DIFFERENT PURIFICATION METHODS AND STRUCTURAL CHARACTERIZATION OF MWCNTS

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Introduction

It is known that, when using catalytic syntheses of multi-wall carbon nanotubes (MWCNTs), the catalyst particles, in the forms of nanocristallites or nanorods of the corresponding metals or metal carbides, occur at different sites both inside and on the apexes of MWCNTs [1, 2]. Besides the catalytic nanoparticles, fresh MWCNTs can contain amorphous carbon, graphite nanocrystallites as well as catalyst metal particles covered with graphite-like shells. The MWCNT purification methods allowing one to avoid such impurities have been developed. Basically, dry and "wet" techniques are employed for the MWCNT purification. The dry methods include oxidation of MWCNTs on air and under O_2 or CO_2. In the "wet" techniques, a treatment of the freshly prepared MWCNTs with concentrated or diluted solutions of inorganic acids at heating or on exposure to ultrasound.

In this work we report the results of investigation the structural changes observed for the MWCNTs obtained by pyrolysis of ferrocene/toluene mixtures and purified to remove the iron impurities in any form.

Results and Discussion

Fe-filled The MWCNTs partially filled with Fe have been prepared as coatings (the thickness was up to 4 mm), consisting of upright-oriented tubes, by MOCVD (700-900 ^oC) of ferrocene/toluene mixtures in a quartz reactor supplied with a two-step system of heating ovens in a flow of Ar, according to the technique described else where [1]. The MWCNT thermal characteristics were studied by the oxidative thermo-gravimetric analysis. The MWCNT oxidation begins at ~520 ^0C and involves one stage.

Analysis of the TEM and HRTEM images of the MWCNTs obtained shows that the graphene shells for the MWCNTs of a small outer diameter (20-50 nm) 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 0.341 nm. As the number of the walls (graphene layers) increases a polygonization of the outer shell is observed (Fig.1).

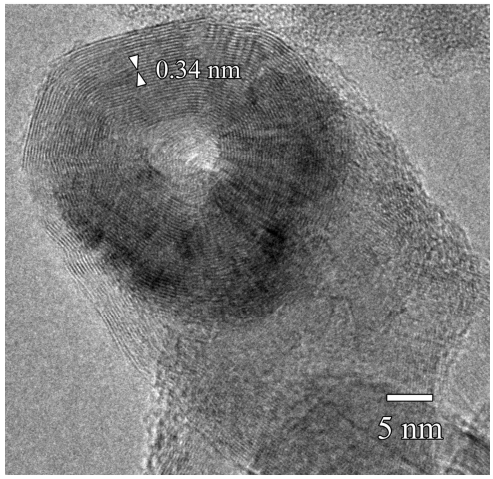

Fig.1. HRTEM micrographs of an end of an open nanotube.

The difractograms of the MWCNT samples (Fig. 2.2) reveal three peaks typical for MWCNTs [(002), (101) and (004)], the strongest one (002) being broader than that for graphite (Fig. 2.1). 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 intervals, the peaks assigned to the α-Fe, γ-Fe and iron carbide Fe_3C phases are also observed. After annealing on air the peaks corresponding to Fe_2O_3 appear. They become stronger as the annealing time increases while the α-Fe, γ-Fe and Fe_3C peak intensity goes down to complete disappearance (Fig. 2.3). In the annealing process, the MWCNT ends are broken up as seen from Fig. 1.

