

# THE EVOLUTION OF IRON AND NICKEL NITRATE FILMS DURING CVD SYNTHESIS OF CARBON NANOTUBES: AN *IN-SITU* HIGH TEMPERATURE X-RAY DIFFRACTION INVESTIGATION

K. Matzinger<sup>1</sup>, A. Lepora<sup>1</sup>, B. Grobéty<sup>1</sup>, and A. Züttel<sup>2</sup>

<sup>1</sup>*Geosciences Department, University of Fribourg, 1700 Fribourg, Switzerland*

<sup>2</sup>*Physics Department, University of Fribourg, 1700 Fribourg, Switzerland*

*Corresponding author e-mail address: bernard.grobety@unifr.ch*

## Introduction

Chemical vapor deposition (CVD) is a widely used technique to produce CNTs in large quantities.<sup>1</sup> The decomposition of gases with carbon containing species (CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> etc.) over a metallic catalyst at temperatures between 600°C and 1200°C leads to the nucleation and growth of CNTs. Much progress has been made from the point of view of the yield, the synthesis costs, and the purity of the products obtained by CVD, but there is still much debate about what really controls CNTs growth. The most active metals are Fe, Co and Ni, but their catalytic action depends on the type of precursor<sup>2</sup>, the type of the substrate<sup>3</sup> and of the reactive gases used<sup>4</sup>. Highly controversial is the actual chemical nature of the active catalyst e.g. if it is present as metal, carbide or as mixed phase. Although carbides are often metastable (e.g. Fe<sub>3</sub>C), because they require carbon activities in the gas phase > 1 to be stabilized, they have often been detected in the reactor and inside the tubes,<sup>5</sup> but there is no agreement about whether they are active species for CNTs growth,<sup>6</sup> or if they are only post-reaction phases<sup>7</sup>

One reason for the uncertainties regarding the catalytic action of metal particles during CNTs synthesis by CVD is the scarce number of *in-situ* analyses of the chemical and morphological evolution of the catalyst. Most *in-situ* analysis concentrated on the growth process of the carbon tubes<sup>8</sup> and the evolution of the reactive gases<sup>9</sup>, but not on the evolution of the catalyst.

This paper focuses on the evolution of iron and nickel-based catalysts under a nitrogen-acetylene atmosphere between 600°C and 750°C. An X-ray diffractometer equipped with a heating stage and an atmosphere controlling system was used to study *in-situ* the evolution of iron and nickel nitrate films, in order to elucidate the nature of the metal phase during the synthesis runs. Quenching experiments with the same furnace were conducted with increasing pyrolysis time, in order to investigate the timing of the nanotubes appearance by *ex-situ* Scanning Electron Microscopy (TEM, SEM).

## Experimental

The catalyst precursors Fe(NO<sub>3</sub>)<sub>3</sub>·9(H<sub>2</sub>O) (Merck, Germany) and Ni(NO<sub>3</sub>)<sub>2</sub>·6(H<sub>2</sub>O) (Fluka, Buchs, Switzerland) were either deposited as crystals or as solution dissolved in ethanol onto glass substrates (0.07 mMol iron- and 0.05 mMol nickel nitrate

hydrate). The crystal samples were used to monitor the catalyst evolution, whereas the solution samples were analyzed for nanotube growth.

The apparatus for the *in-situ* diffractometry was a high temperature X-ray camera (model HTK 10, Anton PAAR, Graz, Austria) mounted on a Philips PW 1830 diffractometer. Gas flow was controlled by two mass flow controllers (AFC-2600, AALBORG, Orangeburg, New York, USA). The phase evolution in the catalyst was studied for two different temperatures: 600°C and 750°C. The goniometer was equipped with a scintillation detector and the phase changes were monitored by scanning individual peaks of the reactant. The diffractograms were recorded in step scan mode (0.02°/step, 1sec/step) between 20° and 80° (2θ). The temperature was raised at a rate of 70°C/min to the desired temperature under nitrogen. After an annealing time of 10 minutes, acetylene (2 vol% or 6 vol %) was added to the nitrogen atmosphere.

The Scanning Electron Microscope (Philips FEI XL30 SFEG SIRIUS) investigations were performed on solution-coated glass substrate (7-10keV acceleration potential). TEM investigations were made with a Philips CM20 microscope, operated at 200 keV and equipped with an EDAX energy dispersive spectrometer.

