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A Method and Apparatus for High-Throughput Controlled Synthesis of Fullerenes and Endohedral Metal Fullerenes

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Abstract—A method for synthesis of carbon nanostructures in a high-frequency arc discharge in the flow of helium (3–4 L/min) is presented. It is shown that the plasma-chemical synthesis of fullerenes and endohedral metal fullerenes (EMFs) can be controlled by changing helium pressure in the chamber. Temperature and electron concentration along the line normal to the discharge axis decrease upon moving away from the axis to the periphery; the larger the pressure, the sharper is the decrease in these parameters. The optimal helium pressure of 98 kPa was found in obtaining the Gd@C_{82} EMF which corresponds to the maximal EMF yield of 5 wt %.

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Unique properties of fullerenes and endohedral metal fullerenes (EMFs) make them not only important materials for electronics and medicine but also a source of fundamental knowledge in the field of quantum mechanics [1]. The main method for obtaining these materials is sputtering of graphite electrodes (which are either impregnated with salt or contain the doping metal in the axial channel for synthesis of EMF) in a dc arc in the helium atmosphere at the pressure of 10 to 26 kPa [2–4]. The drawback of this method is the impossibility of controlling the synthesis parameters. Overly large or small currents and pressure (outside the mentioned range) usually lead to a significant decrease in the fullerene content in the carbon condensate (CC). The method of sputtering of graphite electrodes in HF-arc plasma allows effective obtainment of fullerenes in wider synthesis parameter ranges [5].

In this work, we have shown experimentally that synthesis of EMFs can be controlled by varying the parameters of the HF arc discharge. Measurements of temperature and electron concentration distributions along the axis perpendicular to the arc at different pressures proved that the possibility of controlling the EMF synthesis is due to the possibility to change the mentioned distributions, as well as in the case of obtaining ordinary fullerenes [5]. For the Gd@C_{82} EMF, parameters were found that provide its maximum fraction in the CC.

Discharge was initiated between graphite electrodes in an apparatus that has been described before [6]. Graphite electrodes for emission spectral analysis with the diameter of 6 mm and the length of 100 mm were used (manufactured in compliance with TU 3497-001-51046676-2008). Channels with a diameter of 3 mm and a length of 85 mm were drilled in the graphite rods and filled with a 1 : 1 mixture of graphite powder and metal oxide.

The power supply scheme for the arc discharge is shown in Fig. 1. Voltage from two cophasal outputs of generator *G*1 is applied to the primary coil of transformers *T*1 and *T*2. Secondary coils of these transformers were connected together with a series resonance circuit (*C*1, *R*1, *L*1, *C*2) and the arc discharge with graphite electrodes. The arc discharge took place in a hermetic chamber filled with helium at different pressures where it flowed at the rate of 3–4 L/min. HF current in the arc was kept constant by controlling the electrode feed rate. The current was measured with the aid of current transformer *TA*1. When the current decreased below the given threshold, the electrodes were pushed forward until a designated current value was reached. Recording the optical spectrum and photographing the discharge were carried out through a quartz window in the chamber.

At a constant arc current and frequency (240 A and 66 kHz), the luminous region of the discharge decreased in size as the pressure grew in a helium pressure range of 30–560 kPa. Chord values of the temperature and electron concentration in the plasma were determined from the relative intensities of spec-

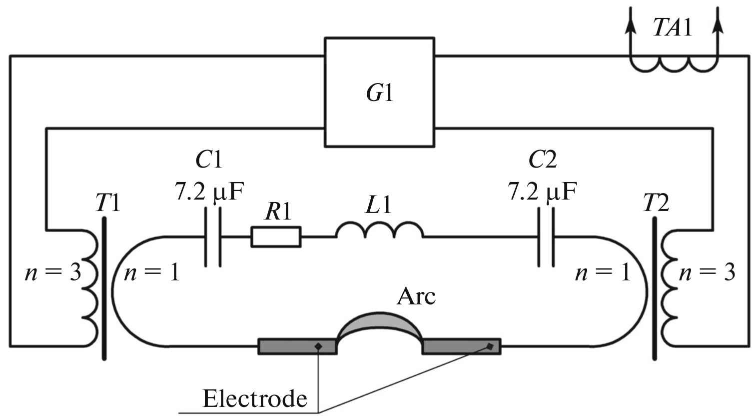

Fig. 1. Schematic diagram of the apparatus.

