PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 1, 01NDLCN10(4pp) (2012)

Electric Discharge Plasmochemical Synthesis of Carbon Nanomaterials

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(Received 26 July; published online 10 August 2012)

High-energy electric discharge technologies (electric breakdown and HF volume discharge in organic media) for a large scale synthesis of amorphous carbon (AC) are developed. A destruction of hydrocarbon molecules into separate fragments occurs during such processing of organic media, what results in AC formation in the process of ultra-fast cooling of the clusters. To investigate the influence of chemical nature of working media, organic liquids and gases from the class of arenes with sp^2-hybridisation of carbon atoms in molecule and alkanes with sp^3-hybridisation were used. Performed XRD, HRTEM and Raman studies showed that produced powders are typical amorphous materials with significant degree of disorder. But only in the case of electric breakdown of alkanes, carbon nanomaterials with complex core-shell structure were discovered. Individual particles of onion-like carbon (OLC) consist of ~ 5 nm core surrounded by graphitic shell of 5-6 layers. Synthesized OLC is used as antifriction additives to industrial oils and as material for electromagnetic waves shielding. The statistical analysis of the atomic structure of the synthesized materials using reverse Monte Carlo and Voronoi-Delaunay methods was performed.

Keywords: Carbon nanomaterials, Electric discharge synthesis, Onion-like carbon, Structure, Voronoi polihedra.

PACS numbers: 52.80. – s, 52.50. – b, 81.05.U – , 81.07. – b

1. INTRODUCTION

Despite the occurrence of the wide variety of methods for the synthesis of carbon nanomateriyals (CNM), a development of technologies for production of different allotropic forms of nanocarbon in large scale, necessary for industrial application, is still actual task. Therefore, high-voltage electrical discharge technologies of CNM synthesis (fullerenes, carbon nanotubes, nanodiamonds, onion-like carbon, amorphous carbon, etc.), based on the use of the methods of electric explosion of graphite rods (exploding wires), electrical breakdown of dielectric hydrocarbons in the liquid and gaseous states and high-frequency (HF) plasma-discharge in gaseous hydrocarbons are of great interest [1-5].

It was experimentally shown that the method of electric explosion of graphite conductors enables to produce a wide spectrum of CNM [1,2]. Their phase composition can be effectively controlled by the amount of specific energy injected into graphite. The phase trajectories of graphite in the process of electric explosion are well described by a system of magnetohydrodynamic and electrodynamic equations [6, 7]. However, regardless of low prices and technological simplicity, the method of electric explosion of graphite does not allow obtain CNM in the scales required for industrial application.

In the Institute of Pulse Research and Engineering and G.V. Kurdyumov Institute for Metal Physics of NAS of Ukraine the high-voltage electric-discharge plasma-chemical methods of synthesis of large scale CNM were designed. In this paper the structural state of the CNM produced by the method of electrical breakdown of hydrocarbons and the method of volume high-frequency discharge in organic gases are studied.

2. ELECTRIC-DISCHARGE TECHNOLOGIES FOR CNM SYNTHESYS

The physical basis of electric-discharge methods for synthesis of various allotropic forms of CNM consists in nonequilibrium plasma formation from initial hydrocarbon medium, in which plasmo-chemical reactions of organic molecules destruction according to the scheme

$$C_nH_k = nC^s + 0.5kH_2$$

with subsequent nanocarbon formation in process of ultra-fast clusters cooling take place.

The plasma is generated as result of high-voltage electrical breakdown of dielectric organic medium with help of generator of powerful current pulses (up to 1 MA, 0.1-10 Hz) or as result of initiation of volume high-frequency (5-50 kHz) gas discharge. The phase composition and structure state of the produced CNM can be effectively controlled by the next:

- through varying an energy injected into working medium by changing the stored energy of a capacitor bank and amount of current pulses;
- through selecting an appropriate working medium – the source of carbon, i.e. use of hydrocarbons of different chemical nature.

