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Synthesis of graphene-like materials by pyrolysis of hydrocarbons in thermal plasma and their properties

R Kh Amirov[1], **I N Atamanuk**[1], **N A Vorobieva**[2], **E H Isakaev**[1], **M B Shavelkina**[1] **and E I Shkolnikov**[1]

[1] Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
[2] Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119991, Russia

E-mail: mshavelkina@gmail.com

Abstract. A method to synthesize graphene-like materials using dc high current divergent anode-channel plasma torch has been developed. Carbon atoms are generated by decomposition of propane–butane and methane in a thermal plasma jet. Products of synthesis are characterized by electron microscopy, thermogravimetry, Raman spectroscopy and porosimetry. Effect of experimental conditions on the morphology, phase composition and porosity of the products of synthesis are investigated. The optimal conditions have been found.

1. Introduction

Graphene has high electrical and thermal conductivity, mechanical strength and transparency, which makes it an interesting material for many applications. At present the most developed fields of their application is the production of composites with improved mechanical and physical properties. There is the production of dual-layer electrodes for ultracapacitors with electric double layer. Currently, supercapacitors, capacitors with high capacitance and low leakage currents are considered candidates to replace conventional batteries in various fields, ranging from miniature electronics to car batteries. In most cases manufacturers of electrodes for ultracapacitors use activated coal. The only drawback of activated coal is that the material is hard and brittle, which does not allow its use in production of flexible ultracapacitors. Graphene could be one of the alternative materials. The main difficulty when using graphene as electrodes is associated with a tendency of aggregation of graphene sheets. This leads to a decrease in the specific surface area of electrodes available for charged particles, and thus lower capacitance. To solve the problem of graphene layers, they should be made in the crumpling form [1].

Most of the available methods to obtain graphene relate to mechanical or chemical cleavage of graphite or epitaxial growth of graphene films. These methods do not provide opportunities for large-surface area graphene and high quality. Significant progress was made recently by the method of chemical deposition of graphene from the gas phase (CVD-method) on Ni-substrate, followed by transferring it onto an arbitrary substrate.

Use of plasma is considered as one of the most promising methods to produce graphene with desired properties. For example, a microwave discharge was used [2]. Graphene output

amounted to 1.8% of the total consumption of carbon. For the synthesis the arc discharge between graphite electrodes was also used. Graphene materials with the number of layers from two to four were synthesized [3]. Hydrogen and helium were used as plasma forming gases [3]. Optimal conditions were found for the synthesis of a small number of graphene layers, wherein the number of defects was less than that in the production of graphenes by chemical methods [4] when the discharge was initiated in a mixture of helium and carbon dioxide. The graphenes become implanted with nitrogen atoms when a mixture of ammonia and helium [5] was used. It should be noted that a standard arc is a discrete and unstable process, and it fails to allow to achieve mass production of high-quality carbon nanostructures [6], as well for the reason of low rate of carbon evaporation.

Nevertheless, to obtain scaling graphenes remains a challenge. From this stand point the application of thermal plasma generated by the plasma torch looks very promising. The advantages of the proposed approach compared with the electric arc method of the graphenes production are: possibility of a substantial increase in productivity by continuous operation; opportunity to work with the starting materials in various states of aggregation; possibility of the optimization of process by independent control over a wide range of pressure, flow ratio of energy input, plasma gas source and carbon containing substance; possibility of forming the stream using a variety of additional devices (nozzles), and by changing geometrical parameters of plasma torch. Using plasma jet reactor based on the dc plasma torch [7] pure layered graphene was obtained. Number of layers of graphene sheets was controlled by controlling the rate of ethanol injection.

