Production of carbon nanofibers by plasma jet of helium and hydrocarbons

M B Shavelkina, R Kh Amirov, V I Kiselev and V A Katarzhis

Joint Institute for High Temperatures of Russian Academy of Sciences, Izhorskaya Street 13/2, 125412 Moscow, Russia

E-mail: mshavelkina@gmail.com

Abstract. The parameters of a non-catalytic process for synthesizing carbon nanostructures during the conversion of methane / helium and propane-butane / helium jets have been studied. The spectral features of the radiation of mixed systems have been investigated. Analysis of the spectra showed that the main part of carbon dimers is withdrawn from the hot region of the plasma in the outlet plasma stream. Synthesized products were been characterized by scanning electron microscopy, Raman spectroscopy, thermal analysis and X-ray photoelectron spectroscopy. It is shown that carbon nanostructures have a bamboo-like morphology and similar properties when using both methane and propane-butane mixture as a carbon source. It has been established that the morphology of synthesized carbon nanofibers is not affected by the pressure of the medium.

1. Introduction

Thermal plasma processing of carbon sources using a plasma jet is one of the universal methods for the synthesis of advanced materials [1-3]. The advanced materials, at present, include various carbon nanostructures (fullerenes, carbon nanotubes (CNTs), carbon fibers, graphene, onions, etc.). Due to their unique electronic and extraordinary mechanical properties, carbon nanostructures have been receiving much attention in a wide variety of applications: electronics and computing, field emitter devices, sensors, electrodes, high strength composites, and storage of hydrogen, lithium and other metals [4,5].

Among the existing types of carbon nanostructures, filamentary carbon nanotubes and nanofibers are the most preferred as potential modifiers of elastomeric compositions. Unlike in a flat graphene sheet, in carbon nanotubes, the common p-electron cloud is deformed, compressed inside the tube and is stretched over the outer surface. The smaller the nanotube diameter the higher is the deformation degree. This affects the strength of the bonds: the greater the curvature of nanotube surface, the smaller degree of the p-orbitals overlapping, the higher is a nanotube capability to chemical reactivity.

In terms of geometry, CNTs are structures with a high aspect ratio, i.e. ratio L / D (length to diameter), because diameter of CNTs is from one to several tens of nanometers, and the length amounts to tens of microns. Therefore, aspect ratio of CNT can reach very high values.

CNTs and nanofibers are mainly produced by CVD technology (the most acceptable in terms of target product yield, energy costs, etc.). The principle of CVD is the decomposition of various hydrocarbons over transition metal supported catalyst. As a result of the above technology application, composition of the filamentary particles contains catalytic particles (metals of variable valence), elements of a catalyst substrate, and also various carbon impurities. In addition, nanostructures synthesized by CVD technology, at the supramolecular level form very strong agglomerates and have various kinds of defects. It means that CNTs and nanofibers have poor technological properties, are
characterized by the complexity of dispersing and uniform distribution in the structuring material matrix.

In this paper, our purpose is to investigate the possibility of direct synthesis of carbon nanofibers in a plasma jet of hydrocarbon / helium without the use of catalysts.

2. Methods

Synthesis of carbon nanostructures was carried out in a flow-type gas reactor. The setup consists of a vacuum chamber, a water ring pump, a plasma generator, a water cooling system, an energy supply system (figure 1). The thermal plasma generator which is a high current divergent anode-channel DC plasma torch was used for the synthesis of graphene materials earlier. When this plasma torch is used for synthesis of filamentary structures its design is adjusted so that the distance between cathode and nozzle is extended to 2 mm in order to increase the flow rate of helium-hydrocarbon mixture (figure 2).

A detailed description of the experimental setup was given in the study [6]. The experiment involved an input of mixture of hydrocarbons with the plasma forming gas into the plasma torch, wherein heating and decompositions occurred in the region of the arc discharge, followed by condensation of the synthesis product on the metal surface of the collector, see figure 1. The rate of hydrocarbons, plasma gas flow and the power of the plasma torch varied independently of each other. For the experimental conditions the electric power of plasma torch was set up to 50 kW. Helium was used as plasma forming gases. Carbon precursors were propane-butane mixture, methane.

