SYNTHESIS OF PLATINUM-CONTAINING CARBON NANOSTRUCTURES

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Introduction

It has been known [1] that besides soot in the course of arc synthesis the growth named deposit [2] forms on a cathode as a by-product.

During evaporation of graphite and any element the deposit may form from two elements and more [4]. Its structure and properties will greatly depend on the properties of the element added. In particular, if this element forms carbides, solid solutions of carbon or does not react with carbon at all [3, 5].

During evaporation of pure graphite the deposit comprises carbon nanotubes and some amount of graphitized mass that is among bunches of nanotubes and mainly in the part that forms a rigid carcass around a core [2].

Graphite and platinum have been evaporated in this investigation. The aim of the investigation is to study structure and morphology of synthetic materials at nano- and micro-levels, and regularities of deposit formation in the presence of platinum vapor.

Results and discussion

The product has been synthesized using the setup for arc evaporation of graphite.

Carbon and platinum have been evaporated in plasma, helium at a pressure of 0.02-0.09 MPa.

In the vertical reactor an anode is fixed and a cathode is moved along the reactor axis.

Platinum wire has been introduced into the anode composition at a ratio of 1:100. Derivatographic studies have been performed using Derivatograph Q-1500D in conditions of dynamic heating from room temperature to 1000 ^{o}C. Studies of microstructure of synthetic products have been performed on the scanning electron microscope T-20. Content of elements in the products has been determined by emission spectral analysis and using X-ray microanalyzer ICXA-733.

Graphite of MPG-7 grade has been used as starting material.

Besides the deposit, the soot that comprises fullerenes and other nanostructures settles on the reactor walls. Nanostructures in the soot have different geometrical forms and structures.

The body of the deposit consists of two main parts, a core and a shell. In graphite evaporation without any catalysts the boundary between the carcass and the core is well defined. However it is very difficult to separate these two parts mechanically. The shell forms from layered structures, which planes are perpendicular to the deposit axis (Fig.1a, b) and densely packed in the united structure.

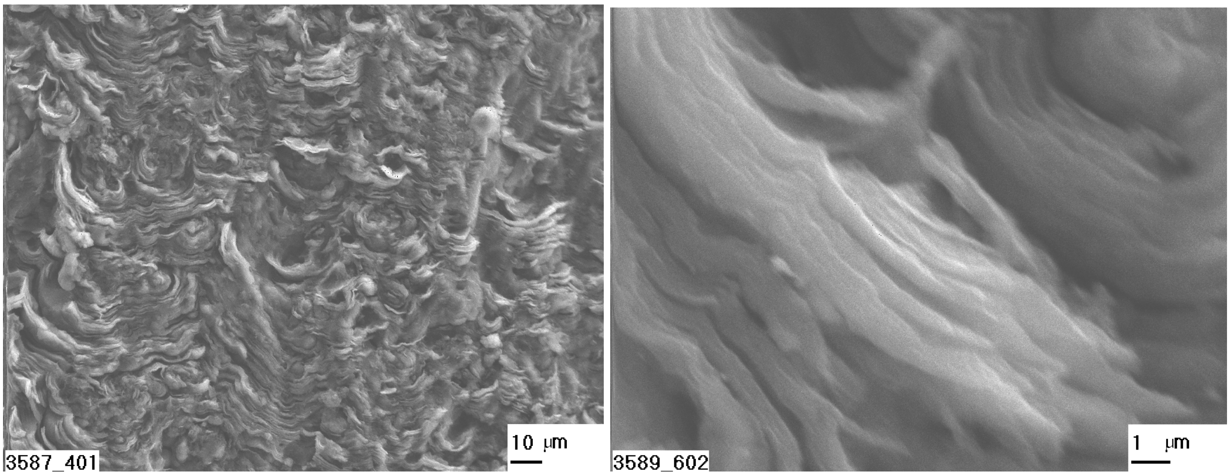
The core of the deposit is more friable and porous. It comprises conglomerates that are oriented along the deposit axis and consist of bunches from carbon nanotubes (Fig.2a, b). Bunches unite multi-wall carbon nanotubes 4-25 nm in diameter.

