Simulation of the equilibrium flow of plasma with the addition of hydrocarbons in the scope of graphene synthesis using a DC plasma torch

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Abstract. Graphene synthesis in the helium and argon plasma jets generated by 40 kW DC plasma torch under the pressure 350 Torr is investigated experimentally and by means of the modeling. Propane-butane mixture and methane are used as the carbon feedstock. Scanning microscopy shows that in the case of helium the structure with lateral size up to 500 nm is being synthesized. In the case of argon the morphology of graphene flakes varies from rumpled to rectified sheets with lateral size up to 2 μm. Temperature and velocity profiles are determined for the helium and argon jets using the numerical simulation. Addition of hydrocarbons into the inert plasma jets creates an environments differing in the composition and the charge concentration.

1. Introduction
Fundamental processes resulting in the transformation of carbon feedstock into the solid ultra-dispersed matter and properties of nanoparticles are nowadays under intensive investigation. The motivation is based on the variety of useful and unique properties of carbon nanomaterials.

This work is aimed to investigate the relationship between the gaseous environment and the morphological properties of graphene layers in the process of conversion of hydrocarbons within plasma jets produced by DC plasma torch.

2. Methods
The set up for plasma-chemical synthesis of ultrafine materials includes: a direct current plasma torch with an expanding output anode, a vacuum chamber, a liquid ring pump, water cooling systems, and power supply systems. A detailed description of the experimental setup was given in the study [1]. The experiment involved a input of mixture of hydrocarbons with a 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 40 kW. Helium, argon, and nitrogen were used as plasma forming gases. Carbon precursors were propane-butane mixture, methane.
For each experiment, the input of hydrocarbons was carried out after establishment of the temperature field in a collector (determined by chromel-alumel thermocouple). Duration of the experiments was 5 - 20 min. The experimental conditions are presented in table 1.

| Power (kW) | Current (A) | Voltage (V) | Gas pressure (Torr) | Ar flow rate (g/s) | He flow rate (g/s) | CH₄ flow rate (g/s) | C₃H₈-C₄H₁₀ flow rate (g/s) |
|------------|-------------|-------------|---------------------|------------------|-------------------|-----------------|---------------------------|
| 30-40      | 350-400     | 60-110      | 350                 | 3.0              | 0.75              | 0.153           | 0.1                       |

Table 1. Technological conditions.

Image (SEM image) and dimensional parameters were recorded using a TESCAN MIRA scanning electron microscope with a standard technique.

The phase composition and thermal stability of the synthesis products was evaluated using a synchronous thermal analyzer STA 409PC Luxx with a QMS 403 C Aeolos quadrupole mass spectrometer (NETZSCH) under heating at a speed of 10 K / min in a dynamic flow of atmospheric air (flow rate 30 ml / min). Resolution of thermal balance is 0.002 g.

### 3. Results and discussions

#### 3.1 Properties of graphene, synthesized in the helium and argon plasmas

Graphene flakes were obtained in the helium and argon plasma jets produced by the 40 kW DC plasma torch under the pressure 350 Torr. Their electron microscopy images are displayed at the Figures 1 and 2. Propane-butane mixture and methane were used as a carbon feedstock. Using the scanning microscopy it is found that in the case of the carrier gas helium the synthesized flakes have lateral size up to 500 nm. In the case of carrier gas argon the synthesized flake-like structures vary in morphology from rumpled sheets to rectified ones with lateral size from several nanometers up to 2 μm.

Thermal investigations of samples have shown (Figure 3 and 4), that in spite of size dispersion the oxidation of samples obtained in case of argon goes on in the narrow temperature range demonstrating their greater purity.

Experimental investigations of the conversion of hydrocarbons in the inert gas plasma jets have shown that under the realized conditions the carbon structures are being formed as graphite fragments – graphene sheets. According to [2] an introduction of hydrocarbons into the heated up to 1700°C volume results finally in the pyrolytic carbon formed as fluffy soot material. The same action at the substrate heated up to 2000-2500°C produces highly oriented graphite. The pyrocarbon is usually formed directly from the carbon vapor, but the soot needs some time to form the soot nuclei. We have performed a visual experiment. When the vacuum chamber is open immediately after the shutdown of plasma torch, reactor surfaces are bare, in 3-4 hours they become black. But those particles have the morphology differing from the soot. The soot morphology is a closed structure in
the form of multilayer spheres. Probably in the experiment there is time enough for the concentric layers to be generated and to cover the nuclei, and the process needs higher temperatures. In the modeling gaseous predecessors of soot are considered as nuclei [3]. In the review [2] nuclei are considered as spheroidal clusters from C60 up to C80, which usually appear in the high temperature range 2300-3000°C as a result of chemical reactions. However, the mechanism of formation of soot particles from those clusters is a subject of intensive investigations.

In this work we have considered the role of carrier gases in the creation of environment favorable for the formation of flake-like structures.

