of the weakest C–C bond in the asphaltene molecule.

The mesophase transformation usually takes place in the temperature range between 400° and 500°C. The conclusion that the same reactions take place over the entire temperature range was reached by Evans and Marsh [20] on the basis of mass-spectrometric data, by Ihnatowicz et al. [5], who demonstrated the constancy of the density of the mesophase and the pitch coexisting with the latter, by Huttinger [6] on the basis of the constancy of the H/C ratio for the mesophase, and by Magiril and Aksenova [22] on the basis of the constant yield of coke relative to the asphaltenes which have reacted and of the reaction rate constant.

Fialkov and coworkers [13,24] and Tyan [25] arrived at a similar conclusion. It has been established by ESR and microscopic methods that, in the range 400–450°C, i.e. from the instant of the generation of the spherolites until the complete conversion of the pitch into the mesophase, the concentration of the free radicals, the line width between the maxima of the derivative ESR absorption line, and the spin–lattice relaxation times remain unchanged, while below and above the limits of this range these characteristics change significantly. The authors concluded that the intramolecular structure of the mesophase responsible for the ESR signal does not change in the range 400–450°C and the formation of the mesophase is due to the increase of the size of the carbon network as a result of thermal degradation and the formation of new C–C bonds.

Thus it may be regarded as established, on the basis of comprehensive studies of the low-temperature carbonisation processes of individual hydrocarbons and their complex mixtures (pitches and tars), that the mesophase transformation involves the ordering of large planar aromatic molecules with formation of nematic liquid crystals accompanied by further condensation with slight losses of hydrogen. As a result of this, the mesophase becomes insoluble. The liquid crystal molecules are formed by reactions involving the thermal dissociation of bonds at the most active site in the molecules and condensation of the resulting free radicals to a large planar aromatic structure.

III. FACTORS INFLUENCING THE MESOPHASE TRANSFORMATION AND THE STRUCTURE OF COKE

The structure of coke is wholly determined by a process involving the generation, growth, and coalescence of the mesophase spheres and the subsequent deformation of the coalesced mesophase on swelling. The study of the factors influencing such processes and of their mechanism is therefore of enormous importance for the solution of the problem of the regulation of the growth of different types of coke.

1. The Coking Conditions

The principal factors influencing the generation and growth of the spheres are temperature and time [3-6,13,16]. There is a limiting temperature below which spheres are not generated even after very prolonged treatment. With increase of the duration of isothermal treatment, a large amount of the pitch is converted into the mesophase, but the time dependence of the increased conversion is asymptotic. At a higher temperature, much less time is needed for the attainment of the specified degree of conversion and the latter is determined solely by temperature. Honda et al. [13] showed that temperature and time are adequate process parameters in the range 390–430°C as regards their influence on the degree of conversion and the properties of the mesophase.

The temperature–time parameters can be used effectively to regulate the structure and properties of coke. Isothermal treatment in the temperature range of the mesophase transformation leads to the formation of coke with a more ordered structure [23]. At the same time there is a significant increase (by 5–8%) in the yield of coke [23,26]. The increase of the rate of coking does not affect the temperature of the onset of the formation of the mesophase, but significantly displaces towards higher temperatures the instant at which the transformation ends, extending thereby the temperature range of the transformation. According to Ihnatowicz et al. [5], a change in the rate of heating of coal pitch from 0.5 to 3 K min^{-1} increases the temperature at which the mesophase transformation is completed by 55 K. At a higher rate of carbonisation, smaller spheres and coke with a mosaic structure are formed. These structural changes are associated with the fact that, when the temperature range of the transformation is displaced towards higher temperatures, there is also an increase in the rate of formation of mesophase nuclei and there is insufficient time for the complete coalescence of the growing spheres.

2. The Composition of the Coking Raw Material

When the influence of the composition of the raw material on the structure of the coke obtained is examined, account must be taken of two aspects—the genetic relation between the structure formed and the composition of the raw material [1,27] and the mutual influence of the components during coking [1,20,28]. The role of the insoluble fractions present in the raw material will be discussed below. The hypothesis that definite components of the raw material are responsible for the formation of a particular type of coke structure [1,27] must be regarded as an exaggeration. The mutual influence of the components is most likely to affect the formation of the structure.

In mass-spectrometric studies of the carbonisation of mixtures of individual aromatic hydrocarbons, intermolecular reactions were not observed, but a decrease of the degree of pyrolysis of the individual components was noted[20]. According to the authors, the latter effect may be a result of the decrease in the intensity of the condensation reactions owing to the mutual dilution of the mixture by the components.

