Summary of Planned Ceramic Composite Program

Composite Development

- Large, uniform composites (mech. properties development and round robin testing)
- Temperature Thermal Conductivity CVI Composite (SiC and graphite fibers)
- Evaluation of NITE composite

Interactive Design Issues

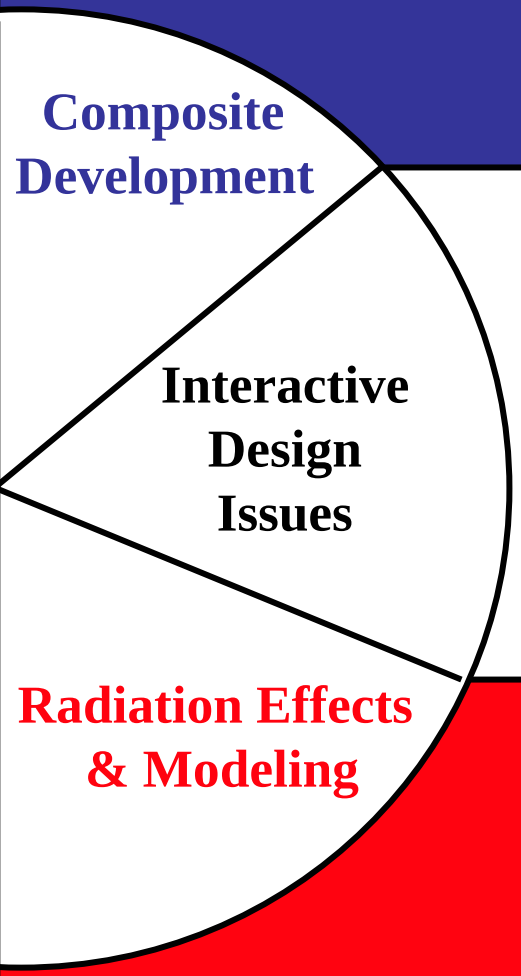
- Determine high temperature corrosion of SiC in LiPb and water vapor
- Crack extension in water vapor containing environment
- Continue surface coatings (glassy, ductile and refractory metals)
- Begin generation of comprehensive data-set on 2D CVI SiC/SiC
- Joining with preceramic polymers
- Determine design space for electrical resistivity of SiC composite

