SYNTHESIS AND INVESTIGATION OF IRON-CONTAINING MWCNTS

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Introduction

Most convenient methods of large-scale synthesis of carbon nanostructures, including multi-wall carbon nanotubes (MWCNTs), are known to be based on the method of vapor-phase thermal decomposition (CVD) of hydrocarbon precursors on catalytic metal (mainly Fe, Co and Ni) nanoparticles deposited on suitable carriers [1]. In the course of investigations [2,3] concerning pyrolysis of the transition element organometallic compounds (OMCs), which contain both a carbon-producing source and a source of the metal nanoparticles – catalysts of the MWCNT growth, it appeared that single-wall CNTs (SWCNTs), MWCNTs and Y-CNTs can be easily prepared from pure transition metal OMCs or from their mixtures with hydrocarbon precursors. The nanostructures obtained are tested for their use as electron emitters, various devices in nanoelectronics, adsorbents (including those for hydrogen storage) and for other applications.

In this work, the results of the investigation of the carbon nanostructure deposition on pyrolysis of the mixtures of ferrocene and benzene or toluene are reported.

Experimental

Fe-filled MWCNTs have been prepared as coatings (the thickness was up to 4 mm), consisting of upright-oriented tubes, by MOCVD (700-900 ^{o}C) of ferrocene/benzene or ferrocene/toluene mixtures (Fig. 1). The MOCVD process was carried out in a quartz reactor supplied with a two-step system of heating ovens in a flow of Ar according to the technique described elsewhere [4]. The conditions of the MWCNT deposition (the reactor size, temperature of ferrocene sublimation, temperature of the oven in the deposition zone, the Ar flow velocity) have been optimized.

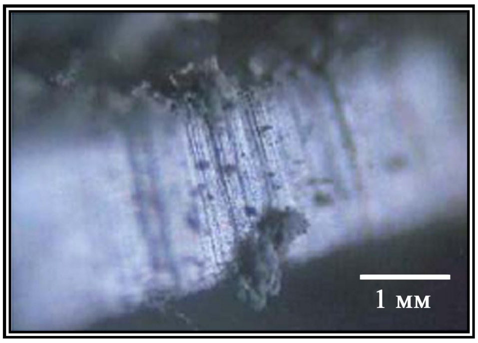

Fig. 1. Side view of the MWNT coating formed on pyrolysis of the ferrocene/benzene mixture in a flow of argon at atmospheric pressure.

For further investigations, the samples obtained in the central zone of the quartz reactor were selected. The data concerning structures and properties of the MWCNTs prepared were collected with use of X-ray powder diffractiometry (X-RPD), oxidative thermo-gravimetric analysis (TGA), high-resolution transmission electron microscopy (HRTEM), X-ray fluorescent (XRF) spectrometry, Raman spectroscopy and magnetic measurements.

Results and Discussion

Analysis of the TEM and HRTEM images for the MWCNTs obtained shows that the coating consists of densely packed MWCNT wisps containing a great number of bundled MWCNTs. The wisps form fibrous structures up to 4 mm length (Figs.1, 2). The graphene shells lie uniformly, parallel to the MWCNT core. They give an equal number of projections on the both sides of the central cavity. The inter-layer distance between the shells is 0.34 nm (Figs.4, 5). The MWCNTs with the outer diameter from 20 to 150 nm and the inner diameter exceeding 3 nm are observed, most of them representing the closed tubes.

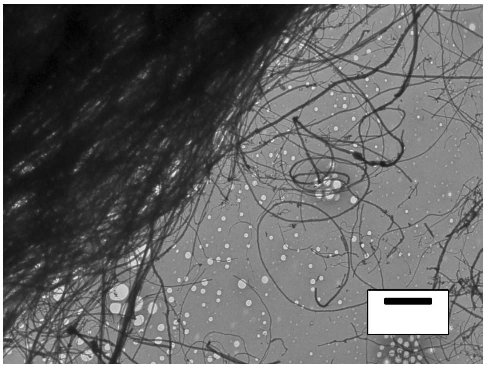

Fig.2 TEM micrographs of a MWCNT bundle. The scale corresponds to 0.4 μm.

