Application of DC plasma torch for synthesis of carbon nanostructured materials

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Abstract. The results of the synthesis of carbon nanostructures at high temperatures using a DC plasma torch are presented. Plasma was generated by introduction of argon, nitrogen and helium into the plasma torch with an anode in the form of an expanding channel. Sustainable modes of the plasma torch operation have been achieved by simultaneous tangential input of a plasma gas with a carbon source. Obtained solid products were studied using electron microscopy, thermogravimetry, Raman spectroscopy and X-ray diffraction to characterize their properties and morphological structures.

1. Introduction

Plasma is a useful tool to synthesize carbon nanomaterials, including diamonds, fullerenes, nanotubes, and graphene, as shown by Gonzalez-Aguilar et al [1]. High temperature of plasma synthesis and anhydrous conditions provide conditions for formation of particles with unique and desirable surface properties and morphology unreachable by other methods. These particle's properties are critical to their performance in application of materials.

2. Methods

For the synthesis of carbon nanostructured materials thermal plasma generator was used which is a high current divergent anode-channel DC plasma torch. A detailed description of the experimental setup was given in the studies [2]. The experiment involved a simultaneous input of hydrocarbons or soot with a plasma forming gas 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 synthesis product on the metal surface of the target in a vacuum chamber, see figure 1. The carbon flow rate, the composition of the catalysts (for solid precursor), plasma gas flow and the power of the plasma torch varied independently to each other. For the experimental conditions the electric power of the plasma torch was set up to 40 kW. Helium, nitrogen and argon were used as plasma forming gases.

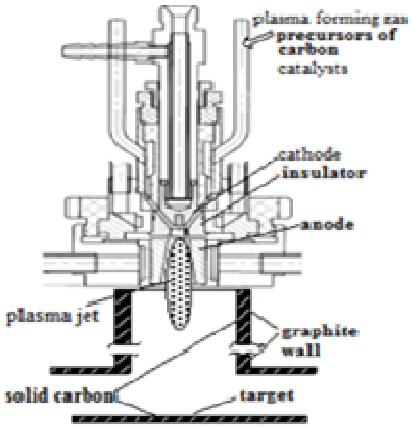

Figure 1. Schematic view of a plasma jet reactor.

For each experiment, the input of hydrocarbons was carried out after establishment of the temperature field in a graphite reactor (determined by the temperature of water in the cooling system) and establishment of the electrical characteristics of the plasma torch. The current value of the plasma torch was constant during the experiment and equaled to 350Å for argon, nitrogen and 400 Å for helium. Arc voltage was changed from 60 to 110 V depending on the gas pressure and the gas flow rate.

Soot, alcohols and hydrocarbons (methane, acetylene, and mixture of propane-butane in the ratio 30:70 mass %) were used as the source of carbon. Decomposition of soot in plasma jet reactor was performed in the presence of catalysts (Y_2O_3, Co, Ni and Fe). Their flow rate varied from 0.008 to 0.035 g/s. Experiments were conducted at various pressures and flow rates of hydrocarbons. Pressure changed from 150 to 720 Torr, and hydrocarbon flow rate varied from 0.05 to 0.37 g/s. Flow rates of alcohols reached 4 ml/min. 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)	Nitrogen flow rate (g/s)	Argon flow rate (g/s)	Soot flow rate (g/s)	Hydro-carbons flow rate (g/s)
30-40	300 - 400	60-110	150-740	0.5-0.9	3.0-3.5	3.0-3.75	0.008-0.035	0.05-0.47

Method of electron microscopy was used to investigate the structure of the synthesized products on a scanning electron microscope of MIRA 3 TESCAN with Schottky field emission cathode in high vacuum regime. Raman spectra were investigated by using the exciting radiation at a wavelength of 532 nm (NTEGRA spectrum). X-ray diffraction data were obtained at the room temperature on a powder diffractometer Stoe Stadi P. To evaluate the specific surface area of materials the classic BET method was applied using a low-temperature nitrogen adsorption analyzer Quadrasorb SI.