3.2 Quasi-one-dimensional modeling
For the considered above options of the synthesis in the helium and argon plasma it is possible to get additional information using the quasi-one-dimensional thermodynamic simulation [1]: temperature and velocity profiles and the plasma composition. Here calculations of local equilibrium state were performed using a list of accounted components including the following individual compounds from the IVTANTHERMO data base: C or C239 – carbon atoms, Cgr or C238 – condensed carbon (graphite) and molecules from C2 up to C5. The list includes also what is found in the literature: fullerenes C40, C60, C80 and carbon nanotubes CNT [4, 5].
Initial equilibrium temperature of the helium plasma with addition of propane-butane mixture was supposed to be 8000K. The most interesting part of the evolution of plasma composition according to the falling axial temperature is presented in Fig. 5. The figure illustrates the process of condensation of carbon from plasma. First of all the early predecessor of solid carbon – C$_3$ appears, further on it is replaced by the immediate predecessor – fullerene C80. The latter at the initial temperature of the condensation very rapidly turns into the solid carbon – Cgr.

Analog of Fig. 6 for the argon plasma looks the same, but has one visible difference: absolute values of mass fractions are much lower because argon flow rate is 4 times greater than helium flow rate. Less visible is the shift of the whole picture for argon towards higher temperatures with relation to the picture for helium. This issue is illustrated in Figure 6 where main curves of Figure 5 are overlapped by corresponding curves for the argon case. The temperature shift is obvious considering the curves C$_3$ and C80. The shift of curves Cgr is barely visible, but there is a difference in the initial temperature of the condensation: 3004 K for He and 3019 K for Ar.

There is a consensus about carbon nanoparticles that their properties usually are determined mainly by the environmental conditions at the beginning of condensation. Plasma composition at the initial temperature of the condensation for the considered above two cases is presented in Figure 7. From the left histogram (a) of Figure 7 the following conclusion may be drawn: in the argon case the concentrations of all hydrogen containing components are substantially greater compared with the helium case, concentrations of the carrier gas and purely carbon components being the same. Concentrations of positive ions are plotted separately in Figure 7 (b). For the helium case only C+ has any significance, but in the argon case ions CH+ and H$_3$+ are increasing substantially the total charge density.

![Figure 5. Evolution of composition of the C$_3$H$_8$-C$_4$H$_{10}$/He plasma along the temperature axis.](image)

Presentation of plasma composition in terms of mass fractions (Figure 5 and 6) makes the carbon balance visible in transformations. Redesign of these figures in terms of concentrations makes the figures less informative: molecules and fullerenes become components of the lower echelons. That’s why, considering the factors affecting the formation of condensed phase, it is easier to deal with parameters of the initial temperature of condensation (Figure 7). Comparison of considered above two cases are presented in Table 2.
Figure 6. Evolution of composition of the CH$_4$/Ar plasma along the temperature axis.

Figure 7. Plasma composition at the initial temperature of condensation for the C$_3$H$_8$-C$_4$H$_{10}$/He and CH$_4$/Ar cases: a) concentrations of main components in m$^{-3}$; b) concentrations of positive ions in m$^{-3}$.

Table 2. Comparison of environmental parameters of synthesis of graphene materials in the helium and argon plasmas

| Parameters                                                                 | He      | Ar      |
|---------------------------------------------------------------------------|---------|---------|
| 1. Temperature, K                                                         | 3004    | 3019    |
| 2. Axial derivative of temperature, K/m                                   | -8474   | -8402   |
| 3. Velocity, m/s                                                          | 113     | 56      |
| 4. Residence time in the temperature range                                 | 2 times more |        |
| 5. Concentrations of carrier gas and carbon containing components         | the same |         |
| 6. Concentrations of H, H$_2$ and hydrocarbons                            | greater  |         |
| 7. Concentration of C+                                                    | the same |         |
| 8. Concentrations of CH+ and H$_3$+                                       | greater  |         |
4. Conclusion
A possibility to control the synthesis of carbon nanostructures during the conversion of hydrocarbons in the helium and argon plasma jets under the pressure 350 Torr is demonstrated experimentally. It is shown that plasma jet composition exerts influence on the morphology and thermal stability of synthesized materials: lateral size of flakes may turn greater or less. Quasi-one-dimensional simulation shows that in the argon plasma there are more of hydrogen and of hydrocarbons. It confirms the theory of the completing the structure after freeing the edges of carbon sheets from hydrogen. Besides, argon environment is rich of ions CH+ and H3+, increasing the charge density. As a result there is a non-uniformity of the growth of particles and the greater variance of their size.

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6. References
[1] Shavelkina M B, Ivanov P P, Bocharov A N, Amirov R Kh 2019 *J. Phys. D: Appl. Phys.* 52 495202
[2] Shi Y, Gao Z, Zhu Q and Kong F 1997 *Carbon* 35(6) 767
[3] Krestinin A V 2000 *Combustion and Flame* 121(3) 513
[4] Scott C D 2004 *J. Nanosci. Nanotechnol.* 4 368-76
[5] S.A. Esfarjani 2013 A modeling framework for the synthesis of carbon nanotubes by RF plasma technology. PhD thesis. University of Toronto