![Figure 1. Schematic view of a reactor.](image1)

![Figure 2. Geometry of the plasma generator: 1 – a cathode, 2 – a water cooled anode with a diverging duct, 3 – plasma forming gas/ hydrocarbon, 4 – symmetry axis.](image2)

For each experiment, input of hydrocarbons was carried out after establishment of the temperature field in a collector (determined by chromel-alumel thermocouple). The current value of the plasma torch was constant during the experiment and equaled to 400 A. Arc voltage was changed from 60 to 110 V depending on gas pressure. Helium (class A) flow rate was 0.75 g/s.

Experiments were conducted at various pressures and flow rates of hydrocarbons. Pressure changed from 150 to 740 Torr, and hydrocarbon (propane-butane technical (PBT) GOST R 52087-2003), methane TU 51-841-87) flow rate varied from 0.05 to 0.37 g/s. Duration of the experiments was 5 - 20 min. The experimental conditions are presented in table 1.
Table 1. Technological conditions.

| Power (kW) | Current (A) | Voltage (V) | Gas pressure (Torr) | Helium flow rate (g/s) | Hydrocarbons flow rate (g/s) |
|------------|-------------|-------------|---------------------|-----------------------|-----------------------------|
| 30-45      | 300 -400    | 60-110      | 150-740             | 0.5-0.9               | 0.05-0.37                   |

Direct registration of the dimensional parameters and images is carried out using a scanning electron microscopy (SEM) - microscope Hitachi S5500 with in-lens technology for obtaining both ultra-high resolution and high sensitivity of EDS analysis. The used modes are DF-STEM, BF-STEM and SE.

The synthesis efficiency, phase composition and thermal stability of carbon products were evaluated by thermogravimetry combined with differential scanning calorimetry (STA 449 Netzsch F3 Jupiter platform) with linear heating in argon in steps of 10 K/min in the temperature range of 20-1000 °C.

Raman spectroscopy (Ntegra Spectra, a laser with 532 nm wavelength) was used to study the structure of nanoscale structures.

A quantitative study of the elemental composition and electronic state of atoms was carried out using X-ray photoelectron spectroscopy (XPS) at room temperature using a Theta Probe spectrometer of ThermoFisher Scientific (UK).

The spectra of hydrocarbons and helium plasma were taken on a three-channel fiber-optic spectrometer AvaSpec 2048 with a spectral resolution of 0.1 ÷ 0.4 nm and spectral range 200 ÷ 1100 nm. The electron temperature was considered for helium plasma, using the method of relative intensities of the same lines of ionization particles (method Boltzmann exhibitors).

3. Results and discussions

All experiments on mixed plasma conversion were carried out in a reactor preheated by nitrogen plasma for 1-2 minutes. After the temperature on the collector surface reached 823 K, pure helium followed by helium – hydrocarbon mixture are tangentially supplied into the plasma torch, as shown in figure 2. Immediately after the input, the temperature of the collector drops to 600 K, but then is restored within 5-6 minutes. The arc voltage with hydrocarbon addition increases by 20 - 30 V. Figures 3-4 show the emission spectra of pure helium and helium plasma with the addition of propane-butane. Figure 3 shows that the spectrum of pure helium recombining plasma jet at atmospheric pressure and an electron temperature of 20,000-30,000 K represents a set of strong atomic lines in the range of 300-800 nm. When propane-butane is added (figure 4), the number of helium lines decreases and lines typical of C2 are observed in the spectrum, whose number grows with distance from the nozzle. The highest intensity of the atomic C lines corresponds to the range 200-400 nm. At the same time both vibrational and rotational temperatures for C2 do not vary over the entire length of the jet. The presence of the CN line is due to the fact that the measurements were carried out in an air atmosphere.

The synthesized products are black color powder. Investigation of the powder by scanning electron microscopy shows that these are filamentary nanoscale structures. Figures 5 - 7 show the morphology of the samples obtained by changing the medium pressure and the precursor type. It can be seen from the figures that the structure in all images is the same and has a "bamboo" appearance with approximately same length of "bamboo fragments" (100 nm) and a diameter of 30-50 nm. This may indicate a periodic nature of the growth process of these carbon nanofibers, which according to [7] is usually associated with the effect of a catalyst.
Figure 3. The emission spectrum of helium plasma without the addition of a hydrocarbon.

Figure 4. The emission spectrum of helium plasma with the addition of propane-butane.

Figure 5. Image of carbon nanofibers obtained by conversion of propane-butane / helium plasma at 710 Torr.

Figure 6. Image of carbon nanofibers obtained by conversion of propane-butane / helium plasma at 350 Torr.