tral lines for two limit pressures achievable in our apparatus, 98 and 363 kPa (with arc current of 240 A and frequency of 66 kHz).

Radial values of these parameters were then calculated in accordance with Abel's theorem (Fig. 2). The diagrams show that the temperature and the electron concentration near the axis of the arc increase with temperature, but decrease at a much higher rate farther from the discharge axis. Extrapolating these results onto the parameters corresponding to the optimal fullerene formation zone, we can conclude that the thickness of the layer with the optimal parameters diminishes as the pressure increases [7]. This is known to decrease the general fullerene content in the formed CC and to increase the relative fraction of higher fullerenes in the extracted fullerenes mixture (FM) [5].

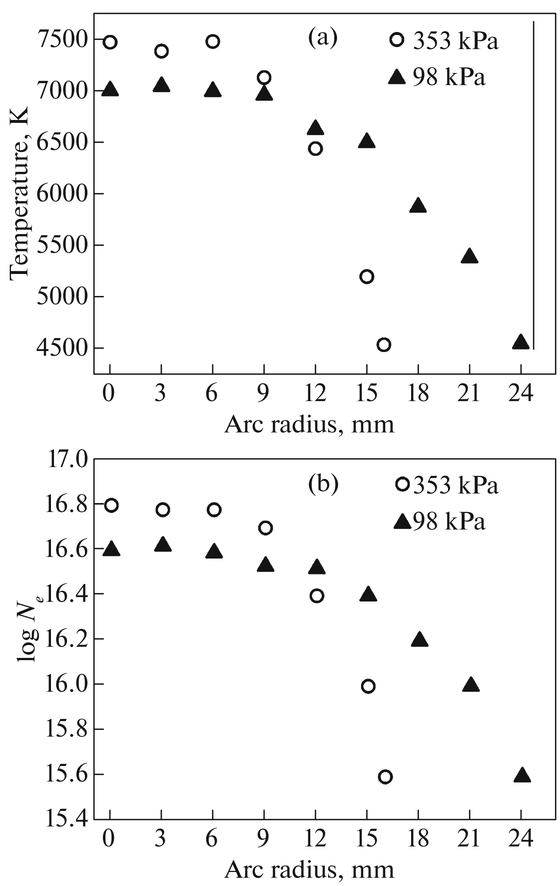

Fig. 2. Dependence of (a) temperature and (b) electron concentration in the arc plasma on distance from the arc axis at pressures in the chamber of 98 and 353 kPa.

Our studies on the influence of the pressure on synthesis of EMFs found no direct correlations. It can be stated that, at pressures above 98 kPa, EMFs with a single metal atom within the molecule are formed, while below that value molecules with two or more metal atoms appear. Determination of the amount of formed EMFs in the obtained and extracted FM is a quite difficult process. An individual fraction containing EMF of only one type needs to be separated and weighted, and then it should be proven by mass-spectrometry that this fraction corresponds to the considered EMF. However, if mass spectrometry shows that the inserted metal exists in EMFs of only one kind and there are no other chemical compounds in the fullerene mixture that contain this metal, then the amount of the EMF can be determined by measuring the metal content. FMs obtained at different pressures with Gd_2O_3 added possess no free gadolinium and no Gd-containing compounds other than EMFs. This allowed us to study the temperature dependence of formation of $Gd@C_{82}$ in the chamber in a relatively simple way.

