Nanocrystalline SiC and Ti_3SiC_2 Alloys for Reactor Materials

- Chuck Henager, Jr. – PI
  - Co-PIs – Nghiep Nguyen, Yongsoon Shin, Kyle Alvine, Weilin Jiang
  - Tech Interns – Tim Roosendaal, Brennan Borlaug, Shelly Arreguin

Pacific Northwest
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Description of Project

- Explore the development of a dense SiC-alloy with Ti_3SiC_2 having high thermal conductivity, high strength, and good fracture toughness
  - SiC-alloy based on displacement reactions used for SiC joining
    - $TiC + Si = Ti_3SiC_2$
  - Novel use of textured Carbon nanotube (CNT) mats for thermal conductivity and fracture toughness
    - Nano and micro imprinting techniques
  - Nanocrystalline SiC from polycarbosilane polymers, SiC-filled and unfilled
- Computational models for theory and for experimental guidance
  - Further development of EMTA code for thermal conductivity and mechanical properties
  - Validation against SiC_f/SiC composite K_{th} data
  - Validation against ZrO_2/CNT fracture toughness data

Current Project Status (Modeling)

- Computational modeling task is ahead of the synthesis task
- Successfully modified EMTA code to describe SiC_f/SiC thermal conductivity (unirradiated and irradiated)
  - Accounts for fibers and fiber/matrix interphase contributions
  - Accounts for temperature effects and porosity
  - Model validated against SiC_f/SiC thermal conductivity data with good agreement
  - One paper published, one in review, and one in preparation
- Modified EMTA code for ZrO_2/CNT composite model of mechanical properties and crack growth resistance curves
  - EMTA bridged to ABAQUS FE code for crack process zone and proper far-filed BCs
  - Model validated against ZrO_2/CNT data with good agreement

Current Project Status (Synthesis)

- Using polycarbosilane (Starfire) for creating slurries and for nanocrystalline SiC synthesis
  - Polycarbosilane crystallizes above 1650˚C to relatively pure SiC
  - Viscosity is about that of water but can be gelled at 60˚C to a soft solid
  - Can be loaded to about 60 volume% with powders and to a lesser extent with CNTs
- We are learning to create gelled powder mixtures and process them into SiC-based alloys with near full density and high thermal conductivity
  - Hot-press in argon at 1800˚C for 2 hours at 20 MPa for densification and crystallization
- CNTs are being prepared separately using unfilled polycarbosilane and high CNT volume fractions using untextured CNT mats
  - Vacuum infiltration and filtration to make dense CNT mats
  - Pellet pressing to high green density and then hot pressing
- Characterization
  - Density
  - Optical Microscopy
  - Thermal conductivity
  - SEM
  - XRD

EMTA Models

- Eshelby-Mori-Tanaka approach to material models with inclusions (pores, fibers, etc.)
  - Mechanics solutions
  - Thermophysical properties

Stress, $\sigma_{ij} \longleftrightarrow$ heat flux, q_i

Strain, $\varepsilon_{ij} \longleftrightarrow$ temperature gradient, ∇T

Stiffness, $C_{ijkl} \longleftrightarrow$ thermal conductivity, k_{ij}

- Linked to ABAQUS FE code for mechanics models

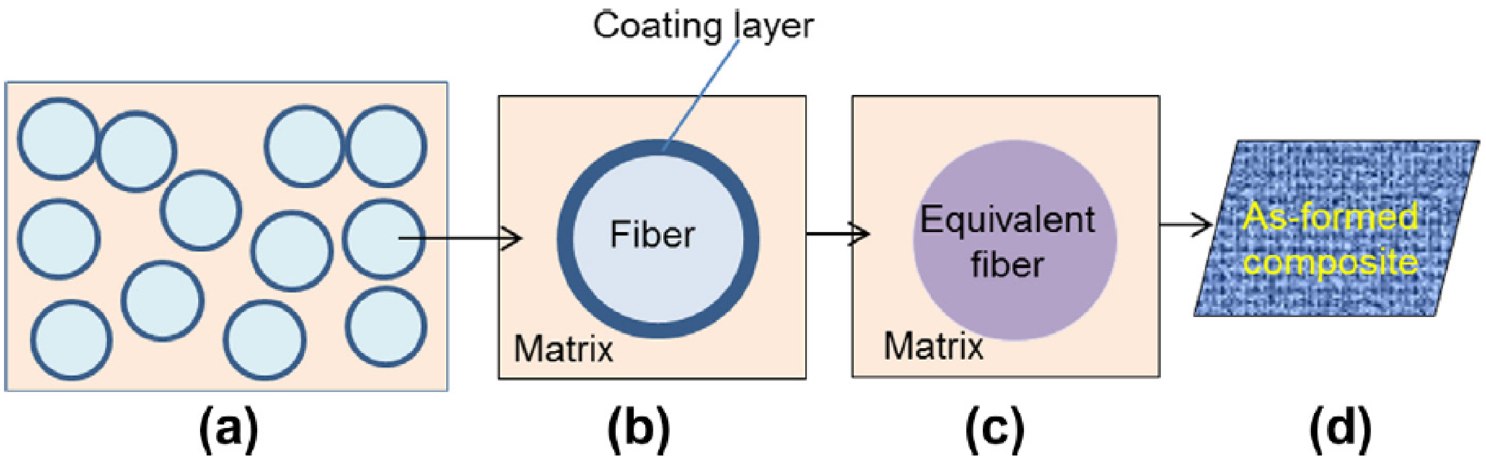


Fig. 1. Schematic of the EMTA computational procedure for homogenization.