Efficiency of the synthesis, thermal stability and phase composition of the carbon products were evaluated by thermogravimetry and differential scanning calorimetry on a synchronous thermal analyzer STA 409PC Luxx (NETZSCH) with the linear heating sample in air at the rate of 10 K/min at temperatures up to 1000°C.

The spectra of argon and helium plasma were taken on a three-channel fiber-optic spectrometer AvaSpec 2048 with the spectral resolution of 0.1 ÷ 0.4 nm and the spectral range 200-1100 nm.

The electron temperature was considered, using the method of relative intensities of the same lines of ionization particles (the method of Boltzmann exhibitors).

3. Results and discussions

Design of the DC plasma torch to 40 kW (figure1) provided for simultaneous input of plasma gas and carbon precursor under angle. Voltage fluctuations in arc plasma torches of this type do not exceed 5%. At transition from one plasma forming gas (argon) to another (helium) and further addition to helium plasma of gaseous hydrocarbon (e.g. methane) there occurs a voltage increase and respective power increase, however, the arc remains stable (figure 2). Figure 3 shows the relative population of excited Ar states calculated from spectral of argon plasma with a liquid hydrocarbon (ethanol). Analysis of such experimental data showed that the maximum temperature of argon plasma at the energy input 40 kW and 350 A was 15700 K. The maximum temperature of argon in the stream of carbon particles was 16700 K. These measurements show that introduction of ethanol into a plasma flow does not cool it. Introduction of a solid carbon also does not affect plasma temperature.

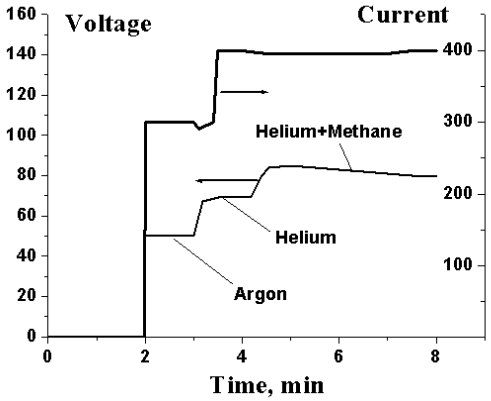

Figure 2. The effect of the stability of the plasma jet.

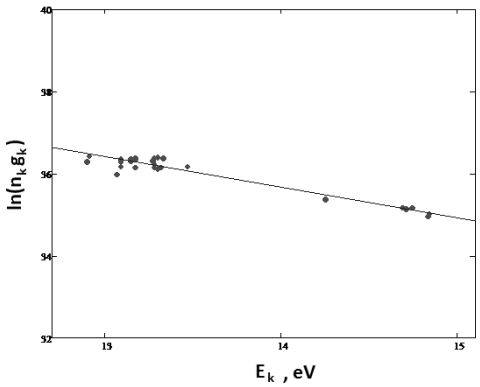

Figure 3. Relative population of excited Ar states.

Figures 4-5 presents the morphology of carbon nanostructured materials obtained by plasma jet.

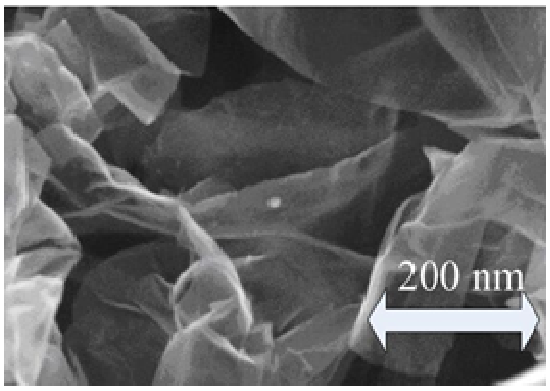

Figure 4. SEM image of graphene sheets produced using helium plasma.