The CC containing fullerenes and EMFs with gadolinium was obtained in the HF arc discharge plasma. The EMF was extracted from the synthesized CC with CS2 in a Soxhlet apparatus. Mass-spectral measurements were performed on a Bruker BIFLEXTM III instrument at the Leibniz Institute for Solid State and Material Research (Dresden, Germany). The studies

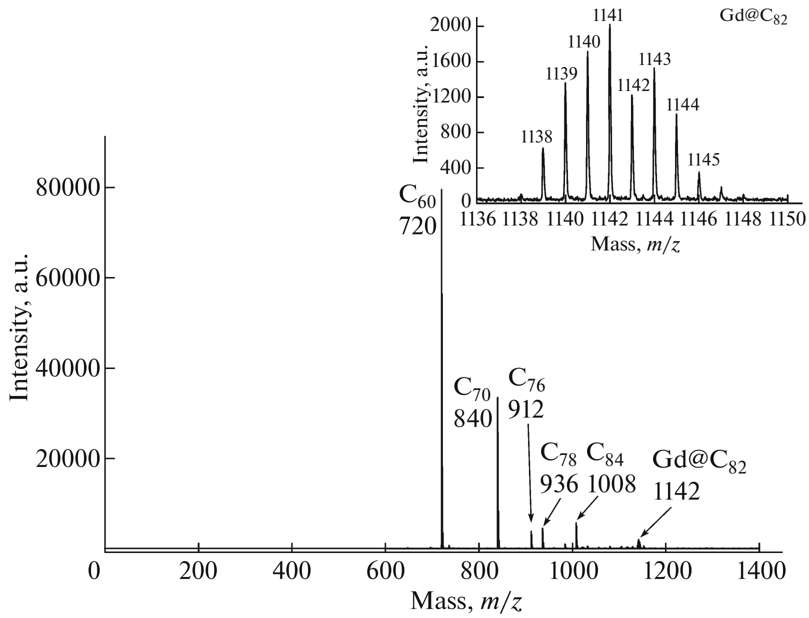

Fig. 3. Results of mass-spectral analysis of the FM obtained with addition of Gd_2O_3 at a pressure of 98 kPa and extracted with pyridine (positive mode).

showed that, in the FMs obtained at various pressures, Gd is present only in $Gd@C_{82}$ (Fig. 3).

Samples of the CC with Gd obtained at pressures of 353, 225, 98, 64.8, and 32.4 kPa were subject to extraction. The extracts were dried, weighted, and then dissolved in the initial solvent to the concentration of 1 mg/mL. Sample solutions were placed into the holes in the graphite rods and then atomized in the arc discharge in a setup for emission analysis [8]. Standard samples were prepared beforehand using solutions with known Gd concentration in the holes in the graphite rods. Obtained data were used for building the concentration curve for analysis using standard samples [9]. Gadolinium content in a given probe was found from the intensity of its line at $\lambda = 335.86$ nm and the concentration curve. Allowing for the mass spectrum that showed that gadolinium is contained only in $Gd@C_{82}$, we thus measure mass fraction of this compound in the fullerene extract. Results of investigation of the $Gd@C_{82}$ content in the fullerene mixture extracted from the CC obtained at various pressures are given in the table.

Dependence of the content of $Gd@C_{82}$ in the FM extracted from the CC obtained at various helium pressures

Pressure, kPa	Gd content in FM, wt %	$Gd@C_{82}$ content in FM, wt %
32.4	0.34	2.5
64.8	0.40	2.9
98	0.40	2.9
225.5	0.42	3.1
353	0.93	5

Thus, the process of EMF formation in the HF arc discharge in the helium flow can be controlled by changing the helium pressure in the chamber, which leads to a change in the plasma cooling rate. The temperature and electron concentration along the normal to the discharge axis decrease from the axis to the periphery. It was shown using the example of obtaining $Gd@C_{82}$ that there is the optimal pressure (98 kPa) corresponding to an optimum product yield (5 wt %).

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