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Technology for Producing Carbon Nanotubes on the Laboratory Setting for Students

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This work presents results of studies of an improved method for producing carbon nanotubes using a low-amperage electric arc and the electromagnetic field of the coil connected in series with the electrodes. Micro- images of nanotubes produced by scanning and transmission electron microscopy are shown. Here we presents developed laboratory setting for laboratory works based on research results.

Keywords: Nanotubes, Laboratory setting, Arc discharge, Carbon nanotubes producing, Nanotubes structure.

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1. INTRODUCTION

The most common way of getting clean carbon nanotubes is an "arc discharge" method. This paper presents an improved method, characterized by introducing into the nanomaterials growth zone longitudinal magnetic field generated by the electromagnetic coils of the heat resistant steel connected in series with the electrodes of the electric arc. [1]

2. DESCRIPTION OF THE OBJECT AND METHODS OF RESEARCH

By introducing into the growth zone longitudinal magnetic field the energy allocated by power supply is distributed in a relatively large amount of a non-isothermal environment within special chamber formed from an upper flange of the cylindrical shell and a lower profiled ring inside which the pole arc is fixed and a plasma generated. Part of this energy is spent on the creation of circulating laminar flow along the surfaces of the rod cathode and the substrate placed on the cowling of the chamber. When introduced into the high temperature region of laminar upward flow of vapor ferrocene Fe $(C_5H_5)_2$, its molecules break up into atoms of iron and C_5H_5 ligands, which diffuse along the downstream of the cylindrical substrate and condense thereon. In a mixture of carbon clusters and formed of nanoparticles iron atoms grow multiwall nanotubes. This is known as the method of growth in the gas phase using a catalyst. The average diameter of the nanotubes growing in the gas phase is in the range of 18-36 nm.

Simultaneously the other way to grow nanotubes on another physical principle – in the current lines of the electric arc directly on the cathode, and deposit is the place of their localization, which is formed from a sacrificial anode material. Examined the effect of the distance between the electrodes in continuous deposit on performance of nanotubes formation. Stabilization of this distance with the required accuracy is achieved at presence of an electromagnetic coil and a special chamber that provide the necessary electrical and thermal inertia of the system [2].

C60 – is the most common fullerene molecule and the most studied in this class of carbon phases. It makes an outstanding high icosahedral symmetry, the highest possible symmetry of the molecule. Because of this molecule has only 46 vibrational modes propagating at 174 vibrational degrees of freedom. Theoretical analysis of the groups revealed a common set of vibrational species as follows: $\Gamma^{vib}_{C_{60}} = 2Ag(Ra) \oplus 3F_{1g} \oplus 4F_{2g} \oplus 6G_g \oplus 8H_g\,(Ra) \oplus A_u \oplus 4F_{1u}\,(IR) \oplus 5F_{2u} \oplus 6G_u \oplus 7H_u$.

Only 8 fivefold degenerate even modes symmetry Hg and 2 non-degenerate even modes Ag symmetry are Raman active. All odd modes either not active or IR active. However, if the molecules are arranged in a crystal, the icosahedral symmetry is broken. Fullerene molecules form a FCC lattice (fullerite). As a result, there is a lowering of the symmetry 37 even modes and they are Raman active.

Electronic structure of fullerite is that the energy of the first allowed electronic transition is 2.6 eV. Therefore, the Raman excitation light in a blue laser in this case is the resonance.

It is known that the analysis of the Raman spectra of higher fullerenes (C70, etc.) is very difficult due to the large number of lines.

One of the main characteristics of fullerenes is so-called pinch pentagonal fashion (PPM), which at ambient temperature yields a Raman peak at 1470 cm^{-1}.

3. OVERVIEW AND RESULTS

In this paper, we studied the effect of asymmetry of cathode organize with respect to the sacrificial anode for stabilization accuracy of this distance. Research has shown that at low currents of electrical arc ≈ 35 A in a helium atmosphere, the cathode axis offset relative to the axis of the anode at a distance Δ, the same distance shifts datum deposit.

Figure 1 shows the deposit formed with the displacement of the electrodes relative to each other.

Its structure is virtually identical to the structure of the deposit, growing with the coincidence of electrodes axes.

On the right image shown a scanning microscope Quanta 200i 3D micro-image of multiwall nanotubes contained in the central part of the deposit. multiwall nanotubes obtained without catalyst and do not contain iron nanoparticles.