In evaporation of graphite and platinum the core has denser structure than without platinum. Columnar structures 100-150 μm in diameter form the core and oriented parallel to the deposit axis. They comprise bunches of carbon nanotubes 4-25 nm in diameter (Fig.3).

However not only hollow carbon nanotubes, but also tubes with different structural anomalies form in this case (Fig.4). The tubes contain some inclusions and have rougher external surface. According to the X-ray microanalysis, the platinum content in the core is a negligible and equals hundred fractions of a percent.

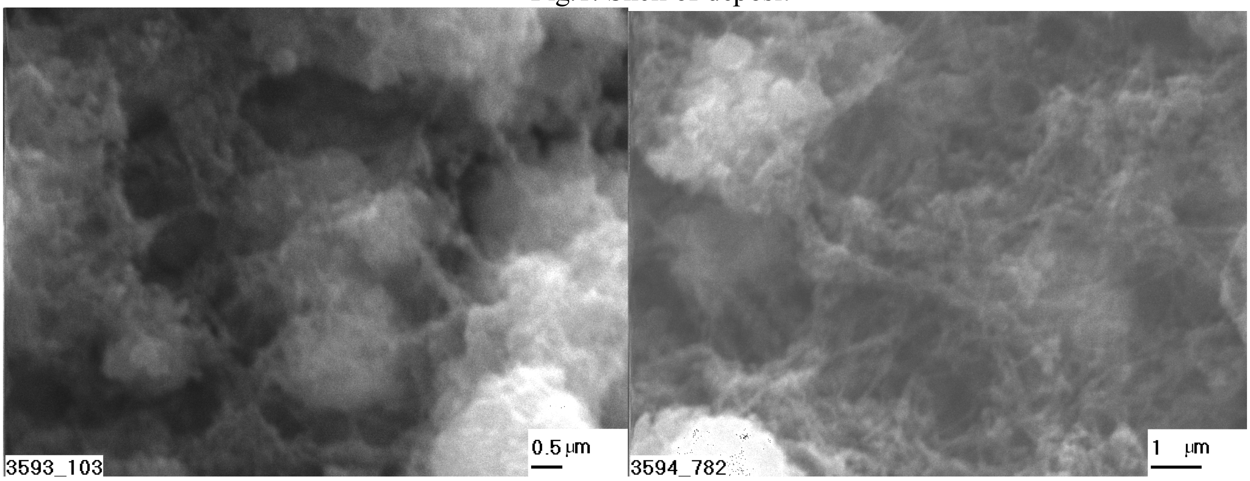
In the course of evaporation of graphite and platinum in electric arc in helium the main mass of metal participates in various plasma chemical reactions to form non-stable Pt-C bonds of σ- and π-types and redistributed among different synthetic products.

According to the emission spectral analysis, the most part of this mass is transferred to the reactor walls by the flow of condensate. The small part of platinum in the cation state under the action of strong electric field and carbon vapor are transferred to the cathode to form the deposit. In spite of high temperature in the condensation zone (above 4000 ^{o}C) that exceeds the boiling point of platinum (3800 ^{o}C), platinum is supposedly present in the deposit composition owing to chemical interaction with carbon atoms.



a) ***b)***

Fig.1. Shell of deposit



a) б)

Fig.2. Core of deposit. (a, b) Bunches of nanotubes

Fig.3. Carbon nanotubes that form the deposit core produced by evaporation of graphite and platinum

Investigation into chemical composition of the deposit has shown that platinum atoms in the deposit are distributed unevenly. Practically the core of the deposit contains traces of platinum. This is supported by the results of emission spectral analysis and studies of the cut surface using the X-ray microanalyzer. The main part of the deposit platinum (less than 1%) is in the deposit bark. It seems likely that the large electron flow that passes through the forming deposit not only has a significant effect on formation of the deposit structure, but also

Higher thermal stability of the platinum-containing bark of the deposit (interaction with oxygen from air starts at 680°C) compared to that of the pure carbon bark (T_{inter}=575 °C) is due to the presence of platinum.

