CONTINUOUS PROCESS OF CARBON NANOPARTICLES GENERATION BY THE PLASMA-LIQUID SYSTEM "TORNADO" TYPE

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Plasma-catalytic system for generation of carbon nanomaterials based on tornado-type discharge (using reverse-vortex gas flow) in a mixture of ethanol aerosol and inert gas was studied. Current-voltage characteristics of the discharge for different modes of the system were investigated. Efficiency of the systems with metal and graphite electrodes was compared. The possibility of continuous operation of such plasma-liquid reactor combined with pyrolytic chamber was demonstrated. It was shown that different morphology of carbon structures (nanorods and nanotubes) generated in such plasma system depends on the temperature of pyrolytic chamber and electrode materials.

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INTRODUCTION

The urgent task to ensure demands for industrial synthesis of carbon nanomaterials (CNM) is continuous process of its production.

Plasma-liquid systems (PLS) can operate in continuous mode k and considerably facilitate a scaling process, in comparison with traditional methods of nanomaterials generation, provide selectivity of target products, safety and profitability [1-5].

Plasma-liquid system of inverse gas flow type vortex tornado with liquid electrode was previously developed by our research group [6, 7]. To generate carbon nanoparticles inert gas - argon and liquid – ethanol (as a carbon source) were used.

However, the alcohol significantly alters its properties in the combustion chamber volume during the discharge burning that leads to the instability of the system. To keep the possibility of plasma in heterophase system with all its benefits, a system with continuous injection of aerosol into the plasma chamber was developed. Besides it is believed that water-cooling metal electrodes in contact with the spray is coated of liquid film and therefore avoids erosion of electrodes.

During the study of the substrate temperature influence on the synthesis process, it was found that CNM production has a peak of effectiveness which corresponds to the specific temperature [8]. This effect is caused by a competition between diffusion and adsorption of carbon atoms, rates of both these processes are determined by the surface temperature. This result is in a good agreement with the most recent theories of CNM synthesis that is based on the investigation of surface models.

Since it have been conclusively proved a decisive influence of the substrate temperature on size and morphology of the final product, formation and removal of produced CNM should be carried out by particles with controlled surface temperature. So the main task of the presented work was to ensure process with continuous formation and removal of the formed carbon material from the reaction volume on the particles with controlled surface temperature.

1. EXPERIMENT

To solve the task mentioned above chemically passive particles used to create carbon nanomaterials growth centres were injected into the pyrolytic reaction chamber. Usage of such particles makes possible to synthesize resulting products outside the system and greatly simplify the process of the purification.

This feature was implemented in an experimental setup consisted of "tornado" type PLS combined with pyrolytic chamber with dust feeding (Fig. 1). A chamber temperature is considered to be the same as a substrate temperature and was maintained by the heating coil. Spray of ethanol, argon as plasmaforming and carrier gas, stainless steel or graphite electrodes were used during the experiment.

Ethanol aerosol was created by the piezocrystal emitter and carry out by the argon stream (feed rate was 3.3 l/min) to the area of raw activation. Alcohol feed rate was 1.7 ml/min. The ethanol aerosol flow was injected with argon into the vessel through the orifice in the upper flange tangentially to the cylinder wall and created a reverse vortex flow of tornado type.

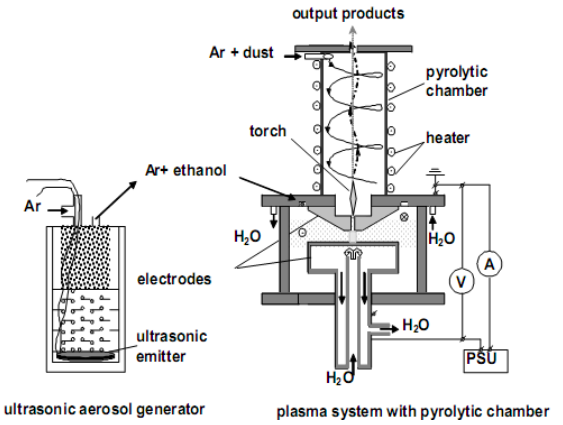

Fig. 1. Plasma-liquid system "Tornado" combined with the reaction pyrolytic chamber

