The growth mechanism of carbon nanotubes within the "cluster volume to surface area" model

J. Kunstmann¹, S. Mandati¹,², F. Börnert², R. Schönfelder³, M. H. Rümmeli³, K. K. Karb³, G. Cuniberti¹

¹ Institute for Materials Science, TU Dresden, 01062 Dresden, Germany
² Indian Institute of Technology, Kanpur, 208016, India
³ IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany

Abstract
The influence of mixed catalysts for the high yield production of carbon nanotubes (CNTs) has been studied systematically. Based on extensive experimental data a "Catalyst Volume to Surface Area" (CVSA) model was developed to understand the influence of the process parameters on the yield and CNT diameter distribution [1,2]. In our study, we present a refined version of the CVSA model developed by combining experiments and simulations.

Experiments
• synthesis of carbon nanotubes (CNTs) by laser ablation with mixed catalysts
• characterization of CNTs by optical absorption spectroscopy (OAS) [1]

Motivation
Want to understand the growth mechanism.

Strategy
• use "cluster volume to surface area" (CVSA) growth model [1,2]
• formulate the model mathematically
• fit measured data to the model and determine the model parameters
• interpret the model parameters in terms of microscopic quantities

Growth Mechanism of Carbon Nanotubes (CVSA)
• after laser evaporation carbon dissolves into the catalyst particle and a liquid metal-carbide is formed
• the bigger the particles the more carbon is inside
• during the condensation carbon precipitates via the surface
• for CNT nucleation, formation of hemispherical cap is necessary
• the catalytic particle size increases with furnace temperature. Why?
  • during cooling the catalytic particles condensate
  • the higher the temperature the longer is the cooling time

Mathematical formulation of the CVSA model
• s(d): catalyst particle diameter distribution
• g(d): Gaussian distribution
• d: catalyst particle diameter
• N: area below s(d)
• a, b: parameters of d(T)

Results: Fit of the CVSA Model to Measured Data
High yield catalyst mix Ni:Co:Mo = 5:4:1

Results: Mathematical Formulation of the CVSA model
• s(d): nucleation window = rectangular function
• s(d): catalyst particle diameter distribution
• g(d): Gaussian distribution
• s(d): growth function
• yield: Y(T) = \int_{S_{CP}}^{S_{MAX}} g(d)\,dn\,dS
  \quad \text{with: } S_{CP} = \text{catalyst particle diameter, } S_{MAX} = \text{CNT diameter}
  \quad \text{a, b: parameters of } d(T)

Catalyst mix with different Ni:Co fractions [1]:
• Results: with increasing Ni:Co fraction
  • the position of s(d) shifts towards smaller diameters
  • the spread of s(d), \(d_{\text{max}}\), changes very little
  • the number of catalyst particles, \(N_{\text{A}}\), changes strongly

Problems:
• fitting procedure needs to have the maximum of the yield in the measured range
• some model parameters are correlated
• measurements at low yields are very noisy = very hard to fit

Outlook
• more measurements are necessary to improve the data density
• unbiased data processing for OAS spectra needed
• improve the model and the fitting procedure
• test reliability of model parameters to allow for a physical interpretation
• interplay of model and measurements to improve our understanding of the CNT growth mechanism

References