Thermodynamic Analysis of Fluid in Hydrothermal Carbon Nanotubes

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Multiwall carbon nanotubes with a high aspect ratio, high degree of graphitization and wide internal channels were synthesized by using a water-based mixture, such as equilibrated C-H-O fluid, in the presence of a catalyst, specifically Ni, at 700-800 °C under 60-100 MPa pressure[1, 2]. Hydrothermal nanotubes have typically 20-70 fringes in walls (wall thickness 7-25 nm) and outer diameter of about 100 nm. Some of the closed-end tubes contained a high pressure encapsulated aqueous fluid, which displayed clearly segregated liquid and gas separated by well-defined curved interfaces. None of the open-ended nanotubes displayed any apparent fluid inclusions.

The goal of this work was to explain the synthesis of carbon nanotubes and to provide analysis of the fluid composition on different stages of the synthesis equilibrium thermodynamics since in-situ experimental analysis is extremely difficult.

ChemSage 4.1GTT software, based on Gibbs energy minimization, was used to model the interaction in the tube between carbon and hydrothermal fluids, assuming closed systems and ideal gases[3]. Dissolution of solid carbon and polymeric precursor (polyethylene) in water and the deposition of carbon from the C-H-O fluid have been analyzed in a broad temperature and pressure range.

During the first stage of the hydrothermal synthesis, dissolution of carbon in C-H-O fluid takes place. The reverse process, deposition of carbon from the supercritical fluid, leads to the tube growth. During the growth of a tube, the synthesis fluid, which is a supercritical mixture of CO, CO_2, H_2O, H_2, and CH_4, exists inside the tube. The pressure inside the tube (after synthesis at 100MPa) was predicted to be up to 30MPa as it depends on the temperature at which the tube closure occurred. The equilibrium fluid composition was calculated to be 85.2% H_2O, 7.4% CH_4 and 7.4% CO_2.

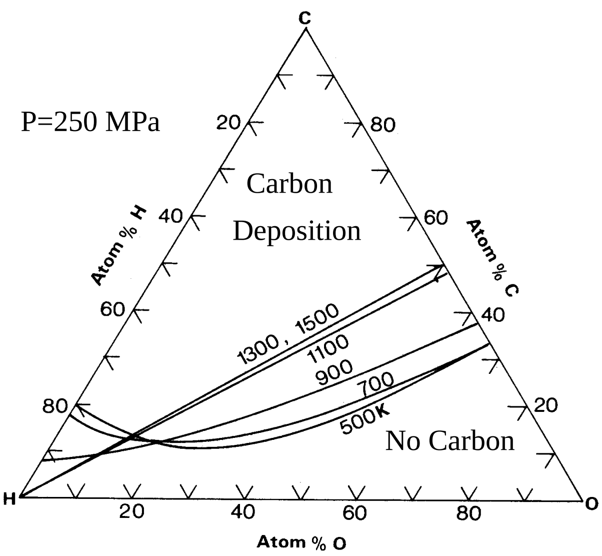

Figure 1: From the carbon stability range in the C-O-H system, by varying the temperature, at a constant pressure, carbon deposition or dissolution can be achieved.

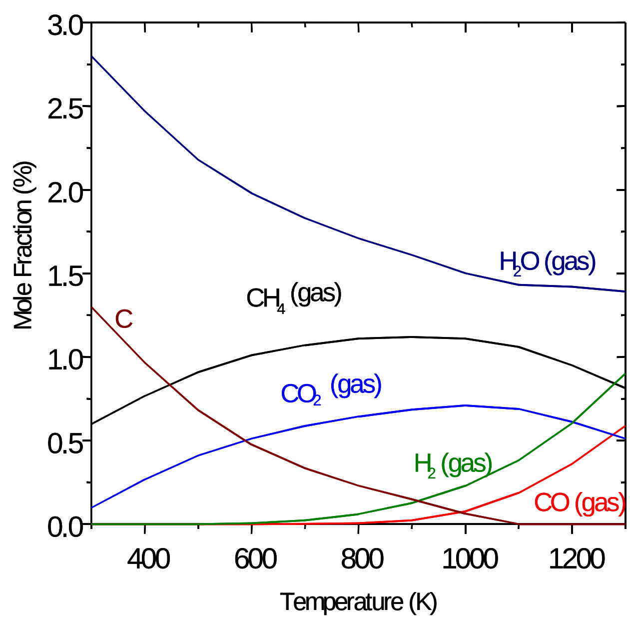

Figure 2: Thermodynamic analysis for the reaction between 1 mol Ethylene Glycol (EG) and 2 mol Water under 80 MPa pressure.

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