Thermodynamic Analysis and Synthesis of Carbon Nanotubes by Chemical Vapor Deposition Using NiO Catalyst and Methane

M.C. Altay, S. Eroglu
Istanbul University, Faculty of Engineering, Dept. Metallurgical and Materials Eng., Avcilar, İstanbul
mcumbul@istanbul.edu.tr; seref@istanbul.edu.tr

Carbon nanotubes were grown on a <100> oriented silicon substrate by chemical vapor deposition technique using NiO catalyst and methane gas. In order to predict the conditions for Ni+C formation, thermodynamic analysis in the system of Ni-O-C-H was carried out at 1 atm by the method of Gibbs' free energy minimization, obeying mass balance constraint [1]. The calculated results are shown in Figure 1 as equilibrium stability diagram for solid phases as a function of temperature and CH_4 mole fraction. As seen from the diagram NiO+Ni, Ni, Ni+C phase fields form successively with increasing CH_4 content. The equilibrium calculations show that free carbon coexists with reduced Ni at temperatures in the range 1100-1300 K for CH_4 mole fractions between 0.5 and ~1. The experiments were initially carried out using bulk nickel oxide powder (~0.3728 g) at a CH_4 flow rate of ~ 15 cm^3/min at 1200 and 1300 K in a tubular furnace with a diameter of 20 mm for various periods (0-30 min). The XRD patterns showed that NiO was reduced progressively to Ni and free C formed along with Ni as the reaction time (or total CH_4 content) was raised. These results were found to be in agreement with the thermodynamic predictions. Based on these studies, temperatures of 1200-1300 K and CH_4 flow rate of 15 cm^3/min were selected for C nanotube synthesis. Prior to the synthesis, the silicon substrate with a <100> crystallographic orientation was dipped into ethanol containing NiO particles after ultrasonic agitation. C nanotube was then grown on the silicon substrate. Carbon coating was obtained at 1300 K for 30 min, indicating that the temperature was too high. Carbon nanotube morphology was, however, observed at a lower temperature of 1200 K for the same growth time. SEM image of the product (Fig. 2) revealed that nanotubes with a mean diameter of ~100 nm were synthesized using pure CH_4.

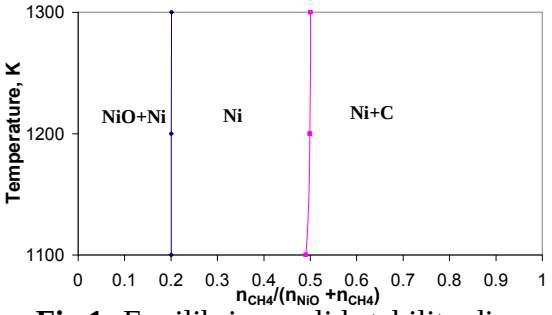

Fig.1- Equilibrium solid stability diagram showing phase fields as a function of temperature and CH_4 mol fraction.

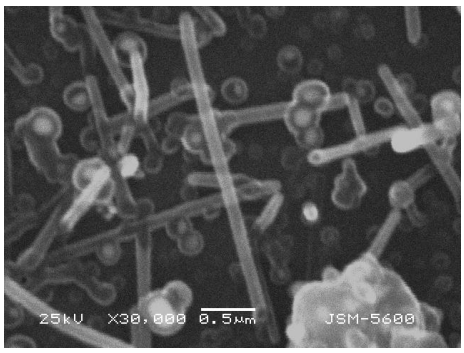

Fig.2- SEM image of the product (1200 K, reaction time 30 min, CH_4 flow rate 15 cm^3/min).

References

[1] S. Eroglu, S.C. Zhang, G.L. Messing, Synthesis of nanocrystalline NiFe alloy powders by spray pyrolysis, J. Materials Research 11 (1996) 2131-2134.