## Results and Discussion

During the heating up stage under nitrogen, the iron nitrate hydrate transformed to an amorphous layer that started to crystallize as hematite ( $\text{Fe}_2\text{O}_3$ ) around 300 °C, the nickel nitrate hydrate dehydrated and the nitrate decomposed at 250°C to NiO. As soon as acetylene was introduced to the iron catalyst, the oxide phases were reduced. At 600°C, hematite disappeared within 2 minutes and was replaced by magnetite ( $\text{Fe}_3\text{O}_4$ ) and wüstite ( $\text{FeO}$ ).

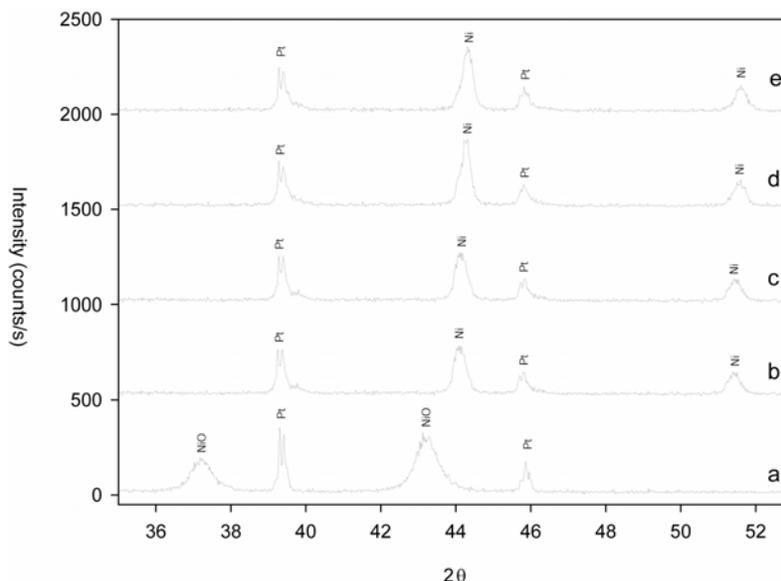


Figure 1: X-ray diffractograms of nickel catalyst samples annealed at 600°C (a) crystals dissolved in ethanol before acetylene exposure. (b) Sample after 30 seconds, (c) after 1 hour, (d) after two hours and (e) after three hours exposed to acetylene (2vol%). Observe the shift in the nickel peak position with increase in acetylene exposure.

The first non-oxide phase, cementite ( $\text{Fe}_3\text{C}$ ), appeared after 1 to 2 minutes. During this first transformation stage no metallic iron could be detected. After 40 minutes the cementite peaks started to decrease and peaks of elemental iron could be detected in the diffractograms. Nickel oxide, however, was reduced within seconds to pure nickel. No nickel carbides were detected neither directly after the  $\text{C}_2\text{H}_2$  flooding of the chamber nor after 3 hours. The nickel peaks, however, shifted to higher  $2\theta$ -values. This shift is interpreted as a change in carbon concentration in solid solution with nickel (Fig. 1). At  $750^\circ\text{C}$  the rate of the reduction reactions for the iron catalyst was considerably accelerated. The main product of the reduction reaction was again cementite and in contrast to the experiments run at lower temperatures no iron could be detected even after prolonged annealing.

After the heating up cycle, the catalyst films formed a polygonal microstructure with an average grain size of 200 nm for hematite and 40 nm for the nickel oxide. The oxide reduction under the acetylene atmosphere reduced considerably the grain size (Fig. 2).

