Synthesis of carbon nanotubes on the surface of the field cathode of X-ray tube

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Abstract. Carbon nanotubes are unique materials being actively investigated in the development of X-ray tubes with a field cathode. The so-called cold-ray tubes. Our contribution in this direction is the use of single crystals W for the anodes and cathodes as substrates. Here are the structures we obtained carbon nanotubes with the catalysts and directly on the surface of tungsten. The report presents results of studies of carbon nanotubes (CNT) formation on metal substrates W and Ni. X-ray microprobe analysis revealed the presence of 8 at. % carbon. Average density of the powder was measured as 5.1 ± 0.1 g/cm3. Calculations have shown that this value corresponds to the density of the carbon content of 8 at. %.

1. Introduction
The aim of this research was studying the possibility of coating the surface of tungsten by carbon nanotubes (CNTs). In case of success it would appear the experimental confirmation of the possibility of formation of CNTs on a tungsten substrate as a field emission cathode of X-ray tubes [1–3].

2. Methods and results
Most of the samples used in the experiments for growing nanotubes were thin metal plates sizes of 10×10 mm mainly made from nickel and tungsten. Before the process of applying CNTs surface samples polished to obtain a developed surface and etched in acid to remove the oxide layer. The liquid catalyst in the form of solution of nickelous nitrate [Ni(NO3)2] was applied on some samples from a tungsten.

The prepared samples were placed into a quartz cuvette, which was placed into the reactor for the synthesis of nanotubes, a circuit diagram is shown in figure 1. Then include heating the reactor chamber at a predetermined rate to a predetermined temperature are controlled thermostatic device. During the heating in the volume of the chamber is injected inert gas argon. Upon reaching required temperature included a heating device of the evaporator and begin feeding in the chamber with sample a pair of ethanol. The process was stopped after a specified time or after the complete evaporation of the ethanol.

In work as a carbonaceous reagent used ethanol, which has a number of advantages compared to other the reagents (e.g. propylene). Under normal conditions the ethanol exists in a liquid state and is easily stored. It is cheap and low toxic, have no high boiling point (78 °C) and decomposition temperature (about 600 °C). From the chemical standpoint feature of ethanol consists that at pyrolysis
of its vapor OH-radicals are formed, which have high reactivity with respect to defective (amorphous) carbon, due to that the CNTs are more pure. Also the OH-radical prevents contamination of the catalyst particles by amorphous carbon which increases time of growth of nanotubes and as a consequence increases the length.

Figure 1. The scheme of the reactor for the synthesis of CNTs: 1 – quartz chamber; 2 – cuvette with the sample; 3 – heating element; 4 – thermocouple; 5 – evaporator with ethanol; 6 – temperature-control systems.

The experimental results (figure 2) showed that on a surface of a sample needle phases were created, and in some places crystalline structures of the faceted form were formed.

Figure 2. The image of the tungsten surface of substrate and a local elementary analysis of this area.

In connection with the foregoing a need to use catalysts, particularly nickel. Figure 3 shows the structure of CNTs on a nickel substrate. These results confirmed prospects of use of nickel as catalyst material. In subsequent experiments, for example, by controlling the thickness of the applied nickel layer can be controlled by the size and number of synthesized nanotubes.

In preparing the tungsten substrates, solution of nickelous nitrate \([\text{Ni(NO}_3\text{)}_2]\) was applied on their surface and then process of synthesis of CNTs was carried out. The results are shown in figure 4.

| Element | Mass., % |
|---------|----------|
| C       | 11.01    |
| O       | 27.20    |
| W       | 59.20    |
Figure 3. Electron microscopic image CNTs on a nickel substrate.

Figure 4. Images of a surface of a tungsten substrate pre-coated Ni(NO$_3$)$_2$ at increase in 50000 (left) and 200000 (right) times respectively.

Based on the results of electron microscopic researches been established that the presence of nickel catalyst leads to stable formation of CNTs on the tungsten surface.

3. Discussion of research results

In the first experiments the modes of synthesis of carbon nanotubes on nickel substrates with ethanol use as carbon source for definition of dependence of process parameters on nanotubes structure such as temperature, time and feed rate of gaseous components were fulfilled. The established laws of formation carbon structures at various parameters are the result of experiments.

Application of carbon nanotubes on substrates from tungsten for receiving nanotubes in the production technology of cathodes for X-ray tubes was the following stage of researches. The nickel catalyst which was applied on substrates from tungsten for formation on their surface of the CNTs arrays was used at the subsequent stage [2].

The thermal tests which showed thermal stability of carbon nanotubes to $T = 1700$ °C were carried out after receiving positive takes of the above researches. Additionally, by scanning electron microscopy radius nanotubes produced was measured, which ranged from 20 to 100 nm. The value of the specific surface was determined by the method of Brunauer–Emmett–Teller, it was 92.64 m$^2$/g. The modes of getting CNTs are worked, and also influence of process parameters of their getting on structure of the nanotubes array on the tungsten surfaces is established.
4. Conclusions
It was established that synthesis of carbon nanotubes by method of a catalytic pyrolysis immediately on the surface of tungsten with ethanol use as carbon source at the chosen modes did not lead to synthesis of CNTs. However, the application of a nickel catalyst on the substrate surface tungsten gave positive results in experiments on synthesis of CNTs on the tungsten surface.

References
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