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GEOCHEMISTRY

Synthesis of Carbon Nanotubes and Fullerite Structures at *PT* Parameters Corresponding to Natural Mineral Formation

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Rare carbon forms, represented by fullerenes and fullerite structures, were experimentally synthesized at temperatures of about 3000–5000°C [6]. The cognate carbon nanotubes vary in shape from barrel-like (practically fullerene) varieties to micrometer-size elongated ones with an outer diameter of several hundred angstroms [6]. The very high temperatures of fullerene synthesis seemingly restrict the application of experimental data to natural mineral formation. These forms were revealed in shungites [5], coals [8], marine carbonate–clayey sediments [9], chondrites [4], and stellar dust [10]. Fullerenes and fullerite structures are known to possess an exceptional potential ability to transport many rare elements as gaseous complexes. Their active participation in the formation of diamond deposits and rare metal carbonatites is assumed in [1]. In most cases, fullerenes are noted in nature in association with graphite. Metamorphic graphite, as is known, is formed at temperatures corresponding to the amphibolite or granulite metamorphic facies. As was demonstrated in [7], graphite can form from methane-containing fluids in the course of metamorphism. All these facts determine the necessity of experimental investigations of the synthesis of these carbon forms under conditions close to natural mineral formation.

We studied the process of graphite formation from methane at 700°C and 500 MPa under reductive conditions. The source of methane was polypropylene, CH_3–[–$CH(CH_3)$–CH_2–]$_n$–$CH{=}CH_2$. The initial material contained additions of potassium ferricyanide, $K_3[Fe(CN)_6]$, that dissociated into C–N complexes on heating. The graphite formation proceeded according to the reaction:

$$CH_4 = C + 2H_2$$

or according to other analogous reactions of dissociation of hydrocarbon gases.

The experiments were conducted using installations of high hydrothermal pressure [2] at the Institute of Experimental Mineralogy of the RAS. The design of an external heating electric furnace allowed us to create a 50-mm-long, almost gradientless (2–3°C) zone in the reactor, into which an ampule with the initial material was placed. The temperature was measured with an accuracy of ±5°C by a chromel–alumel thermocouple. The installation was set up into the experimental regime in 1.5–2 h. The samples were quenched by cold air. During 10–12 min of the quenching, the initial temperature decreased to 150–200°C. The pressure was measured with an accuracy of ±10 MPa by a tube manometer. All experiments were conducted in welded gold ampules with 0.2-mm-thick walls. Taking into account that the high-pressure vessels generate the oxygen fugacity close to that created by a nickel–bunsenite (NNO) buffer mixture, we applied the double-ampule method. The initial mixture (30 mg) was placed into the inner ampule (diameter 3 mm, length 40 mm). The ampule was welded up and placed into a larger ampule (diameter of 5 mm, length 50 mm). Into the outer ampule, 1000 mg of carbonyl iron and 100 mg of water were added to provide the oxygen fugacity corresponding to the Fe–wustite (FW)/wustite–magnetite (WM) buffer mixture. To increase the duration of the buffer mixture functioning, a nickel container (length 30 mm, diameter 5 mm) filled with quartz–fayalite–magnetite (QFM) buffer mixture was placed near the outer ampule. The experiment duration was 5–7 days.