Levinter et al.[28] observed a decrease of the yield of coke in the simultaneous coking of asphaltenes and oils compared with the coking of asphaltenes alone. As a result of the mutual influence of the components, such a mixture behaves during coking as a single group component with intermediate properties. The capacity for graphitisation of the coke derived from asphaltenes alone is poorer than that of the coke obtained from the mixture. Levinter et al.[28] reached the conclusion (similar to that of Lewis and Singer[19]) that dilution of asphaltenes by oils decreases the rate of formation and growth of coke "crystallites", which favours an increase in the degree of order of the coke structure.

In a study of the kinetics of coke formation, Magaril[29] also concluded that there is a relation between the differences in the kinetics and the amounts of coke formed and the differences in the properties of the solvent used in the coking of asphaltenes. The addition to a poor solvent for asphaltenes of an effective solvent lowers the yield of coke, while in the decomposition of asphaltenes in an effective solvent coke formation begins only after the attainment of a threshold concentration. The authors explained their latter finding by the solvation of asphaltenes, preventing their condensation and the onset of coke formation.

The presence in the raw material of certain chemical elements, particularly oxygen, sulphur, and nitrogen, plays an important role in the coking process. In pitch, they usually form part of heterocyclic compounds. During pyrolysis, the presence of the above elements promote, on the one hand, dehydrocondensation accompanied by the formation of partly stable intermediate products and, on the other, the formation of cross links[30,31]. The appearance of such links at the early stages of aromatic condensation leads to the formation of rigid carbon with an extremely non-ordered structure. The formation of cross links and of a three-dimensional network at later stages gives rise to the formation of a highly condensed aromatic system. When the raw material contains halogen atoms (Cl, Br), the thermal stability of the compounds falls, since the energy of the C–Cl and C–Br bonds is smaller than that of the C–C and C–H bonds. Owing to their high affinity for hydrogen, fluorine and chlorine act like dehydrogenating agents[30].

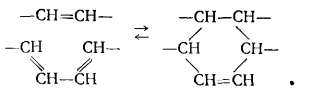
The influence of oxygen and sulphur on the mesophase transformation has been most thoroughly investigated. Ihnatowicz et al.[5] and also Tyan[25] established that the presence of more than 7% of oxygen in the raw material leads to the complete suppression of the mesophase transformation and to the formation of non-graphitising coke. When the oxygen content is less than 5%, the structure differs little from that of the usual graphitisable coke. Oxygen greatly narrows the temperature range of the mesophase transformation by reducing the temperature of its completion. When the oxygen content is 5–7%, coke with a pseudoisotropic structure is obtained. Sulphur has a similar influence on the mesophase transformation[31]. The presence of a small amount of sulphur does not cause appreciable changes in the properties of the mesophase, but, when its content exceeds a limiting concentration, for example 5% for PVC pitch, the fluidity of the mesophase and the temperature determining the limit of its plastic state decrease sharply. When the sulphur content is between 5 and 8%, fine spheres and a two-phase structure are formed. The presence of more than 8% of sulphur leads to the formation of an isotropic structure.

Kipling et al.[31] explain the effect of sulphur by the formation of cross links at the early stages of pyrolysis. They suggest the possibility of a catalytic effect of sulphur. It is postulated that the principal function of sulphur is to increase the degree of unsaturation of the molecules of the initial material:

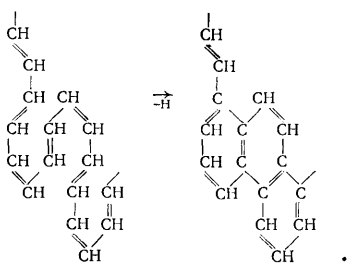
$$-CH_2-CH_2- + S \rightarrow -CH=CH- + H_2S\ .$$

The polyenes formed undergo Diels–Alder condensation reactions, which may be accompanied by dehydrogenation:

(a) intermolecular condensation:



(b) intramolecular condensation:



At a fairly high temperature, one may expect that aromatisation will take place with elimination of hydrocarbons and hydrogen, which combines with sulphur to give hydrogen sulphide.