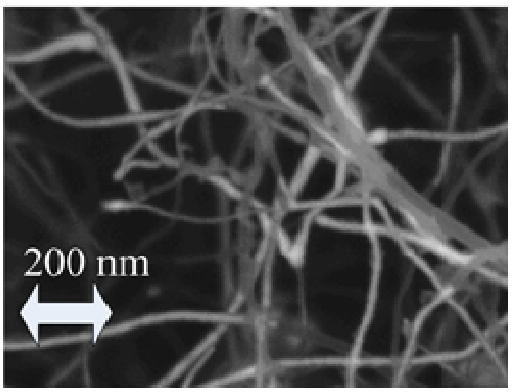

Figure 5. SEM image of carbon nanotubes produced using nitrogen plasma.

Investigation of the synthesis products derived with the help of plasma jet has shown that by varying the medium pressure, plasma flow speed and rate of hydrocarbon materials input, it is possible to obtain various nanostructures of carbon – graphene (figure 4) as well as carbon nanotubes (figure 5). By varying the ratios of plasma gas and precursor in plasma jet it is possible to produce single-layer and multi-layer carbon nanotubes, in the shape of individual structures or collected in bunches, that is, bound nanostructures. The maximum production of carbon nanotubes was observed in helium plasma at combination Ni/Co/Y_2O_3 – 1.46/1.47/1.29 at.%, when the pressure was 500 Torr, arc current was 400 A and consumption of the mixture was 0.45 g/min. The diameter of the synthesized carbon nanotubes changed from 16 to 74 nanometers. Large graphene flakes having transverse lateral dimensions of 600 nm were synthesized at helium pressure of 350 Torr at the rate of 0.75 g/s. Distance between adjacent graphene flakes is 1-2 nm. Graphene materials may consist of one or 5 layers.

Typical bands were received on the Raman spectra of the investigated samples (figure 6) which are specific to carbon nanotubes and graphene – same as in the work [3].The sensitivity of the positions, widths and intensities of the D, G and 2D peaks–have made it possible to probe a variety of morphologies of graphene produced from different hydrocarbon materials decomposed by plasma jet.

X-ray diffraction patterns (figure 7) of carbon products synthesized from decomposition of methane in helium plasma of pressure of 350-710 Torr show rather narrow and sharp reflexes that are identified generally as the metal lines and hexagonal graphite.

Thermal oxidative behavior has shown the shift of oxidation temperature interval toward the higher temperatures area. It is believed that the obtained structures are single-phase and have a few defects. In some circumstances graphite appears as a second phase. The carbon nanostructures have different thermal stability formed by the pyrolysis of the carbon black with the catalysts and hydrocarbons decomposition. Less stable are graphene materials derived from methane (curve 1) and mixture of propane and butane (curve 2) (figure 8).

Specific surface area of the samples with the lateral size of 300-600 nm was 350-400 m^2/g measured using the BET method. Figure 9 presents the comparison of pore size distribution for two gas pressures used in the experiment. The main range of pore radii was in the region of 10-70 Å, corresponding to mesopores.

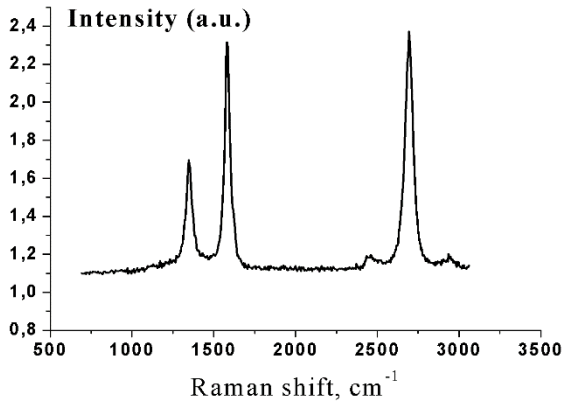

Figure 6. A typical Raman spectrum of few-layered graphene obtained from decomposition of methane by helium plasma. The three intense features are the D band at 1334 cm^{-1}, the G band at 1580 cm^{-1} and the 2D band at 2660 cm^{-1}.