B.N. Nguyen, C.H. Henager Jr. / Journal of Nuclear Materials 440 (2013) 11–20

EMTA Results

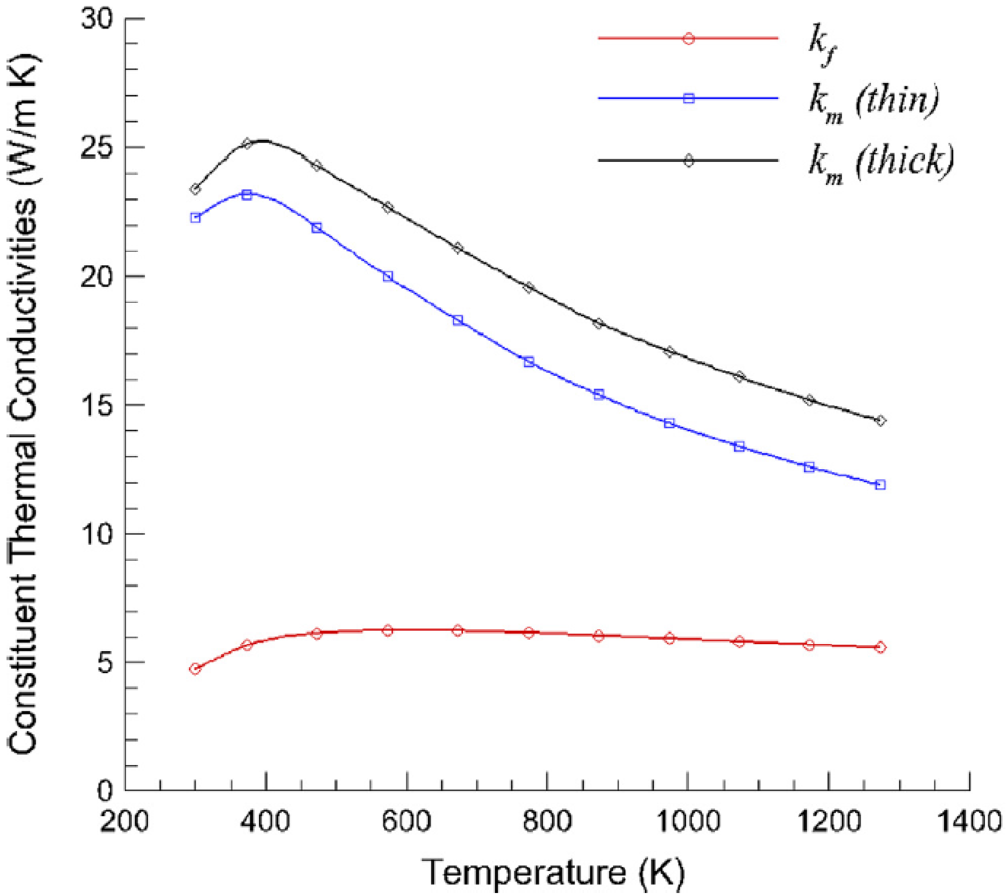
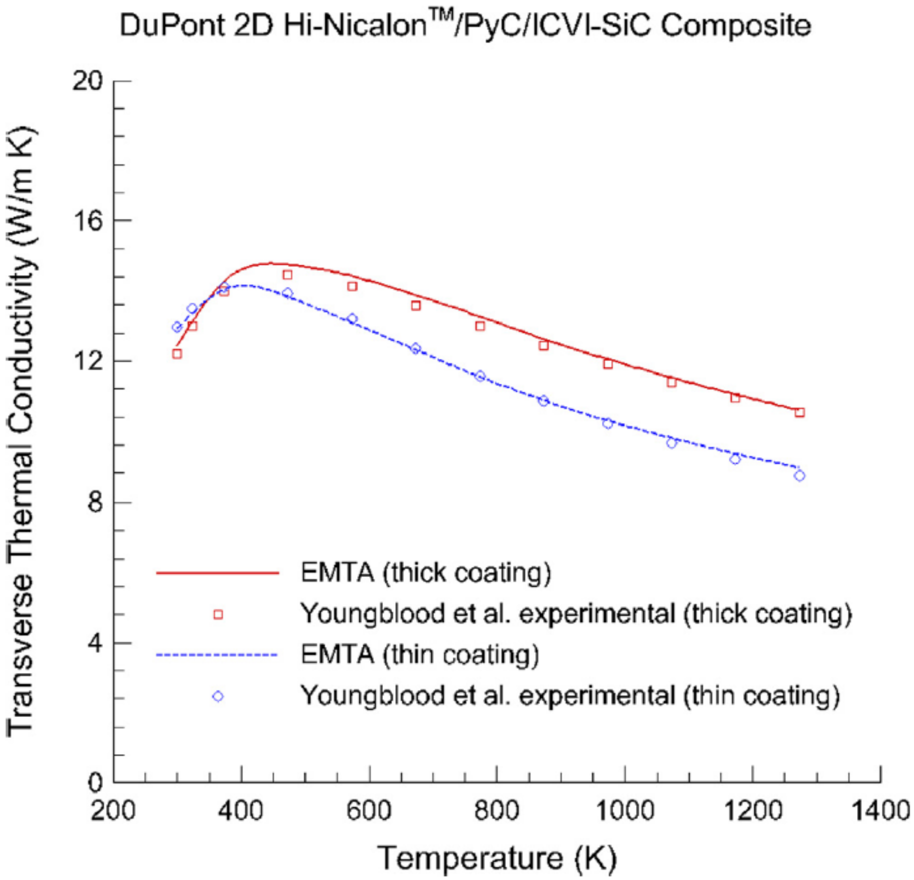
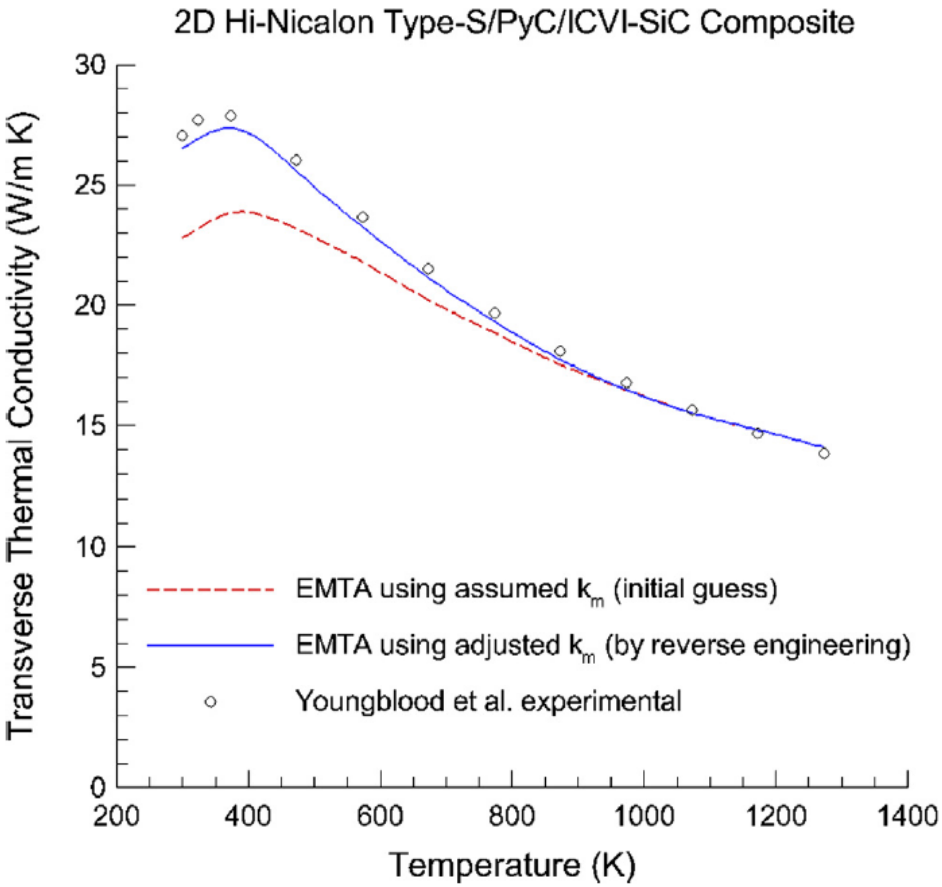


Fig. 2. Thermal conductivities of the constituent materials, SiC fibers and SiC matrices in the thin and thick versions of the SiC/SiC composite [7].

- Thermal conductivity data (Youngblood et al.)