The reaction of sulphur with the free radicals produced in the pyrolytic process results in the incorporation of a certain amount of sulphur in the resulting structure:

$$\rangle\dot{C}H + S_n \rightarrow \rangle CH-\dot{S}_n\ ;$$
$$\rangle CH-\dot{S}_n + \dot{C}H\langle \rightarrow \rangle CH-S_n-CH\langle\ .$$

The radical formed, being comparatively long-lived, can react with other hydrocarbon radicals, forming cross links, which prevent the mutual orientation of the molecules.

It has been noted[15] that, despite the wide variety and complexity of the pyrolytic reactions, they can be characterised by the structure formed as a result of the coalescence of the mesophase spheres. Microstructure studies on different types of semicoke derived from starting materials with different contents of heteroatoms demonstrated a decrease in the size of the mesophase spheres with increase of the sulphur content. This finding can be accounted for by the increase viscosity of the mesophase due to the formation of cross links at early

stages of the pyrolysis. The influence of increasing viscosity has also been noted by Kipling et al.[31]; the increase in viscosity complicates the reorientation of the molecules in the liquid stage.

3. The Influence of Additives

The influence of various additives on the coking processes has been investigated in many studies. All the additives employed can be divided, in terms of the nature of their activity, into chemically active, catalytic, and plasticising[32].

The most common way in which the properties of the coking raw material are affected is by oxidation with atmospheric oxygen or various chemical agents. When oxygen is passed through the starting material, peroxides are usually obtained in the first instance and are then converted into stable compounds on subsequent decomposition. The decomposition of peroxides may result in the formation of cross links leading to the formation of a rigid carbon structure[30]. The role of oxygen probably reduces to the initiation of the condensation and polymerisation reactions of multicomponent aromatic compounds present in the pitch owing to the formation of free radicals during oxidative dehydrogenation. The radicals can give rise to peroxide compounds, which initiate the subsequent process and also interact with one another, forming molecules capable of further growth[32].

Various substances are used to initiate the oxidation reactions. Variable-valence metal salts are familiar catalysts and the mechanism of their action has been investigated in detail[33-36]. The valence of the metal changes during the process and free radicals are formed, probably as a result of the direct involvement of the catalyst in the reaction between oxygen and the hydrocarbon. The role of the catalyst reduces to initiating the oxidation reaction in the initial stage of its development, which ensures as high a rate of chain initiation. However, Denisov[35] suggested the involvement of the catalyst also in the chain propagation processes, assuming that the catalysis takes place throughout the reaction via a sequence of macroscopic stages and not via a single mechanism. Peroxy- and azo-compounds are frequently used as initiators. Gas-phase initiation, where nitrogen dioxide produces the maximum effect, has been employed.

Apart from passing air through the starting material, many different oxidising additives are used; the influence of any of these can be accounted for by its effect on dehydrogenation and polycondensation processes. Sulphur is an agent closest to oxygen as regards its action. A mechanism has been put forward for its interaction[30]. When sulphur is added, the dehydrogenation temperature falls, and and, in addition, sulphurisation leads to aromatisation. The hydrogen liberated combines to form H_2S. Kipling et al.[31] made a detailed study of the mechanism of the catalytic action of sulphur present in the starting material. When sulphur is introduced at later stages of the pyrolysis, its role is to the dehydrogenation and aromatisation processes. In practice, when the pitch is treated jointly with sulphur and air, the carbonisation process is accelerated. The influence of aluminium chloride has been considered in a number of investigations[30,32,37]. Its catalytic action is probably based on the formation of intermediate complexes of the catalyst and the reactants.

Fitzer et al.[30], who investigated the influence of anhydrous $AlCl_3$ on the pyrolysis of different types of pitch, concluded that small amounts of the catalyst (0.1–0.5%) produce appreciable changes when the electron density in the aromatic ring is increased, for example by the presence of phenolic groups. Such compounds are always present in pitch. The favourable influence of the introduction of nitro-groups (NO_2) has been noted[38,39], the oxidative dehydrogenation of pitch being promoted. Such treatment of pitch is useful in connection with the reactivity of the nitro-group in dehydrogenation reactions and with its initiating effect on hydrocarbon oxidation processes[32].

The influence of boric acid and ammonium sulphate on the coking of petroleum residues has been examined[37]. It is suggested that these substances dissociate at 140° and 330°C respectively and promote the oxidative condensation of hydrocarbons of comparatively low molecular weights.

The influence of metals on coke formation in catalytic cracking is also noteworthy. Masagunov and Tikhanovskaya[40] concluded that the influence of the metal on coke formation depends on its dehydrogenating activity. Highly dehydrogenating metals (nickel, copper, and cobalt) lead to a sharp increase of coke formation even when their content is negligible.

