Carbon nanotubes with Co-filling: HRTEM studies

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Carbon nanotubes possess many interesting properties. In particular they can be considered as reaction nanochambers. It is known that in certain cases nanotubes are able to obtain and to keep high pressure phases of materials, which are unstable under normal conditions [1 - 3]. The purpose of the present work is to synthesize carbon nanotubes, filled with Co, and to examine the resulting nanostructures, paying special attention to their crystallographic features.

In the present study carbon nanotubes filled with Co were synthesized in the High Isostatic Pressure (HIP) apparatus at temperature 720 ± 20 °C and under pressure 0.05 GPa (500 bar) in the mixture of carbon monoxide and nitrogen. The TEM analysis has shown presence of fcc-Co (fig.1), hcp-Co (fig.2) and disordered polytypic structure of Co (fig.3). The fcc-Co lattice often appears to be twinned. We observed three different orientations of fcc-Co particles relatively to the nanotube axis: [112], [110] and [111]. Moreover, additional orientations [552] and $[1\overline{14}]$ were observed in the twins of such particles. For hcp-Co we observed orientation [634]_{hcp} and [001]_{hcp}.

The formation of all three structures of Co in nanotubes can result from the process of segregation from the melt leading to the formation of closely packed structures. It was shown, that in our work the origins of Co deformation were, most probably, the thermal stress, the surface tension and the variation of the nanotube cross-section size. This deformation leads to the twinning for fcc-Co and to the sliding and numerous stacking faults for hcp- Co. The elastic deformation, resulting both from the cooling of the nanotube (the coefficients of thermal extension of Co and graphite are different), and from the surface tension, leads to the plastic deformation of Co including its extrusion inside the nanotube. The value of this deformation depends on the diameter of the nanotube and its variation along the nanotube. Variety of the {111} twinning planes (fig.1) can be explained by different direction of the forces acting on the Co filling of the nanotube. These forces depend on the shape of the particle, profile of the nanotube, growth rate of the inner walls and other factors.

[1] L.Sun, F.Banhart, A.V.Krasheninnikov, J.A.Rodriguez-Manzo, M.Terrones, P.M.Ajayan, Carbon nanotubes as high-pressure cylinders and nanoextruders, Science, v.312, 2006, 1199-1202.

[2] D.Golberg, Y.Bando, T.Sato, N.Grobert, M.Reyes-Reyes, H.Terrones, M.Terrones, Nanocages of layered BN: Super-high pressure nanocells for formation of solid nitrogen, Journal of Chem. Phys., 116, 19, 2002, 8523-8532.

[3] V.D.Blank, B.A.Kulnitskiy, I.A.Perezhogin, Yu.L.Alshevskiy, D.V.Batov, N.V.Kazennov, Nanotube as a reaction chamber. Deformation processes in nanotubes, Materials Sciences Transactions, 1, 2007, 42-48.



Figure 1. Two systems of twins in the fcc-Co particle, located inside the carbon nanotube.



Figure 2. Hcp-Co particle inside the carbon nanotube.



Figure 3. Polytypism in the Co-particle, located inside the nanotube. The periodic introduction of stacking faults produces satellite spots. The only two solitary reflections, which are seen at the diffraction pattern correspond to $(111)_{fcc}$ either $(002)_{hcp}$.