As a result of analysis of a sample, it was found that direct measurement of the fullerene soot provides

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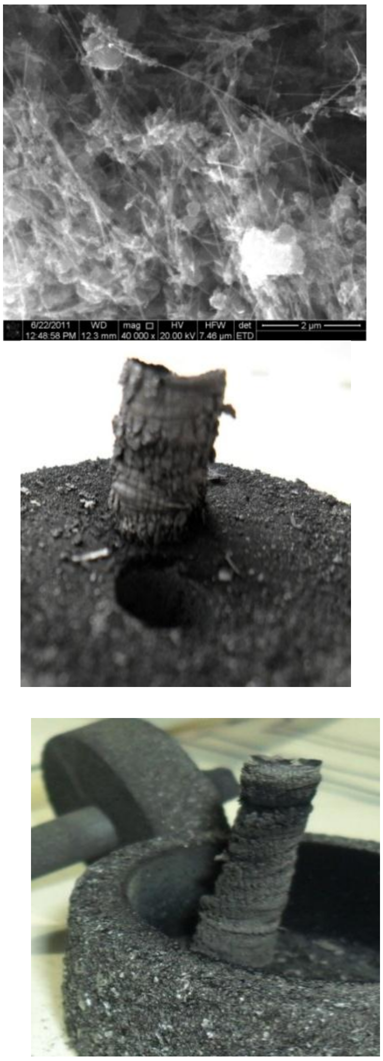

Fig. 1 – The deposit growth in the flat and hollow cathode and multiwall nanotubes contained in the central part of the deposit

a Raman spectrum typical of amorphous carbon. Therefore, carbon black powder was pre-dissolved in benzene for 12 hours, and was then coated and dried on a glass substrate. Because prolonged exposure to laser radiation can lead to polymerization of fullerenes, then avoid this accumulation technique used Raman signal when the sample is constantly moving. Pump wavelength is 473 nm (blue laser), the speed of movement of the sample – about 2 microns per second. As a result of the measurement data was obtained by the spectrum shown at Figure 2.

Peaks at 269, 713 and 1427 cm^{-1} are even symmetry modes Hg. A strong peak at 1470 cm^{-1} - corresponds to the pentagonal pinch mode of C60. The appearance of additional peaks in the spectrum (e.g. intense peak Hu symmetry at 1567 cm^{-1}), which should not be Raman active for the free C60 may indicate that there may be a place of partial polymerization of fullerenes and fullerite formation. Raw Raman spectrum are shown at Figure 3

Positive feature of the technology and installations for producing nanotubes is relatively short preparation time of pumping chamber to pre-evacuation and degassing electrodes with fasteners occurring simultaneously with the process of heating the substrate – all it takes no more than 20 minutes. Figure 4 shows a graph of temperature increase of the substrate (top) and the annular casing temperature of ferrocene container placed below the arc column. It is seen that the periodic shorting of sacrificial anode and cathode with a growing deposit, the substrate temperature rises monotonically and after 15 minutes to stabilize at 800 ± 500 °C.

