THE PROCESS OF CARBONIZATION AND GRAPHITIZATION OF PETROGRAPHIC COMPONENTS OF HARD COALS
PART I. PROPERTIES AND STRUCTURE AND THE COKING PROCESS OF PETROGRAPHIC COMPONENTS OF HARD COALS

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The basic petrographic components of hard coals-vitrinites, exinites, micrinites, fusinites, differ considerably in their properties and structure even within particular ranks of coals [1-12].

Despite numerous investigations on the behaviour of coals on heat treatment there is missing a full discernment in the literature even on the coking process of petrographic components separated from coals of a full coalification scale and no investigations were carried out on their process of graphitization.

In the paper the results of investigations on the separation, properties and structure of petrographic components from coals of the Polish Coal Basins /The Upper and Lower Silesian Coal Basin/, with a peculiar regard to their behaviour on heat treatment are presented.

Separation of petrographic components

The basic petrographic components - vitrinite, exinite, micrinite and fusinite - were separated from coals of various ranks: flame coal /79,%C/, gas-coking coal /85,3%C/, orthocoking coal /89,3%C/, meta/semicoking coal /87,2%C/ and anthracite /91,7%C/.The separation of the petrographic components was carried out by the organic heavy liquids method /carbon tetrachloride and toluene/.All the petrographic components: vitrinite, exinite, micrinite and fusinite could be isolated in case of flame and gas-coking coal.From the remaining coals only vitrinite and fusinite were isolated.In the most pure form, the vitrinites /97,2-99,2%/ and fusinites /93,8 - 98,4%/ were isolated, the lower degree of purity of the obtained exinites /90,4 and 93,8%/ is caused by appearance of a strong fusion of exinite with other components. The isolated micrinites are the concentrates containing 50% of the pure component.

Properties and structure of petrographic components

The petrographic components within all ranks of coals, show that there are differences which appear in the physico-chemical and technological properties and in the structure.Most visibly they are marked in the coals of lower rank.

The content of volatile matters decreases towards: exinites-vitrinites-micrinites -fusinites.The content of C element is the lowest in the vitrinite, higher in exinite and micrinite, and the highest in the fusinite.The content of hydrogen falls towards:exinite-vitrinite-micrinite-fusinite The highest content of oxygen have the vitrinites and micrinites, the lowest fusinites.Most of aliphatic and alicyclic compounds /2930,2860,1450,1380 cm^{-1}/ appear in exinites, considerably less in vitrinites, not much in micrinites.The vitrinites and the exinites in comparison with correspondent micrinites contain higher quantities of aromatic hydrogen /910 - 750 cm^{-1}/.The aromatic groups of the hydrogen in case of vitrinites are the best developed in gas-coking and orthocoking coals.A great part oxygen functional groups in exinites and vitrinites are the hydroxyl groups of phenolic type /3700 - 3100 cm^{-1}/, which in micrinites and fusinites appear in very small quantites. The content of functional groups changes in a characteristic way with coalification.In exinites, vitrinites and micrinites with the rise of their coalification degree the content of aliphatic and alicyclic compounds as well as of the oxygen groups decreases.

The fusinites show an insignificant content of the functional groups.During the coalification process the fusinites do not undergo essential changes.

Exinite compared with other components shows in all coals the lowest degree of coalification.Exinite is distinguished by the highest content of volatile matters, hydrogen, non aromatic hydrocarbon groups and by a high content of aromatic CHgroups

The participation of non aromatic configurations in petrographic components decreases towards:exinite-vitrinite-micrinite-fusinite and with the rank of coal.

The intensity of interference bands appearing on the X-Ray diagrams of vitrinites and the calculated values of structure parameters, show that there is a process of ordering of the vitrinite structure in coalification process.Particularly strong increase of structure packing degree is observed when passing from the vitrinite of the gas-coking to the orthocoking coal.

The appearance of weakly shaped 002, 100 band and of visible γ band on X-Ray diagrams shows that the structure of exinites is weakly ordered.

The micrinites are distiguished by the best packing of their structure /the smallest interplanar spacings d_{002}/.