Demidova[32] examined the influence of various types of additives, both chemically active (aluminium, bismuth, and potassium nitrates) and catalytic (finely dispersed nickel powder), directly on the mesophase transformation. The addition of aluminium, bismuth, and potassium nitrate increases the coking capacity as a result of condensation processes leading to the preferential growth of the content of carboids. The addition of finely dispersed nickel increases coke formation owing to the intensification of the dehydrogenation reactions of the low-molecular-weight compounds in the pitch in the range 200–300°C.

ESR and differential thermal analysis (DTA) data have shown that thermal degradation and the formation of the polymer structure of semicoke in modified types of pitch occur at lower temperature. Demidova[32] suggests that the formation of the semicoke structure in the modified pitch is completed at an earlier stage than in the initial pitch, as a result of the initiation of dehydropolycondensation processes mainly by the solid oxides derived from the decomposed metal nitrates. The introduction of condensing and catalytic dehydrogenating additives also promotes the initiation of the formation of mesophase spheres at 410°C. Mainly fine spheres are formed in the presence of additives. According to the author, the formation of the spheres and the limitation of their growth in pitch with added nitrates occur either in consequence of the shielding of their surface by the solid phase of the additive or because of the multiplicity of crystallisation centres, which may consist of finely dispersed oxides produced from the decomposed nitrates.

The decrease in the size of the spheres during oxidation was also noted by Averina[41], the increase in the number of spherical particles and the decrease of their dominant size being promoted by the increase of temperature and the rate of oxidation. An appreciable increase of the number of nuclei of the mesophase particles in the oxidised starting material was observed following the addition of catalysts, particularly iron(II) oxalate. According to the author, the catalyst prevents the coalescence of the mesophase particles, which leads to the formation of a fine-grained structure.

Oxygen and sulphur also increase the viscosity and the period of the mesophase transformation[15,31]. Kipling et al.[31] assume that the increase of viscosity, due to the increase of the degree of cross-linking of the molecules, complicates their reorientation and the formation of an ordered structure.

4. The Influence of Dispersed Additives; Mechanical and Other Influences

The influence of dispersed additives on crystallisation of high-molecular-weight compounds from the melt is generally known and is widely used to modify their structure. These additives are usually nucleus-forming agents and are present in the centres of the growing spherolites [42].

Brooks and Taylor [3] investigated the influence of various dispersed insoluble additives on the mesophase transformation and the structure of coke. They found that any solid surface constitutes the preferred site for the formation of the mesophase, but, in contrast to the crystallisation of polymers, dispersed additives remain on the surface and are never detected within the growing mesophase spheres (see Fig. 1). This factor significantly restricts the scope of the regulation of the structure and complicates the process. Because of this, the influence of dispersed particles on structure formation in carbonisation must be treated not only from the standpoint of the formation of nuclei but also taking into account their behaviour at the mesophase–pitch interface. Dispersed particles are almost always present in the starting materials from which coke is obtained. They differ significantly in structure and their behaviour in the coking process is likewise different [6,7,43,44].

Sedimentation of the dispersed components of pitch during its conversion into coke leads to large structural inhomogeneities along the height of the coke "pie" [6,44-46]. Numerous point structures, consisting of aggregates of the dispersed components of pitch, are observed in its lower part. The smallest particles remaining in the pitch at the instant of the onset of the mesophase transformation are distributed non-uniformly. After the appearance of the mesophase, they collect on the surface of the spheres and prevent their growth by depriving them of the ability to coalesce (Fig. 3). [16] The pitch phase is then liberated from the dispersed particles and the new spheres formed in it grow to a much greater size via coalescence. As a result, when the pitch is fully converted into the mesophase, the fine spheres blocked by the dispersed particles give rise to mosaic structures and the large spheres give rise to acicular, fibrous, streaming, or oriented structures (the differences between them are merely a matter of terminology).

The structure of coke obtained from starting materials containing dispersed particles is extremely inhomogeneous. In most cases where a readily graphitising coke is required with a homogeneous acicular or layer structure, one endeavours to liberate the fused pitch from the dispersed component with the aid of various technological procedures (filtration, centrifugation, etc.) [47,48]. It is also possible to obtain a homogeneous mosaic structure by introducing dispersed additives, which form a three-dimensional coagulation network throughout the bulk of the material and prevent the coalescence of the spheres [49].

