SYNTHESIS AND CHARACTERIZATION OF MWCNTS COATED WITH TITANIUM CARBIDE THIN FILMS

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Abstract

We synthesized multiwall carbon nanotubes (MWCNTs) arrays with the 80 nm average outer diameter of nanotubes by metalorganic chemical vapor deposition (MOCVD) at 825 °C. Ferrocene and toluene were used as precursors. Deposition of titanium carbide nanocoating on the surface of MWCNTs was performed by MOCVD with titanium-containing organometallic as precursor. Titanium carbide nanocoatings with various morphology and structure depending on the synthesis parameters were synthesized. We obtained titanium carbide thin films with thickness of 2 - 15 nm on surface of MWCNTs. Composition and structure of hybrid material TiC/MWCNT were investigated. The data of the structures and properties of the samples were obtained by X-RAY, TGA, SEM and HRTEM.

Keywords: nanotubes, composite, MOCVD, nanocoating, TiC

1. INTRODUCTION

Hybrid materials based on multiwall carbon nanotubes with various metal-containing nanoparticles or coatings deposited on their surface are promising sources for new reinforced composites with polymer and metal matrices as well as for construction of new catalytic and sensor devices. It is especially interesting to obtain MWCNTs coated with titanium carbide nanocoating on the surface, which, in particular, can be used as catalytic systems, additives in various alloys, additives in acrylate adhesive compositions and as gas sensors.

2. SOURCE MWCNTS

To create a new composite material based on MWCNTs and titanium carbide it is important first of all to synthesize a high quality source MWCNTs with certain parameters. So it is necessary to get clean smooth MWCNTs with an external average diameter up to 100 nm without any impurities. MWCNTs suitable for creating new nanocomposite were synthesized on the created MOCVD-installation and are characterized by various analytical methods.

2.1 Synthesis of the source MWCNTs

Synthesis of the source MWCNTs was carried out by MOCVD method and is described in detail in [1]. Ferrocene and toluene were used as precursors. The ferrocene evaporator furnace temperature was 95 °C. The temperature of pyrolysis furnace was 825 °C. Flow rate of argon was 450 cm^3/min. Scheme of MWCNTs deposition installation is shown on Figure 1.

In this reactor argon (inert carrier gas) passes through the bubbler with toluene and carries toluene vapor in the zone of the evaporator furnace. Ferrocene vapor joins toluene vapor in this zone. This mixture is carried by the flow of argon to the pyrolysis furnace. Decomposition of hydrocarbons and organometallic compounds occurs in this furnace forming arrays of nanotubes on cylindrical inner liners.

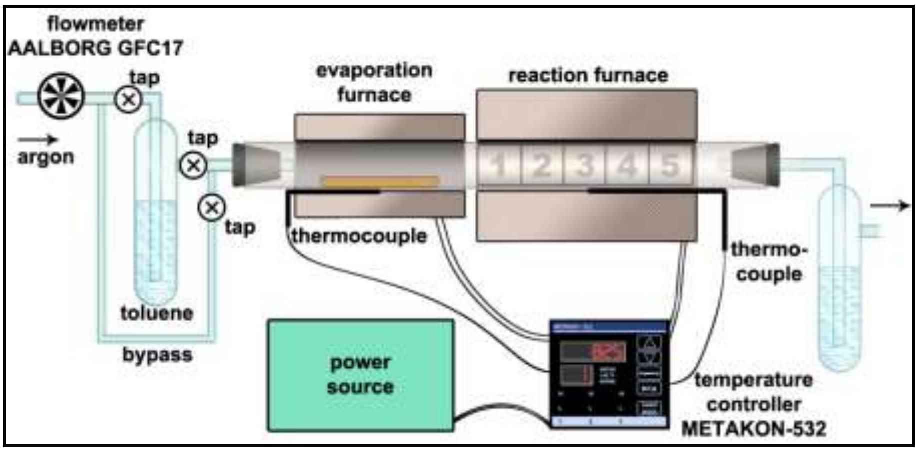

Fig. 1 Scheme of the MWCNTs synthesis reactor

Thus the macroscopic hollow cylinders with walls made of radially oriented MWCNTs were obtained by the synthesis at 825 °C. Such macroscopic cylinders can be up to 50 mm long, with wall thickness up to 3 mm and weight up to 4 g. The outer diameter of the cylinder is 17 mm. Then such macroscopic cylinders are milled to obtain the powder of MWCNTs suitable for deposition of various nanoparticles on it.

a. Characteristics of the source MWCNTs

Synthesized source MWCNTs were analyzed by various physicochemical methods. Investigation of morphology and form of the synthesized MWCNTs were performed by a scanning electron microscope Carl Zeiss SUPRA 50VP. Figure 2 shows the image of MWCNTs array obtained by the scanning electron microscope. It shows that most of MWCNTs have almost the same thickness.

