APPLICATION OF DUSTY PLASMA FOR SYNTHESIS OF CARBON NANOSTRUCTURES

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The synthesis and investigation of carbon substances which are formed in the arc at atmospheric pressure with feeding by currents with industry frequencies, currents with kHz frequencies, and by direct current (dc) are carried out. The influence of the current frequency on the yield of fullerenes and nanotubes, which were formed under synthesis, is explored. It is shown that a change of the local electron concentration by introducing particles of different substances has negative influence on the yield of fullerenes.

Introduction

Since the discovery of fullerene [1], many explanations of its formation have been attempted. Usually, in the considered models, only chemical interactions of carbon atoms were considered [2—4]. Within the framework of these models, the effective synthesis of fullerenes at atmospheric pressure, which was realized in our setup (it works successfully since 1994) [5], is impossible. It is necessary to note that, during a long time, researches could not synthesized fullerenes at atmospheric pressure [6]. We demonstrated that the electron concentration is an important parameter which affects the coagulation of carbon clusters, because the cluster charges depend on the magnitude of electron concentration in plasma [7]. The idea of a controlling role of electron concentration was used in the optimization of our setup aimed at the synthesis of fullerene and fullerene derivatives.

1. Experimental Section

In this report we present the results of the investigations of carbon structures which were synthesized in a low-temperature carbon-helium plasma at atmospheric pressure. The arc was generated between two graphite electrodes at the feeding by currents with frequencies of 44 kHz and 50 Hz and by dc. Evaporated carbon condensed on the chamber walls and on an electrode, which was cooled most effectively. The carbon condensate from the walls (soot), fullerenes which were extracted from soot by benzene, and the carbon condensate from the electrode (thermolysis residual [8]) were analyzed.

The structure and composition of samples were investigated by electron microscopy (transmission electron microscope PREM-200), mass spectrometry (Bruker Biflex TOP-MS time-of-flight mass-spectrometer), X-ray powder diffraction (DRON-4 diffractometer) and UV-vis spectroscopy (Uvikon 943 double beam spectrometer).

2. Results and Discussion

The ratio of soot and thermolysis residual, which were synthesized under different regimes of arc feeding, is presented in Table 1. One can see that this ratio changes and the yield of fullerene contained in soot changes as well.

The maximal fullerene yield from soot was achieved at the 44-kHz current feeding. 80% of soot, 10% of thermolysis residual, and 10% of graphite loss with a helium flow were formed from the evaporated carbon. At this frequency, the high yield of fullerenes was observed in a wide range of currents from 100 to 300 A. During the analysis of the fullerene composition in soot, it was determined that, despite the significant difference between the yield of fullerenes synthesized at different frequencies, the ratio of fullerenes in a mixture changed insignificantly (Table 1).

The X-ray powder diffraction studies showed that the current frequency did not influence the structure of formed thermolysis residual (Fig. 1). The main part of thermolysis residual was graphite with a distance of 3.40 Å between its layers.

By electron microscopy, it was found that multiwall nanotubes were only in the content of thermolysis residual, and different amounts of nanotubes were obtained at different frequencies of current (Table 2 and Fig. 2). The maximum nanotube yield (bundles of nanotubes) (Fig. 2) was achieved at dc. Individual nanotubes were obtained at 44 kHz. This amount was significantly less than that of nanotubes obtained at dc. There were no nanotubes in the thermolysis residual synthesized at 44 kHz.

In Table 3, we show the results of the comparison of fullerene mixtures obtained under injection of different elements with those without injection of any elements. The synthesis was carried out at 44 kHz (maximal fullerene yield). The powders were introduced with the helium flow by a device for the feeding of powder samples [9]. The analysis of the obtained results allowed us to determine that the injection of Ir particles leads to increasing the amount of C_{60} by 10 % and the formation of oxide dimers. The amounts of C_{70} and higher fullerenes increased in the case of the injection of Ni, Fe, and Se. The influences of these elements on the yield of fullerene oxides were different: Se and Ni led to, respectively, decreasing and increasing their yield, and Fe gave the zero yield of fullerene oxides.

As one can see from Table 3, all these elements have different effects on the contents of a fullerene mixture.