Compact coagulation in the pitch phase, which is usually characteristic of the dispersed component of pyrolytic tars, leads to the formation of aggregates in the form of grains, whose size ranging from 0.5 to 5 mm upwards, known in the literature [43,46] as spherulitic structures. As a result of partial sedimentation, the content of spherulitic structures increases at the bottom of the coke "pie". When the viscosity of the pitch phase is fairly high, for example in the coking of the oxidised residues, the spherulites remain distributed throughout the bulk of the coke [44]. The dispersed components of the starting material, distributed in the main bulk of the coke, have the greatest influence on its properties. Thus insoluble dispersed particles play a very important role in the formation of the structure of coke and can be used to control it.

Apart from the factors described above, mention should be made of the effect of mechanical influences and the magnetic field on the structure of the mesophase. Simple stirring of the coke material at the stage of the mesophase transformation improves the coalescence of the spheres and rotary stirring, apart from intensifying coalescence, gives rise to a coaxial orientation of the aromatic layers in the coalesced mesophase and leads to the formation of textured coke [3,4].

The application of a 6.0 kG magnetic field for 1.5 h during the mesophase transformation causes the orientation of the *C*-axes of the spheres parallel to one another and to the direction of the magnetic field. Sanada et al. [50] suggest that such orientation of the spheres is caused by the forces arising from the effect of the magnetic field on the magnetically anisotropic polycondensed aromatic molecules in the spheres. These forces have been estimated approximately as 1–3 dyn g^{-1} from measurements of the magnetic susceptibility. The coalescence of the spheres results in an oriented mesophase, but defects are observed in the arrangement thus produced. According to the author, the forces generated by the magnetic field applied in the coalescence stage are too low to form a defect-free structure.

A specific type of mechanical influence on the coalesced mesophase of gaseous coking products plays a very important role in the formation of the coke structure. It is known [1,51] that the maximum rate of gas evolution in the coking process is observed at the temperature corresponding to the end of the mesophase transformation. Since the mesophase has a much higher viscosity than the pitch phase, it prevents free gas evolution and swells under the pressure of the gases evolved. During swelling, the volume of the coking mass increases by a factor of 4–9 [1] and its very rapid solidification, the mechanism of which has not so far been investigated, takes place. After swelling, the coalesced mesophase consists of a porous material with a spongy structure.

During the swelling process, the mesophase matrix is extended and deformed and its constituent layer structures are oriented in the direction in which the stretching stresses are applied. The mesophase is deformed most markedly at the sites which have become the walls between the pores and to a lesser extent at the functions of several walls. The layers of the mesophase are oriented along the walls, forming a texture within the limits of each. The instant at which swelling comes to an end and mesophase solidifies can be regarded from the morphological point of view as the instant of the termination of the formation of the coke structure. Intra- and inter-molecular rearrangement processes occurring on further increase of temperature do not have an appreciable influence on the structure.

Among the factors discussed above, influencing the mesophase transformation, the following have found the most extensive practical applications: regulation of the behaviour of the dispersed components of the starting material, isothermal treatment in the temperature range of the mesophase transformation, oxidation of the starting material at a temperature below the onset of the mesophase transformation. The first two factors are usually employed to obtain anisotropic types of coke with a distinct oriented layer structure, which are readily converted into graphite and have a high electrical conductivity and reactivity. For this purpose, the coking starting material is freed from solid particles at a temperature below the onset of the

mesophase transformation by filtration, centrifugation, or by being allowed to stand[47,48]. Oxidation of the starting material is used to obtain coke with isotropic properties[41].

IV. STRUCTURAL CHARACTERISTICS OF VARIOUS TYPES OF COKE

The structures of all types of graphitising coke are based on layer structural elements formed in the stages of the mesophase transformation and on subsequent deformation during the swelling of the mesophase. In this sense, the structure of each type of coke can be fully described by the dimensions and nature of the relative disposition of these structural elements[41]. Furthermore, different industrial types of coke have structural features, which are wholly determined by the composition and properties of the starting material from which they are obtained, mainly by its content of insoluble substances, its reactivity, and the degree of its oxidation[1,16,41,43,45,46].

