

Synthesis and Properties of Plasma-Deposited Carbon Condensates

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Received March 20, 2003; in final form, June 2, 2003

Abstract—Structural data, thermal characteristics, and theoretically calculated binding energies are reported for a graphite condensate obtained by carbon deposition from plasma. It is demonstrated that this condensate can be effectively used in self-propagating high-temperature synthesis processes. © 2003 MAIK “Nauka/Interperiodica”.

Elementary carbon is available in a variety of forms exhibiting different, sometimes opposite characteristics. On the one hand, this material is extremely active, being capable of forming ten times more compounds than all other elements together, while, on the other hand, carbon is absolutely inert with respect to some of the most aggressive reactants.

It is a peculiarity of graphite that samples can significantly differ in their structure and properties, depending on the conditions of synthesis [1–5]. In the course of thermal treatment, graphite exhibits an increase up to 3.44 Å in the spacing between layers, which are parallel to each other but possess no mutual azimuthal orientation. This type of graphite is well known and called turbostratic [5].

This paper reports on the results of our investigation of a product of this kind that was synthesized as reported previously and called thermolysis residue

(TR) [6]. The TR was obtained in a plasmachemical reactor described in detail elsewhere [7]. In this setup, a carbon–helium plasma is generated by sputtering spectral-purity carbon rods made of the graphite referred to below as initial, possessing a hexagonal structure with the crystal lattice parameters $a = 2.462$ Å and $c = 6.732$ Å. A TR deposit was formed in the course of rapid cooling and crystallization from carbon–helium plasma and deposited on a relatively cold external ring electrode of the reactor.

The results of our investigation showed that the structure of this graphite condensate is determined by the conditions of cooling of the ring electrode on which deposition takes place. At an average temperature of this electrode not exceeding 400°C, a deposit is formed with the same lattice parameters as those of the initial graphite. At higher temperatures, a carbon condensate formed on the electrode contains both the initial graph-

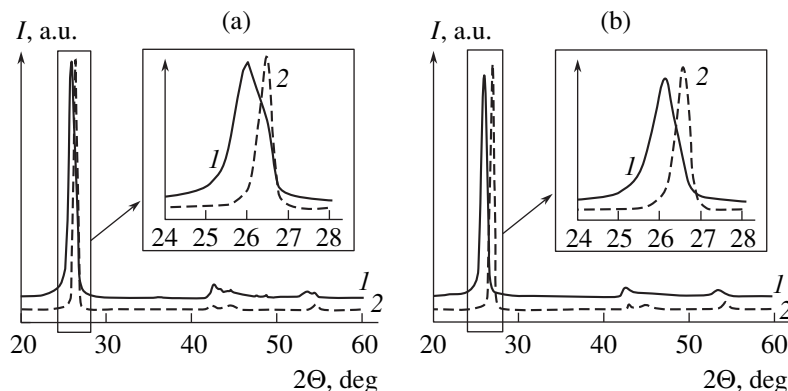


Fig. 1. X-ray diffraction patterns of (a) initial graphite with TR and (b) pure TR condensate showing sample peak (solid curves 1) in comparison to the diffraction peak (dashed curve 2) of the initial graphite.

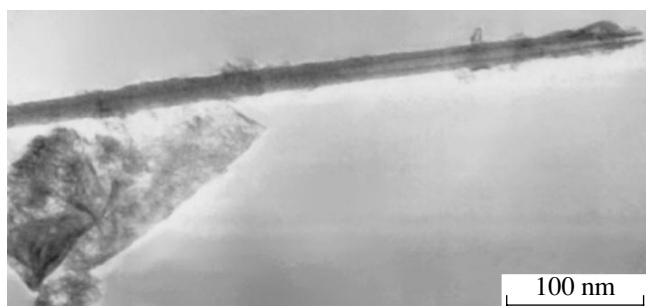


Fig. 2. Electron-microscopic image of a carbon condensate, showing a multiwall nanotube and a turbostrate graphite particle.

ite and TR phases (Fig. 1). When the electrode temperature is increased up to 800°C or above, the condensate consists entirely of TR. In this material, the spacing between graphite layers is increased by 0.06 Å ($a = 2.462$ Å and $c = 6.852$ Å) as compared to that in the initial graphite. These conclusions are based on the results of X-ray diffraction measurements performed for powder samples on a DRON-4 diffractometer. An increase in the interlayer distance is usually explained by random packing of graphite layers in the course of rapid condensation of carbon from the plasma [5].