The method of electrical breakdown has been implemented in a chamber with a coaxial system of electrodes filled with the working medium - liquid or gaseous hydrocarbons, which are differ in the degree of hybridization of carbon atoms and the structure of the molecule:

- benzene (C_6H_6) - belongs to a class of arenes with sp^2-hybridization of the carbon atoms in a planar ring molecule,
- cyclohexane (C_6H_{12}) - belongs to a class of cycloalkanes with sp^3-hybridization of carbon atoms in a nonplanar ring molecule,

- acetylene (C_2H_2) - belongs to a class of alkynes, with sp-hybridization of the atoms,
- mixture of propane and butane (C_3H_8 + C_4H_{10}) - belongs to the class of alkanes, with sp^3-hybridization of the carbon atoms.

After series of electrical discharges (up to 20,000 pulses), working liquid containing colloidal solution of carbon nanoparticles was decanted from the discharge chamber and centrifuged during 0.3-2 hours. The produced material is exsiccated at the sparing temperatures (up to 500 K) with a purpose to form dry powder.

The experimental equipment for the synthesis of CNM by HF method consists of:
- reactor, in which the mobile and stationary electrodes with the channels for the supply of gaseous feedstock and removal of reaction products are installed;
- high-voltage HF pulse generator with adjustable output voltage from 3 to 30 kV and pulse repetition rate from 1 to 100 kHz.

HF electric discharge synthesis was conducted in an environment of propane-butane and acetylene for various configurations of electrode systems at ambient and slightly elevated pressure and temperature in the reactor.

Investigation of the nanocarbon microstructure was performed using high resolution electron microscope JEOL JEM-2100F. X-ray diffraction studies were carried out on a standard diffractometer with monochromated Mo K_α radiation in the washing beam geometry.

3. STRUCTURE STATE OF THE SYNTHESIZED CARBON NANOMATERIALS

3.1 Exeperimental results

As result of the performed experiments, carbon powders with low bulk density (~ 10 kg/m^3) and developed surface (S_{BET} ~ 50-300 m^2/g) were synthesized on the electric discharge equipment in the above mentioned hydrocarbon media using the methods of electrical breakdown and HF electric discharge. High-resolution electron microscopy showed that produced carbon nanomaterials possess an onion-like structure (Fig. 1a) in the case of use of hydrocarbons with sp^3-hibridization (cyclohexane, propane-butane) as the working medium. It can be clearly seen that the particles are collected in agglomerates (Fig. 1b). The individual particles have a spheroidal shape and size of ~ 5-10 nm. Deviation of graphene layers in a particle from the ideal spherical shape, inherent in the onion-like structures, can be explained by incompleteness of the synthesis process. In the case of use of acetylene, amorphous carbon with disordered structure has been formed (Fig. 1c).

Raman spectroscopy investigation has validated that the products of electric discharge treatment of various hydrocarbons are typical amorphous carbon material.

The representative Raman spectra of the amorphous carbon are characterized by intensive broad G- and D- bands (Fig. 1). The standard positions of D (1350 cm^{-1})- and G (1580 cm^{-1}) -bands for graphite are indicated in the figures. The structural parameters calculated from the ratio of intensities of D-and G-bands have proved a strong structural disorder of the carbon powders: the value of L_a does not exceed 8 nm what correlates with that obtained from the high-resolution electron microscopy and structural data.

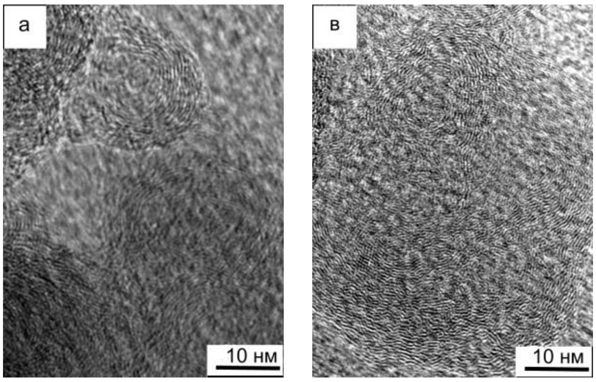

Fig. 1 – High-resolution micrographs of products of electric discharge treatment of propane-butane mixture (a), acetylene (b)

