Synthesis of carbon nanotubes by high current divergent anode-channel plasma torch

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Abstract. In this study we propose the high-performance technology to produce carbon nanotubes (CNT) in plasma jet reactor by means of a direct current plasma torch. This technology provides excellent opportunities to investigate a direct evaporation of materials and their subsequent condensation on the carbon surface. Experiments were carried out at the electric power of a plasma torch up to 30 kW. Helium and argon served as plasma gases. CNT synthesis at pyrolysis of soot was catalyzed by the metal disperse powders of Ni, Co, Y₂O₃. We applied x-ray diffraction and electronic microscopy to investigate the structure of obtained products. Also we utilize the thermogravimetric analysis to determine the phase structure of carbon nanomaterials. Using available experimental data we were able to sequentially scale the production process of CNT of desirable space structure. Finally we established that structural and morphological properties of CNT produced at evaporation of soot in the presence of high-percentage combined catalysts depend upon the catalyst structure.

1. Introduction
Although the mechanisms of synthesis for carbon nanotubes are not fully understood nowadays, the key methods of their production were already described. So the question is which of these methods are most suitable for commercial manufacturing. In this respect it is known that the methods using vacuum or high pressure are less productive than the methods of synthesis at atmospheric pressure. Evaporation of graphite by an electron or ion beam and also usage of diamond anvils restrict the productivity of the methods. Also damaging effects are defects of the electrolysis or the explosive synthesis. It is concluded [1-3] that the most widespread for laboratory usage are the arc and laser methods.

During CNT synthesis in the electric arc the direct current is generated between the anode and the cathode situated at the several millimeters from each other. This process generates the plasma arc with a small distance between the electrodes. On the carbon surface (for example, graphite) the carbon evaporates from the anode and subsequently condenses on the cathode forming carbon nanotubes. In the arc method [4] any external magnetic field generated by constant magnets or electromagnets was not used and there was no recirculation of the evaporated carbon. With the help of this method one adds the various chemical catalysts into the anode. This increases the production of CNT and affects the diameter of nanotubes. In order to improve an arc method the cathode and the anode were made in the form of a plate on a tip to create the interplanar micro-discharge. Also the plasma volume was

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slightly increased [5]. An idea for the future development is to increase the synthesis productivity by increase of arc current or electrode diameter. The later is considered impracticable because the precipitated carbon nanotubes evaporates again from the cathode. To sum up the standard arc method is discrete and unstable process and by this method it is not possible to reach mass production of high-quality carbon nanotubes [5].

The much bigger quantities of carbon nanotubes (CNT) can be obtained in a continuous manner by plasma torch method and other chemical vapour deposition methods [6, 7]. Using plasma torch method in particular and other similar methods in general one can significantly increase productivity and synthesis time by transition to volume synthesis. Since 2001 several scientific centers [6-16] were investigating the synthesis of carbon nanotubes in the plasma jet reactors with the help of plasma torch method. In the study [7] the serial plasma torch of induction type in the plasma jet reactor was described as a perspective method for future development. The presented data indicated the high productivity of CNT synthesis, which considerably exceed the analogues results reached with the help of arc and laser methods of synthesis. The quality of synthetized CNT remains as high as in the arc and lasers methods.

Among existing variety of designs and schemes of direct current plasma torch with self-established length of an arc the common feature for all of them is the cylindrical channel. The technological disadvantages of such plasma torch are faults in volt-ampere characteristic, the low efficiency and an unstable operating mode. The arc discharge in such plasma torch is characterized by strong heterogeneity of electro-physical and heat-physical properties. Using the extending channel of the output electrode in the plasma torch one can significantly increase the velocity of cold gas at the entrance to the channel and intensify heat exchange between an arc and plasma-forming gas. This process aims to reduce length of the arc discharge and obtain uniform distribution of thermal streams in electrode walls. The arc column can occupy the considerable volume of a discharge gap, and its anode short circuit is achieved by micro-arcs that considerably reduce the average density of current and the thermal stream in the anode. Thus uniform magnetic field of current is established and as a result stability of arc column is achieved by expansion of an output electrode [17]. Another feature of the plasma torch with the extending channel of the output electrode is that the length of the arc discharge is not fixed and strongly depends on the gas type, gas flow and intensity of the current. It allows effective usage of this type plasma torch in various plasma technologies, especially in those where the considerable change of parameters of a mode is required during technological process [17, 18].

The advantage of this type plasma torch system was demonstrated by comparison to several developed technologies. Among these technologies were plasma hardening and nitriding of railway wheels, plasma coating for recovering and manufacture of railway frogs and plasma coating of copper with wear resistant refractory layer [17, 18]. On the basis of these technologies the plasma jet reactor was developed and the experimental investigation of synthesis of carbon nanotubes was started to investigate the mechanisms of their synthesis, structure assembly and yield increase.

The main aim of the present study is to obtain experimental data on synthesis of carbon nanotubes from soot in the presence of catalysts by means of the direct current plasma torch with the extending channel of an output electrode. The synthesis depends on a sort of plasma-forming gas, its pressure, the consumption of soot and structure of catalysts.

