NANODIAMONDS FROM FUEL

B A Timerkaev¹, R B Shakirov¹, A A Zalyalieva¹, R K Gevorgyan¹, R R Shaikhattarov¹
¹KNRTU-KAI, Kazan, Russia

btimerkaev@gmail.com

Abstract. In this paper, we present the results of the synthesis of nanodiamonds from carbon nanostructures and diamondoids in an arc discharge. The electrodes used in the experiments were a molybdenum cathode and a copper anode coated with carbon nanostructures such as carbon nanotubes and diamondoids. The formation of carbon nanostructures on the surface of a copper electrode was carried out in an electric arc sunk into fuel oil. At the next stage, these carbon nanostructures served as a source of atomic carbon and diamondoids from the surface of the arc discharge anode. The use of fuel oil as a feedstock for creating the electrode material probably led to the retention of diamondoids contained in fuel oil during two vaporizations. It was found that, in addition to carbon nanotubes, nanodiamonds also formed on the cathode surface.

1. Introduction

Diamond is one of the most important and sought-after materials, on the one hand, as the hardest material on Earth, on the other hand, as an exceptional piece of jewelry. Therefore, the search for simple methods of artificial synthesis of diamonds has not stopped for almost a century and a half. There are two ways to create diamonds. The first method is a method of converting graphite into diamond under high pressure and high temperature. To do this, it is necessary to force carbon atoms to overcome the quantum potential barrier and rearrange into the crystal structure of diamond. In this way, diamond crumbs are created and sufficiently large diamonds are grown. The second method is the synthesis of diamonds by the CVD method in the presence of catalysts and diamond nuclei. Now a new way of creating nanodiamonds is emerging. For instance, the works [1, 2] reported on the synthesis of nanodiamonds under high pressure and temperature from adamantanes (diamonds) (chemical formula (CH₄)₄(CH₂)₆). A sensational article [3] reports on the synthesis of nanodiamonds from diamondoids. Diamondoids are the smallest (typically 0.5 to 2 nm) form of hydrogen-terminated carbon cells that can be superimposed on the diamond lattice. According to the spatial arrangement of carbon atoms, such a molecule is similar to one, two or three cells of the diamond crystal lattice. Composed entirely of sp³ hybridized bonds, diamondoids combine some of the exceptional properties of bulk diamond and hydrocarbon molecules, such as rigidity, thermal stability, and uniformity at the atomic level. The authors of this work used diamondoids as promising precursors for laser-induced synthesis of diamonds under high pressure at high temperature. The lowest pressure and temperature (P-T) at which diamond was obtained were 12 GPa (at ~2000 K) and 20 GPa (at ~900 K), respectively. At a pressure of 20 GPa, the transformation of diamondoid into diamond occurred in 19 μs. Molecular dynamics modeling showed that after dehydrogenation, the remaining diamond-like carbon cells rearrange into diamond-like structures at high
pressure and temperature. The results of plasma-chemical synthesis of carbon nanostructures from hydrocarbons are given in [9–10]. In [11–13], methods for increasing the stability of electric discharges in the processes of synthesis of various nanostructures were studied.

Despite the success achieved in the synthesis of large diamonds and nanodiamonds by the above methods, the synthesis process requires compliance with very stringent conditions. As reported in [4], the synthesis of even microscopic diamonds can take several days.

The synthesis of nanostructures can be successfully carried out only if the temperature regime is strictly observed. That is, the synthesis temperature cannot exceed the melting temperature of the nanostructure. Therefore, information about the distribution of temperature fields in the region where the synthesis of one or another nanostructure is supposed to be carried out should be known in advance. Each type of nanostructure has its own synthesis temperature. The traditional technique for the synthesis of carbon nanotubes involves the evaporation of graphite at a temperature of 4000K and their deposition on the cathode. In this case, there should be a section on the cathode with a temperature of about 1800K. This is exactly the temperature at which the synthesis of nanotubes occurs. It would be much better if the evaporation temperature of carbon atoms also corresponded to the same temperature. Therefore, for the implementation of the synthesis of carbon nanostructures, it is advisable to use easily evaporating structures. In this work, we used an anode consisting of fullerene soot, nanotubes, and diamondoids as an anode.