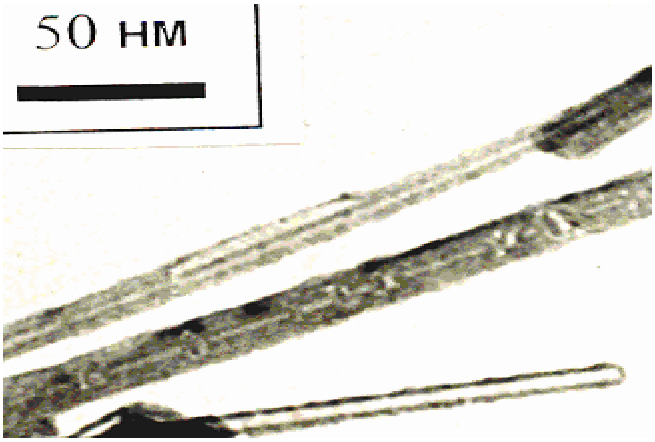


Fig.4. Anomaly in nanotubes (inclusions and branching.

The deposit core, that practically forms from bunches of carbon nanotubes with a very low content of platinum, also exhibits higher thermal stability (interaction with oxygen from air starts at 640 °C) compared to that of the pure carbon bark (T_{inter}=575 °C). Thermal analysis has shown that the deposit core produced in the presence of platinum has two phases that interact with oxygen from air at 800 and 910 °C.

Conclusions

The forming hollow carbon nanotubes 5-25 nm in diameter and 1.5-2 in length are not distinguished from those produced without platinum apart from some anomalies. The deposit has hexagonal graphite structure with impurity of a rhombohedral phase. Platinum in the synthetic products is distributed as follows: separates platinum atoms.
the deposit core – less than 0.001%, the deposit shell – less than 1%, the wall soot – more than 1%. The parts of the platinum-containing deposit are more stable than those without platinum. The synthetic products can be used to produce fuel cells.

References

1. Trefilov V.I., ShChur D.V., Tarasov B.P., Shul'ga J.M., Chernogorenko A.V., Pishuk V.K., Zaginajchenko S.J. Фуллерены - a basis of materials of the future//the Monography, Publishing house ADEF-Ukraina, Kiev - 2001, page 1-148.
2. Tarasov B.P., Muradyan V.E., Shul'ga Yu.M., Krinichnaya E.P., Kuyunko N.S., Efimov O.N., Obraztsova E.D., Schur D.V., Maehlen J.P., Yartys V.A., Lai H.-J. Synthesis of carbon nanostructures by arc evaporation of graphite rods with Co-Ni and YNi_2 catalysts // Carbon, V. 41, 2003, P. 1357-1364.
3. Rogozinskaya A.A., Schur D.V., Timofeeva I.I., Klochkov A., Simanovskiy A.P., Rogozinskiy A.A. X-ray structural study of deposit formed on electric arc sputtering of Me_1-Me_2-C composites // NATO Science Series II - Mathematics, Physics and Chemistry, volume nr. 172, 2004, P. 307-312.
4. Shulga Yu.M., Schur D.V., Baskakov S.A., Simanovskiy A.P., Rogozinskaya A.A., Rogozinskiy A.A., Mukhachev A.P. XRD patterns of cathode deposits formed in electric arc sputtering Zr-Me-graphite electrodes // NATO Science Series II - Mathematics, Physics and Chemistry, volume nr. 172, 2004, P. 137-142.
5. Zaginaichenko S.Yu., Schur D.V., Matysina Z.A. The peculiarities of carbon interaction with catalysts during the synthesis of carbon nanomaterials // Carbon, V. 41, 2003, P. 1349-1355.