2. Experimental setup and procedure

The detail description of experimental setup was given in the study [19]. Shown in the figure 1 is the scheme of the experiment. Photo of plasma torch and reactor is listed in figure 2. The main difference of our approach from the arc method is that the original materials for synthesis of nanotubes (carbon and disperse metal catalysts) are put together in plasma torch with used gas (argon, helium) under the electric power equalled 10-30 kW. The evaporation of these materials takes place in plasma jet with the further rapid cooling process during which from the formed carbon vapour and catalysts the synthesis of carbon nanotubes occurs in gas volume as well as on a surface of reactor. Evaporation of
carbon and metal catalysts occurs not only in plasma jet but also in the vicinity of the arc discharge by processing the original disperse materials. The flow rate of carbon mass, quantities of catalysts substances, used gas and powers of plasma torch are controlled independently from each other. By changing geometry of a reactor, pressure and velocity of a plasma jet it is possible to widely manipulate the rate range of used cooling carbon vapour. Time of continuous work of plasma jet is limited by the lifetime of the tungsten cathode. The pressure of gas is within the range from 10 to 760 Torr.

Soot was used in the form of powder or small granules. Synthesis of CNT was conducted by pyrolysis of mechanical mixture of soot and the metals Ni, Co and Y\textsubscript{2}O\textsubscript{3} in the powder form. The concentration of a pair Ni + Co was fixed. For a combination of Ni+Co+Y\textsubscript{2}O\textsubscript{3} catalysts the wide range of concentrations were used. Substance combinations were made in such a way that there was a variation in each component concentration from minimum to maximum allowed value. In the arc methods a mixture of two catalysts is more commonly used rather than a mixture of three and more substances [20].

In each experiment the mixture was injected only after stabilization of a temperature distribution in the graphite reactor. Stabilization usually takes 5-10 min and was indicated by measuring the water temperature in cooling system. Table 1 lists the typical operating conditions.

The methods of x-ray diffraction and electronic microscopy were used to investigate the structure of original materials and their synthesized products on a scanning electronic microscope of MIRA 3 TESCAN and a raster electronic microscope LEO SUPRA 50 VP (Germany) with the powerful dispersive X-ray Oxford X-MAX micro spectral analyzer (Great Britain).

The method of thermo gravitation measurements was used to measure the efficiency of synthesis and describe the phase structure of carbon products (STA 449 the Netzsch firm F3 Jupiter platform). Also using this method the data was obtained on thermal stability, purity, structural perfection and uniformity of samples with UNT depending on catalysts substances quantitates in mixture with soot. For this technology the large amount of various materials was used. The sample weights for the analysis ranges from 0,58 to 6,8 mg. As a gas an atmospheric air was used. Temperature was increased with the rate 10 degrees a minute starting from room temperature to 1000\textdegree C. The method takes into account a range of stability conditions for various carbons forms and also considers impurity of metals.
during their heating in the oxidative environment. The efficiency of nanotube synthesis and its discharge characteristics (voltage, current, pressure, composition of gas) can be controlled by the velocity of a gas stream, the sizes of the reactor and its configuration, the nature and purity of materials of electrodes and other parameters. The main parameter affecting the nanotube synthesis is the growth rate, which in turn depends on many parameters. The growth rate is used for scaling and currently there is a lack of theoretical models for exact quantification of the growth rate. Nowadays there is no quantitative model to explain influence of catalyst type on CNT synthesis. To make progress in modeling the experimental measurements should to be obtained for the broad range of system parameters.

Table 1. Technological conditions.

| Parameter                  | Value                      |
|---------------------------|----------------------------|
| Power                     | 10-30 kW                   |
| Current                   | 100-400 A                  |
| Voltage                   | 35-80 V                    |
| Plasma gas                | Argon, Helium              |
| Gas flow rate             | 1-3.6 g/sec                |
| Pressure                  | 50-760 Torr                |
| Flow rate of solid carbon | 0.2-2.2 g/min              |
| Carbon precursors: soot   | < 10 μm                    |
| Catalyst <15% on weight   | Ni, Co, Y₂O₃              |
| Size of catalyst          | < 10 μm                    |
| Time of continuous work   | 1 hour                     |

3. Results of experiment

For the experimental conditions the electric power of a plasma torch was set up to 30 kW. Helium and argon were used as a plasma gases. Helium was taken under pressure of 350-710 Torr with gas flow rate from 0.5 to 1 g/sec. The argon flow rate ranged from 1.5 to 3 g/sec with pressure interval from 450 to 600 Torr. CNT synthesis at pyrolysis of soot was conducted at the presence of catalysts. The consumption of soot with catalysts set as 0.3-2.1 g/min. For the analysis the products of carbon condensation were taken from different part of the metal target [3] under different concentrations of catalysts, pressure and rate of the gas flow. The soot was analyzed in advance. According to the thermogravimetric analysis the synthesis product contains about 4 % of amorphous carbon, 48.37 % of a graphitic phase of soot and 38.21 % of polycrystalline graphite.