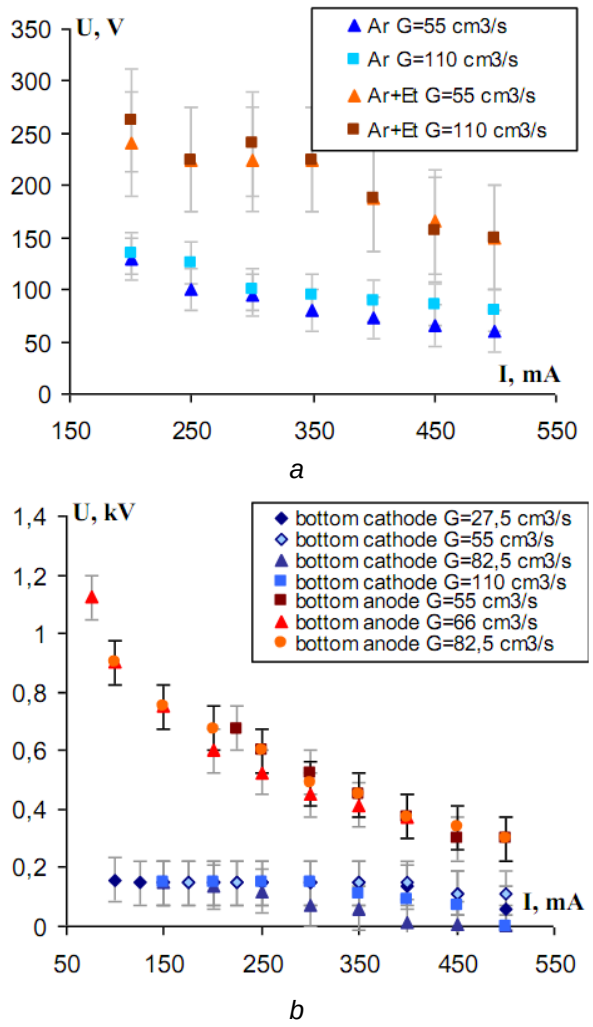

Fig. 2. Current-voltage characteristics of the discharge, the inter-electrode gap of 3 mm: a – in pure argon and mixture argon/aerosol alcohol, b – for the two polarities of discharge in mixture argon/aerosol alcohol, for different flows of working substance

The electrical discharge burned between the bottom and the upper electrode. The both electrodes were made from stainless steel or graphite (EG-2), which was attached to the holder from stainless steel and have water cooling. The interelectrode gap e was 3 mm. Plasma torch was blown by stream of argon through the outlet in the top electrode (∅ 3.4 mm) in the pyrolytic chamber. The formation of carbon nanomaterials was occurred on the surface of chemical passive microparticles (so-called dust) in the the pyrolytic chamber. The flow rate of argon for filing dust was 10-15 L/min. The temperature of pyrolytic chamber was controlled by the system of thermocouples.

With aerosol injection into the discharge chamber the voltage significantly increased (Fig. 2,a). Such peculiarity of the current-voltage characteristics of the discharge in the presence of alcohol aerosol can be explained by appearance of negative ions O^- and CO^-, leading to a significant increase of the recombination rates, and hence to maintain the discharge the voltage increase the is needed. Besides, voltage increase on the discharge may be connected with cooling of electrodes by aerosol.

The discharge weakly depends on the gas flow at interelectrode gap of 3...5 mm (Fig 2,b).

The carbon deposit with the graphitized outer wall was formed on anode in aerosol plasma system with metal electrodes (Fig. 3). When the anode was lower electrode, carbon deposit was fairly stable, in the case when the anode was upper electrode - carbon deposit was easily destroyed and taken out by the gas flow in the process. The deposit formation in the interelectrode space leads to a breach of the discharge and continuous system operation. We supposed that it can be avoided by the using of graphite electrodes.

CVCs, discharge character, and physical phenomena in the discharge chamber (aerosol extinction in the discharge volume) were significantly changed when metal electrodes were replaced by graphite ones. This phenomenon can be explained by high absorptive capacity sprayed graphite electrodes.

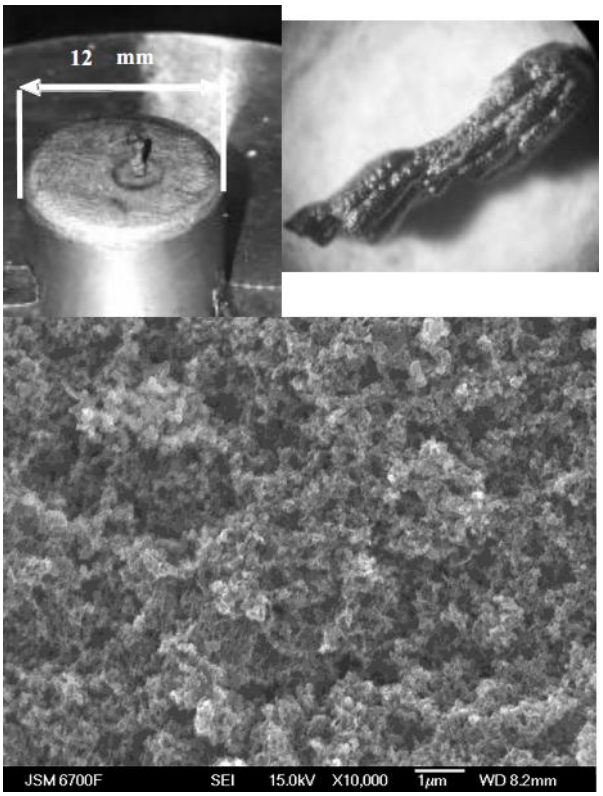

Fig. 3. Carbon deposit on the anode, appearance and internal structure

Significantly increased voltage on the discharge, and decreased difference discharges with different polarity, compared with metal electrodes (Fig. 4). Uneven heating of the cooled electrodes has the main influence on the current-voltage characteristics.