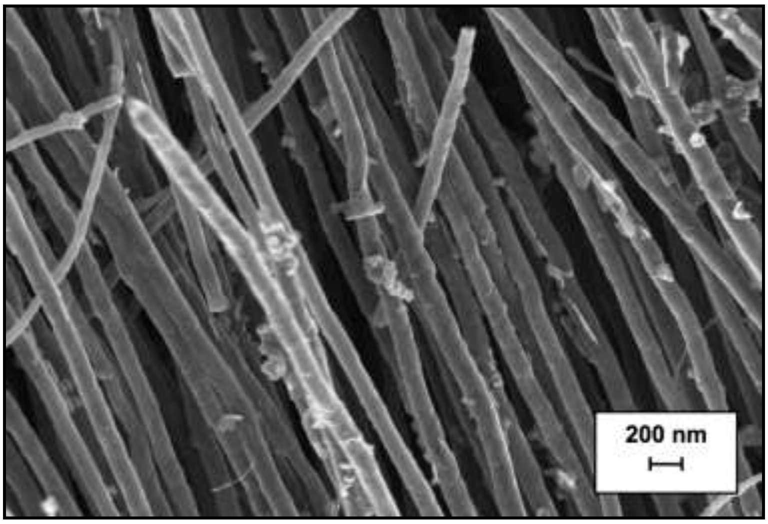

Fig. 2 SEM image of the source MWCNTs

After collecting the statistical data it was established that the average outer diameter of MWCNTs is about 80 nm. However both very thin (5 - 20 nm) tubes and the relatively thick (>100 nm) tubes are always found in the sample.

The surface quality and internal structure of the source MWCNTs were investigated by using transmission electron microscope Carl Zeiss LIBRA 200MC. Typical high-resolution transmission electron microscopy image of thin carbon nanotube is shown on Figure 3. On this picture the nanotube walls made of carbon layers and the inner channel inside tube are clearly visible.

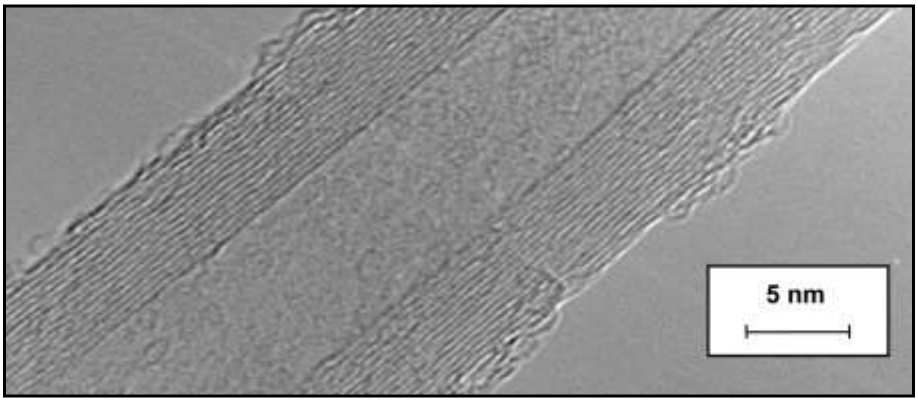

Fig. 3 HRTEM image of the source MWCNT

The source MWCNTs were also investigated by thermogravimetric analyzer Pyris 6 TGA. It was found that the oxidation of the source MWCNTs starts at 490 °C. The maximum oxidation rate is reached at 588 °C.

The phase composition of the source MWCNTs was investigated by using X-ray diffractometer Bruker D8 Discover. Apart from carbon phase, gamma-iron phase and iron carbide phase were found. This is a consequence of the source MWCNTs growth on iron catalyst. Thus the synthesized nanotubes comprise nanosize iron particles in their internal channels.