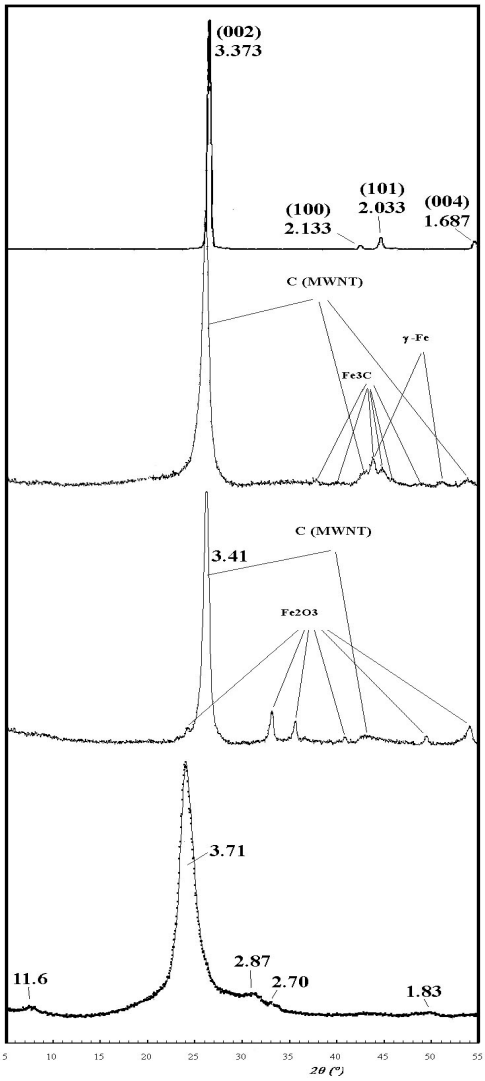

Fig.2. Difractograms of the carbon material samples. 1- graphite (a standard); 2- a sample of starting MWCNTs; 3- a sample of MWCNTs after annealing on air at 500 ^{0}C; 4- a sample of MWCNTs after annealing on air and a subsequent treatment with a mixture of concentrated H_2SO_4 and HNO_3 (3:1) at 140 ^{0}C for 45 min.

The treatment of the oxidized MWCNTs with a 3:1 mixture of concentrated H_2SO_4 and HNO_3 at 140^{0}C for 45 min results in substantial changes of the X-ray diffraction picture. The peak at $2\Theta=26^0$ shifts to $2\Theta=24^0$. Weak features appear at $2\Theta=7.6^0$, 31^0, 33^0 and 50^0. The $2\Theta=24^0$ peak position corresponds to an increase in the MWCNT sp^2 –carbon interlayer distance from 0.341 to 0.371 nm. It is worth mentioning that the resulting material keeps its new properties when stored on air. If an interlayer distance increase exceeds some determined value, a structural phase transition occurs and the symmetry group changes. The graphite-like MWNT structure P63/mmc characterized by the enlarged d_{002} value (3.41 Å) transforms into a new phase. A difractograms of the sample (Fig. 2.4) reveals peaks arising from another planes with d=11.6, 3.71, 2.87, 1.83 Å. A co-existence of the two phases was observed also, depending on the etching conditions. The difractograms of the sample was interpreted as that of a two-phase system. The lattice parameters were refined by the Ritvelds method with use of the FullProf Suite program package. The following parameters of the hexagonal lattices have been obtained: the

MWCNT graphite-like phase – a = 2.463, c = 6.85 Å; the second phase – a =2.46, c = 11.361 Å. The possible symmetry group is P 6/mmm. The divergence criteria R_p=19.7, χ^2=0.97 are quite satisfactory for such a defective structure. These results are confirmed when studying MWCNTs by the HRTEM method. We obtained the MWCNT photomicrographs where both MWCNT regions with interlayer distances of 0.341 nm and MWCNT regions with increased interlayer distances of 0.371 nm are observed. A possible mechanism of this phase transition is discussed.

Conclusions

Fe-filled MWCNTs have been prepared by pyrolysis of ferrocene/toluene mixtures. A structural phase transition in MWCNTs has been observed after an oxidation of obtained MWCNTs on air and a subsequent treatment with a [H_2SO_4+HNO_3(3:1)] mixture at 140 ^{0}C. The graphite-like MWCNT structure (P63/mmc) with an increased d_{002} value (0.341 nm) transforms into a new phase with the P 6/mmm possible symmetry group and d_{003} = 3.71 nm.

Acknowledgements

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References

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