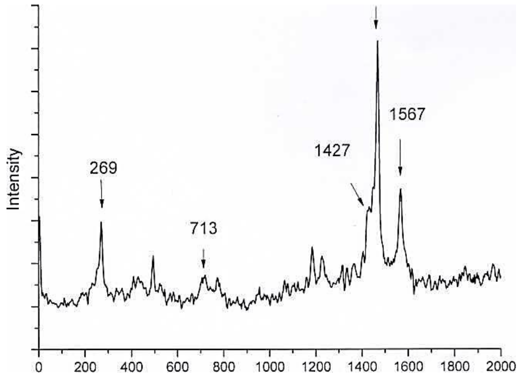

Fig. 2 – Raman spectrum of fullerene soot

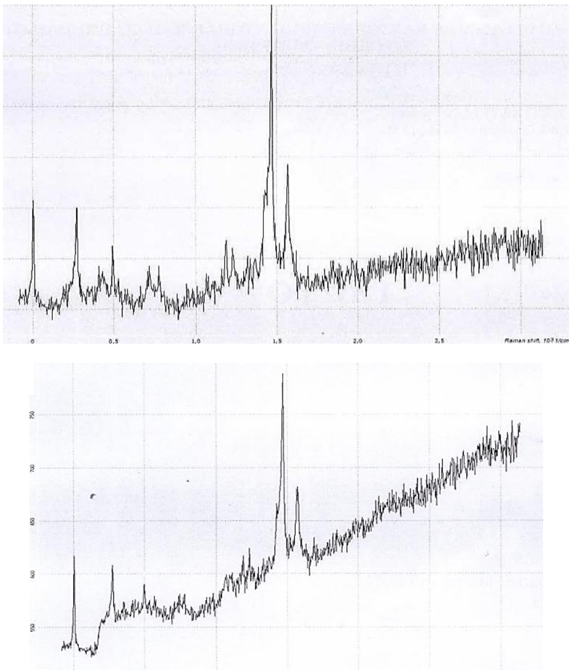

Fig. 3 – Original (raw) Raman spectrum of fullerene soot

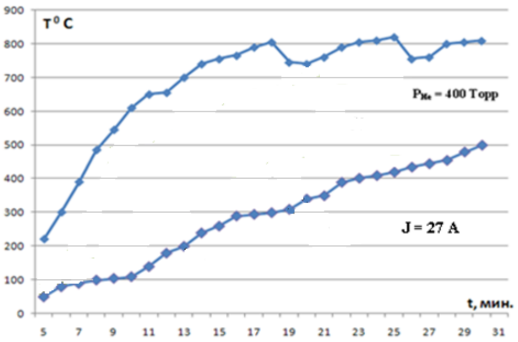

Fig. 4 – Temperature changes in the substrate (top) and the ferrocene container

During researches we obtained the totality of technological parameters when the rate of evaporation of the anode and cathode deposit growth are approximately equal. It is noted that these modes of operation allow to obtain multi-wall nanotubes in a gas phase with fewer amount of amorphous carbon.

The structure of multi-walled nanotubes is studied using a transmission microscope JEM-100CX (voltage U – 100 kB). Figure 5 shows the typical micro-image of multiwall nanotubes produced with a catalyst of iron. The picture shows amorphous carbon particles attached to the nanotubes.

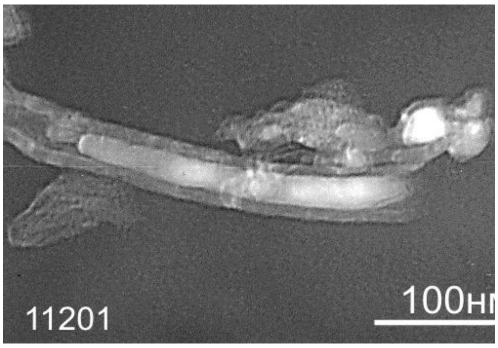

Fig. 5 – Nanotube structure with encapsulated iron nanoparticles obtained in a transmission microscope JEM-100CX

Along with the nanotubes in a gas phase amorphous carbon is formed, which also diffuses to the surface of the substrate and contaminate the resulting intermediate product, which requires a lot of effort for the subsequent purification of the nanotubes.

Conducted a comparative evaluation of the energy costs of producing nanotubes by two most common methods – CVD in a tube of flow quartz reactor with usage of carbon-containing liquids and catalysts and improved arc method with low-amperage arc. It is shown that for the same average temperature of the reaction chamber, heat losses in the production of multi-walled nanotubes are almost identical. In the arc chamber heat loss reduction achieved by setting heat shields inside the vacuum volume and normal thermal insulation on the outer surface. It debunks the understanding of arc method as a process with large energy losses. In contrast, transfer of nanotubes production into low-amperage area ≈ 40 A lowered the costs of electricity and raw materials.

We obtained the following competitive advantages of advanced technology for production of nanotubes in the gas phase:

– in the process of pumping, substrate and the work surfaces degassed and heated to the desired temperature, after which occurs the injection of ferrocene molecules. After closure of technological process the substrate with nanotubes removed from the reactor, placed in unfolds into ultrasonic field, wherein soft purification from amorphous carbon is conducted, without fear of destruction nanotubes;

– temperature ≈ 4000 °C in the arc column serves to intensify the collapse of ferrocene molecules using a strong tool – radiation and charged plazma particles, meanwhile hydrogen obtained by the decomposition of C_5H_5 ligand reduces the amount of amorphous carbon within condensable nano products;

– formed radial gradient of temperature and concentration of carbon clusters promotes intensive growth of multiwall nanotubes in the region of the substrate at relatively low temperatures ≈ 750 °C.

4. CONCLUSIONS

In connection with the opening in Universities in the Republic of Kazakhstan nanotechnology faculties there is a problem in equipping them with relatively inexpensive domestic equipment. Based on advanced arc technology we have developed installation for education and research works for students, which is represented in Figure 6.

Fig. 6 – Educational and research installation for students

Feature is the safety of the installation, provides by usage of low-voltage power supply, the lack of need in carbon-containing liquids and their waste disposal unit. A wide thematic spectrum of conducted laboratory work provided by offered snap to each of them, and two works reproduce the historical experiences in the field of carbon plasma for the results of which were awarded the Nobel Prize in Chemistry. The cost of our educational and research installations is much lower than similar installations of foreign firms (Ulvac, Atomate, NanoLab) and two times lower than Russian «CVDomna».

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