3. DEPOSITION OF TITANIUM CARBIDE COATINGS ON MWCNTS SURFACE

Deposition of titanium carbide coatings was carried out in vacuum glass reactor. Cp_2TiCl_2 and source MWCNTs were used as precursors and were placed into reactor before synthesis. Then reactor was heated up to 900 °C. The reactor was continuously pumped out to remove reaction byproducts. The scheme of synthesis reaction is as following:

$$Cp_2TiCl_2 \xrightarrow{900^\circ C} TiC + reaction\ byproducts \quad (1).$$

4. ANALYSIS OF THE SYNTHESIZED MATERIALS

Synthesized hybrid materials were analyzed by various physicochemical methods. First of all phase composition of synthesized materials was established using X-ray diffractometer. Figure 4 shows the experimental diffraction pattern of the hybrid material TiC/MWCNTs and theoretical diffraction patterns of MWCNTs and titanium carbide. This fact proves that decomposition of Cp_2TiCl_2 leads to deposition of TiC what is depicted on reaction scheme (1). Thus it is unequivocally confirmed that the synthesized material is the composite of titanium carbide and MWCNTs without any impurities.

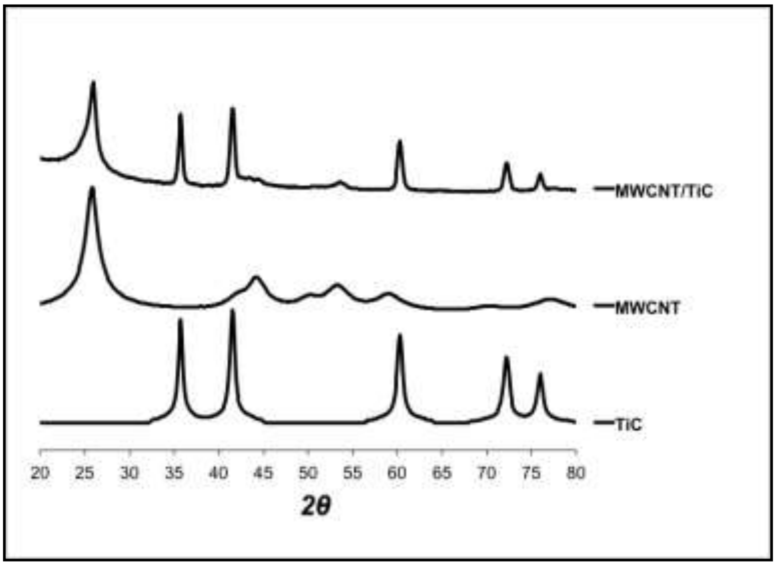

Fig. 4 Experimental XRD pattern of the synthesized hybrid material TiC/MWCNTs and theoretical XRD patterns of MWCNTs and TiC

Figure 5 shows the image obtained by a scanning electron microscope of MWCNTs array covered by TiC. It can be seen that the titanium carbide coating completely covers the surface of MWCNTs.