Figure 3. Structure of synthesis products in the presence of catalyst ratios Ni/Co/Y₂O₃ - 1.06/1.06/0.94 at.%.

Figure 4. The SEM image of synthesis products with catalyst ratios: Ni/Co/Y₂O₃ - 1.46/1.47/1.29 at.%, the pressure set as 500 Torr, current is 400 A and consumption of soot with catalysts is 0.45 g/min.
The formation of the quasiamorphous structure of plastically deformed material with the coating of Ni and Co particles was detected under experimental conditions helium pressure 600 Torr and the soot content of catalysts Ni/Co - 0.64/0.64 at.%. The quasiamorphous state fills boundary areas connecting randomly situated nanoelements forming a dendrite structure.

The single extended cylindrical structures of a fixed diameter were formed from a quasiamorphous matrix with the following experimental conditions: mixture Y$_2$O$_3$ with the soot was done according to the ratio Ni/Co/Y$_2$O$_3$ = 1.06/1.06/0.94 at.%, helium pressure was decreased to 500 Torr, the current set as 400 A and the consumption of soot was fixed as 1.25 g/min. Shown in the figure 3 is the SEM image of nanotube at above experimental conditions.

The key difference of the created cylindrical nanostructure from known CNT [1] is the formation of clusters of the ordered framework with the open end and rather pure walls. Diameter of cylindrical structures is 60 nanometers. One can see in figure 3 the structural features of nanoelements of soot in figure 3. They have more deformed surface but smaller degree of disorder then previously described CNT [1]. Also if Y$_2$O$_3$ concentration is less than Ni concentration and relates to the concentration of Co when the single-wall nanotubes with characteristic defective structure are formed with the consumption of soot with catalysts reduced twice.

**Figure 5.** The results of thermogravimetric analyses of synthesis products with catalysts taken with the ratios Ni/Co/Y$_2$O$_3$ 1.46/1.47/1.29 at.%; the pressure was 500 Torr, current was 400 A and consumption of soot with catalysts was 0.45 g/min.

The CNT production was increased by decrease of a soot consumption with catalysts taking ratios Ni/Co/Y$_2$O$_3$ 1.05/1.05/0.73 at.% to 0.32 g/min and with pressure of He 500 Torr. Thus the distribution of CNT diameter was observed. Many CNT situated on a quasiamorphous surface of a matrix of soot but not perpendicular to it was with the mishaped struture.

The difference in the structure of formed products was detected on the center of the target and on the periphery. On the periphery polyhedral particles formed nanostructures. We noted that the formation of CNT with helium is more effective then with argon. A large amount of amorphous carbon and spheroidal nanoparticles is formed using argon.

Diameter of carbon nanotubes ranged from 16 to 74 nanometers depending on experimental conditions. The maximum production of carbon nanotubes was observed in helium with the following experimental conditions: ratio Ni/Co/Y$_2$O$_3$ 1.46/1.47/1.29 at.%, the pressure 500 Torr, current of arc 400 A and a consumption of mix 0.45 g/min. Shown in the figure 4 is the structure of the synthesis products at optimized conditions. SEM images corresponded to the thermogravimetric data. In the figure 5 there are results of thermogravimetric analyses of synthesis products at optimized conditions. According to the thermogravimetric analysis the maximum weight ratio of nanotubes was 13%. At temperatures ranges from 310 to 380°C and from 380 to 473°C the oxidation of black particles to
amorphous and quasiamorphous structure on the air took place. Further increase of temperature to ranges 450-660°C and 660-820°C was accompanied by appearance of two peaks on DSC curve related to production of CO and CO2. This result was confirmed by comparison of distribution curves for intensity of dispersion of X-rays in experimental data for different combinations of catalysts in soot mixture and literature data. Figure 6 illustrates the example of X-ray analyses.

To sum up the experimental data allowed sequential scaling process of CNT production to obtain required structures. The structural and of the morphological properties of CNT produced at soot evaporation at the set of highly concentrated catalysts depended upon the catalyst composition.

4. Conclusions
We investigated of synthesis of carbon nanotubes at soot pyrolysis in the presence of metal Ni+Co+Y2O3 catalysts in the plasma jet reactor using the direct current plasma torch with the extending channel anode in plasma-forming gas helium and argon.

It was possible to influence the production of the carbon nanotubes and their spatial structure by changing the gas flow rate, pressure and type of plasma-forming gas. The spheroidal particles have been formed in the presence a large amount of amorphous carbon in argon. The decreased arc current increased the impurity amount in the different forms of nanoparticles and amorphous carbon in products of synthesis.

The catalyst structure influenced structural and morphological properties of the carbon nanostructures produced at pyrolysis of soot in the presence of highly concentrated catalysts containing nickel, cobalt and yttrium.

To sum up the experimental data allowed sequential scaling process to produce CNT of required spatial structure.

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