

THE PROCESS OF CARBONIZATION AND GRAPHITIZATION OF PETROGRAPHIC COMPONENTS  
OF HARD COALS  
PART II. THE CHANGES OF PROPERTIES AND STRUCTURE OF COKES FROM PETROGRAPHIC  
COMPONENTS IN THE PROCESS OF GRAPHITIZATION

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The papers of Franklin [1], Blayden, Riley and Gibson [2], Jasienko and coworkers [3, 4, 5] have shown that the cokes obtained from hard coals may be divided into three groups of substances: non-graphitizing -cokes from low rank; graphitizing-cokes from coking coals; graphitizing at very high temperature-cokes from anthracites.

In the literature no investigations on the graphitization processes of cokes obtained from petrographic components were found.

The cokes obtained from petrographic components: exinites, micrinites and fusinites separated from hard coals of different rank /Part I/ have been subjected at 1500, 2000, 2500°C to the process of graphitization. The chemical properties and the structure of carbonization and graphitization products was examined.

Changes of chemical composition of the cokes in the process of graphitization

The mentioned changes takes place at different rates and their intensity and range depend on the kind of coke.

On high temperature treatment of cokes generally may distinguish the following stages: 1000-1500°C changes in the elemental composition leading to the formation of new structural elements, but with weak increase of their ordering; 1500-2000°C - ordering of structural elements within the planes, the formation of turbostratic structure; 2000-2500°C spacial ordering of the structure.

In the process of graphitization of the cokes of all the studied petrographic components, the changes of chemical nature have a very similar course. The highest intensity of these changes takes place up to 1500°C. In the graphitization products obtained at 1500°C the content of the C element is above 99.99%, 99.99-99.99%, the content of hydrogen ~0.2%. The sulphur components show a higher thermal resistance than those of carbon and hydrogen; their decomposition takes place with a variable intensity within particular temperature ranges up to 2500°C. In the products of graphitization obtained at 2000°C of cokes from fusinites and from exinites as well as from vitrinites of flame coal there is about the same content of sulphur /0.1%. Sulphur components of higher thermal resistance appear cokes from vitrinites of orthocoking coal, also meta/semicoking coal and anthracite.

The decomposition of mineral substance proceeds the easiest in the process of graphitization of cokes from fusinites, the slowliest in the cokes from exinites.

Changes of structure of cokes in the process of graphitization

**Microscopic Examinations.** The cokes of vitrinites from flame and gas-coking coals remain optically isotropic; the structure of coke of vitrinite from orthocoking coal in principle does not change; the cokes of vitrinite from meta/semicoking coal and vitrinite from anthracite show a strong increase of intensity optical anisotropy, mainly at 2000-2500°C.

In cokes of exinites an insignificant increase of the range and of intensity of the optical anisotropy appears.

In the process of graphitization of optically isotropic cokes-micrinites, and fusinites a small quantity of anisotropic phase appears at 2000-2500°C. In all the types of the studied coals the fusinites with a well preserved cellular structure remains entirely optically isotropic in the process of graphitization up to 2500°C.

**X-Ray Examinations.** The cokes from petrographic components differ essentially by their susceptibility to ordering the structure in the process of graphitization /Fig. 1-3/. In case of cokes from vitrinites and exinites a strong dependance of the quantity of structural changes on the degree of coalification of the original petrographic components appear.

The cokes of vitrinites from flame and gas-coking coals behave as the non-graphitizing substance, they give products of a very stable ordering of the structure, taking place only in two dimensional system. The process of graphitization of the coke of vitrinite from the orthocoking coal leads to a gradual development of the graphitoidal structure /at 2500°C  $G=0.47$ /. The coke of vitrinite from meta/semicoking coal shows only an insignificant susceptibility to graphitization, /at 2500°C  $G=0.16$ /. The coke of vitrinite from anthracite within the temperature up to 2000°C behaves as the non-graphitizing substances. An intense ordering of its structure appears however above 2000°C temperature, after destruction of the cross linking bonds. The product of graphitization obtained in 2500°C achieves a better formed graphitoidal structure than the analogous graphitization products of cokes of other examined petrographic components.

The cokes of exinites from flame and gas coking coals are characterized by a considerably higher ability to ordering of their structure than the cokes of corresponding vitrinites.