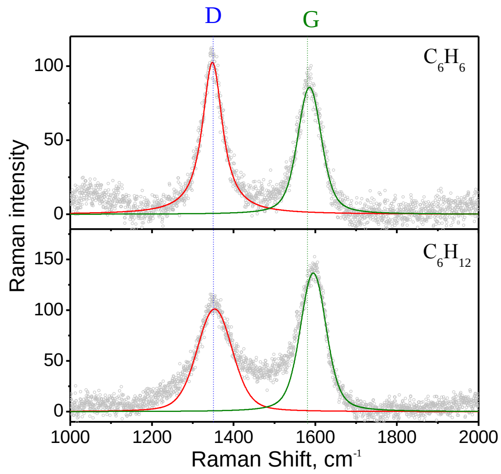

Fig. 2 – Typical Raman spectra of amorphous carbon obtained by electrical discharge treatment of benzene (a) and cyclohexane (b)

To determine the type of short-range order the method of radial distribution of atoms was used. Structure factor (SF) and radial distribution function were calculated from the experimental diffraction data for all synthesized materials (Fig. 3). It is clearly seen that SF of all powders is characterized by intense line S_1 = 1.8 Å^{-1}, whose position is typical for graphite.

Thus, the powders, synthesized at electrical discharge treatment of gaseous and liquid hydrocarbons, are amorphous carbon with a graphite type of short-range order. It is also well confirmed by the analysis of the radial distribution function of atoms.

Synthesized carbon nanomaterials were utilized as antifriction additives to industrial oils and as material for effective electromagnetic waves shielding. The reflection factor and absorption factor measurements of the CNM samples were made in the frequency range from 25 to 37 GHz. The absorption coefficient of the OLC sample is in the band of 28-34 dB.

3.2 Statistical analysis of structure state of the CNM

Structural models of atomic configurations of carbon nanomaterials produced from gaseous hydrocarbons have been reconstructed employing experimental curves of the structure factor by means of the reverse Monte Carlo method [8]. Agreement of experimental and calculated structure factors (Fig. 3 c, d) indicates that the resulting model of the atomic positions corresponds to the realistic structure of the studied objects. For the models of generated atomic configurations of the synthesized amorphous carbon, bond angle distributions have been calculated (Fig. 4).

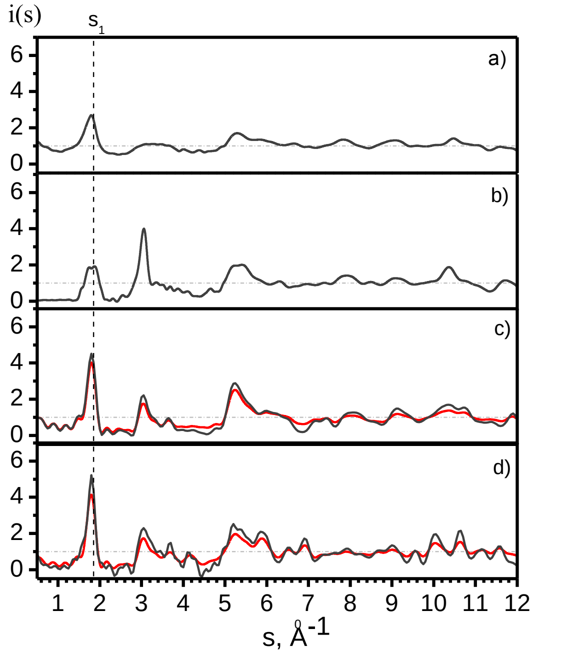

Fig. 3 – The structure factor of CNM produced by electric discharge treatment of liquid and gaseous hydrocarbons (a - benzene; b - cyclohexane; c - mixture of propane and butane, d - acetylene)
— experiment
— modeling

Bond angle distributions are characterized by a broad intense peak at 60°, which is absent in the ones calculated for graphite and UDA (Fig. 4). From a crystal-chemistry point of view, this fact can be interpreted as an insertion of additional atoms into the centre of some hexamerous fragments of curved graphene layers of amorphous carbon. A less intensive maximum which occupies an intermediate position between the ones of graphite and UDA is also presents on the bond angle distributions for the synthesized materials (Fig. 4 a, b).

To analyze the local atomic structure the model ensemble of atoms was divided into Voronoi polyhedra (VP) and Delaunay simplexes. The most widely applicable forms of the statistical geometrical analysis of random systems by VP are topological (distribution of the number of faces and the number of edges per face and topological types) properties and metric (distribution of VP volumes, distribution of VP face areas, the radial distribution of geometrical neighbors, the sphericity coefficient, etc.) ones [9].