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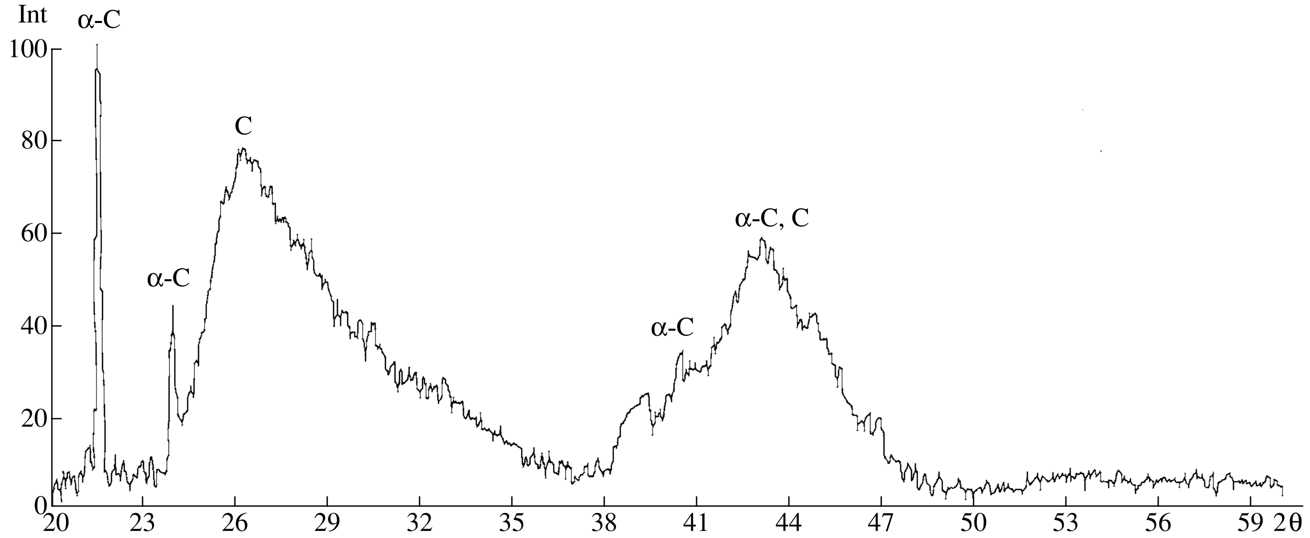

Fig. 1. X-ray diffraction pattern of the synthesis products obtained on a Siemens D-500 diffractometer. The major peaks are related to graphite (C) and α-carbine (α-C).

Fig. 2. Fullerite multilayer structures (magn. ~300 000).

Fig. 3. Carbon nanotube (magn. ~300 000).

On treatment with concentrated HCl to remove possible metallic phases and iron oxides, the synthesis products were studied using the X-ray diffraction method on a Siemens D-500 diffractometer. The reflection data were obtained using the CuK_α radiation (Ni filter). The measurements were carried out within the range 2θ = 20°–60° with a step of 0.02° and an exposure of 12″. Using this method, graphite and another hexagonal phase of C (α-carbine) were identified in the synthesis products (Fig. 1). After this, the synthesis products were treated with concentrated $HClO_4$ to remove the graphite admixture. Then, the samples were dried, doped with 2–3 ml of chemically pure toluene, and subjected to an ultrasonic treatment for 10 min at a frequency of 22 kHz on a MSE-100W instrument (UK). A drop of the obtained suspension was placed on an electron microscope net with a carbon plate and, after evaporation of the volatile components, was observed on a JEM-100S transmission electron microscope (JEOL, Japan) at magnifications of 20000–100000 with recording on the FT-41MD film. As a reference preparation, we used carbon nanotubes obtained from a fullerene-producing device and kindly presented by ZAO Astrin. In our samples, fullerite multilayer formations with diameters from 200 to 800 Å were found. The diameter of the inner cavity or channel in these structures varied from 20 to 60 Å (Fig. 2). These formations are analogous in appearance to short, closed multilayer carbon nanotubes formed during fullerene synthesis under vacuum discharge conditions at ~5000 K. In

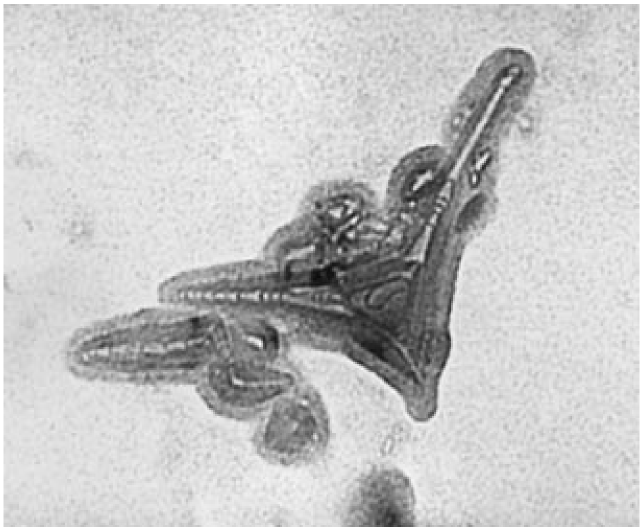

Fig. 4. Combination of a fullerite structure with segmented carbon nanotubes (magn. 300 000).

addition, a small amount of thin (10–20 nm in diameter) elongated (0.5–1 μm) nanotubes were found (Fig. 3).

The results of this work allow us to conclude that the origin of fullerenes and carbon nanotubes found in natural rocks is directly related to reduced hydrocarbon fluids.

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