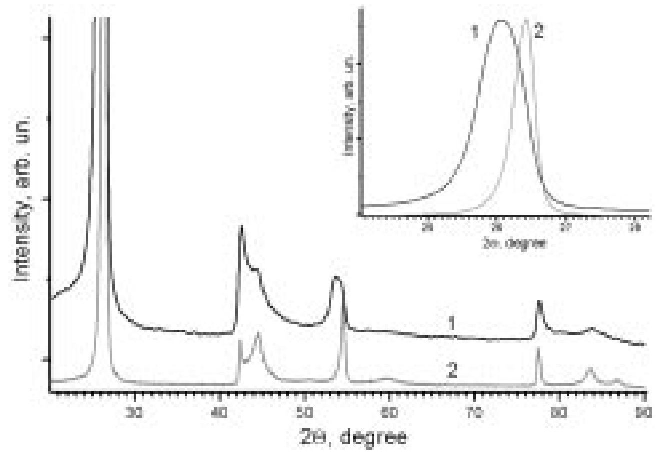


Fig. 1. X-ray powder diffraction data of thermolysis residual obtained at the feeding by current with a frequency of 50 Hz (*1*) and initial graphite (*2*)

According to our model [7], an additional injection of substances varies the electron concentration in plasma. The main parameters which determine the charge of clusters or small particles are the ionization potential and electron affinity [10]. The magnitudes of these parameters are presented in Table 4.

These data show that the magnitudes of ionization potential and electron affinity of injected substances influence significantly the relative content of different fullerenes in the mixture rather than the total fullerene

T a b l e 1. Ratio of fullerenes which are formed in a carbon-helium plasma at currents with different frequencies

Current frequency, Hz	C_{60}, %	C_{70}, %	C_{60} and C_{70} oxides, %	High fullerenes, %
0	77	17	1	4
50	84	13	<1	3
44×10^3	80	15	1	4

T a b l e 2. Percent content of carbon substances synthesized upon the condensation from a carbon-helium plasma at currents with different frequencies

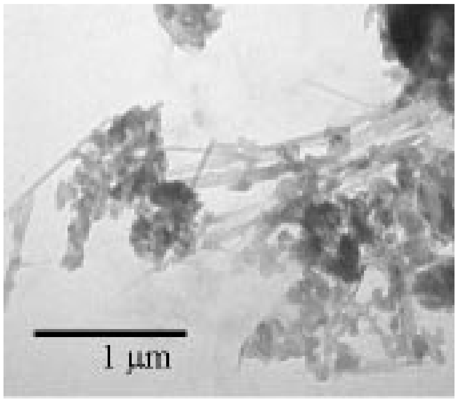
Current frequency, Hz	Current, A	Soot, % (including fullerenes, %)	Thermolysis residual, % (including nanotubes)
0	55—200	27—73 (1—4)	73—21 (bundles)
50	100—200	69—70 (1—3)	18—22 (absence)
44×10^3	100—300	78—80 (7—8)	9—10 (individual)

T a b l e 3. Influence of elements which were injected in plasma on the composition of a fullerene mixture

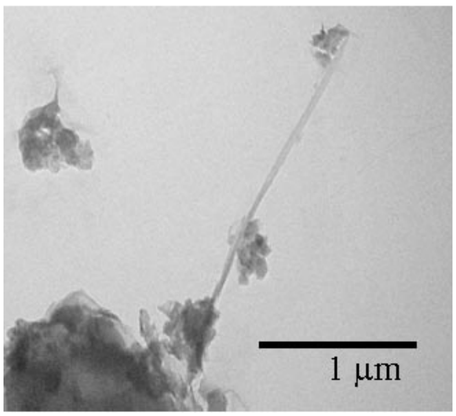
Element	C_{60}	C_{70}	C_{60} and C_{70} oxides	High fullerenes
Na	↓ negligibly	no influence	no influence	↑ by 2 times
Gd	↑ negligibly	↓ negligibly	↓ negligibly	↑ negligibly
Se	no influence	no influence	↓ by 3 times	↑ by 2 times
Fe	↓ negligibly	↑ negligibly	↓ up to zero	↑ by 2 times
Ni	↓ by 1.4 times	↑ by 2 times	↑ by 10 times	↑ by 2 times
Pt	no influence	no influence	↑ by 2 times	↓ by 1.5 times
Ir	↑ by 1.15 times	↓ by 1.6 times	dimers	↓ by 2 times

↑ – increasing the relative content in a fullerene mixture.

