Carbonization and Graphitization of the Mesophase Separated from Coal Extract

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The coal extracts in the process of carbonization pass through a stage mesophase formation [1,2,3]. This stage plays an important role in the formation of structure susceptible to the ordering in the higher temperatures. It seemed to be advisable to examine properties and structure of the mesophase in different stages of its development.

In order to separate the mesophase from its mother isotropic liquid their various solubility in quinoline was used, defining the insoluble fraction in a boiling quinoline as mesophase.

Experimental

The anthracene oil extract from orthocoking coal /75°C softening temperature, 1,26% A^a, 66,4% V^{daf}, 89,5% C^{daf}, 5,6% H^{daf}/ was carbonized at temperatures 430, 440,450, 460, 475°C and from the obtained carbonization products the mesophase was separated. The mesophase yield determined in the process of extraction and microscopically, is presented in Fig. 1.

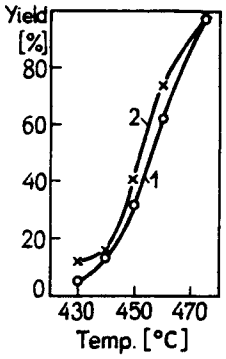


Fig. 1 The yield of the mesophase with extraction by quinoline-1, from microscopic analysis - 2

The development of the mesophase in the extract with the rise of carbonization temperature and also the picture of the separated mesophase, is presented in Fig. 2, while the physico-chemical properties of the mesophase in Fig. 3. The results of X-ray structural examination of the mesophase, are given in the Table 1.

Carbonization and Graphitization Processes of the Mesophase

The carbonization products of extract on various stage of mesophase transformation and the mesophases separated from them were carbonized at temperature 600°C and the obtained semicokes graphitized at temperature 3000°C.Distinct differencies in the behaviour of these two substances during heat treatment, were observed.

Table 1
Structural parameters of the separated mesophase

Sample N°	Temperature of carbonization °C	Interlayer distance d_{002} nm	Height of crystallites L_c nm
1	430	0,3469	2,20
2	440	0,3466	2,27
3	450	0,3466	2,39
4	460	0,3466	2,39
5	475	0,3466	2,96

Discussion

The extract from the orthocoking coal in the process of carbonization passes within 430-475°C through the stage of mesophase formation. The successive stage of mesophase transformation are strictly connected with the temperature of the process :

430°C - appearance of anisotropic mesophase spheres of 2-4 μm in diameters in the isotropic mass,

430-440°C - increase of spheres size /up to 15 μm/ at the expense of the isotropic mass, beginning of the coalescence,

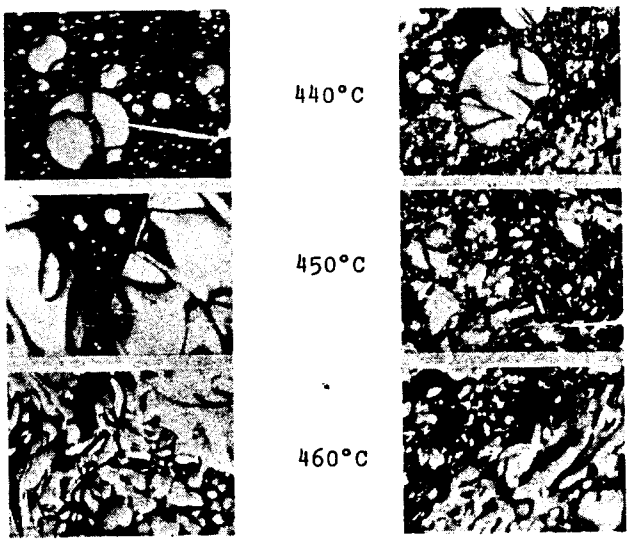
440-450°C - a further increase of sheres size /above 20 μm/, development of the coalescence, beginning of formation of larger anisotropic regions,

450-460°C - coalescence on larger surface, deformation of the mesophase,appearance of large anisotropic areas,

460-475°C - end of mesophase transformation, a total deformation of the mesophase in anisotropic structures /coarse, flow, leaves and domain/

The yield of the mesophase separated from carbonization products in the process of extraction with quinoline is lower than that determined microscopically, what shows that the mesophase forming compunds in the condition of extraction are partly dissolved. The extraction conditions caused the cracks and the destruction of single anisotropic forms, what maybe seen clearly in the mesophase texture.