Statistical analysis of Voronoi polyhedra, constructed for the models of atomic configurations of amorphous carbon, generated by RMC method, showed that the VP with faces number of 15 dominate in the synthesized materials. It is also established that the Voronoi polyhedra are mainly characterized by pentagonal faces, which do not correspond to crystal structures

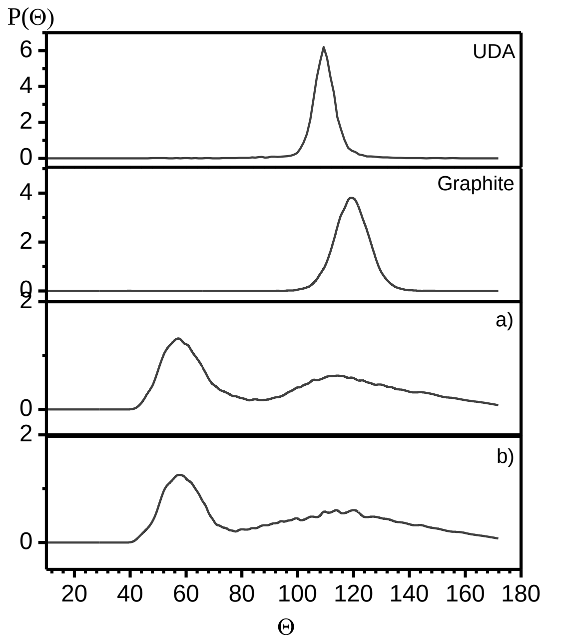

Fig. 4 – Bond angle distribution, calculated for models of atomic configurations generated by the RMC method: a – mixture of propane and butane,
b – acetylene

and provide an amorphous state. The volume distributions of VP of different carbon materials, calculated by presented in [10] algorithm, are shown in Fig. 5. It is clearly seen, that the curves for the produced nanocarbon, as opposed to crystalline graphite and UDD, are characterized by an asymmetry and prolating toward higher volume values. Such kind of the volume distribution of VP indicates to a fact that the system is heterogeneous, namely, the presence of large pores in atomic structure of AC.

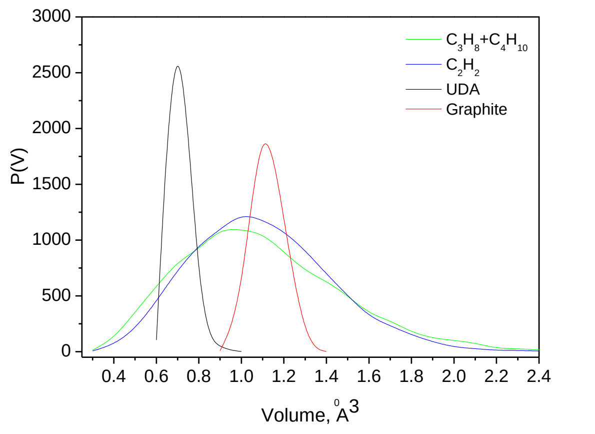

Fig. 5 – Volume distribution of Voronoi polyhedra for synthesized carbon nanomaterials

4. CONCLUSIONS

High-energy electric discharge technologies (electric breakdown and HF volume discharge in organic media) for a large scale synthesis of amorphous carbon are developed. The synthesized materials possess almost homogeneous morphology: up to 90% of individual particles have a similar shape with size of 10-20 nm. AC, produced by HF plasma-discharge in gaseous hydrocarbons technique, practically consists of pure carbon. It eliminates the need of its separation and purification, what results in essential decrease of prime cost of the CNM.

The structure of amorphous carbon produced by the technique of electric discharge treatment of organic media directly depends from chemical nature of the working medium – source of carbon. The fact of onion-like carbon synthesis by electric discharge treatment of hydrocarbons with sp^3-hybridization (cyclohexane and propane-butane mixture) is established.

Onion-like carbon was utilized as antifriction additives to industrial oils and as material for effective electromagnetic waves shielding.

AKNOWLEDGEMENTS

This work was partially supported by the joint project of SFBR of Ukraine (#F41/220-2012) – RFBR of Belarus (T11K-130).

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