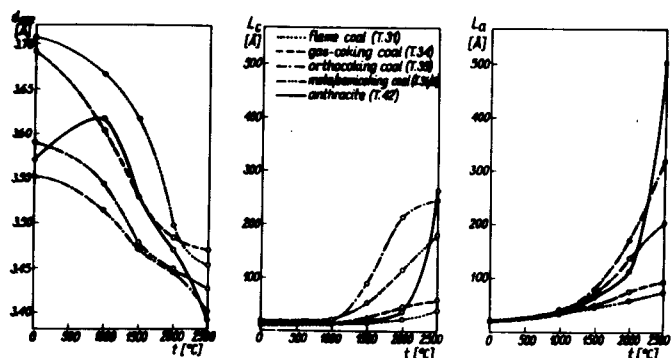


Fig. 1 Changes of structure parameters of cokes from vitrinites on the graphitization.

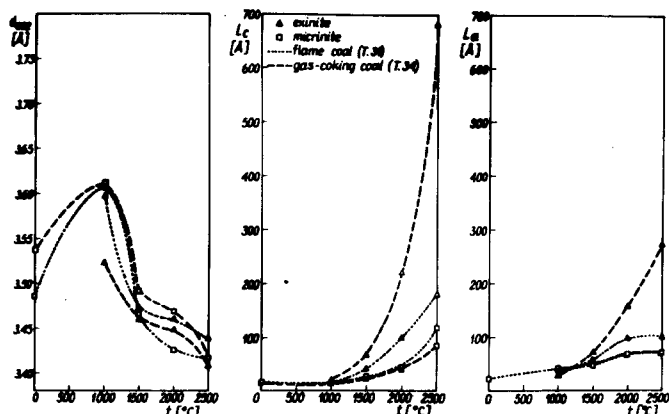


Fig. 2 Changes of structure parameters of cokes from exinites and micrinites on the graphitization.

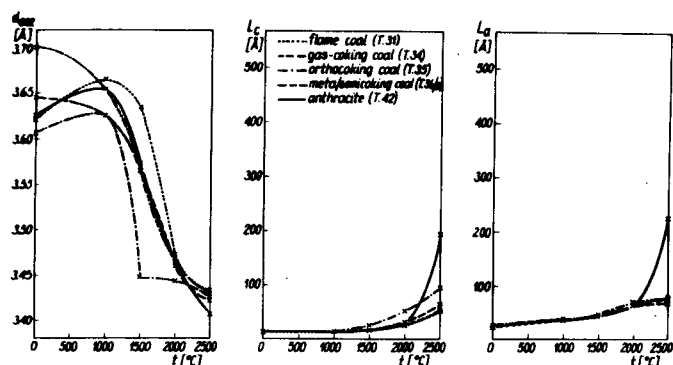


Fig. 3 Changes of structure parameters of cokes from fusinites on the graphitization

To a higher of coalification of the exinite corresponds the higher intensity of structural changes appearing in the process of graphitization. The product of graphitization obtained at 2500°C of the coke of exinite of the flame coal shows only the turbostratic-structure. An analogous graphitization product of exinite from gas-caking coal has features of a graphitoidal structure. In the process of graphitization of cokes from of exinites the tendency to a parallel arrangement of layers decidedly dominates over the increase of layer planes.

The cokes of micrinites have a limited susceptibility to ordering of the structure in the process of graphitization. In the products of graphitization of cokes from micrinites there is strong packing of layers, considerably better than in corresponding products of graphitization of cokes from non-graphitizing petrographic components. The three dimensional ordering of the structure does not appear.

The cokes of fusinites from all the investigated coals, characterized by a very low susceptibility to ordering of the structure belong to the groups of non-graphitizing substance. The cokes of fusinite behave very like, except the coke of fusinite from anthracite. An exception found in the case of the cokes from fusinite from anthracite where a distinct increase of the degree of structure ordering at 2000-2500°C is observed, might result from a considerable quantity of vitrinite inclusions as well as of the presence of intermediate forms between vitrinite-semifusinite appearing in the original fusinite.

### Conclusions

The behaviour of cokes from petrographic components on high temperature heat treatment /graphitizing or non-graphitizing/ is a logical consequence of their structure.

The cokes of exinite from gas-caking coal and of vitrinite from orthocaking coal behave as graphitizing substances; the cokes of vitrinite of flame coal, the cokes of micrinites and fusinites separated from coals of different degree of coalification, belong to non-graphitizing substances; the cokes from anthracite undergo the process of graphitization not below 2000°C.

The obtained results give also essential information about the possibility to use the hard coals as raw material, to obtain carbon and graphite materials. It seems that the cokes from vitrinites of flame coals may be useful to obtain materials like "glassy carbon". The cokes from orthocaking coal may be a raw material for electrode industry. From coals and anthracite, which will be used as a raw materials for the production of carbon and graphite materials macerals of inertinite group should be removed.

### References

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