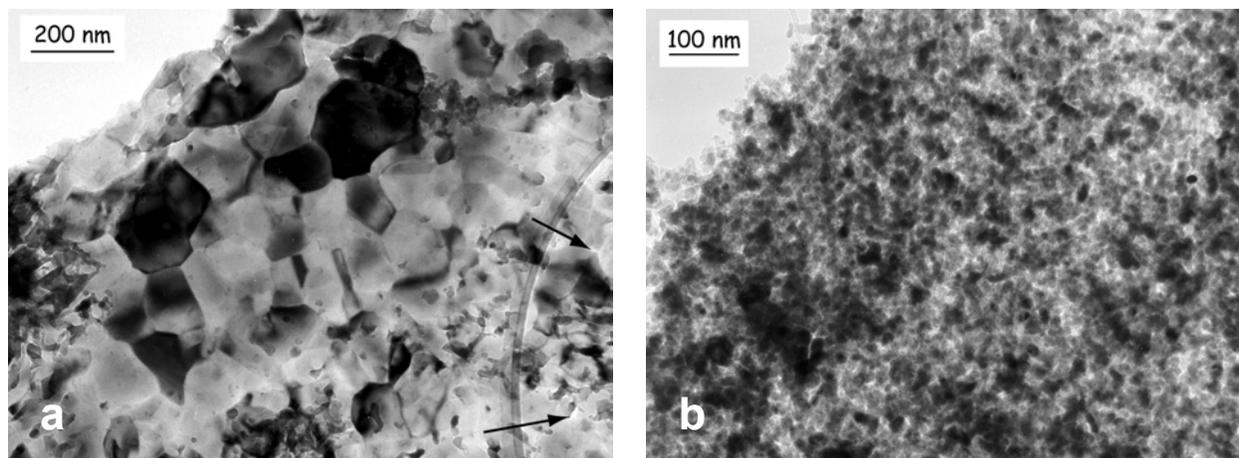


Figure 2. Bright Field TEM images of iron catalyst samples annealed under acetylene at  $600^\circ\text{C}$  for (a) 30sec: Polygonal iron oxides layer (center); a change of grain size is visible towards the rim. The sample has been annealed. The arrows point to intergranular pores. Texture obtained after 5 minutes of annealing. A clear reduction of the grain size is visible. Most cementite grains and interstitial pores are covered/filled with carbon. (d) After 10 minutes the first carbon nanotubes are visible.

The final microstructure is a sponge-like aggregate of cementite (Fig. 2b) and metallic nickel respectively. The iron carbide grains had a large size distribution ranging from a few, up to 80 nm whereas the nickel particles had a more homogeneous grain size e.g. around 20 nm. CNTs were only nucleating on grains smaller than 40 nm in diameter. The first tube-shaped carbon deposition for both catalysts were observed 1 minute after the addition of the acetylene and consisted of rods several tens of nanometer thick and some hundred nanometers in length.

Yields and size homogeneity for both catalysts appeared to be proportional to the acetelyne concentration (Fig. 3) and inversely proportional with film thickness. Areas with a thick catalyst layer showed heterogeneous deposits of amorphous carbon,

encapsulated particles, and nanotubes with a large diameter. In general, the tube diameter was correlated with the grain size of the catalyst.

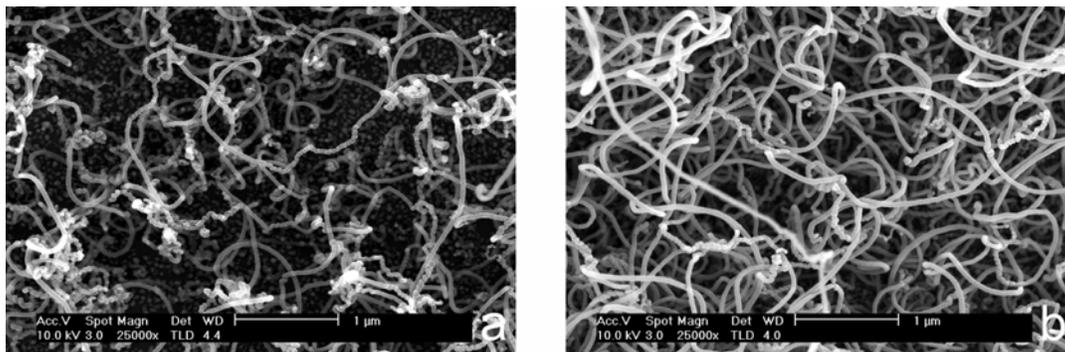


Figure 3. SEM images of samples (0.05 mol/l nickel nitrate hydrate dissolved in ethanol) (a) sample exposed for 1 hour to 2% acetylene and (b) to 6% acetylene.

The wall thickness determined from TEM images showed that the CNTs are multiwalled. Both open and closed tips are present, often enclosing catalyst particles. The carbide nature of the iron containing particles was confirmed by electron diffraction. A temperature increase of 150°C had a strong enhancing effect on nanotubes production for the iron catalyst, not so for the nickel catalyst. The reason is probably the stronger tendency of nickel metal particles to coalesce. After short time at this temperature, most nickel particles were too large to serve as nucleation site for the tubes.

