INFLUENCE OF TEMPERATURE CONDITION ON THE PROCESS OF CNM GENERATION

Iu.P. Veremii, V.Ya. Chernyak, S.A. Filatov, S.V. Olszewski, V.O. Forostyanij

Taras Shevchenko National University of Kyiv, Faculty of Radiophysics, Dept. of Physical Electronics, Kyiv, Ukraine, E-mails: tin@univ.kiev.ua , chernyak_v@ukr.net

Role of surface in processes of carbon nanomaterials generation in plasma-liquid system was analyzed. Qualitative analysis of samples was supplied by spectrophotometrical methods, X-rays microanalysis and scanning microscope. Influence of substrate temperature on carbon deposited nanostructures was shown. Possibility of obtaining carbon nanostructures with metal inclusions in plasma-liquid systems from ethanol was presented.
PACS: 52.77.-j

1. INTRODUCTION

On our days the basic methods of receipt of carbon nanomaterials (CNM) were practically formed. It is a receipt of CNM in a voltaic arc, at the laser or sun ablation of graphite, pyrolysis of hydrocarbons in the presence of catalysts, HiPco-process [1-5]. Each of them has the advantages and failings. Therefore it is continuing develop a principal new methods, or methods based on combinations from above-listed. In spite of numerous works on the generation of CNM, there is an unexplained role of surface and volume in the kinetic mechanism of nanoparticles formation. Therefore, receiving of CNM in the system, where it is possible to change the temperature of substrate, at permanent other parameters, was of interest.

Influence of substrate temperature on process efficiency of CNM synthesis was considered in this work.

Feedstock reforming for carbon nanoparticles generation was performed in plasma-chemical reactor on base of secondary discharge. The unconventional discharge system allows creating plasma with the high degree of nonequilibrium in area of electrodes. It allows receiving active particles with untraditional energy parameters. Reception possibility of CNM in such system was shown in previous papers [6].

2. EXPERIMENTAL

Experimental set-up for study influence of substrate temperature on the process of CNM synthesis shown on the Aig.1. Reactor consisted from the metal cylinder (1), which was closed by the cover (3). Free jet argon ran from the nozzle (4) across two opposite coaxial electrodes (5) and formed a bright crescent-shaped electric arc of auxiliary discharge. The exhaust gases came out of a reactor through two holes (6). Liquid was put into the system through the hollow electrode (2) with the heater (H1) and come into the reactor as vapour. The current of secondary discharge runs through plasma (7) of arc discharge and vapour of liquid. Another electrode of the secondary discharge was plasma of auxiliary discharge.

The secondary discharge is powered by the DC source. The polarity of secondary discharge was determined by polarity of electrode (2).

For the decision of assigned task, in the construction of reactor were brought some changes [6]. The substrate (S), which preheat a heater (H2) is added. Temperature of substrate is controlled by the system of thermocouples of (T1), (T2) and (T3). Feasible temperature range was from 170 to 350 °C.

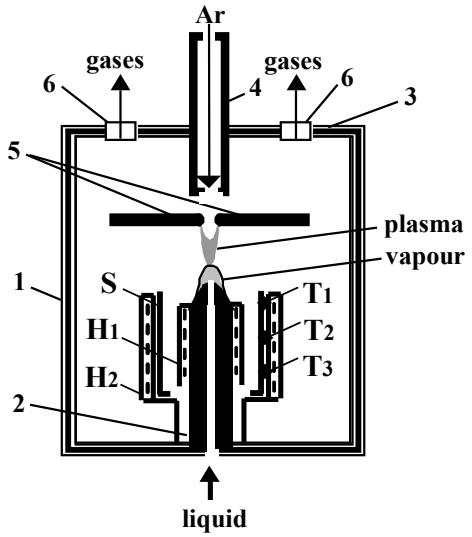

Fig.1. Experimental set-up for study influence of substrate temperature on the process of CNM synthesis

Stainless steel was chosen as a material for surface. An electrode of secondary discharge is made from kovar (Ni-Co alloy).

Auxiliary discharge parameters was up-to-date Is = 300 mA, Us = 0,6 kV, secondary discharge – Id=200 mA, Ud = 0,6…0,8 kV.

During our experiments we treated ethanol (C_2H_5OH) solution with 0.004% of catalyst admixture – ferrous acetate $Fe(CH_3COO)_2$. Supply velocity of the solution in discharge area was near 1cm^3/min. Saturated vapor of liquid (ethanol etc.) set by temperature of coldest element of reactor (in our case – inner wall with water cooling).

The soot, got on substrate at a certain temperature, weighed and passed preparation for diagnostics. The qualitative analysis of obtained soot was provided by spectrophotometrical methods [7], X-ray microanalysis and scanning microscopy.