Figure 7. Image of carbon nanofibers obtained during the conversion of methane/helium plasma at 350 Torr.

Figure 8. The Raman spectrum of carbon nanofibers, obtained by conversion of methane/helium plasma at 350 Torr (1), propane-butane / helium plasma at 710 Torr (2).
Figure 9. Thermogravimetry of carbon nanofibers obtained by conversion of propane-butane/helium plasma at 350 Torr (1), methane/helium plasma at 350 Torr (2).

Figure 10. XPS C 1s spectra of carbon nanofibers obtained by conversion of propane-butane/helium plasma at 350 Torr (1), methane/helium plasma at 350 Torr (2), HORG (3).

Catalyst was not used during the experiments in this work. Heterogeneity of the surface, apparently, is associated with formation of internal overlaps. Such structure corresponds to nanofiber [8].

Figure 7 shows a typical Raman spectrum for carbon nanofibers samples synthesized in a helium plasma jet system. The spectrum of the samples reflects a unique feature of the G-band: because of localization and curvature of graphene layers in formation of nanofibres [9].

Studies of the thermal stability of the samples show that the mass loss occurs in the temperature range of 673-873 K which is typical for purified carbon nanostructures. However, the amount of mass lost in the oxidation of samples synthesized in conversion of propane-butane/helium plasma at 350 Torr and in conversion of methane-helium plasma at 350 Torr, differs by 46 mass % by weight in air (figure 9). This is due to the different surface structure formed in the gas phases of different composition. This result agrees with the X-ray photoelectron spectroscopy data.

As can be seen from figure 10, some difference in the peak widths of the samples is caused both by the samples inhomogeneity and by the presence of several chemical states of the carbon atoms. For their interpretation and determination of relative values, account of surface charge has been conducted with isolation of a state with sp²-hybridization, to which energy of 284.44 eV is attributed. For the samples synthesized from methane-helium plasma, the fraction of sp²-hybridization is slightly less than for the samples synthesized from propane-butane/helium plasma.

Thus, we have developed a method for synthesizing carbon nanostructured materials by plasma jet without the use of catalysts. The resulting carbon fibers have fewer defects than those generated using chemical methods [11].

4. Conclusion
The possibility of non-catalytic synthesis of carbon nanofibers in the conversion of a mixed plasma: helium / hydrocarbon, where propane-butane or methane is used as a hydrocarbon has been demonstrated experimentally. Analysis of the emission spectra of these systems showed that the amount of carbon dimers increases at the exit of the stream from the zone of arc discharge. The study using physicochemical methods of synthesis products obtained in different helium plasma systems has been showed that the bamboo-shaped morphology of carbon nanofibers and their properties do not change when the pressure of the medium and the type of carbon source change.

5. Acknowledgements
The authors gratefully acknowledge Russian Foundation for Basic Research for the support by grants No 16-08-00145, 16-08-00057, 16-08-00081 and 18-08-00306.
6. References

[1] Ostrikov K and Murphy A B 2007 J. of Phys. D: Appl. Phys. 40 2223

[2] Gonzalez-Aguilar J, Moreno M and Fulcheri L 2007 J. Phys. D: Appl. Phys. 40 2361

[3] Boulos M I 1991 IEEE Trans. Plasma Sci. 19 1078

[4] Mostofizadeh A, Li Y, Song J and Huang Y 2011 J. of Nanomater. 2011 Article ID 685081 21 pp

[5] Carbon Nanostructures Series Ed.: Araujo Paulo Springer: Berlin, Germany 2018

[6] Shavelkina M B, Amirov R H, Katarzhis V A, Kiselev V I 2017 J. of Phys.: Conf. Ser. 748 012021

[7] Ivanov V, Nagy J B, Lambin P, Lukas A, Zhang X B, Zhang X F, Bernaerts D, Tendeloo G, Amelinckx S and Landuyt J. 1994 Chem. Phys. Lett. 223 329

[8] Volodin A A, Fursikov P V, Kasumov Y A et al. 2006 Russ Chem Bull 55 1425

[9] Ferrari A C 2007 Solid State Commun. 143 47

[10] Naumkin A V, Kraut-Vass A, Gaarenstroom S W and Powell C J 2012 NIST Standard Reference Database 20, version 4.1

[11] Che G, Lakshmi B B, Martin C R and Fisher E R 1998 Chem. Mater. 10 260