The predominance of carbides for the iron catalyst at the onset of CNTs formation seems to be in contradiction with the arguments put forward by Rodriguez.<sup>10</sup> Based on the fact, that activation energy for CNTs growth on a given metal is very close to the activation energy of carbon diffusion in the same metal, and that experiments made with pure iron carbide catalysts were unable to produce CNTs, he concluded that carbides play no active role in CNT formation. The diffusion data<sup>11</sup> were obtained by measuring growth rates of single NTs on different metal nanoparticles *in-situ* by Controlled Atmosphere Electron Microscopy (CAEM). No *in-situ* structural analyses of the nanoparticles have been presented in this paper, so the nature of the catalyst during the experiment is not really known. The authors observed fragmentation of iron nanoparticles during the experiments, which may well be explained by decarburization and associated metal wasting. The absence of nanotube growth in the presence of iron carbide particles may be related to the fact, that the catalyst in CNT synthesis has *two* roles to play. Poor performance in the first catalytic process, e.g. the breakdown of the carbon bearing gas species, does not preclude the ability to serve as nucleation site for CNTs and vice versa. The low temperature growth of CNTs on Co-Ni particles as an example, is only possible when a co-catalyst (Pd, Pt, Cr) is added to break down acetylene.<sup>13</sup> The large quantities of CNTs produced in the present experiments at 750°C, during which no iron is formed, show that iron carbide particles are able to serve as CNT nucleation sites. The role of cementite in the breakdown of acetylene is less

clear, because in the sample strip in the HTK-camera is made of platinum, an excellent catalyst for that process.

## Conclusions

The experiments have shown that iron and nickel catalyst under typical NT synthesis conditions behave differently. Strictly speaking, iron is not a "catalyst" but an active reactant of the system. For both catalysts, the morphological and crystallographic nature of the catalyst at the end of the synthesis does in no way translate the complex transformations occurring during the run, and the above experiments show the valuable information that can be gained from *in-situ* analysis of the catalyst. Both morphological and chemical changes such as size reduction and metal dusting (iron) influence the timing and the yield of nanotube formation. Differences in yields and morphology of nanotubes for synthesis performed under different run conditions may, therefore, not be related to intrinsic changes in the nanotube growth rates, but to differences in the evolution of the catalyst. Similar behaviors can be expected from other transition metals used as catalysts for NTs growth.

## References

- [1] M.S. Dresselhaus, G. Dresselhaus, K. Sugihara, I.L. Spain, and H.A. Goldberg, *Graphite Fibers and Filaments*, Springer Series in Materials Science 5, (Springer Verlag, New York, 1988)
- [2] A. Fonseca, K. Hernadi, P. Piedigrosso, J.F. Colomer, K. Mukhopadhyay, R. Doome, S. Lazarescu, L.P. Biro, P. Lambin, P.A. Thiry, D. Bernaerts, J.B. Nagy, *Appl. Phys. A-Mat. Sci. & Proc.*, 67, 11 (1998)
- [3] A. Kukovecz, Z. Konya, N. Nagaraju, I. Willems, A. Tamasi, A. Fonseca, J.B. Nagy, I. Kiricsi, *Phys. Chem. Chem. Phys.* 2, 3071 (2000)
- [4] O.A. Nerushev, S. Dittmar, R.E. Morjan, F. Rohmund, E.E.B. Campbell, *J. Appl. Phys.* 93, 4185 (2003)
- [5] H.Q. Hou, A.K. Schaper, Z. Jun, F. Weller, A. Greiner. *Chem Mat.* 15, 580 (2003)
- [6] Ivanov, A. Fonseca, J.B. Nagy, A. Lucas, P. Lambin, D. Bernaerts, X.B. Zhang, *Carbon* 33, 1727 (1995).
- [7] P. Coquay, A. Peigney, E. De Grave, R.E. Vandenberghe, C. Laurent, *J. Phys. Chem. B*, 106, 13199 (2002)
- [8] D.H. Kim, H.S. Jang, C.D. Kim, D.S. Cho, H.S. Yang, H.D. Kang, B.K. Min, H.R. Lee, *Nano Let.*, 3, 863 (2003)
- [9] Y.S. Woo, D.Y. Jeon, I.T. Han, N.S. Lee, J.E. Jung, J.M. Kim *Diamond Rel. Mat.* 11, 56-66 (2002)
- [10] N.M. Rodriguez, *J. Mater. Res.* 8, 3233 (1993).
- [11] T.K. Baker, J.R. Alonzo, J.A. Dumesic, and D.J.C. Yates *J. Catal.* 77, 74 (1982).
- [12] C.J. Lee, J. Park, J.M. Kim, Y. Huh, J.Y. Lee, and K.S. No, *Chem. Phys. Lett.* 327, 277 (2000).