

  ROBL-CRG	Experiment title: In-situ XRD and XRR during the chemical vapour deposition of carbon nanotubes (CNTs) and graphene	Experiment number: MA-1150
Beamline: BM 20	Date of experiment: from 29.06.2011 until 05.07.2011	Date of report: 12.03.2013
Shifts: 18	Local contact(s): Dr. Carsten Baehtz (baehtz@esrf.fr)	<i>Received at ROBL:</i>
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Results

Despite the immense application potential of carbon nanotubes (CNTs), the state of the catalyst during chemical vapor deposition (CVD) of CNTs is still a matter of intense debate, partly originating from contradictory results in the literature [1].

During the beamtime, we studied the iron-catalyzed CVD of CNTs by complementary *in-situ* grazing-incidence X-ray diffraction (XRD) and *in-situ* X-ray reflectivity (XRR). We find that typical oxide supported Fe catalyst films form widely varying mixtures of bcc and fcc phased Fe nanoparticles upon reduction, which we ascribe to variations in minor commonly present carbon contamination levels. Depending on the as-formed phase composition, different growth modes occur upon hydrocarbon exposure: For γ -rich (fcc) Fe nanoparticle distributions, metallic Fe is the active catalyst phase, implying that carbide formation is not a prerequisite for nanotube growth. For α -rich (bcc) catalyst mixtures, Fe_3C formation more readily occurs and constitutes part of the nanotube growth process (Figure 1). We propose that this behavior can be rationalized in terms of kinetically accessible pathways within the bulk iron-carbon phase diagram

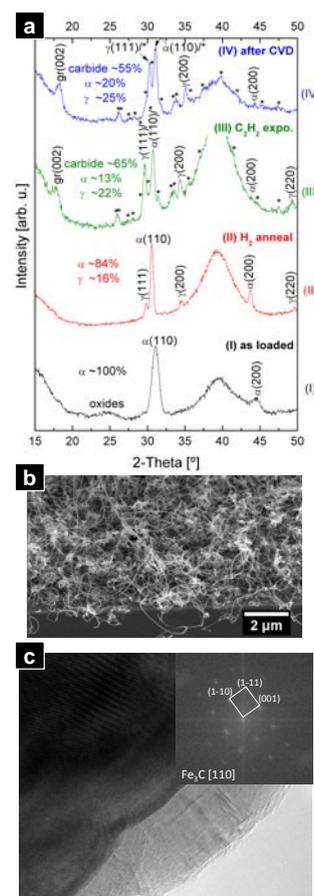


Figure 1: Typical evolution for α -rich Fe catalyst: (a) *In-situ* XRD scans showing CNT growth involving Fe-carbide (*) formation. (b) Obtained CNTs. (c) HR-TEM confirms presence of carbide. From [2].

with the inclusion of phase equilibrium lines for metastable Fe_3C . The integral *in-situ* XRD and XRR results were further correlated with nanotube CVD in an *environmental* transmission electron microscope. Our results emphasize that kinetic effects dominate the complex catalyst phase evolution during realistic CNT growth recipes (Figure 2). Our findings were published in *Chemistry of Materials* [2].

References

- [1] Tessonnier, Su *ChemSusChem* **2011**, 4, 824
 [2] Wirth, Bayer et al. *Chem. Mater.* **2012**, 24, 4633

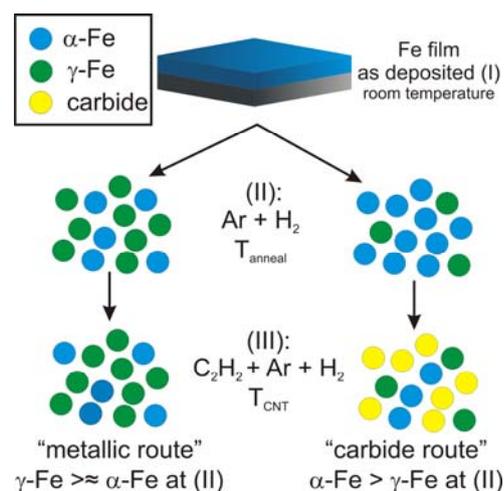


Figure 2: Schematic representation of the reaction pathways summarized as "metallic route" and "carbide route". For equi-percentile α/γ ratios and high γ -Fe content growth proceeds via the "metallic" route (without formation of a carbide), while for high α -Fe content the appearance of CNTs is accompanied by the formation of cementite Fe_3C (the "carbide route"). From [2].