There is as yet no established terminology in the literature for the structure of coke. This is because studies on the structure of coke have been carried out for a long time without understanding the mechanism of its formation. For this reason, the apparent wide variety of structures could not be treated systematically and each investigator, concentrating attention on a particular aspect of the same layer structure, characterised it by a specific terminology based mainly on morphological considerations. Thus terms such as acicular[47,48], fibrous[45,52], and streaming[41,43] structures arose to characterise sections of the mesophase structure with layers oriented in the direction of stretching on swelling. Much attention has been given to problems of terminology in a study by Averina[41]. Some of the morphological terms and the associated errors have been criticised[16,46], but this problem is outside the scope of the present review.

The following concepts can be used to characterise the structure of coke. The structure of coke is understood as the collection of all the structural elements and their combinations which are encountered within coke. The structure can be simple or complex depending on whether it consists of one or several types of structural elements; it can be homogeneous or inhomogeneous depending on whether the elements are of equal size and have the same orientation and on whether or not their distribution in the bulk phase is uniform. When structural elements of a single type form accumulations in a complex structure in the form of grains or other aggregates, then regions with a structure of the same type are usually referred to as structural components. Finally, a structural element is understood as a morphological unit with optically definable boundaries, characterised by a particular shape and internal structure.

The formation of coke with a specified structure and properties by active interference with the coke formation process has not yet been developed widely on an industrial scale and this is why industry produces a limited range of types of coke, the structure and properties of which are wholely determined by the type of raw material used in the coking process. The starting materials for the preparation of graphitising coke are the heavy residues from petroleum processing and the products of the processing of the tars resulting from the coking of coal and bituminous shale[1,41,51]. The temperature conditions in the prepration of the coking raw material have a definite influence on the structure of coke. Accordingly, all kinds of raw material can be divided into three types[41]: low-temperature raw material—the cracking residue obtained at 500–600°C and virtually free from solid particles; moderate-temperature raw material—the pyrolysis tars obtained at 650–800°C and containing different amounts of 0.5–4 μm solid spherical particles with a radial ray internal structure; high-temperature raw material—coking tars obtained at 800°C and above and containing solid soot particles smaller than 0.1 μm. The insoluble dispersed components of the raw material are the basic cause of the formation of the complex and inhomogeneous structure of coke[16,41-46]. Certain characteristics of the different types of raw material, based on the data published by Krasyukov[1] and Stepanenko et al.[51], are presented in Table 1.

Table 1. Characteristics of different types of coking raw material.

Parameter	Cracking residue	Pyrolytic tars		Coal tar pitch
		mild regime	severe regime	
Density, g cm^{-3}	0.94	1.12	1.17	1.33
"Ring and sphere" softening temperature, °C	liquid	liquid	liquid	145
Group composition, wt.%	74	82	66.5	28
Tar malthenes	21	9.8	8.7	
Asphaltenes	5	7.1	12.3	24
Carboids	0.3	1.0	12.5	48
Sulphur content, %	0.4	0.5	0.5	0.7
Coking number, %	9.0	18.1	30.4	74.0

The temperature of the processes in which the coking raw material is obtained determines not only its content of dispersed components and their structure[41,44] but also its reactivity and a number of other properties[1] influencing its behaviour in coking and the structure of the coke obtained.

We shall now consider the structural characteristics of the commonest industrial types of coke. The petroleum-cracking electrode coke (PCEC) is obtained by the coking in stills of a low-temperature raw material–the petroleum cracking residues[1]. This coke has the simplest and most, homogeneous structure among all industrial types of coke, consisting only of lamellar structural elements, forming sections of a structure with a parallel orientation in the walls between the pores and sections with a randomly oriented structure at the junctions of several walls (Fig. 3). The formation of a simple structure is ensured by the absence from the coking material of dispersed components and the only structural inhomogeneity is the orientation inhomogeneity, unavoidable in coking within the bulk of any raw material and associated with the inhomogeneous deformation of the coalesced mesophase on swelling.

Petroleum pyrolytic coke is obtained by the coking in stills of a moderate-temperature raw material—pyrolytic tars[1]. Depending on the pyrolysis temperature, tars corresponding to mild (650–700°C) and severe (750 to 800°C) regimes are distinguished. The mild regime tar is distinguished by a much higher content of carboids. The carboids in pyrolytic tars consist of solid spherical particles with a specific radial ray structure (Fig. 4), which are converted into the coke structure without a change in morphology[43]. For this reason, a characteristic feature of all pyrolytic types of coke is a layer structure consisting of two types of structural elements—spherical elements with a radial ray internal structure and lamellar

elements forming the base of the coke. The behaviour of the spherical particles in the coking of mild or severe regime pyrolytic tars is significantly different; this determines also the difference between the structures and properties of the corresponding types of coke.