It was shown in [5] that two regions can be distinguished in a carbon arc, defined as the core of the arc and the periphery of the arc. These areas have very different temperatures and densities of carbon formations. At the colder periphery of the arc, diatomic carbon molecules (C2) predominate, which are in the minority in the core of the hot arc. These differences are due to the extremely uneven distribution of the arc current, which is mainly conducted through the arc core filled with carbon atoms and ions. Thus, the ablation of the graphite anode is driven by the core of the arc, while the formation of carbon molecules occurs at the colder periphery of the arc.

It is reported in [6] that the growth kinetics of nanostructures in plasma is affected by Coulomb forces between charged particles. In a stationary plasma, the unipolar charge of particles leads to a slowdown in growth and to a limitation in the particle size. In a non-stationary atmospheric pressure arc discharge, a bipolar charge distribution is formed. Large formations are positively charged, while atoms are negatively charged. In this case, the Coulomb forces accelerate the formation of particle growth on a millisecond time scale.

2. Materials and methods

2.1. Plasma-chemical method

In this work, in contrast to HPHT, CVD methods and methods for the synthesis of microdiamonds by arc evaporation of graphite, a plasma-chemical method for the synthesis of nanodiamonds in arc plasma by evaporation of carbon nanostructures, such as carbon black containing nanotubes and diamondoids, is proposed.

In the first stage, a cathode assembly consisting of carbon black containing nanotubes and diamondoids was synthesized in an arc plasma with electrodes embedded in fuel oil. In the second stage, this cathode unit was used as the anode of the electric arc discharge.

The effectiveness of an arc discharge with electrodes recessed into fuel oil for the synthesis of carbon nanotubes is described in detail in [7–8]. The advantage of this method for the synthesis of carbon nanomaterials is the fact that electrodes are placed directly in the raw material. Therefore, both the temperature of the electrodes and the temperature of the plasma itself are moderate. On the surface of the electrodes, the temperature distribution turns out to be such that there are corresponding regions that are optimal for the synthesis of certain carbon nanoobjects. Copper rods 5 mm in diameter were used as electrodes in this work. After this stage of the experiment, nanotubes and carbon deposits formed on the surface of the copper cathode. Next, this copper electrode with carbon deposits was placed in a vacuum
chamber and served as an anode in the nanodiamond synthesis facility. The synthesis was carried out in an argon medium at a pressure of 500 Torr with an arc current of about 30 A. The experiment lasted for about 30–40 s. During this time, the carbon build-up from the anode surface was transferred to the surface of the molybdenum cathode.

2.2. SEM imaging

Carbon nanoformations on the surface of the molybdenum cathode were studied using optical and electron microscopes.

3. Results and discussion

Nanoformations in form represent a carbon buildup on the cathode surface. The middle part of this outgrowth contains carbon nanotubes to a greater extent, while the periphery contains nanodiamonds.

![Figure 1. An electron micrograph of a carbonaceous build-up on the cathode. Magnification 8000 times.](image)

On Fig. 1 shows an electron micrograph of deposits on the cathode. As can be seen from the figure, these deposits are nanodiamonds with dimensions of about 300–500 nm. Nanodiamonds are quite densely located relative to each other, and fluctuations in their sizes are insignificant. Carbon nanotubes are also visible there. The lengths of nanotubes vary within 2–4 µm, and the diameters are about 50 nm.

Figure 2 shows photographs of smaller nanodiamonds. Their sizes are more than 10 times smaller than the sizes of diamonds shown in Fig.1. Characteristically, nanotubes are not observed in this region.

The following figure (Fig. 3) shows an electron micrograph of even smaller nanodiamonds in the form of a diamond placer. The diamond placer is located on the surface of the graphene sheet.

In Fig.2, nanodiamonds have approximately the same dimensions of about 40–50 nm. The appearance of practically all nanodiamonds is the same. Some of them are pyramidal in shape.

The nanodiamonds shown in Fig. 3 have more regular shapes. Their sizes are less than 20 nm.
4. Conclusion
Thus, the plasma-chemical synthesis of nanodiamonds in an electric arc plasma was carried out by evaporating carbon nanostructures containing carbon nanotubes and diamondoids, followed by their deposition on the surface of a molybdenum cathode. The anode material was one of the electrodes of an electric arc embedded in fuel oil.
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