EMTA Results

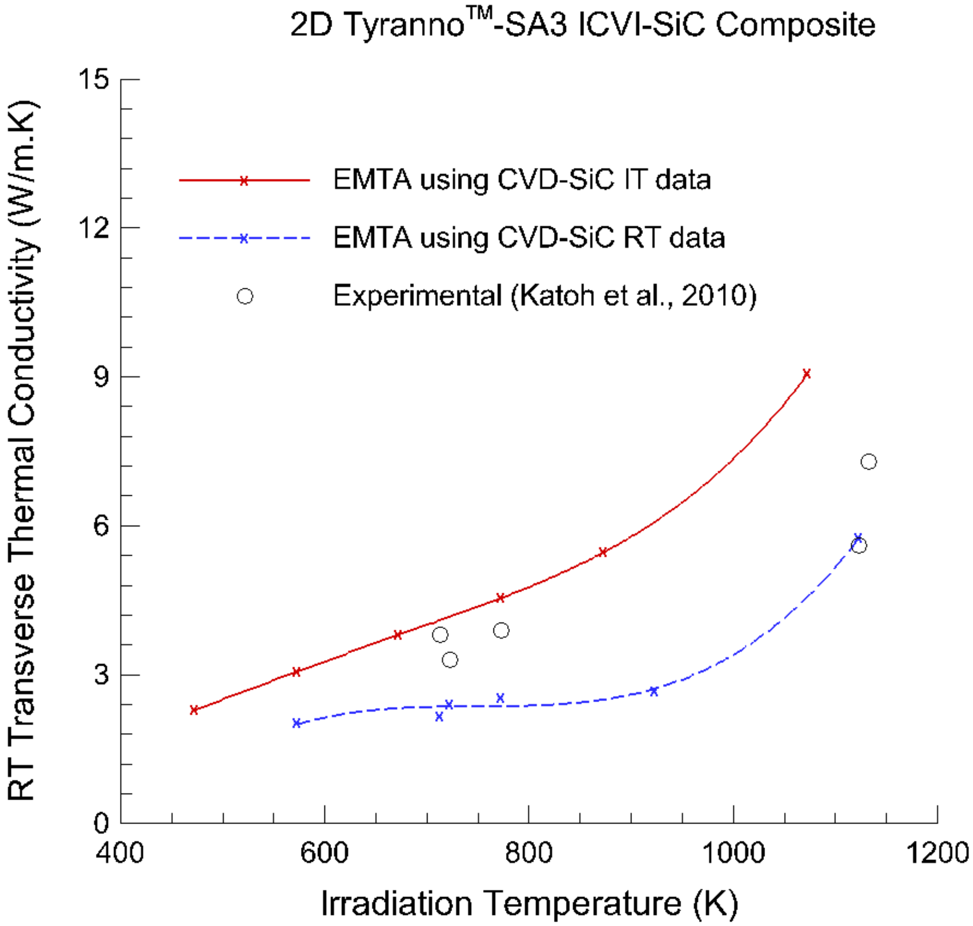

DuPont 2D Hi-Nicalon™/PyC/ICVI-SiC Composite


2D Hi-Nicalon Type-S/PyC/ICVI-SiC Composite

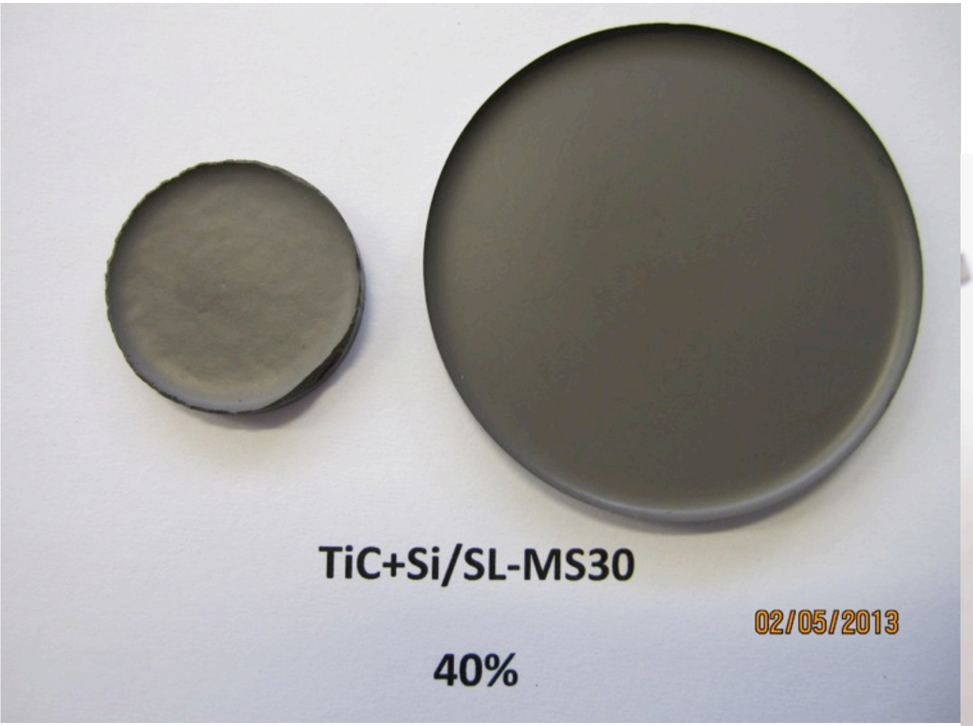
- Model validation for two fiber types
  - Hi-Nicalon
  - Type-S

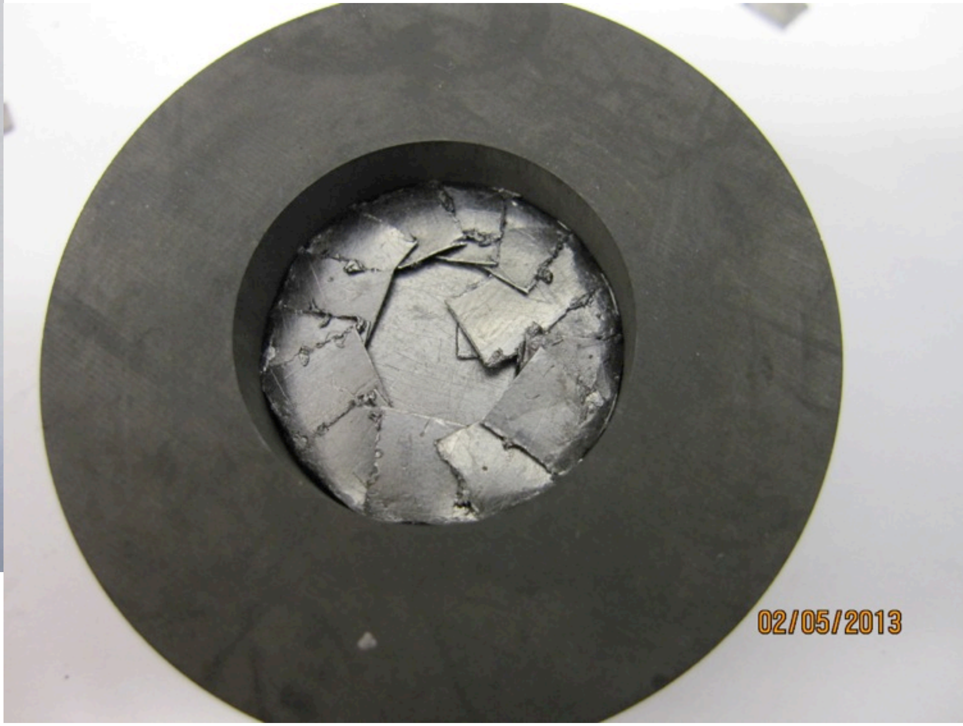
EMTA Results Irradiated Composites

- Further validation using irradiated SiC_f/SiC data
  - Assume damage only in the SiC-matrix
  - Katoh, Y., L.L. Snead, T. Nozawa, S.Kondo, and J. Busby, “Thermophysical and mechanical properties of near-stoichiometric fiber CVI SiC/SiC composites after neutron irradiation at elevated temperatures,” JNM, 2010, **403**: 48-61.



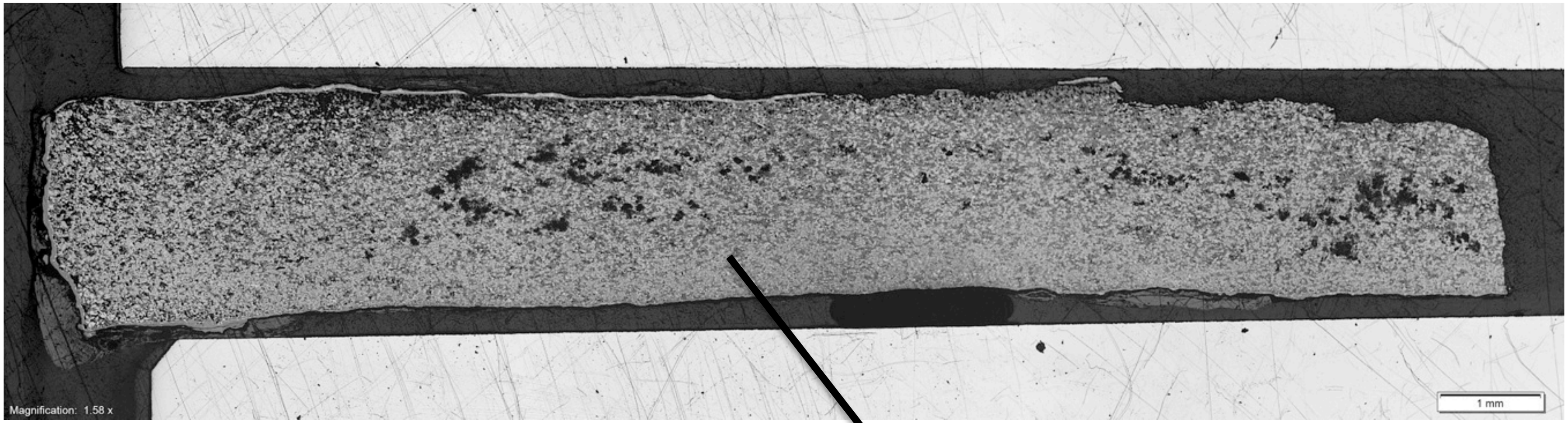
SiC-alloy Synthesis



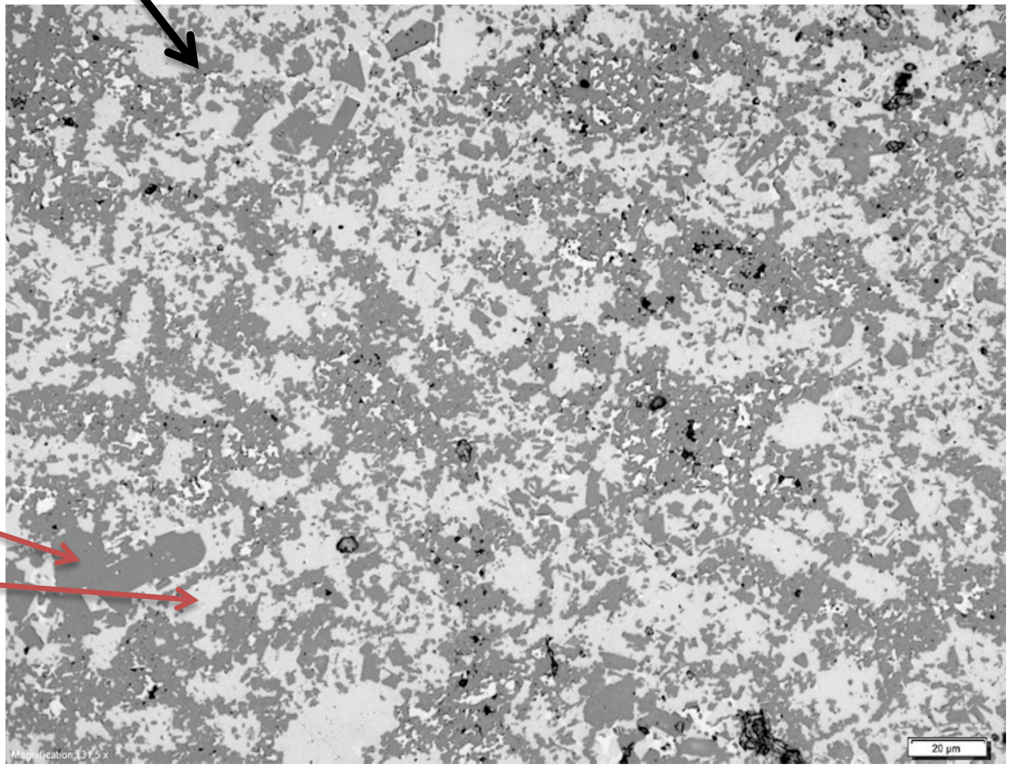


- Gelled SiC-based materials for hot-pressing
  - Cast into 1” molds
  - Wrapped in graphite paper and pressed in graphite dies