With the rise of the temperature,the content of carbon in the mesophase increases,while the content of hydrogen decreases, but these are however negligible changes. In the lower temperatures the containing heteroatoms compounds



(a) (b)

Fig. 2 Microscopic photographs of the formation of the mesophase, a-carbons, b-separated mesophase /polarized light, ×250, nicols+/

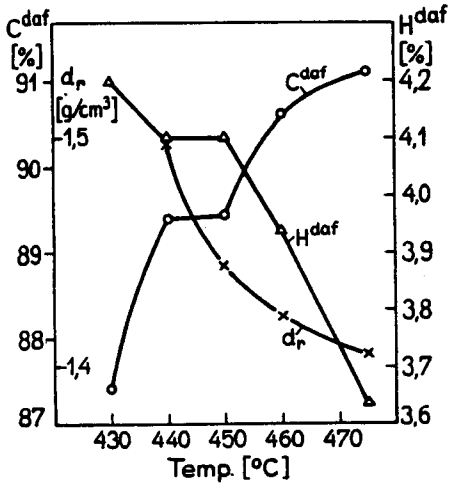
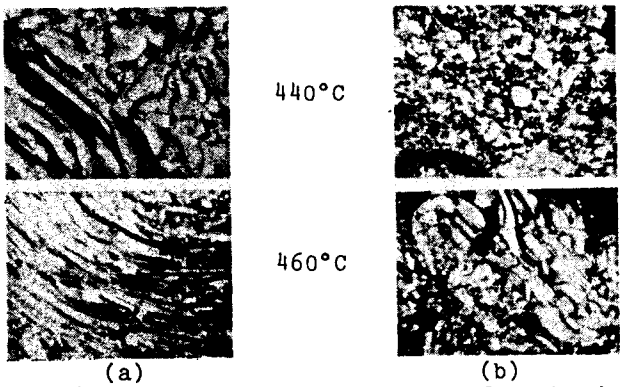


Fig. 3 Characteristics of the mesophase.

occuring in the extract, take part in the formation of the mesophase molecules, while in higher temperatures, they decompose partly.

The separated mesophase is characterized by a close structure, independently of the degree of mesophase transformation. In its composition, the condensed aromatic compounds in form of layers free from functional groups and



(a) (b)

Fig. 4 Microscopic photographs of carbonization products / 600° / a-carbons, b-mesophase /polarized light, ×250, nicols+/

long side chains occur. Heteroatoms - oxygen, nitrogen and sulphur occur in the condensed ring system and also as a bridges between aromatic layers. In the whole range of temperatures mesophase transformation, the mesophase structure does not change essentially.

The structure of the mesophase causes its high thermal resistance. The heated mesophase does not soften, and the obtained semicoke indicates the structure of its original substance, contrary to the carbonization products which are reactive and during heat treatment, they continue to change, giving semicoke characterized by a highly developed anisotropic structure /Fig. 4/.

The action of a high temperature, causes a distinct increase of the degree of mesophase structure ordering up to the formation of a three dimensional graphite structure, however, the degree of graphitization as well as the size of crystallites are lower than in the case of graphitization products of carbons from the extract /Table 2/.

The structural changes appearing in the heat temperature treatment of the coal extracts are connected not only with the formed mesophase, but also with medium in which the mesophase is formed.

References

1. Jasieńko, S., Świetlik U., 14th Biennial Conf. on Carbon, Pennsylvania State Univ. 1979 p. 383-385
2. Jasieńko S., Świetlik U., 15th Biennial Conf. on Carbon Philadelphia 1981 p. 210-213
3. Świetlik U., Jasieńko S., 6th Carbon and Graphite Conf. London 1982, p. 206-208

Table 2 Structural parameters of graphitization products /3000°C/

N°	Sample	Interlayer distance d_{002} nm	Height of crystallites L_c nm	Diameter of crystallites L_a nm	Degree of graphitization g	Density /in methanol/ d_r g/cm³
1	carbonization product 440°C	0,3370	78,6	87,4	0,82	2,237
2	mesophase	0,3376	48,2	59,3	0,74	-
3	carbonization product 450°C	0,3371	78,6	88,2	0,80	2,238
4	mesophase	0,3376	58,3	68,4	0,74	2,208
5	carbonization product 460°C	0,3369	80,1	89,9	0,83	2,238
6	mesophase	0,3377	58,3	76,9	0,73	2,209