The main aim of the present study is to obtain experimental data on synthesis of graphene-like materials from carbon atoms generated by decomposition of propane–butane and methane in a thermal plasma jet by means of the direct current plasma torch with the extending channel of an output electrode. The advantage of this type of plasma torch system was demonstrated by comparison with several developed technologies. These are the technologies of hardening and nitriding of railway wheels, plasma spraying for recovery and manufacturing railroad crossings and plasma deposition of copper with wear-resistant refractory layer [8,9]. On the basis of these technologies a plasma jet reactor was designed and the experimental study of synthesis of carbon nanotubes was developed to investigate the mechanisms of their synthesis, structure assembly and yield increase [10].

2. Experimental setup and procedure

For the synthesis of graphene materials the thermal plasma source was used which is a high current divergent anode-channel dc plasma torch [8–10]. A detailed description of the experimental setup was presented in the article [11]. The experiment involved a simultaneous input of hydrocarbons with the working gas (helium, argon) into the plasma torch, wherein heating and decompositions occurred in the plasma jet and in the region of the arc discharge, followed by condensation of the synthesized product on metallic surfaces. Consumption of carbon, plasma forming gas and plasma torch power were changed independently from each other. For the experimental conditions, the electric power of plasma torch was set up to 40 kW. Helium and argon were used as plasma gases. The experimental conditions are presented in table 1.

Natural gases used as carbon source were: propane–butane in the ratio 30:70%, technical methane and methane of high purity (99.99%). The main parameters were varying pressure in the range from 200 to 730 Torr and gas flow rate. Hydrocarbon flow rate ranged from 0.87 to 6.49 g/s for a propane–butane mixture, and methane from 0.48 to 3.66 g/s. The experiment duration was 10–20 minutes. Upon completion of the synthesis of carbon materials samples were collected from the target surface [11] and from the trap. Samples were not purified and were analyzed in the form in which they were synthesized in the reactor. Methods of electron

Table 1. Technological conditions.

Power	20–40 kW
Current	200–400 A
Voltage	35–100 V
Plasma gas	Helium, Argon
Gas flow rate	0.5–3.75 g/s
Pressure	50–750 Torr
Time of continuous work	20 min

microscopy were used to investigate the structure of the synthesized products by a scanning electron microscope of MIRA 3 TESCAN. Efficiency of synthesis, thermal stability and phase composition of carbon products were evaluated by thermogravimetry and differential scanning calorimetry on synchronous thermal analyzer STA 409PC Luxx (NETZSCH) with linear heating sample in air at the rate of 10 K/min at temperatures up to 1000°C. Raman spectra were investigated by using the exciting radiation at a wavelength of 532 nm (Ntegra spectrum). To determine the characteristics of the porous structure (pore volume, pore radius, surface area) we used a relatively new method of adsorption "Limited Evaporation" [12] based on the analysis of the kinetics of evaporation of the adsorbate from the test material. Using the model of one-dimensional diffusion of vapor the isotherm of desorption have been calculated. Applying approaches of Broekhoff-de Boer theory and Dollimore-Heal equation cumulative and differential distribution of pore volume as function of their radius have been found. It is assumed slit-like pore form [12] to evaluate the specific surface area of materials the classic Brunauer, Emmett and Teller method was applied using a low-temperature nitrogen adsorption analyzer Quadrasorb SI. In each experiment, the mixture was injected only after stabilization of temperature distribution in the graphite reactor. Stabilization usually takes 5–6 min and was indicated by measuring water temperature in the cooling system.

3. Results of experiment

The investigation has confirmed the formation of graphene-like materials. Experiments on the decomposition of propane–butane mixture show that depending on the pressure and value of the gas flow rate a nanostructure with various morphologies is formed. At low pressures of helium (200 Torr) a large amount of amorphous carbon (37%) and the graphitized particles are produced. Increase of the pressure leads to formation of graphene flakes. At 350 Torr their transverse dimension was the highest and the geometric parameters were used to define the size of each sheet length and width, which was in the range of 600 nm, but the amorphous carbon was present. Further increase of pressure decreases the content of this phase and reduces the size of graphene flakes. When reaching a pressure of 710 Torr of helium, the synthesized samples contain 2% of amorphous carbon and 81% of graphene flakes. If the arc current is reduced at a pressure of 350 Torr, then the amount of the amorphous carbon increases again. The flow rate of helium, in fact, had no effect on the morphology of the flakes (ranged from 0.45 to 0.95–1.0 g/s). The products of synthesis by using propane–butane mixture and argon have transverse dimension not exceeding 100 nm. As in the case of using helium with increasing argon pressure, the amorphous carbon is formed together with graphene flakes.