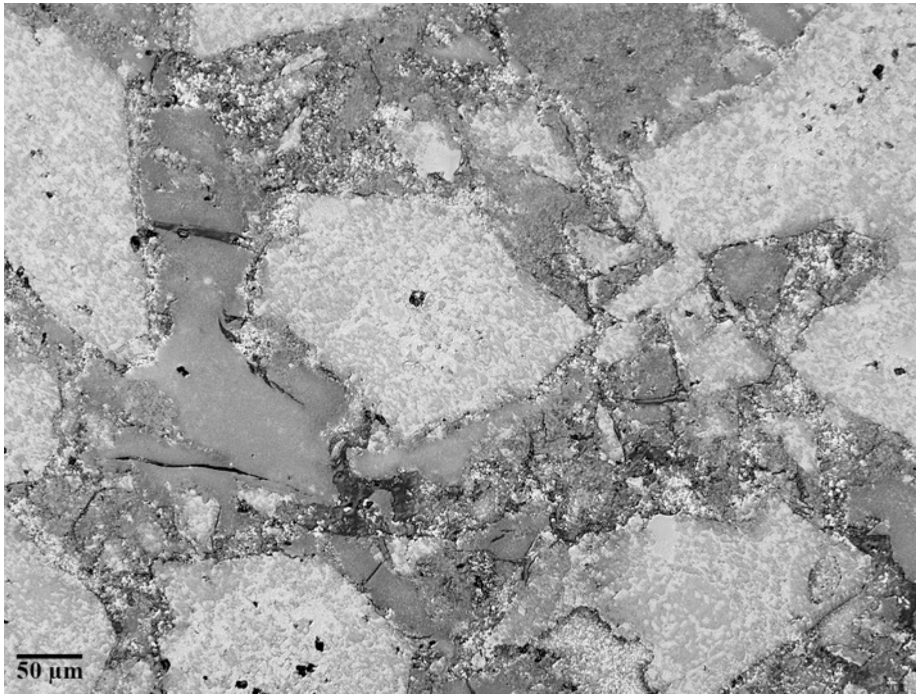
Optical Microscopy Analysis of SiC-alloy

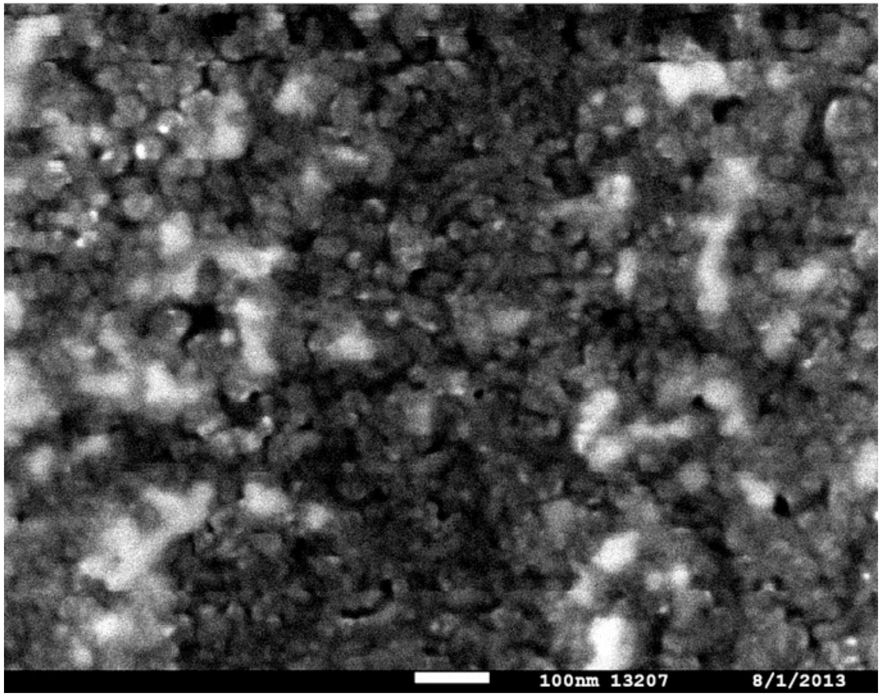


- Hot-pressed sample in cross-section
  - 1750˚C, 20 MPa
  - 3.1 g/cm^3
  - 60wt% TiC+Si powders in 30 wt% SiC-filled polymer creates a thick slurry
  - K_{th} = 56.1 W/mK (~ 50% of Hexoloy SiC value)
- Microstructure is typical SiC + Ti_3SiC_2 interpenetrating
- Issues to solve
  - Gradients
  - Porosity



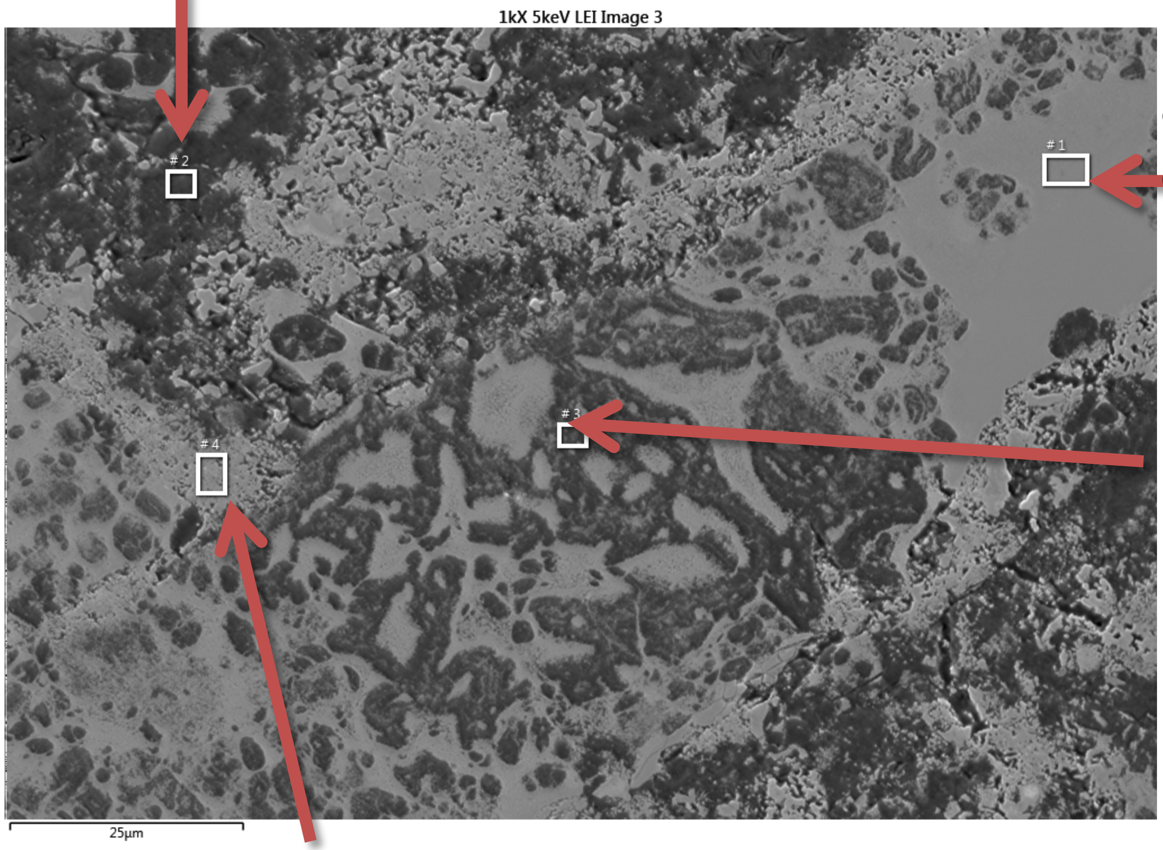
OM and SEM of CNT Pellet





- Pellet-pressed, hot-pressed dense CNT material
  - Observe separate CNT regions and SiC-rich regions due to agglomeration during processing
  - K_{th} = 50 W/mK (Hexoloy = 110 W/mK)
  - Approximately 80% CNT plus Polycarbosilane (SiC)
  - Hot-pressed 1600˚C, 5 MPa, 2 hours