In the case of graphite electrodes carbon deposit did not formed that allows to increase the life of continuous discharge significantly. Despite the presence a liquid aerosol in the reactor graphite electrodes were sputtered significantly. Concentric nature of the sputtering areas in the electrodes is due to the presence of the vortex gas flow.

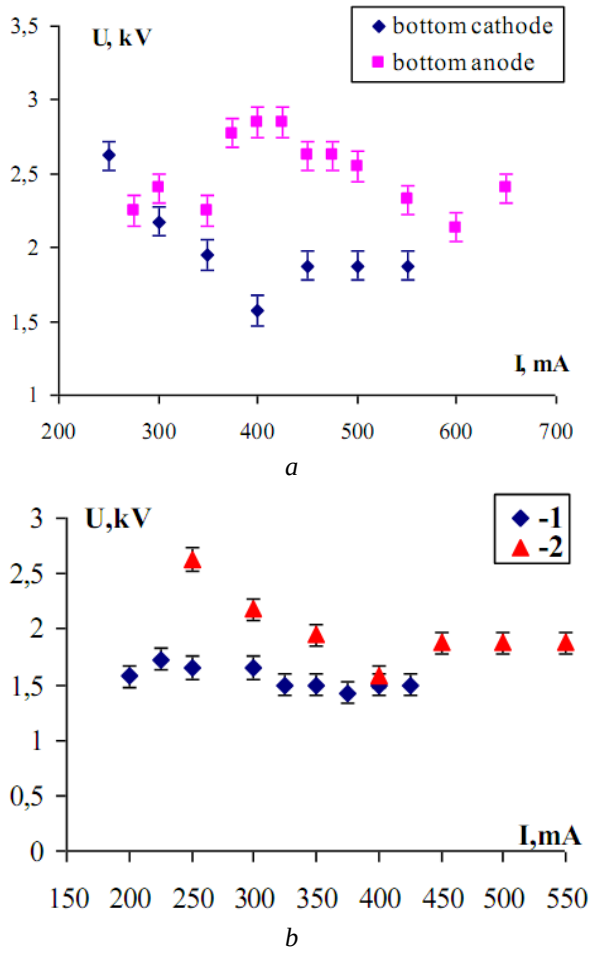

Fig. 4. Current-voltage characteristics of the discharge with graphite electrodes: a – for different polarities; b – between metal electrodes (1), between graphite electrodes (2)

It was shown that effectiveness of the nanomaterials formation f is much higher in the case of graphite electrodes using. But the increasing of productivity is likely due to the included scattered electrode material into the final product. This conclusion was made by comparing emission plasma spectra of discharges with different electrodes. The intensity of atomic carbon emission line significantly increases in the case of graphite electrodes using. It indicates the increasing of the concentration of activated carbon in the bulk at the same temperatures of excited levels population of the carbon molecule (C_2).

2. METHODS AND RESULTS

The outlet material was collected by decantation method, when chemically passive particles removed by acid derived. CNM sample was washed in distilled water several times. Then the material annealed in a muffle oven at 500^0C (0.5 h) to remove amorphous carbon component, and sonicated in the ultrasonic bath with frequency 42 kHz and power 50 W (0.5 h in ethanol, which is then evaporated) to avoid clumping of particles.

Formation of carbon structures with different morphology was found in samples obtained at high temperatures (600°C and higher). Accumulation of carbon rods with a diameter of 70...100 nm and a length of 10 mm placed randomly was observed in the samples at the pyrolytic chamber temperature of 600°C. (Fig. 5). A small number of carbon nanotubes with a diameter of 10...50 nm were presented in samples at temperatures over 650°C. Mixture of carbon structures in samples may be caused by the specifics of the formation as well as the influence of cleaning procedures.

Purified samples obtained in the system with graphite electrodes are almost entirely composed of entangled carbon nanotubes of different diameters 10...80 nm (Fig. 6).

This difference in the products of synthesis can be explained by better atomization of carbon in the discharge zone possibly due to the sputtering of graphite electrodes. It promotes to the formation of nanostructures with smaller dimension.

Thus it can be concluded that working with graphite electrodes are more productive, but requires constant control of the electrodes. The procedure of the samples purification is the same.