The best conditions for the production of graphene-like flakes were as follows: helium pressure of 710 Torr, flow rate of propane–butane 0.87 g/s. Content of the amorphous carbon in the
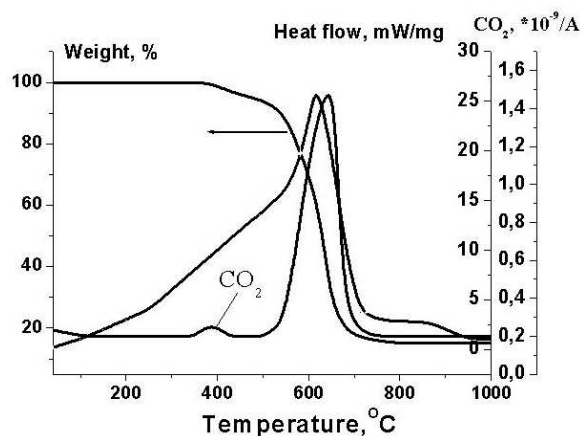
Figure 1. The results of thermogravimetric analyses of synthesis products produced by decomposition of propane–butane at a pressure of 710 Torr. Plasma forming gas is helium.
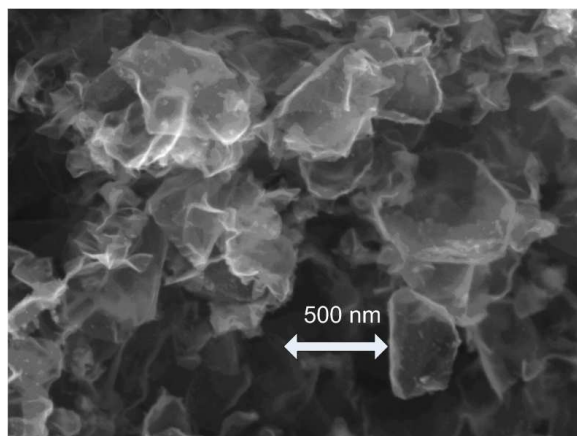

Figure 2. The morphology of synthesis products from the decomposition of propane–butane at a pressure of 350 Torr. Hydrocarbon flow rate is 2.7 g/s and helium flow rate is 0.75 g/s.
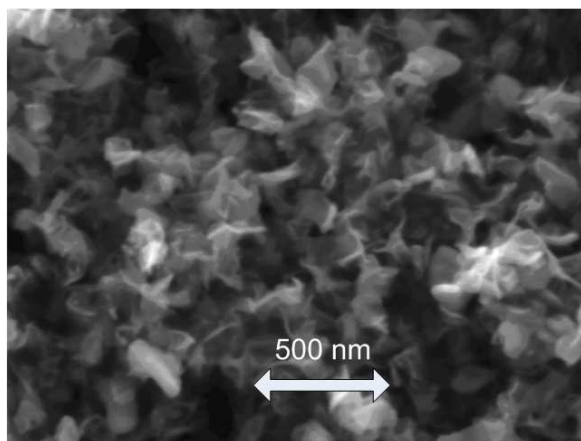