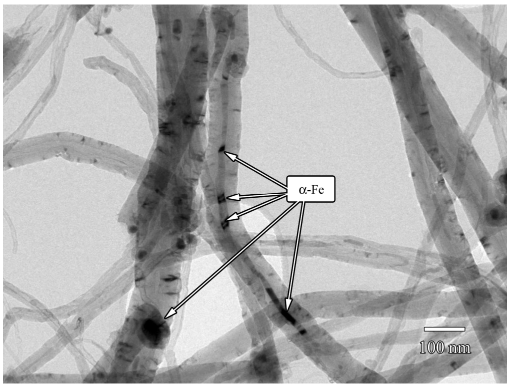

Fig.3. TEM micrographs of MWCNT showing partial infill of a nanotube with the α-Fe nanocrystals and nanorods.

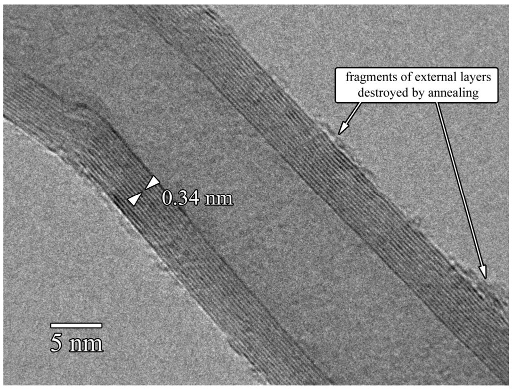

Fig.4. HRTEM micrographs of a section of a MWCNT annealed at 500 ^{0}C.

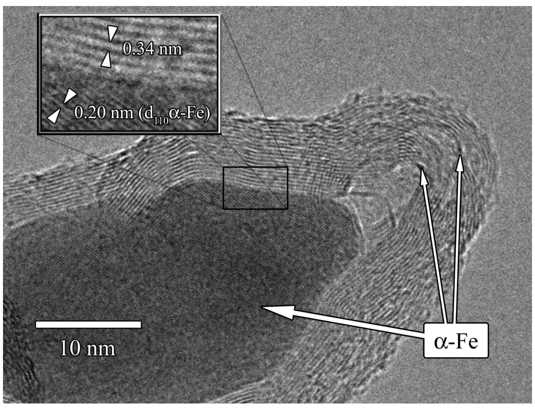

Fig. 5. HRTEM micrographs of α-Fe catalytic nanoparticles on the MWCNT cap.

Nanocrystals of α-Fe occur on different sites of MWCNTs, in particular as nanocrystallites and nanorods of few tens nanometers length at the tips (caps) of MWCNTs (Figs.3, 5). The X-RPD patterns for the MWCNT samples show three characteristic MWCNTs peaks [(002), (101) и (004)], the strongest one (002) being somewhat broadened as compared to graphite. The 002 peak position corresponds to an increase in the sp^2 carbon interlayer distance from 0.336 nm (graphite) to 0.343 nm (MWCNT). In the 37^o-57^o 2Θ angle interval, the peaks assigned to α-Fe, γ-Fe and iron carbide Fe_3C are also found. Iron in the MWCNT samples occurs predominantly in the forms of non-oriented iron carbide and supermagnetic α-Fe nanoparticles (the sizes exceed 3 nm) as indicated by the Moessbauer spectroscopy. The iron concentration in the MWCNT samples obtained at 850 ^{o}C was determined by XRF as (2.4±0.5) % (mass).

Conclusions

The conditions for preparation of multi-wall upright-oriented Fe-filled carbon nanotubes by pyrolysis of the ferrocene/benzene and ferrocene/toluene mixtures have been optimized. Up-to 4-mm thick MWCNT coatings have been obtained. The iron concentration in MWCNTs has been shown to be not less than (2.4±0.5) % (mass), depending on the synthetic conditions. Iron occurs in MWCNTs as nanoparticles and nanorods of α-Fe, γ-Fe or Fe_3C which sizes exceed 3 nm.

Acknowledgements

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References

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