Figure 3. Petroleum cracking electrode coke. Randomly oriented structure. Replica; magnification × 3500.



Figure 4. Spherulitic structural component of petroleum pyrolytic electrode coke. Replica; magnification × 7000.

The petroleum pyrolytic electrode coke (PPEC) is obtained from mild regime tars. In the coking of such tars, the spherulites coagulate with formation of dense aggregates in the form of grains whose size ranges from a fraction of a millimeter to 4–5 mm [43,46]. Such aggregation takes place until the onset of the mesophase transformation and for this reason the spherulites of the starting material do not have a significant influence on the growth of the mesophase spheres. As a result of aggregation, the spherulitic structural elements form the spherulitic structural component of the PPEC, which is usually located at the base of the coke or in the form of grains at the junctions of several interpore walls. The base of the coke, made up of the mesophase deformed on swelling, consists mainly of a larger structure with parallel orientation. Thus the PPEC structure can be characterised as complex and inhomogeneous, having spherulitic and lamellar structural components with parallel orientation (Fig. 5).

The special petroleum pyrolytic coke (SPPC) is obtained from severe regime tars. Despite the much higher content of sperulites in such tars, they do not coagulate on coking. Remaining uniformly distributed in the coking raw material, the dispersed spherulites prevent the growth and coalescence of the mesophase spheres. This factor and also the packing defects introduced by the spherulites into the structure on deformation of the mesophase matrix during the swelling process rule out the possibility of the formation of structures with parallel orientation. Because of this, SPPC has a complex relatively homogeneous structure consisting of a matrix comprising lamellar randomly oriented structural elements and filled by spherulitic structural elements. Such a structure is referred to [41] as impregnated-spherulitic. The spherical structural elements are sometimes encountered in the form of aggregates, but the latter do not form a clear-cut boundary with the rest of the matrix. The causes of the different types of behaviour of spherulites during the coking of mild and severe regime tars have not as yet been elucidated. It is suggested [41] that the absence of coagulation is associated with the lower reactivity and greater viscosity of the severe regime tars.



Figure 5. Petroleum pyrolytic electrode coke; magnification × 49.

The pitch electrode coke (PEC) is obtained from a high-temperature raw material—coal tar pitch. The starting material consists of coal tar pitch—a side product from the coking of coal containing, apart from various hydrocarbons, a fairly large amount of soot particles, formed in the coking furnace from gaseous coking products in the concluding stage of the process at temperatures of 900°C and above, and also very small solid particles consisting of certain components of coal. Coal tar is converted into pitch by oxidation, usually carried out by blowing hot air through the tar at 250–300°C. The purpose of the oxidation is further condensation and increase of the yield of coke. PEC has a complex inhomogeneous structure, the formation of which is determined mainly by the behaviour of the soot particles of the raw material in the mesophase transformation stage [16]. The partial sedimentation and aggregation of the largest particles lead to the formation of the so called point structural components (Fig. 6). The smallest of these also remain distributed in the pitch at the instant of the formation of the two liquid phases evolved from it on the surface of the growing mesophase spheres,

blocking their growth and preventing their mutual orientation and coalescence. The distributed particles significantly increase the proportion of defects in the lamellar structural component of the pitch coke (Fig. 7).



Figure 6. The point structural component of pitch electrode coke. Replica; magnification × 7000.



Figure 7. Pitch electrode coke; magnification × 350.

Different types of shale coke, obtained from the heavy residues remaining after the processing of bituminous shale, have been used increasingly in recent years in the manufacture of carbon-graphite materials. Depending on the purpose of the processing (the formation of petrol, gaseous hydrocarbons, etc.) and its temperature, the residues obtained differ significantly in composition and properties, which determines the wide variety of structures and properties of shale coke [43]. Thus the shale coke from the pyrolytic tars of shale petrol has a structure analogous to that of PPEC, while the structure of the coke from the "gas" tar is analogous to that of PCEC.

Table 2 presents some of the properties of industrial types of coke in accordance with the USSR Government Standards GOST 3278-62 and GOST 3213-58 as well as other data [1,41,45]. Ultimately, almost all the properties of coke are determined by the degree of development of structural anisotropy, arising at the mesophase transformation stage, and by the structural characteristics associated with the dispersed components of the coking raw material. In terms of increasing anisotropy, the types of coke described above can be arranged in the following sequence [41]: PEC < SPPC < PPEC < PCEC. The density of coke is associated directly with the structural anisotropy: the smaller the degree of development of anisotropy the lower the density (Table 2).

