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A Possible Mechanism of Formation of Fullerene Nanoparticles in Shungites

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Abstract—A mechanism of formation of fulleroid nanoparticles in shungites, adequate to the principal structural features of these particles (a cavity filled with nothing but water traces, the absence of the catalyst nanoclusters, and some other) was suggested.

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Natural mineral shungite is extremely promising from the viewpoint of nanocarbon science and applications. Some of these applications, e.g., water treatment, are known for at least 300 years, while others, e.g., coke substitution or addition to building materials, are now under development [1, 2] or research [3].

Fullerene and carbon nanotube (CNT) science treats shungite as an important natural material unique in containing fulleroid particles such as multilayer fullerenes and, probably, true fullerenes. Data on the presence of true fullerenes are contradictory. The first encouraging results obtained in mass-spectrometric experiments [4] were disproved by the results of extraction with conventional organic solvents, but those studies were underlain by the views on the molecular character of the bond for fullerenes in shungites. Covalent and donor–acceptor compounds of fullerenes, yielded by their reactions with nucleophilic molecules, are being actively studied today. It is believed that specifically the chemical character of the bonding of fullerenes in shungites complicates their detection [5].

By contrast to fullerenes, the existence of fulleroid particles as multilayer globules, nanotubes, nanobarrels, and onion-like nanocarbons with an internal cavity is beyond question, and they were repeatedly observed [6, 7]. Like carbon in shungites on the whole, fulleroid structures are rigidly connected to the aluminosilicate matrix [7]: Both phases are uniformly distributed even in particles prepared by

micrometer grinding. Along with noncrystalline carbon and aluminosilicates, shungite contains a small amount of a bituminous organic material.

The richest in carbon (up to 90 %) is shungite-I [8]; however, it is fairly expensive, and its deposits are extremely limited. Evidently, more promising is shungite-III containing 30–40% carbon [8, 9] (with the remaining 60–70% accounted for primarily by aluminosilicates). The total resources of the shungite rocks of the Onega basin exceed 1 bln tons, and the explored reserves of the largest Zazhoginskoe deposit are estimated at ca. 150 mln tons.

Typical electron micrographs of the nanostructures of shungite-III were obtained after chemical recovery of the carbon component (the resulting material was named MNS, modified nanoshungite). The sequence of the operations in removal of the mineral components was described in [10]. The samples were analyzed on a JEM-100S (JEOL, Japan) transmitting electron microscope at a magnification of 10^4 – 10^5 . Figure 1 shows one of compact accumulations of the nanoparticles, irregularly distributed over the bulk of the material. The micrograph shows a closed-end multilayer CNT with a cavity, comprising numerous layers, with the channel diameter of ca. 3 nm, outside diameter of 20 nm, and length of ca. 0.2 μm , as well as nanobarrels with a cavity and onion-like nanocarbons without cavity. All the nanostructures are clearly separated from the silicate matrix.

The morphology of the carbon filling the inter-