CNT Pellet Not Homogeneous Yet



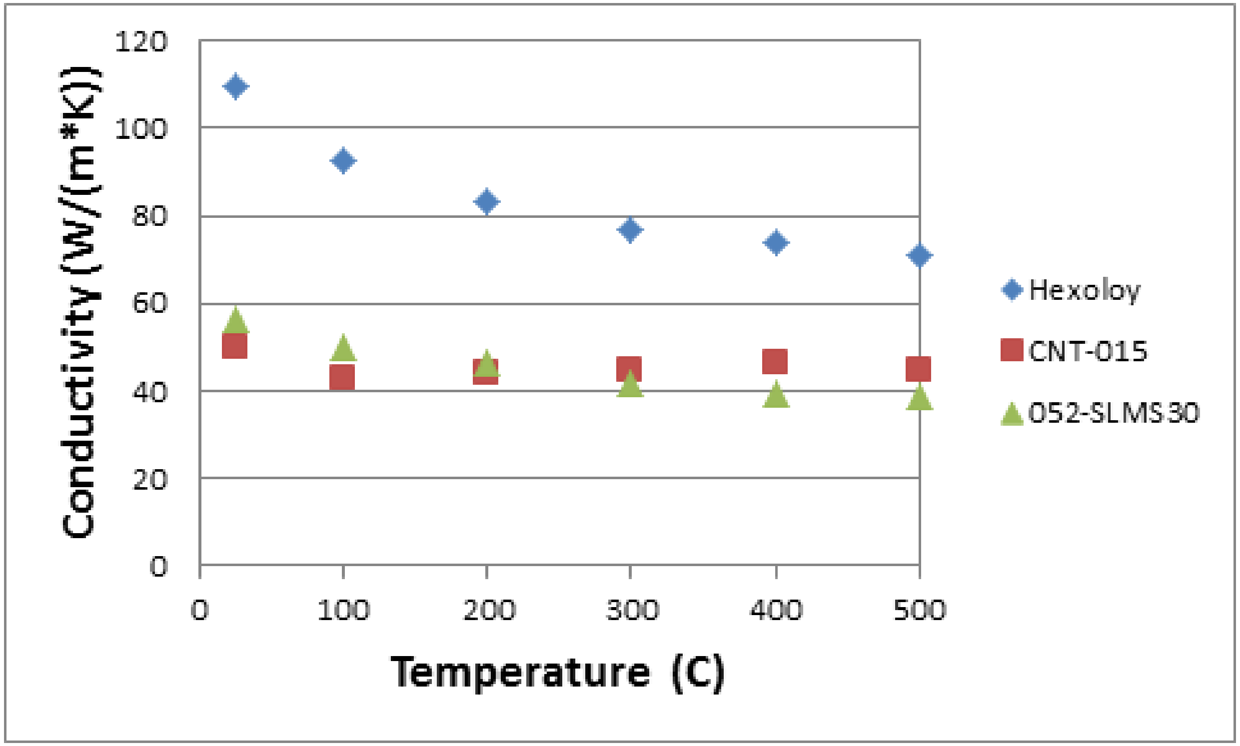
6% SiC, 90% CNT, 5% O

95% SiC, 4% CNT, 0.1% O

30% SiC, 69% CNT, 1% O

99% SiC, 0% CNT, 1% O

Thermal Conductivity



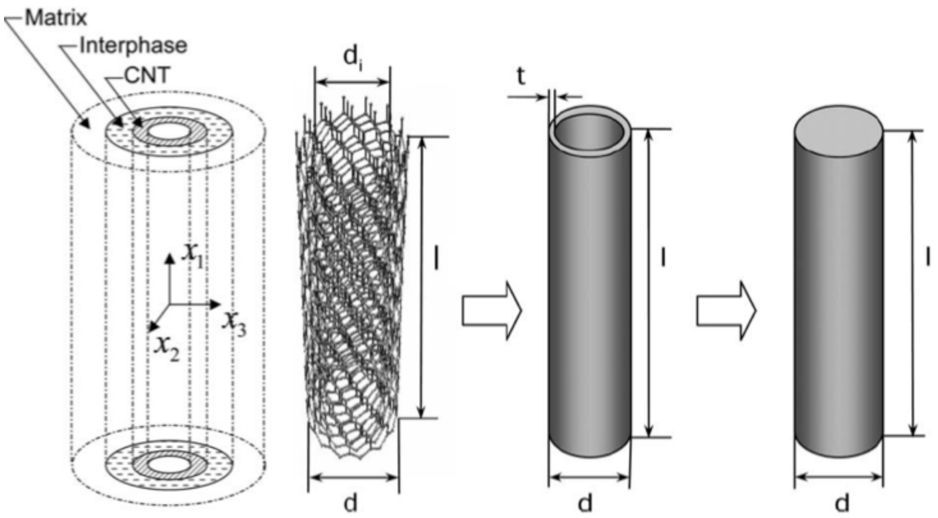
Sample	Hexoloy	CNT-015	052-SLMS30
Temperature (C)	Avg (W/(m·K))	Avg (W/(m·K))	Avg (W/(m·K))
25	109.51	50.20	56.1
100	92.41	43.10	49.71
200	83.51	44.20	46.47
300	77.13	44.80	41.99
400	74.07	46.60	39.11
500	70.78	44.62	38.99

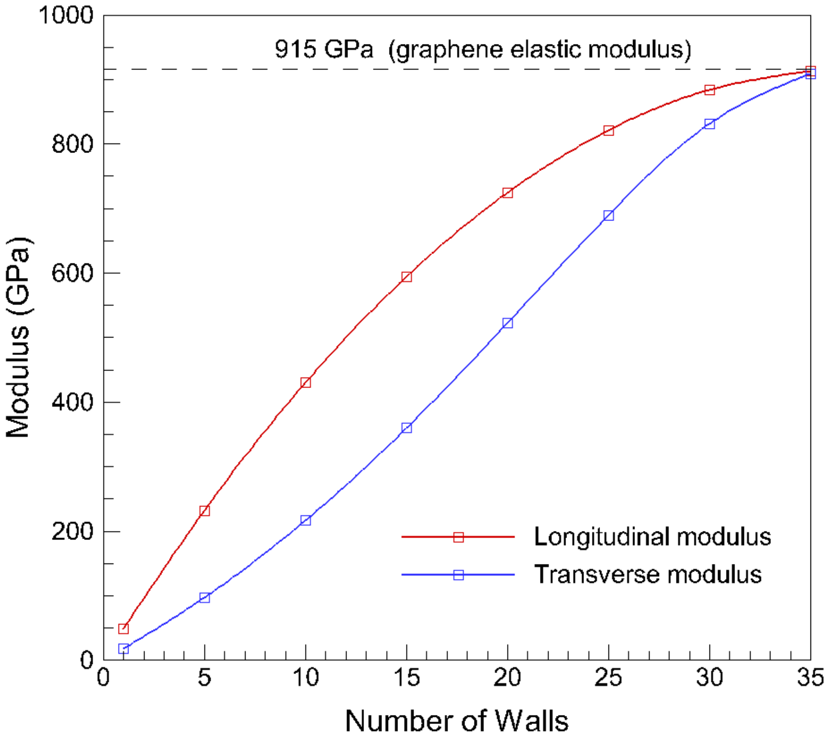
EMTA Mechanics Modeling for CNTs

- EMTA-ANLA/ABAQUS associated with an MBL model
  - Small scale damage and fracture in a process zone under plane strain and Mode I loading
  - The damage model developed for MWCNT reinforced ceramics is used to describe damage in the process zone leading to crack initiation and propagation
  - The loading at crack initiation defines *fracture toughness*
  - Comparison to Mazaheri et al.'s experimental results (*Composites Science & Technology.*, 2011, 71: 939-945)

Constituent Data for EMTA & EMTA-NLA

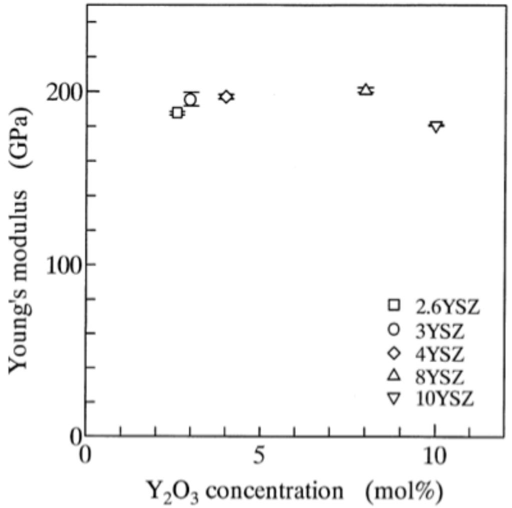
- MWCNTs
  - Interphase between CNTs and matrix enhances composite stiffness/toughness
  - Large numbers of walls achieve isotropy and enhanced mechanical properties