Electron-microscopic investigations performed using a scanning electron microscope (SEM) of the REMMA-202 type (Russia; magnification, $\times 300$) showed that the TR phase consists of sintered spheroidal species with dimensions ranging from 0.3 to 10 μm . We have finely comminuted a TR sample by grinding and studied the material in a transmission electron microscope (TEM) of the JEM-100C type (JEOL, Japan). It was found that the TR phase contains, besides graphite species, multiwall carbon nanotubes (Fig. 2). Most of these nanotubes have lengths ranging from several dozen up to several hundred and even thousands of nanometers, with internal diameters from a few to several dozen nanometers. The electron diffraction patterns obtained from TR species and nanotubes coincide, from which it follows that the spacing of graphite layers in both TR graphite species and nanotubes is the same (about 3.42 Å). Quantitative estimates showed that the fraction of nanotubes is usually small, within 1–2%.

Experimental data on the particle size and combustion front velocity in powdered titanium–carbon mixtures

Mixture composition	Carbon particle size, μm	Combustion front velocity, mm/s
Titanium–graphite	10	8
Titanium–soot	10^{-2}	10
Titanium–TR	10	18

The binding energies of carbon for the TR and usual graphite structures were calculated within the framework of the density functional formalism using a VASP program package [8]. The results showed that a difference between the energy per mole of carbon in the TR phase and initial graphite amounts to 5.8 kJ, which implies that 5.8 kJ/mol would be liberated upon the transition from TR to the initial graphite. Therefore, TR can be expected to exhibit a higher chemical activity related to the greater potential energy stored in the TR structure. This has to be manifested in a greater efficiency of chemical reactions involving carbon in the TR form.

We have studied the samples of initial graphite and TR by means of differential thermal analysis on a Q-1000 (MOM, Hungary) derivatograph, whereby the samples were heated from 24 to 1000°C. It was established that the initial graphite burns in the temperature interval from 660 to 890°C, while the TR burns in the interval from 570 to 850°C, the process being exothermal. The fact that the TR burns at lower temperatures is evidence that the TR phase is actually more chemically active than the initial graphite, in agreement with theoretical estimates.

The next check for chemical activity of the TR phase was a practically important reaction of the formation of titanium carbide by method of self-propagating high-temperature synthesis (SHS). The initial components were titanium and TR powders (see table). For comparison, the SHS process was also performed with the carbon component in the form of initial graphite and X-ray amorphous soot. The average size of titanium particles was 100 μm . The initial mixture contained titanium and carbon taken in a stoichiometric ratio, and the initial charge was pressed to a density of about 0.5 g/cm³. The samples were placed into an SHS reactor chamber evacuated to a residual pressure of 10^{-3} Pa. The SHS reaction was initiated by heating the sample end (occurring at an initial temperature of 24°C) through contact with a red-hot graphite rod.

The SHS synthesis of titanium carbide using carbon in the form of graphite and soot proceeded at a combustion wave front propagation velocity corresponding to the published data [9]. In the case of a reaction involving the TR, the combustion front velocity was about twice as large as that for graphite and soot (see table).

In summary, the results of our investigations showed that the thermolysis residue consists of spheroidal carbon species including turbostrate carbon and multiwall carbon nanotubes. The distance between graphite planes in both turbostrate graphite and nanotubes is 3.42 Å. Quantum-chemical estimates showed that the energy difference per mole of carbon in the TR and initial graphite is 5.8 kJ, so that this amount of energy had to be liberated upon the TR–graphite conversion. It was demonstrated that the energy saturation of TR can be effectively used, for example, in the SHS synthesis of refractory carbides.

Work on the synthesis and investigation of TR condensates with variable content of nanotubes is in progress. We will also study the possibility of using such materials in various applications, for example, as sorbents for chromatography.

Acknowledgments. This study was supported by the INTAS Foundation (grant no. 01-2399), the Russian Foundation for Basic Research (project no. 03-03-32326), and the Federal Targeted Scientific-Technological Program "R&D in Selected Science and Technology Directions."

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Translated by P. Pozdeev