3. POST-PROCESSING METHODS

Preparation of probes for X-ray microanalysis and scanning microscope. First powder was processed with concentrated hydrochloric acid about 30 minutes (for metallic catalyst removal). Then it was washed by distillate many times, and dried out at 100ºC. Then samples was annealed in muffle oven with air access (0,5 hour at 450º C) for amorphous carbon and low graphite structure particles oxidation.
Refined in such way powder was placed by glass stick on special carbon sticky tape, which was glued on a target of scanning microscope.

Preparation of probes for spectrophotometry. For a spectrophotometry probes prepared as follows. At first unrefined soot (0,5…1 mg) put into solvent (10 ml, n-hexane or toluene), shook up during 10 minutes and enabled settled. For the best fullerenes dissolution the prepared solutions added treatment an ultrasound during 1 hour. For research of absorption spectrums in a visible spectral region and near UV quartz cuvettes were used.

4. RESULTS

Carbon powder obtained at a certain temperature was scraped off from steel substrate and weighted.

Nonmonotonic maximum exists on dependence on the CNM mass from substrate temperature (Fig.2.). Every point in curve was tested 2–3 times.

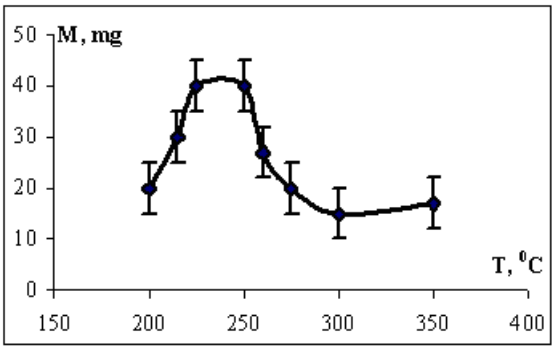

Fig.2. Dependence of mass of obtained CNM from the temperature of substrate

Photos of refined CNM samples, obtained by scanning electron microscopy Supra55 (Carl Zeiss) shown on Fig.3. Major part of sample presented by spherical formations with diameter in range 500 nm to 10 μm.

Similar structures can be seen in samples for all temperatures of substrate. But for regimes, which correspond to maximum of temperatures dependence, shown on Fig.2, averaged diameter of structures is larger.

Information about chemical composition of spherical formations, obtained with help of x-ray microanalysis (system INCA 350, Oxford Instruments) shown on Fig.4. As possible to see, such carbon nanostructures contain large amount of metals: catalyst metals and material of secondary electrode (Ni, Co). Question of metal distribution in bulk of spherical nanostructures remains unsolved, because most probable chemical structure - metal carbides (Fe_3C, Ni_3C, Co_3C) is impossible in the view of stehiometry.