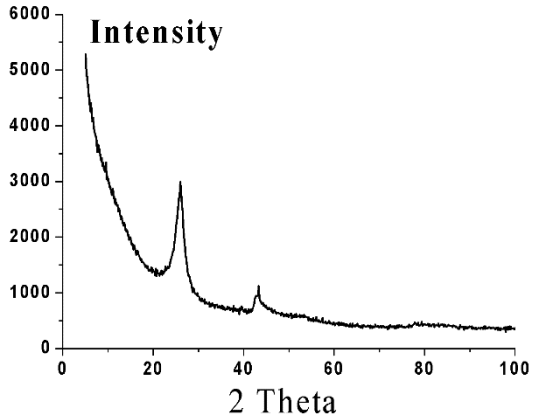

Figure 7. XRD pattern of graphene synthesized from decomposition of methane by helium plasma.

Thus, we have developed a method for synthesizing carbon nanostructured materials by plasma jet. The resulting few-layered graphene sheets and carbon nanotubes have fewer defects than those generated using chemical methods [4].

4. Conclusion

The efficiency of DC plasma torches with divergent channel anode, capacity of up to 40 kW for the synthesis of nanostructured carbon materials was demonstrated. Changing geometry of a reactor, pressure and velocity of plasma jet it is possible to vary the rate of carbon vapor cooling within a wide range. By varying the rate of carbon vapor cooling it is possible to obtain a wide range of carbon nanostructures with high yield of pure deposit.

On the basis of the research of the synthesis products conducted with the use of electron microscopy, thermogravimetry and X-ray analysis, the optimal conditions for the synthesis of each type of material: carbon nanotubes, carbon nanofibers and graphene were determined. Graphene structures synthesized using plasma jet are active for new catalysts.

As a whole, the experimental data allow step by step to scale the process of production of graphene and carbon nanotubes of desirable morphology.

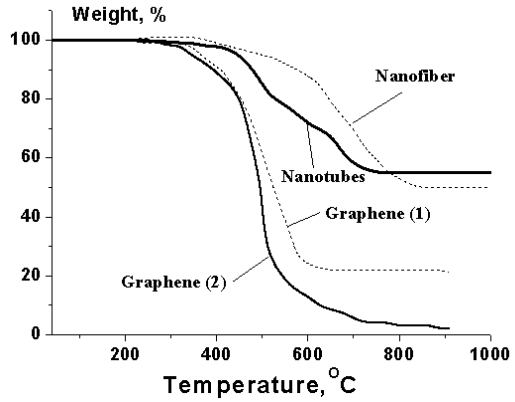

Figure 8. Comparison of the thermal stability of plasma jet synthesis products from various precursors: solid (nanofibers and nanotubes), gaseous methane (Graphene 1) and propane-butane (Graphene 2).

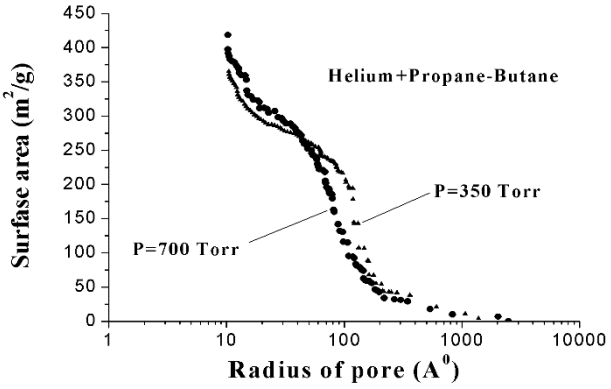

Figure 9. Specific surface area as a function of the pore radius.

Acknowledgements

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