Figure 3. Morphology of synthesis products by decomposition of propane–butane at a pressure of 500 Torr.
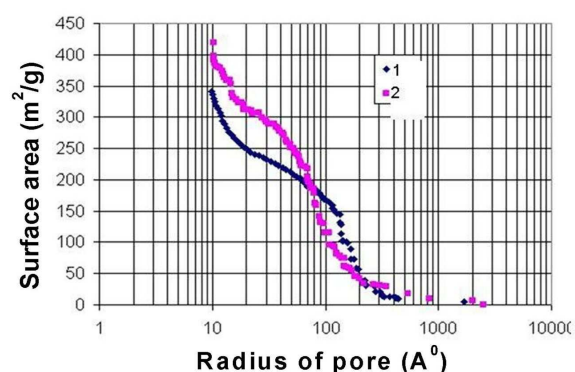

Figure 4. Specific surface area as a function of the pore radius for the samples synthesized using helium at a pressure of 350 Torr (1) and 710 Torr (2). Carbon source is propane–butane.

products of synthesis was 4 wt.% and the graphitized particles were less than 2%. Figure 1 shows the results of thermogravimetric analyses of synthesis products at this case, figure 2 presents an example of SEM image at a pressure of 350 Torr and the morphology of synthesis products by decomposition of propane–butane at a pressure of 500 Torr is shown in figure 3. Specific surface area of the samples synthesized at 350 Torr of helium was 350 m^2/g, and for those synthesized at 710 Torr it was 400 m^2/g. Sufficiently large number of pores is in the size range of 10-40 nm, which corresponds to the mesoporous structure. Figure 4 presents pore size distribution.

With a large decrease in consumption of propane–butane, a large quantity of amorphous
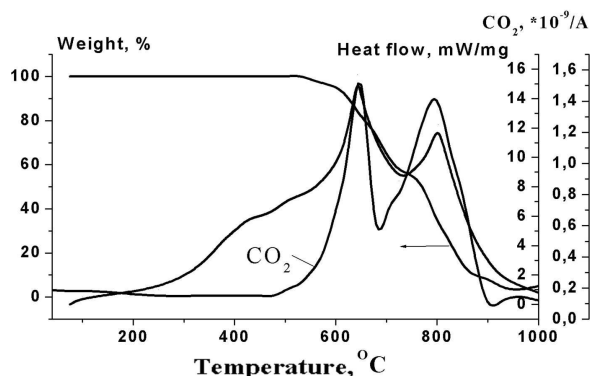
Figure 5. The results of thermogravimetric analyses of synthesis products produced by decomposition of propane–butane in argon at low gas flow rate at a pressure of 730 Torr.
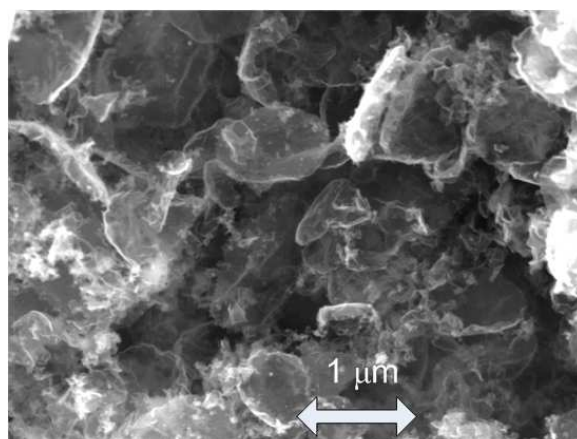

Figure 6. The morphology of synthesis products from the decomposition of methane at a pressure of 350 Torr. Plasma forming gas is helium.

carbon was found 37% using helium at a pressure of 500 Torr and at a pressure of 730 Torr when argon was used. The same effect was observed when the current arc in helium decrease at a pressure of 350 Torr. Under such conditions on thermogravimetric curve one can observe the formation of two areas of weight decrease of the sample, followed by two anomalies on the curve of calorimetry oxidation process which is explained by the formation of carbon nanotubes [10]. The results of thermogravimetric analyses for this case are shown in figure 5. Optimal conditions for the synthesis of graphene materials obtained by decomposition of methane differ mainly in higher precursor consumption. According to the electron micrographs and thermogravimetry, synthesis products during decomposition of pure methane in helium and argon at a pressure of 350 Torr and expenditure 0.75 g/s and 3.5 g/s up to 77% graphene-like material is formed with a transverse dimension of 400–600 nm.