Fusinites show higher dimensions of layers in comparison with the remaining petrographic components, these layers, however are weakly packed.The degree of ordering of fusinites structure depends in small degree on the rank of coal.The differences which appear in the distances of interplanar spacing and the dimensions of crys-

tallites between the investigated fusinites, may be explained by the petrographic heterogeneity of fusinites.

The differenes appearing in the chemical composition and in the structure between the petrographic components are the cause of their different behaviour in the coking process.The thermal resistance increases towards:exinite-vitrinite-micrinite-fusinite.The exinite behave as fluido-plastic substances.Among the investigated vitrinites, plasticity, caking and coking properties and expansion pressure on coking show only the vitrinites which occupy the mediumposition in the coalification scale, the gas-coking coal ,orthocoking and meta/semicoking coals.The best coking properties show the vitrinite from orthocoking coal/RI-87,FSI=9,b=140%,α_{max}=2620%/min/.The vitrinites from coals which occupy the extreme positions in the coalification series those from flame coal and from anthracite do not soften during the heating.The micrinites in principle should be numbered among the inert components.The fusinites remain completely inert in the coking process.

Properties and structure of cokes obtained from petrographic components

The petrographic components were coked in Gray-King apparatus in a temperature of 1000°C.In the obtained carbonization products chemical properties and structure were tested by applying the ultimate and proximate analysis and the structural microscopic and X-Ray examinations.

As results of an intense thermal decomposition of less resistant structural configurations, the content of volatile matters decreases /1,1-3,3%/ and also of hydrogen /0,4-1,0%/, while the content of C element increases /95,4-98,5%/.

In the coking process, essential changes of optical properties in the products of carbonization appear.The petrographic components may remain optically isotropic,or they may form areas which show an optical anisotropy of different range and intensity.In case of coking of vitrinites and exinites the type of developing anisotropic texture is strictly connected with rank of coal.

The cokes of vitrinites from flame and gas-coking coals are optically isotropic. The cokes of vitrinites from orthocoking, meta/semicoking coal and anthracite are optically anisotropic.

The coke of vitrinite from orthocoking coal is distinguished by a very large variety of anisotropic forms which are formed during coking.Areas of structure showing a fine-grained,coarse-grained, shell, fibrous and band anisotropy with predominant shell and fibrous anisotropy are formed passing into the band anisotropy.In the cokes of vitrinites from meta/semicoking coals and anthracite,mainly the areas showing a lump anisotropy and a small number of areas with band anisotropy appear.

The coke of exinite from the flame coal contains very small areas showing an optical anisotropy, in form of a fine grained anisotropy of a low intensity.The coke of exinite from gas-coking coal consists of areas showing a strong anisotropy in form of small and middle sized shells.The cokes of micrinites and fusinites are optically isotropic.

The structural X-Ray examinations have shown that largest dimensions of crystallites and the best packing of layers show the cokes obtained from vitrinites of ortho and meta/semicoking coals and the coke from exinite of a gas-coking coal/Fig.1/.

The smallest heights of crystallites and the weakest packing of layers show the cokes from vitrinites of lower coalificated coals as well as the cokes obtained from fusinites and micrinites.The cokes obtained from inertinites show relatively high dimensions of crystallites diameters.

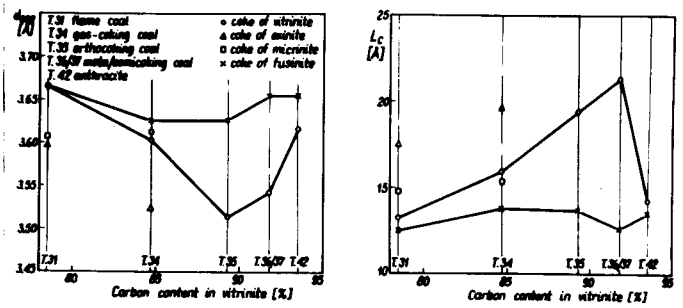

Fig.1 Structure parameters of cokes from petrographic components of hard coals

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