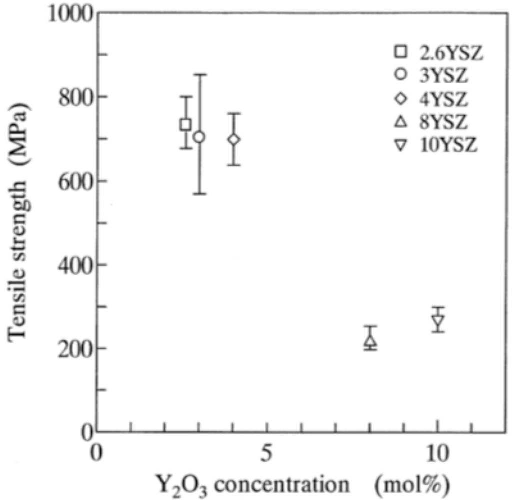


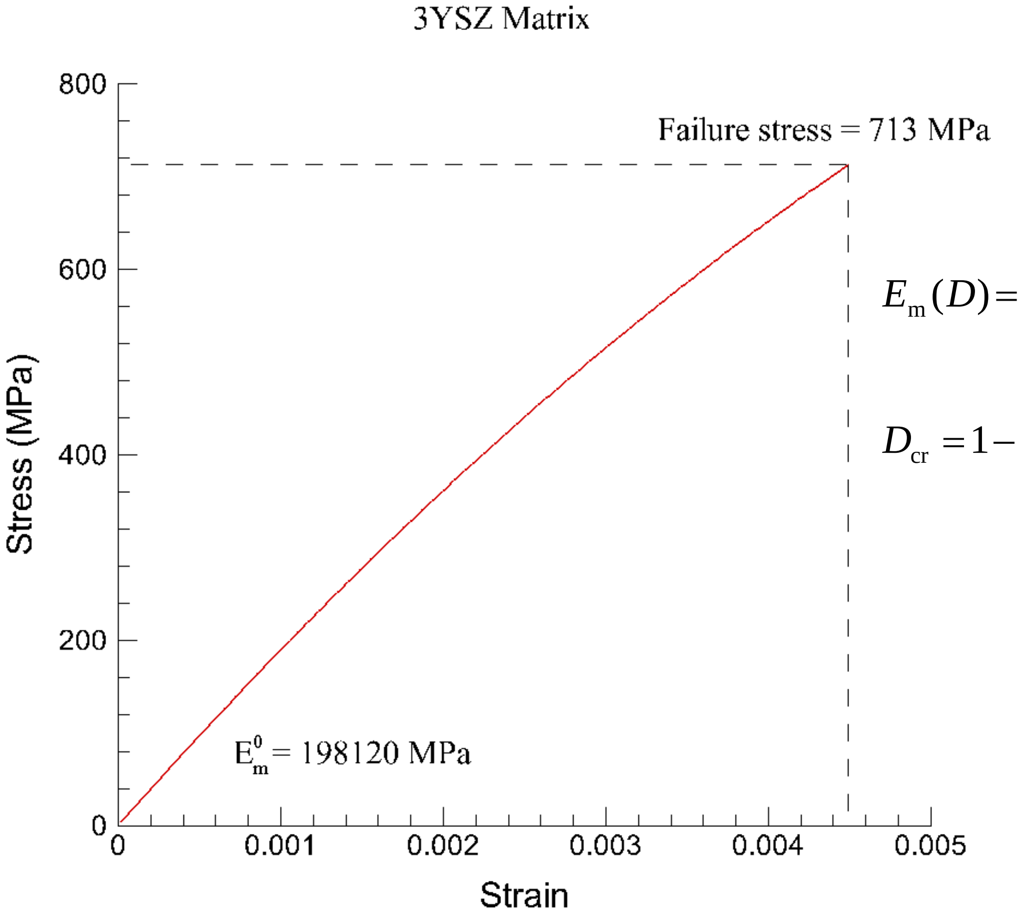


Constituent Data for EMTA & EMTA-NLA

- 3YSZ (3mol% yttria stabilized zirconia)





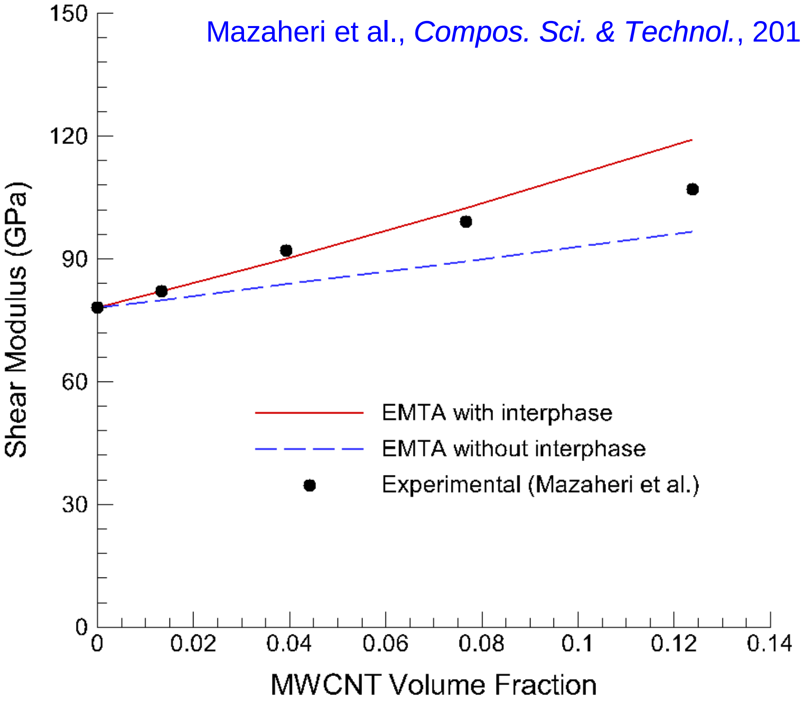


$$E_{\mathrm{m}}(D) = E_{\mathrm{m}}^0 (1 - D)$$

$$D_{\mathrm{cr}} = 1 - \frac{E_{\mathrm{m}}(\sigma_{\mathrm{f}})}{E_{\mathrm{m}}^0} = 0.2$$

