

## Nanosized carbon forms in the processes of pressure–temperature-induced transformations of hydrocarbons

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### Abstract

The products of thermal conversions of naphthalene, anthracene, pentacene, perylene, and coronene at 8 GPa in the temperature range up to 1300 °C have been studied by scanning electron and high-resolution transmission electron microscopies. As a result, it has been established that various nanometer-sized carbon species (spherical and coalesced two-core onion-like carbon particles, faceted polyhedral particles, graphitic ribbons, graphitic folds, and nanocrystalline diamonds) are present in the conversion products together with micron-sized crystallites of graphite and diamond.

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### 1. Introduction

Thermal conversions of carbonaceous compounds under pressures present a complex sequence of physico-chemical transformations associated with the carbonization of the original materials and the successive structural organization of the carbon residues formed. The final stages of the evolution of such systems under high pressures are the formation of graphite or diamond. Up to now, both these stages have been studied fairly comprehensively on the bulk micrometer scale level [1–10]. In such type of studies, X-ray diffraction and Raman spectroscopy, which provide for characterization of the evolution of the carbon states in some detail depending on pressure, temperature, or the duration of treatment, are usually the main

methods of investigations of carbon materials. Microscopic investigations of the materials by scanning (SEM) and high-resolution transmission electron microscopy (HRTEM) normally play an ancillary role. In the study of graphitization, they illustrate the processes of the lateral growth of graphene layers, the increase of the number of the parallel graphene layers and their structural ordering in the layer packing, and the change of the microtexture of the material as a whole [3,4,6]. In the case of diamond formation, they allow a clear demonstration of the size, composition, and morphology of crystals of the diamond fractions obtained [8,10].

At the same time, theoretical investigations of the problems of the relative stability of the different nanometer-sized carbon structures [11–16] have shown that the initial nanosized stages of the structural organization of the carbon residue can be accompanied by the formation not only of graphite and diamond, but also of other forms of

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carbon. According to the thermodynamic analysis carried out by several authors using different approaches [11–16], a number of the size-dependent phase transitions between the various nanostructures of carbon can take place in the products of carbonization. Usually, fullerenes, spherical onion-like and polyhedral particles, bucky diamond, diamond and graphite nanoparticles are considered as such nanoforms of carbon [11–16]. Therewith, the existence of sized ranges of thermodynamic stability is predicted almost for each of these nanoforms of carbon in fairly wide intervals of  $p$ ,  $T$ -parameters. Taking into account this fact and the substantial “kinetic” stability of the nanostructures, it can be expected that some nanostructures formed at high pressures and temperatures can be separated at ambient conditions. In the present study we have shown experimentally the possibility of the formation of different carbon nanostructures in the processes of the thermal conversions of aromatic polycyclic hydrocarbons (PAHs) at high pressures and temperatures.

The investigation of high-pressure high-temperature (HPHT) transformations of PAHs at 8 GPa on the bulk micrometer-sized scale was carried out by us previously [10]. It was shown that the main product of HPHT treatment of naphthalene, anthracene, pentacene, perylene, and coronene at 8 GPa and temperatures above  $\sim 1100$  °C is graphite with a high degree of crystalline perfection. At treatment temperatures of 1280 °C and higher, diamond becomes the main product of the conversion for all hydrocarbons investigated. Subsequent microscopic investigation allowed us to establish that in addition to graphite and diamond the products of PAHs treatment contain minor fractions of different nanometer-sized forms of carbon, which became the subjects of this study.

## 2. Experimental

High-pressure states, obtained as a result of naphthalene, anthracene, pentacene, perylene, and coronene treatment at 8 GPa and different temperatures up to 1300 °C in a “Toroid”-type high-pressure apparatus, were quenched under pressure to room temperature and then studied at ambient conditions by X-ray diffraction, Raman spectroscopy, SEM, and HRTEM. Experimental details of HPHT treatment, X-ray and Raman studies were described previously [10]. Microscopic investigations of the samples were carried out by using a DSM 982 Gemini (Zeiss) scanning electron microscope. A HRTEM study was performed on a FEI F-20ST (Philips) field emission gun transmission microscope equipped with super-twin polar pieces and operated at 200 kV. Images were recorded at approximately Scherzer defocus on a CCD multiscan camera after astigmatism corrections, and eventually filtered via the Digital Micrograph software. Materials for HRTEM investigations, prepared by ultrasonic dispersion of the samples in ethanol for 5 min, were deposited on a copper grid coated with holey carbon. The deposited suspensions were thereafter dried in air prior to TEM experiments. To avoid

any electron irradiation damage that could induce allotropic transformations of carbon materials and, in particular, gives rise to the formation of onion-like carbon (OLC) particles [17], we used a reduced beam intensity. Since we observed no changes in the carbon structures studied during the whole period of the irradiation of the samples, we believe that the formation of different carbon nanostructures observed by us takes place not in the electron microscope but immediately in the high-pressure apparatus during the process of thermal conversions of the hydrocarbons.

## 3. Result and discussion

The high-pressure states obtained as a result of HPHT treatment of different PAHs at 8 GPa and 1280 °C were studied most extensively. Preliminary investigations of these samples by X-ray diffraction, Raman spectroscopy, and SEM showed that the micron-sized formations of graphite and diamond are their basic components regardless of the structure of the initial hydrocarbons. According to the SEM data, the diamond fraction consists of the diamond crystallites with the sizes of 5–40  $\mu\text{m}$  (Fig. 1(A)). Graphite platelets with rounded edges constitute the graphite fraction. Typical lateral sizes of the graphite particles are equal to 3–30  $\mu\text{m}$ . The main reason for the simultaneous presence in the samples of two basic carbon states is the availability of detectable axial and radial gradients of temperature in the high-pressure apparatus used. For this reason, the pure diamond fraction is concentrated in the hottest part of reaction zone where the temperature matched its nominal value of 1280 °C.

Subsequent detailed microscopic investigations revealed that, besides bulk graphite and diamond, various nanometer-sized carbon forms are present in the samples. These nanoforms of carbon manifest themselves microscopically in the form of individual globules and aggregates (Fig. 1(B)). Study of these formations by HRTEM allow imaging of a number of the most characteristic nanostructures of carbon being incorporated into the observed globules and aggregates (Fig. 2).

According to Fig. 2, the separated lighter fractions of the dispersed samples consist, as a rule, of matrixes of non-organized carbon with inclusions of spherical OLC and coalesced two-core OLC particles, faceted polyhedral particles, graphitic ribbons, arched graphene sheets or graphitic folds, and nanocrystalline diamonds.

Typical sizes of the spherical OLC particles are equal to 15–30 nm. The two-core OLC particles are of approximately 5–10  $\times$  20–30 nm size, and polyhedral particles of about 7–10 nm size. The graphite ribbons built of packings of graphene layers with the numbers of layers ranging from 4–7 up to 20–35 show a length of several tens of nm. The 0.34 nm spacing of lattice fringes observed in Fig. 2(D) is a little more than that for the (002) planes of perfect graphite. The sizes of diamond nanoparticles are 3–8 nm. These diamond nanoparticles have shown different orienta-

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