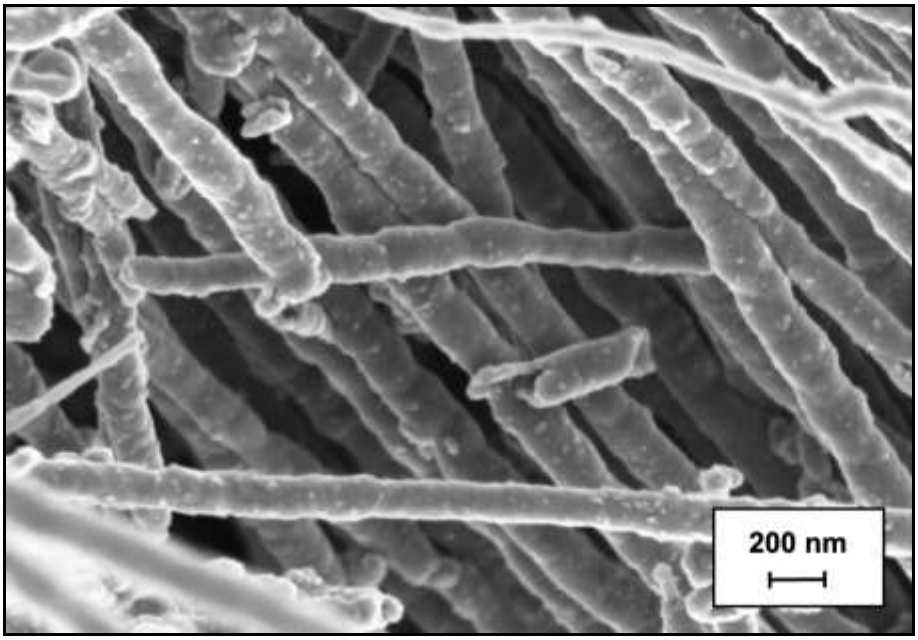

Fig. 5 SEM image of the TiC/MWCNTs material

Structure of the coating of titanium carbide on the surface of MWCNTs was investigated by high-resolution transmission electron microscopy. The images presented in Figure 6 clearly demonstrate the features of the formation of titanium carbide coating. It is also can be well seen that the coating has a good uniformity. In addition, the HRTEM images show that the TiC coating thickness was about 10 nm.

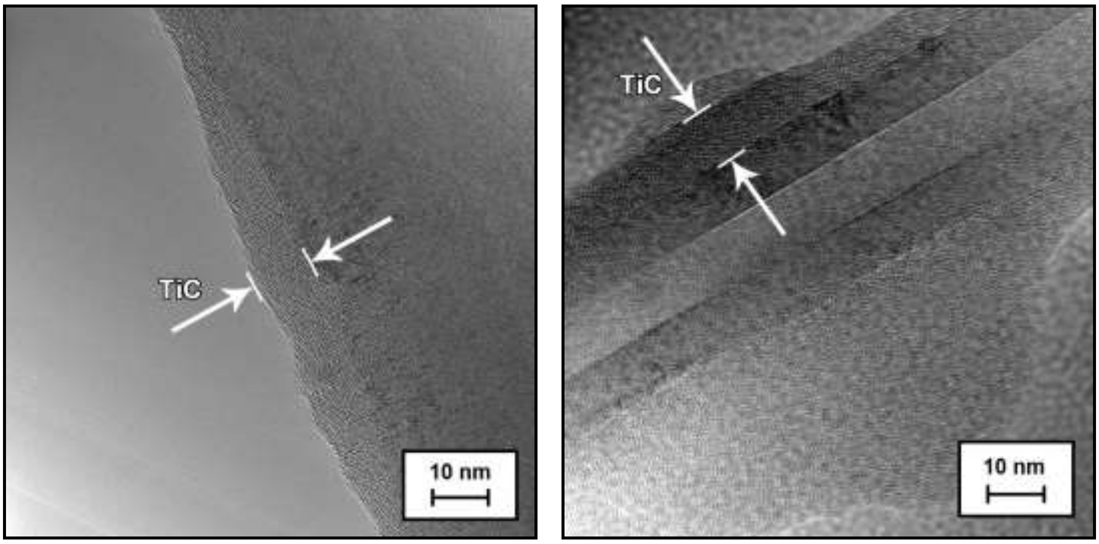

Fig. 6 HRTEM images of the TiC/MWCNTs material

However, the titanium carbide coatings can have thickening up to hundreds of nanometers. Such a structure of the coatings on the surface of MWCNTs confirms that almost all of the source MWCNTs are completely covered with titanium carbide. Of course the coating thickness essentially depends on the initial ratio of precursors in the reactor. With a minimum initial amount Cp_2TiCl_2 taken the coating of titanium carbide managed to get thickness of about 3-4 nm. Thus by changing the initial ratio of the reaction precursors different coating thickness of titanium carbide on the surface of MWCNTs can be achieved.

5. CONCLUSION

We synthesized new hybrid materials based on MWCNTs and titanium carbide nanocoatings. We used various physicochemical methods of analysis to investigate this material. This material is a powder of MWCNTs coated with thin films of TiC. The average outer diameter of MWCNTs is about 80 nm. The coatings of titanium carbide have an average thickness of 2-15 nm. Synthesized hybrid material consists only of iron-containing MWCNTs fully coated with titanium carbide thin films without any impurities.

ACKNOWLEDGEMENTS

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LITERATURE

[1] OBIEDKOV A.M., KAVERIN B.S., EGOROV V.A., SEMENOV N.M., KETKOV S.Yu., DOMRACHEV G.A., KREMLEV K.V., GUSEV S.A., PEREVEZENTSEV V.N., MOSKVICHEV A.N., MOSKVICHEV A.A., RODIONOV A.S. *Macroscopic cylinders on the basis of radial-oriented multi-wall carbon nanotubes*. 2012, Letters on Materials, V. 2, P. 152-156.