Kondoh et al., J. Alloys & Compounds, 2004, 365: 253-258

MWCNT/3YSZ Elastic Properties

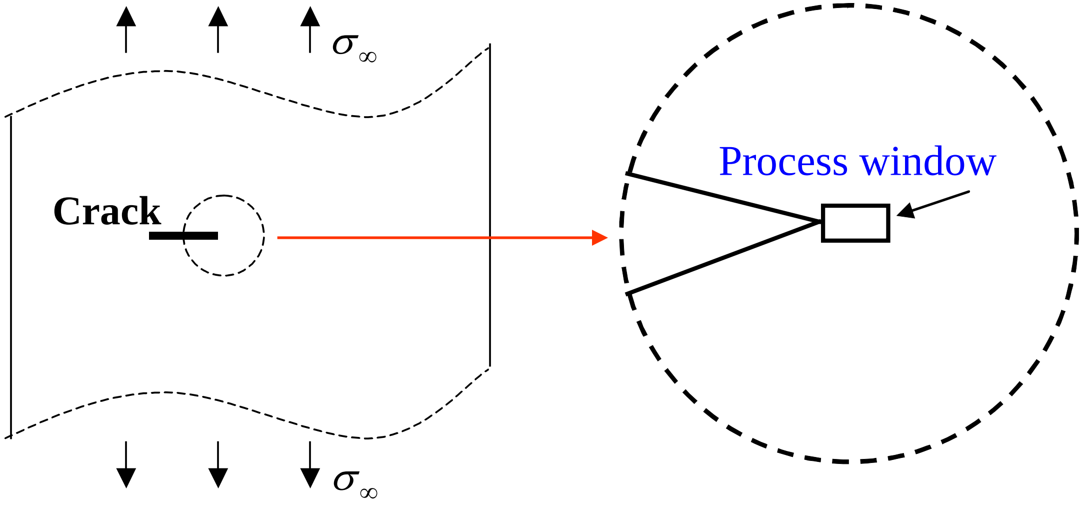


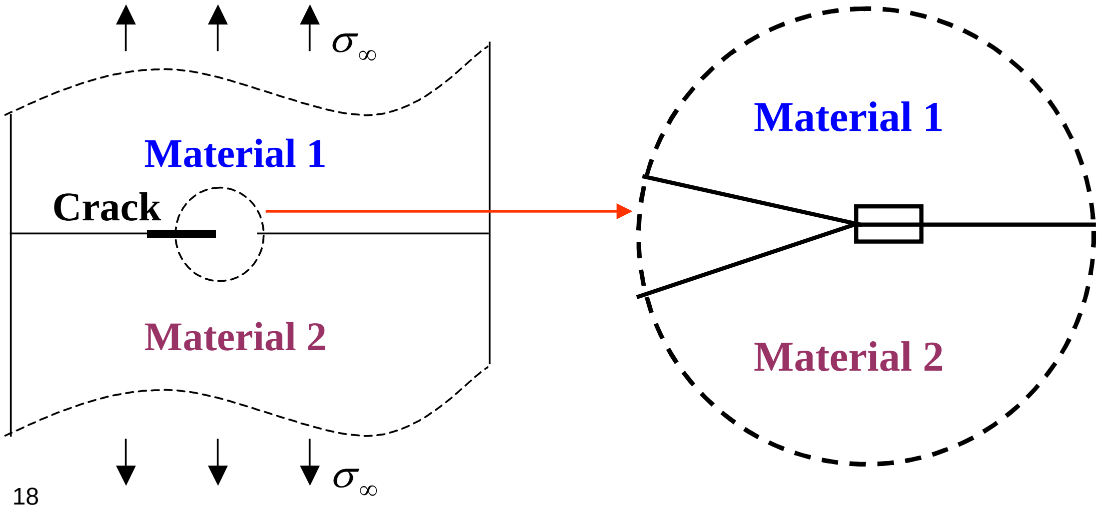
Mazaheri et al., *Compos. Sci. & Technol.*, 2011, 71: 939-945

Shear Modulus (GPa)

MWCNT wt%	**0 wt%**	**0.5 wt%**	**1.5 wt%**	**3 wt%**	**5 wt%**
Experimental (Mazaheri et al.)	78 ± 6.5	82 ± 5.4	92 ± 4.3	99 ± 3.8	107 ± 3.8
EMTA with interphase	78	82 (0%)	90.06 (2.1%)	102.35 (3.4%)	119.19 (11.4%)
EMTA without interphase	78	79.92 (2.5%)	83.71 (9%)	89.32 (9.8%)	96.63 (9.7%)

Modified Boundary Layer (MBL) Modeling Approach

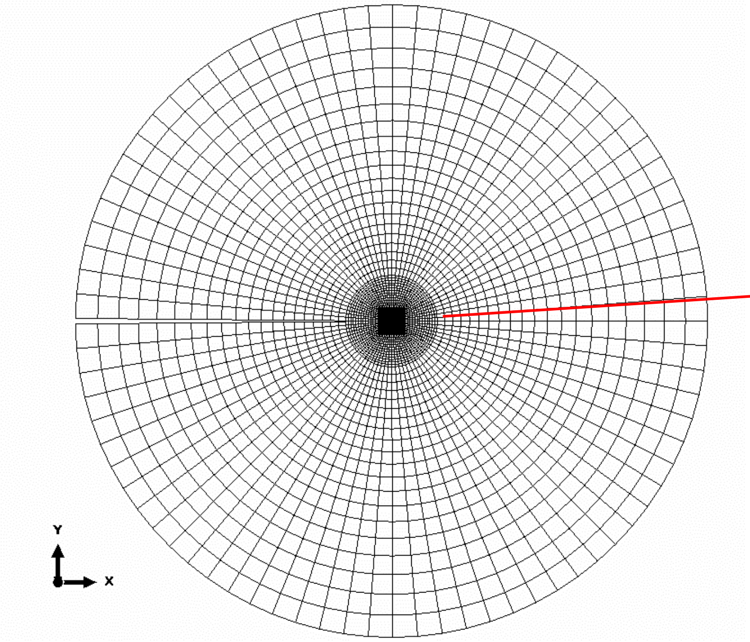


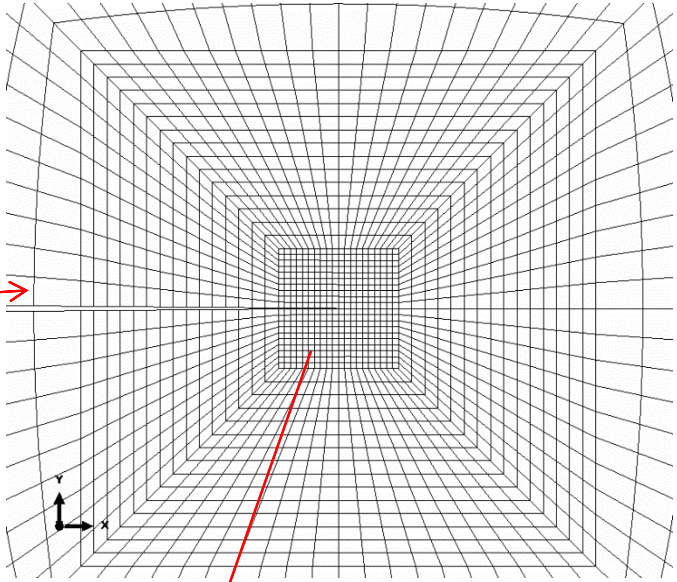


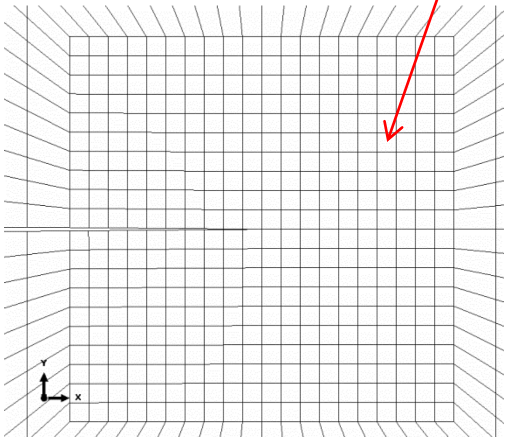
Principle of the MBL modeling

- An existing crack is assumed inside a material or at the interface
- A small circular region around the crack tip is analyzed
- Elastic crack-tip fields are applied as boundary conditions
- Damage & fracture are allowed to occur in a small process window finely discretized
- Crack propagation is captured by a vanishing element technique.

Finite Element Model for MBL Analysis







Damage in the process window is described by a damage model for MWCNT reinforced ceramics