↓ – decreasing the relative content in a fullerene mixture.



a



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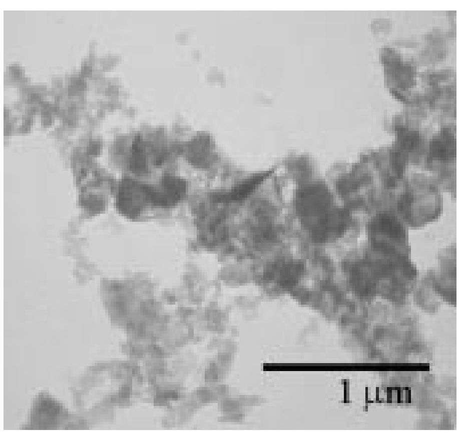

c

Fig. 2. TEM images of nanotubes in residual graphite synthesized at DC (*a*), at currents of frequencies of 44 kHz (*b*) and 50 Hz (*c*)

element with the yield. From the X-ray powder spectra of soot (Fig. 3) synthesized under injection of different elements, it was determined that a small fullerene yield was in the case where soot had particles of an injected

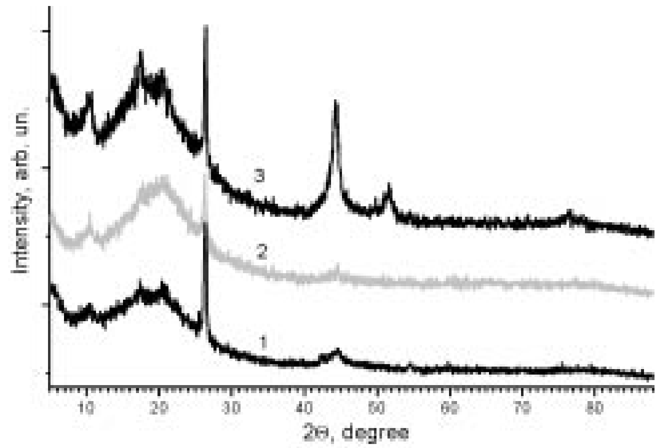

Fig. 3. X-ray powder diffraction data for soots obtained without injection of any substance (*1*), with the injection of Fe (*2*) and Ni (*3*)

size of tens of nanometers and more. It was realized under injection of Ni, Pt, and Ir to the plasma. In the presence of amorphous particles of a size of some nanometers and less in soot, the fullerene yield was maximal, and it matched to the synthesis without injection of substances. These results are in agreement with our idea of a controlling role of electron concentration in the fullerene synthesis [4]. Big particles have large electron affinity and influence strongly the density of free electrons. This process leads to a local decrease of the electron density and a deviation from the zone of optimal synthesis.

Conclusions

The results of the investigation of substances synthesized in a carbon-helium plasma arc at atmospheric pressure at different frequencies of the feeding current show that the fullerene ratio and the yield of nanotubes depend on the frequency. The parameters of the synthesis with maximal fullerene yield and maximal nanotube yield are found. It is necessary to use currents in the kHz range for the realization of the effective fullerene synthesis in plasma and to use dc for the realization of the effective synthesis of nanotubes in plasma.

The additional injection of the Ni, Pt, and Ir powders, which usually increase the yield of nanotubes, into a carbon plasma leads to a decrease of the fullerene yield because of a low atomization of these substances and to a local increase of the electron concentration. So, the formation of fullerenes and nanotubes are two

T a b l e 4. Fullerene yield upon the injection of different elements, ionization potential and electron affinity for these elements, and the presence of particles in soot.

Element	Fullerene yield, %	Ionization potential, eV	Electron affinity, eV	Presence of amorphous particles in soot
–	8	–	–	–
Na	6	5.1	0.3	–
Gd	6	6.2	–	–
Se	7	9.75	2	–
Fe	8	7.87	0.5	–
Ni	4	7.6	1.3	+
Pt	4	9.0	2.6	+
Ir	4	9.2	2	+

competitive processes which depend on the plasma parameters. One can control the plasma parameters by introducing the powders of different elements and changing the frequency of a feeding current of the arc.

The results of the investigation of the substances obtained in plasma at different current frequencies allowed us to determine that the current frequency influences the fullerene ratio and the structure of formed thermolysis residual.

Earlier, we found that the feeding of the arc discharge by the 44-kHz current leads to its stratification, i.e. to fluctuations of the electron density [11]. One can obtain a more complete interpretation of the results (Tables 3 and 4) if the electron concentration and temperature will be measured experimentally. In the future, we plan to combine the fullerene synthesis with experimental measurements of the electron concentration and temperature in a fullerene plasma by spectral methods.

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ЗАСТОСУВАННЯ ЗАПОРОШЕНОЇ ПЛАЗМИ
ДЛЯ СИНТЕЗУ ВУГЛЕЦЕВИХ НАНОСТРУКТУР

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Р е з ю м е

Проведено дослідження синтезованих вуглецевих субстанцій, які формуються в електричній дузі під атмосферним тиском в умовах протікання постійного струму, струмів промислової та кілогерцової частоти. Досліджено вплив частоти струму на продуктивність одержання фулеренів і нанотрубок, котрі формуються в процесі синтезу. Показано, що на продуктивність негативно впливає зміна локальної концентрації електронів, яка відбувається як наслідок введення частинок різної природи.