Table 2. Characteristics of certain types of coke.

Parameter		PCEC	Streaming component	Spherulitic component	SPPC	PEC
Pyknometric density, g cm^{-3}	1300°	2.10	2.08	2.02	2.04—2.08	2.085
	2400°	—	2.26	2.20	2.19	2.23
Graphitisability d_{002}, Å		3.364	3 369	3.385	3.388	3.380
Degree of graphitisation, %		—	54 5	36.5	70	—
Porosity, % (1300°C)		67—69	64—65		—	55—57
Press characteristics						
Relaxation coefficient, %		—	5.2	8.1	15.2	—
Coefficient of elastic expansion, %		10.4	14	6.7	8.4	7.3
Microhardness, kgf mm^{-2}	1300°	115	124	195	180	180
	2400°	7.2	10.5	30.2	21.5	13.6
Susceptibility to wear, %		6.0	10.5		6.4	8.0
Compressive strength	1300°	—	48		65	—
	2400°	—	16—44		38—43	—
Reactivity						
Oxidation in air						
	crude	97.0	92	—	—	—
	1300°	17.0	2.0	—	—	—
	2400°	0.10	0.17	0.32	—	—
Reduction in a stream of CO_2						
	crude	77.8	9.7		—	16.9
	1300°	17.0	7.5		—	6.0
	2400°	4.8	4.9		—	—

The decrease of the anisotropy of coke is a result of the comminution of the mesophase spheres during coking or of the oxidation of the coking raw material (PEC) or it occurs under the influence of the dispersed components (PEC, SPPC, PPEC). The latter cause the greatest decrease of density when they remain distributed within the bulk of the coke, as, for example, in PEC and SPPC. In this case, the decrease of the density of coke is associated not only with packing defects at the boundaries of the former mesophase spheres but also with the structural defects, which arise at the boundaries between the dispersed particles and the mesophase at the instant of the deformation of the latter on swelling. These defects consist of wedge-shaped pores, apparently mostly closed pores, since they arise as a result of the breakdown of continuity in the microvolume on deformation and not as a result of gas evolution; the pore size depends on the size of the dispersed inclusions. For example, the density of SPPC with 0.5–4.0 μm dispersed particles is significantly lower than the density of PEC with dispersed particles whose size is less than 0.1 μm.

Structural anisotropy is closely related to the capacity of coke for graphitisation (their capacity for conversion into graphite at temperatures above 2300°C), which

determines in its turn very many properties, for example electrical conductivity, strength, reactivity, and antifriction properties. The conditions necessary for a satisfactory graphitisability, first formulated by Franklin[53], involve a mutually parallel orientation of crystallites and the absence of cross links between the aromatic layers at the edges of the crystallites.

The oxidation of the coking raw material at a temperature below the range of the mesophase transformation has the strongest influence on the graphitisability of coke. Oxidation immediately impairs both conditions for satisfactory graphitisability, since, together with the comminution of the mesophase spheres and the sharp decrease of anisotropy, cross links are formed in the oxidation process between the aromatic layers in the form of oxygen bridges. The dispersed components of the raw material affect only the first condition for graphitisability.

Among the types of coke described above, PEC graphitises least satisfactorily, since it is obtained from the types of pitch described above which contain a large amount of dispersed components, while PCEC graphitises most satisfactorily.

Structural anisotropy and the properties associated with it determine to a large extent the technological behaviour of coke and the properties of the articles made from it.

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The advances in recent years in the understanding of the mechanism of structure formation of graphitising coke have served as a basis for the development of new methods for the preparation of coke with a specified structure and properties. The development of a new class of one-component carbon-graphite materials, the so called "mesophase carbons" with a regulated structure and properties, is being prosecuted at the present time on the basis of the above advances. At the same time, vigorous research is being continued on the structure and properties of mesophase products of different origins and also on the synthesis of new substances, the heat treatment of which results in the formation of a mesophase with the required properties and capable of being converted into carbon on subsequent carbonisation without a significant change in structure. Further study of the mechanism of the mesophase transformation and of the formation of the structure of graphitising coke is one of the fundamental trends in the chemical technology of carbon and the science of carbon-graphite materials.

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