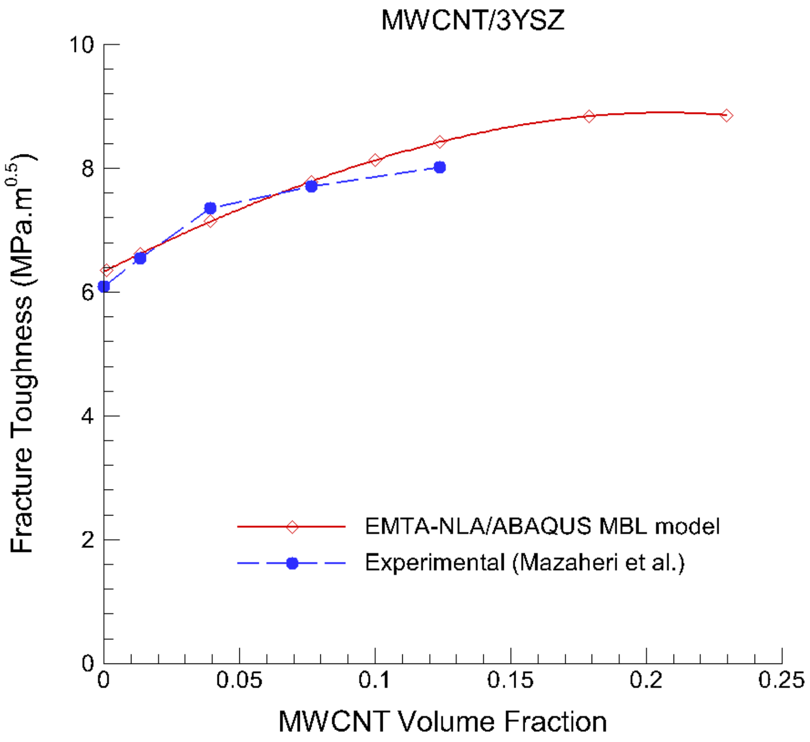
Boundary condition

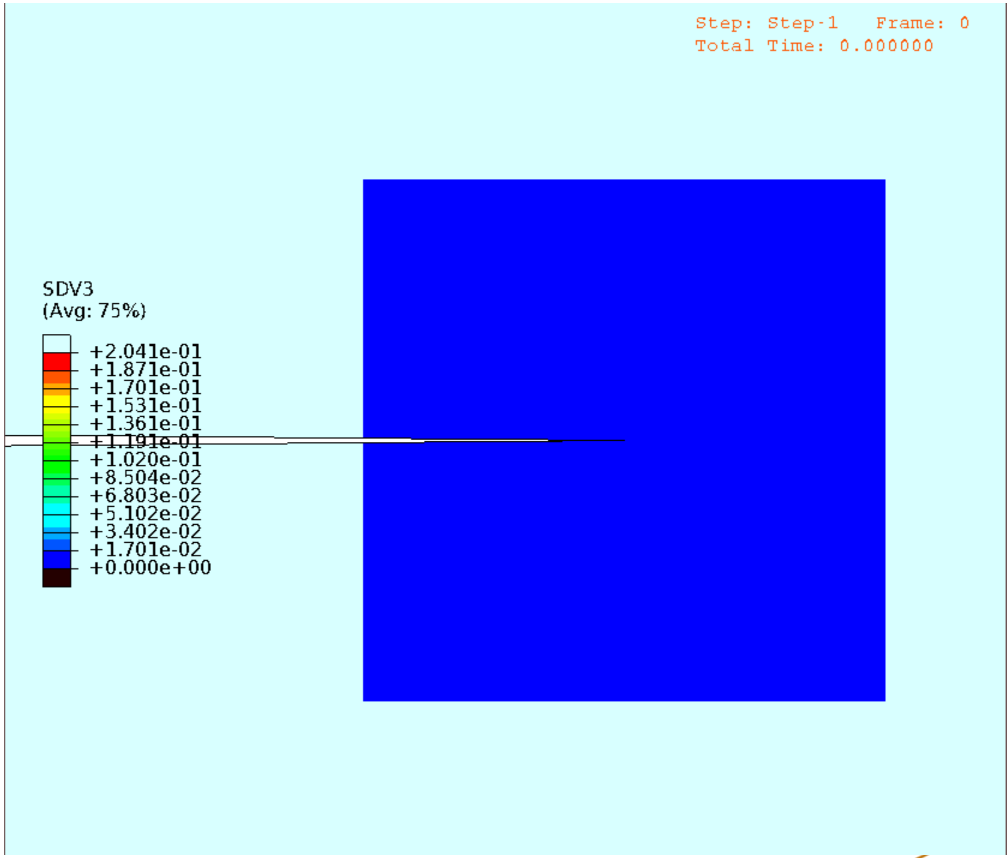
$$u_1 = \frac{K_{\mathrm{I}}}{2\mu}\sqrt{\frac{r}{2\pi}}\cos(\frac{\theta}{2})[\kappa - 1 + 2\sin^2(\frac{\theta}{2})],$$

$$u_2 = \frac{K_{\mathrm{I}}}{2\mu}\sqrt{\frac{r}{2\pi}}\sin(\frac{\theta}{2})[\kappa + 1 - 2\cos^2(\frac{\theta}{2})]$$

Fracture Toughness Prediction for MWCNT/3YSZ

- EMTA-NLA/ABAQUS predictions agree well with Mazaheri et al.' s test data from SEVNB specimens subjected to bending

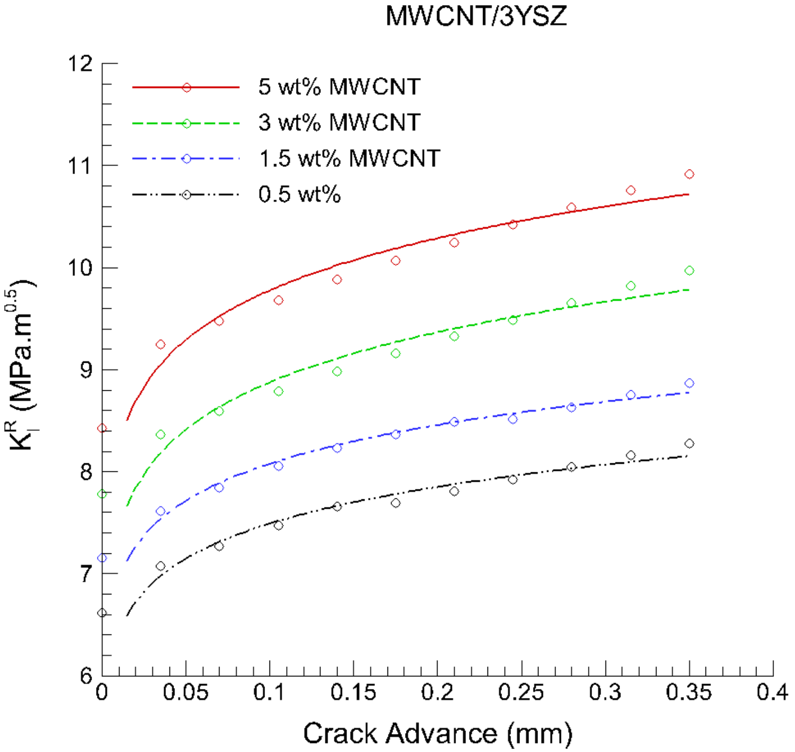




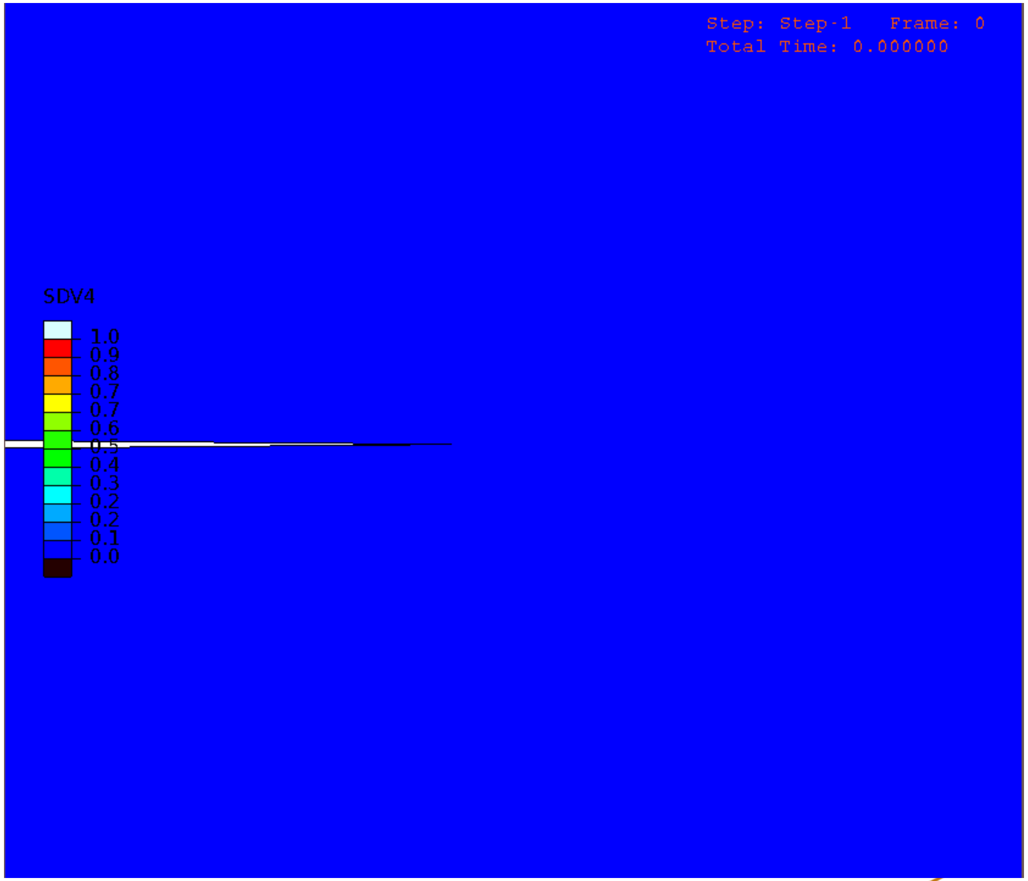
- The model predicts toughening saturation at about 20 vol% CNT loading
  - This is in broad agreement with literature on CNT toughening
  - Model result points to the need for additional toughening mechanisms

Crack Propagation and Resistance Behavior

- Stress intensity factor vs. crack advance defines crack resistance



$$K_I^R = k\, c^{\alpha}$$



Ramachandran et al., *J. Am. Ceram. Soc*. 74 (1991) 2634
Sarkar & Das, *Mater. Sci. Engn. A* 531 (2012) 61

Conclusions

- SiC-alloy processing has two tasks that are making good progress but have issues remaining to be resolved
  - Polymer plus powders has gradient and porosity issues to resolve
  - SiC-alloy microstructure forms as expected
  - CNT processing more difficult
    - CNT agglomeration issue
    - Texturing remains to be done
  - Density and K_{th} are promising at this stage
- Modeling is far ahead of processing
  - Thermal conductivity models using EMTA are quite powerful
  - Crack growth resistance models indicate limited toughening due to CNTs
  - Suggest that textured mats will be required if toughness issue is to be resolved
- Density and Thermal Conductivity can be addressed
- Toughness is more difficult to accomplish
- Task on Fission Product Diffusion was not covered here but is progressing using Ag-implantation and RBS