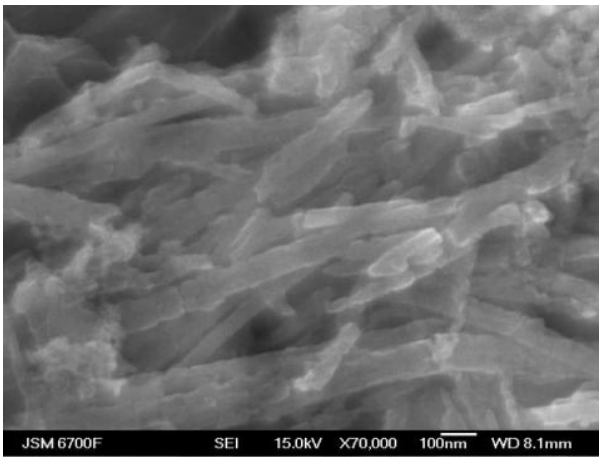

Fig. 5. Photo purified sample CNM obtained in the system with metal electrodes

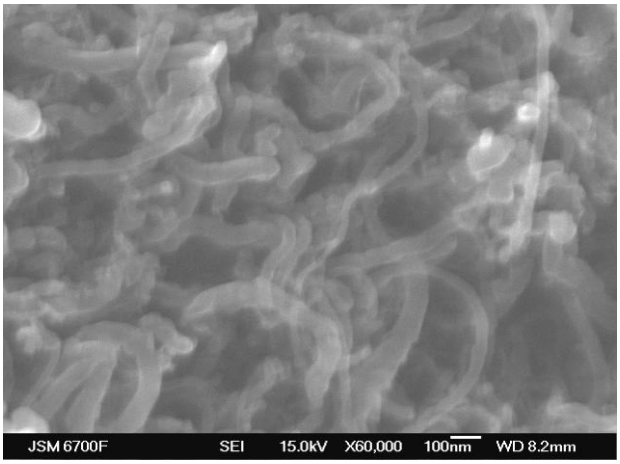

Fig. 6. Photo purified sample CNM obtained in the system with graphite electrodes

CONCLUSIONS

It was found that samples obtained at "Tornado"-type PLS mainly consist of nanostructured carbon. The possibility of carbon nanomaterials removal from plasma by chemically passive dust particles was shown. The cleaning process of material obtained in this work is much simpler than clearing CNM synthesized by conventional methods. It was concluded that working with graphite electrodes is more productive.

The main advantages of the investigated PLS are: a long service time; ability to maintain uninterrupted working cycle; ability to control chemical composition of produced nanoparticles by using aerosols of different hydrocarbon liquids or by changing material of electrodes and microparticles injected into pyrolytic chamber. It was shown that the temperature of the pyrolytic chamber significantly affects on the morphology of final products of and its value can vary in wide range.

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НЕПРЕРЫВНЫЙ ПРОЦЕСС ГЕНЕРАЦИИ УГЛЕРОДНЫХ НАНОЧАСТИЦ В ПЛАЗМЕННО-ЖИДКОСТНОЙ СИСТЕМЕ ТИПА "ТОРНАДО"

Ю.П. Веремий, К.В. Юхименко, М.М. Касумов, Т.Е. Лиситченко

Представлены плазменно-каталитические системы для генерации углеродных наноматериалов на основе разряда типа "торнадо" (с использованием обратно-вихревого потока газа) в смеси аэрозоля этанола и инертного газа. Рассмотрены вольт-амперные характеристики такого разряда для различных режимов работы системы. Проведено сравнение эффективности системы с металлическими и графитовыми электродами. Показана возможность непрерывной работы такого плазменно-жидкостного реактора в сочетании с пиролитической камерой. Показана возможность образования в такой системе углеродных структур различной морфологии (наностержней и нанотрубок) в зависимости от температуры пиролитической камеры и материала электродов.

НЕПЕРЕРВНИЙ ПРОЦЕС ГЕНЕРАЦІЇ ВУГЛЕЦЕВИХ НАНОЧАСТИНОК У ПЛАЗМОВО-РІДИННІЙ СИСТЕМІ ТИПУ "ТОРНАДО"

Ю.П. Веремій, К.В. Юхименко, М.М. Касумов, Т.Є. Лиситченко

Представлено плазмово-каталітичні системи для генерації вуглецевих наноматеріалів на основі розряду типу "торнадо" (з використанням обернено-вихрового потоку газу) в суміші аерозолю етанолу та інертного газу. Розглянуто вольт-амперні характеристики такого розряду для різних режимів роботи системи. Проведено порівняння ефективності системи з металевими та графітовими електродами. Показана можливість безперервної роботи такого плазмово-рідинного реактора в поєднанні з піролітичною камерою. Показана можливість утворення в такій системі вуглецевих структур різної морфології (нанострижнів і нанотрубок) в залежності від температури піролітичної камери та матеріалу електродів.