Figure 6 shows an example of SEM image of synthesized products from the decomposition of methane using helium. With increasing pressure of argon and helium to 500 Torr in experiments with technical methane, the size of graphene structures on the target increases. In helium yield of graphene materials amounted to 91%. Decreasing the gas pressure down to 150 Torr increased the amount of graphite and amorphous carbon phase. The maximum yield of 82–88% of graphene materials with crumpling sheets was observed in argon at 650–670 Torr and a high flow rate of methane 2.8 g/s. Figure 7 presents the results of thermogravimetric analyses of synthesis products at these conditions. The primary pore volume of the samples obtained by the decomposition of methane is also concentrated in the pore radius range of 40 nm. The porosity of the products of synthesis is the same whether propane–butane or methane were used. Specific surface of products generated using methane according to BET method material is 400 m^2/g. Figure 8 shows the comparison of distribution volume for the pore radius at methane (1) and propane–butane (2) decomposition.

Graphene-like materials produced from decomposition of methane at optimum conditions, are less stable at high temperatures than the synthesis products generated using propane–butane. Figure 9 show the results of thermogravimetric analyses of synthesis of different carbon material products at optimized conditions including nanotubes [10].

Raman spectroscopy is a rapid and easy way to obtain an indication of the structure and quality of carbon materials including graphenes [4,7]. In the Raman spectra of the synthesized
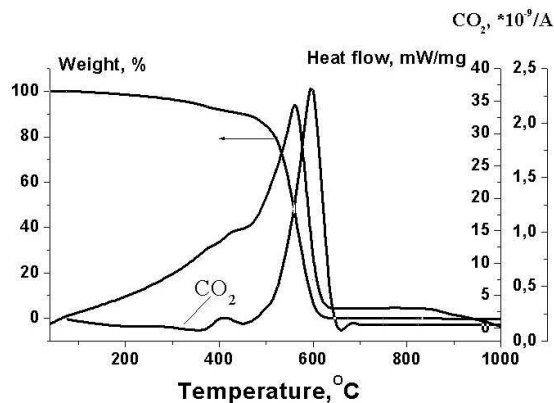
Figure 7. Results of thermogravimetric analyses of synthesis products produced by decomposition of methane at a pressure of 670 Torr. Plasma forming gas is argon.
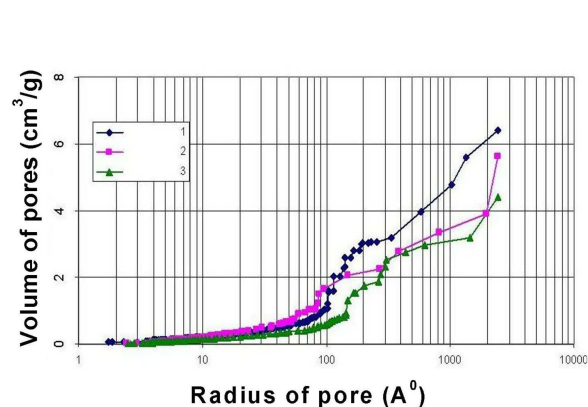

Figure 8. Volume of pore as a function of the pore radius. (1) Pressure is 710 Torr, plasma gas is helium, carbon source is propane–butane. (2) Pressure is 710 Torr, plasma gas is helium, carbon source is methane. (3) Pressure is 350 Torr, plasma gas is helium, carbon source is acetylene
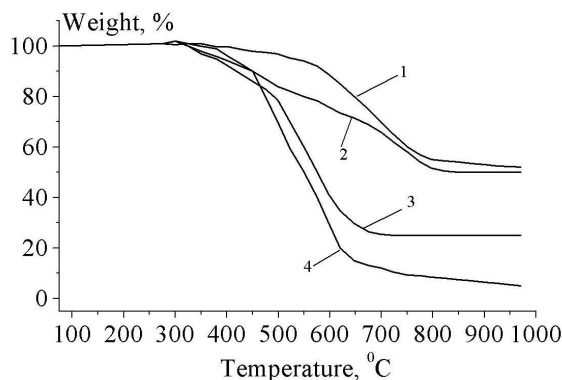