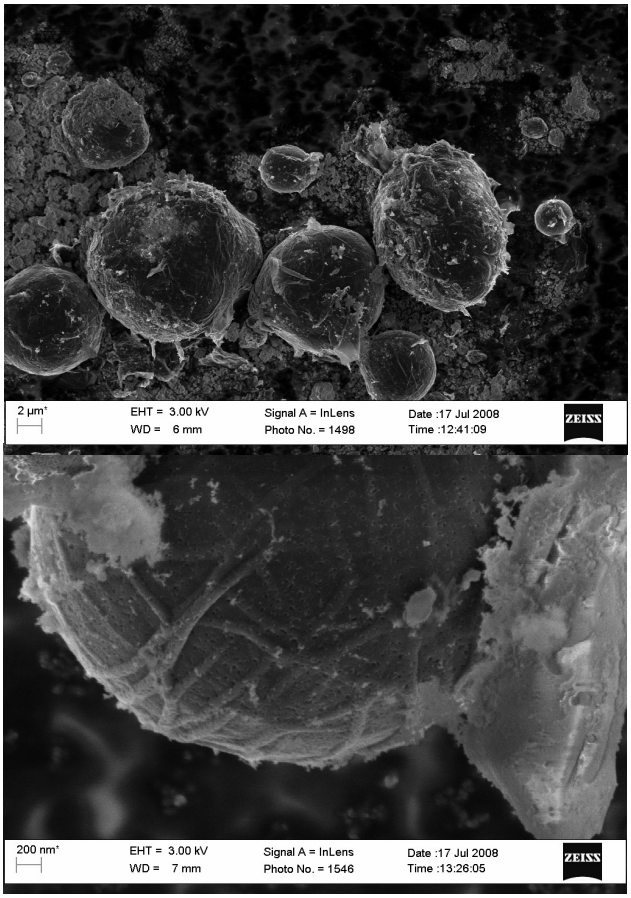

Fig.3. Photos of probes obtained by scanning microscope

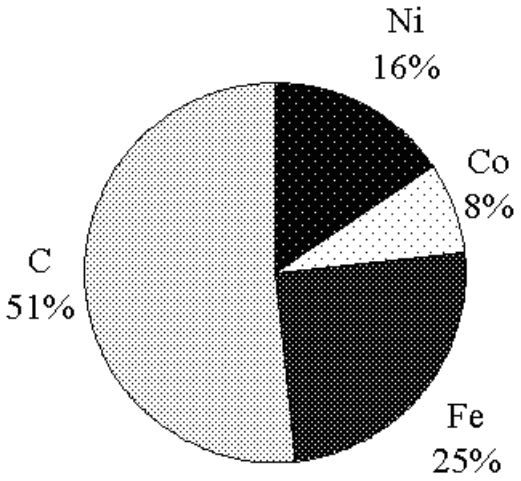

Fig.4. X-ray microanalysis chemical composition of spherical formations (adduced in weight percents)

In despite the fact, that amorphous component of sample is different by its composition (amorhous carbon, pyrografite, metal oxydes), spherical formations stay uniform in all probes.

It is necessary to notice, that material of auxiliary discharge electrodes (copper) is present in amorphous part of CNM, but wasn't found in spherical formations. Probably this fact can be explained that Ni or Co, like Fe serves as catalyst for carbon structure growth, but copper is not.

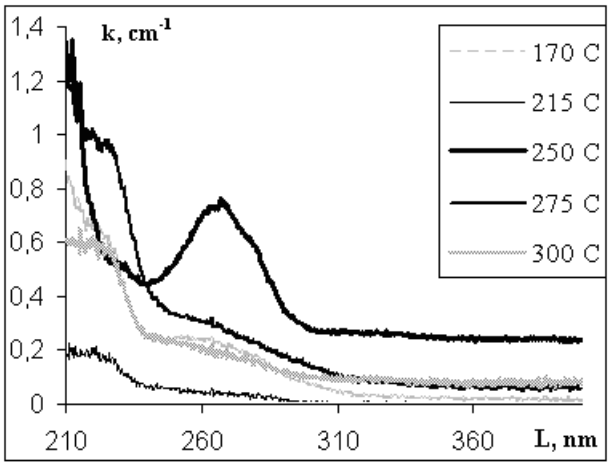

Fig.5. Spectrophotometry of samples soot dissolved in n-hexane for different temperature of substrate

Comparison of absorption spectrums of samples obtained at different substrate temperature presented on Fig.5. Samples soot dissolved in n-hexane with USD-treatment in accordance with the conditions of preparation from work [7].

A peak on a wave-length 270 nm can be ascribed to the molecule of phulleren C_{60} [7]. Then it is possible to suppose, that spherical formations is association of phullerenes, which contain atoms or molecules of metals – endometalphullerenes.

CONCLUSIONS

A surface plays a substantial role in formation of the final carbon nanomaterials:

1. Nonmonotonic maximum on dependence of CNM mass from the temperature range of substrate exists.
2. Influence of surface temperature on final product morphology is shown.
3. Possibility of obtaining carbon structures with large amount of metals inclusion is presented.

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Article received 27.10.08

ВЛИЯНИЕ ТЕМПЕРАТУРНЫХ УСЛОВИЙ НА ПРОЦЕССЫ ФОРМИРОВАНИЯ УНМ

Ю.П. Веремий, В.Я. Черняк, С.А. Филатов, С.В. Ольшевский, В.О. Форостяный

Исследована роль поверхности в процессах генерации углеродных наноматериаллов (УНМ) в плазменно-жидкостной системе с вторичным разрядом. Качественный анализ образцов проводился с помощью спектрофотометрической методики, рентгеновского микроанализа и сканирующей микроскопии. Показано влияние температуры подложки на полученные УНМ. Продемонстрирована возможность получения углеродных наноструктур с включением значительного количества металлов.

ВПЛИВ ТЕМПЕРАТУРНИХ УМОВ НА ПРОЦЕСИ ФОРМУВАННЯ ВНМ

Ю.П. Веремій, В.Я. Черняк, С.А. Філатов, С.В. Ольшевський, В.О. Форостяний

Досліджено роль поверхні в процесах генерації вуглецевих наноматеріалів (ВНМ) у плазмово-рідинній системі на базі вторинного розряду. Якісний аналіз зразків проводився за допомогою спектрофотометричної методики, рентгенівського мікроаналізу та скануючої мікроскопії. Показано вплив температури підкладки на вихідні ВНМ. Продемонстровано можливість отримання вуглецевих наноструктур з включенням значної кількості металів.