Figure 9. The results of thermogravimetric analyses of different carbon nanomaterials: (1) carbon nanofibers, (2) carbon nanotubes, (3) graphene-like materials produced by the decomposition of propane–butane, (4) graphene-like materials produced by the decomposition of methane.
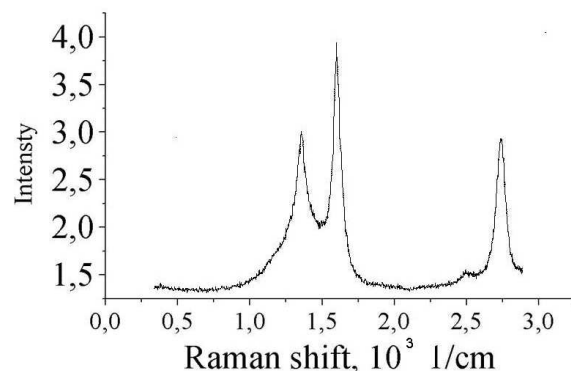

Figure 10. The Raman spectrum of the sample from the decomposition of propane–butane in helium plasma at a pressure of 350 Torr.

samples, characteristic features of graphenes materials were observed. Figure 10 presents a typical Raman spectrum of carbon nanomaterials produced by the decomposition of propane–butane. The three intense features are the D band at 1335 cm^{-1}, the G band at 1580 cm^{-1} and 2D band at 2661 cm^{-1}.

In our study, we used the well-known approach to make conclusions about the presence of graphene materials and about the number of layers of graphene structures in accordance with the work [13]. The number of the graphene layers can be estimated from the 2D peak position and peak intensity G. It was concluded that the synthesized graphene flakes had a number of

layers, which was less than ten. The analysis of the Raman spectra showed that the majority of the synthesized products had one or two layers of graphene using helium and up to five graphene layers using argon as the plasma gas. Our results are in agreement with the results published in the articles [7]. In this article the conclusion was made that graphene-like materials of similar type were produced in plasma jet reactor of similar type when the same methods of diagnostic was used. The main difference of our work is that as the carbon source we used gases instead of liquid. It has allowed increasing the rate of formation of graphene-like materials by the factor of a hundred. In addition, it also allowed us to investigate the effect of gas composition and pressure.

Summing up the experimental data allowed sequential scaling process of graphene-like production to obtain required structures. The structural and the morphological properties of graphene-like materials produced at hydrocarbon decomposition depended upon pressure and gas flow rate.

4. Conclusions

We have investigated the synthesis of graphene-like materials at decompositions of hydrocarbons in the plasma jet reactor using the direct current plasma torch with the extending channel anode in plasma-forming gas helium and argon. Possibility of producing a wide range of graphene materials with different morphology and structure has been shown. The optimal conditions for the synthesis of graphene materials and the influence of synthesis parameters on the structure of the surface and specific pore area have been found. Relationship between the morphological properties of graphene materials produced in the plasma jet with their porous structure has been investigated. The possibility that the selection of hydrocarbons and their flow rate can increase the yield of graphene-like materials has been demonstrated. It was found that depending on the synthesis conditions the geometry of graphenes alters (from curved petals to disk with the diameter of 100–700 nm). The quantity of graphenes in the synthesized products also alters from 58 to 95%. The experimental data to scale gradually the process of production of graphene-like materials with the desired morphology has been obtained.

Acknowledgments

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