Radiation Effects & Modeling

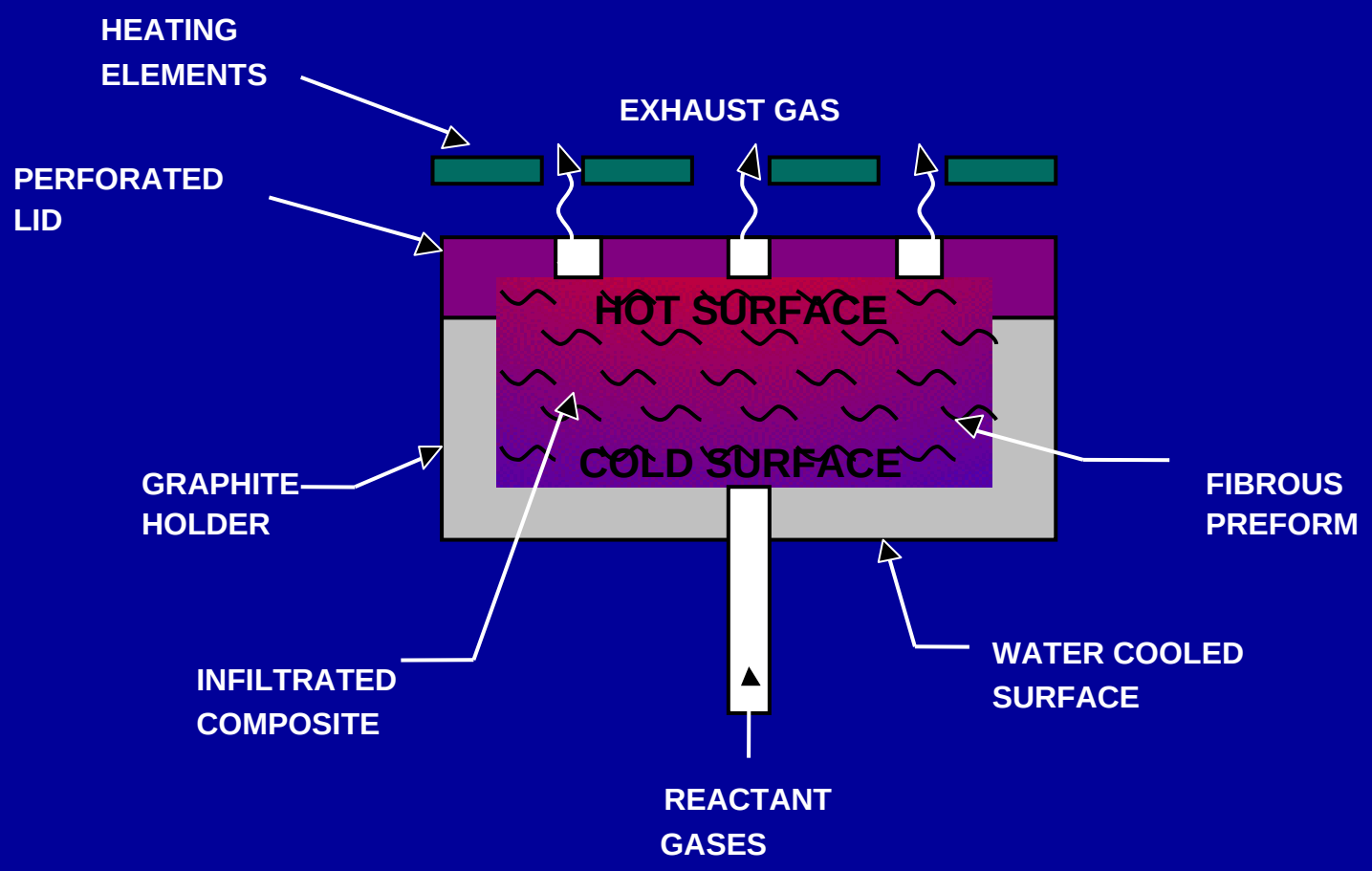
- Mapping of swelling and microstructure of SiC at high T
- Constitutive modeling of composite fracture under irradiation
- Extend irradiation effects database on SiC and SiC/SiC to higher dose
- Thermal conductivity modeling and development of practical algorithm

Summary of Planned Ceramic Composite Program

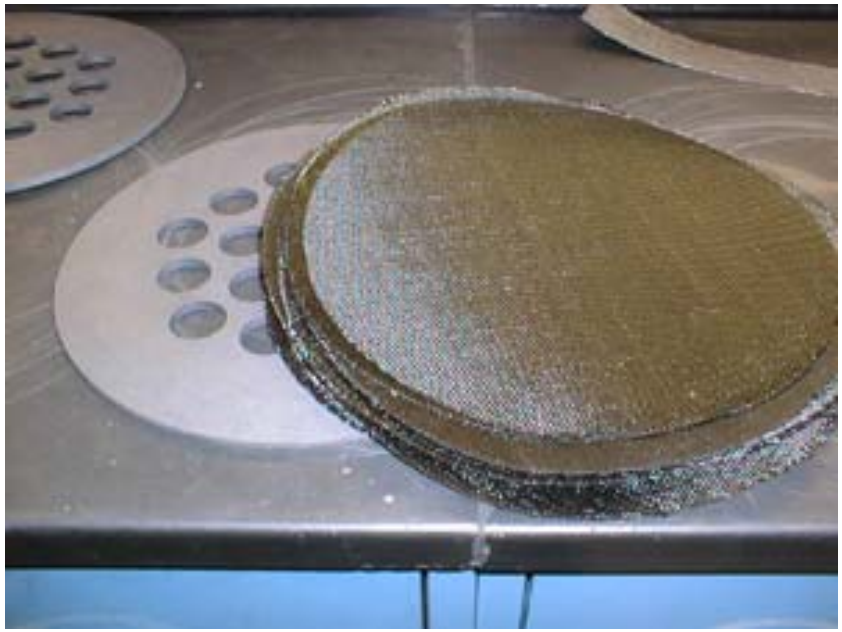
Large, uniform composites (mech. properties development and round robin testing)

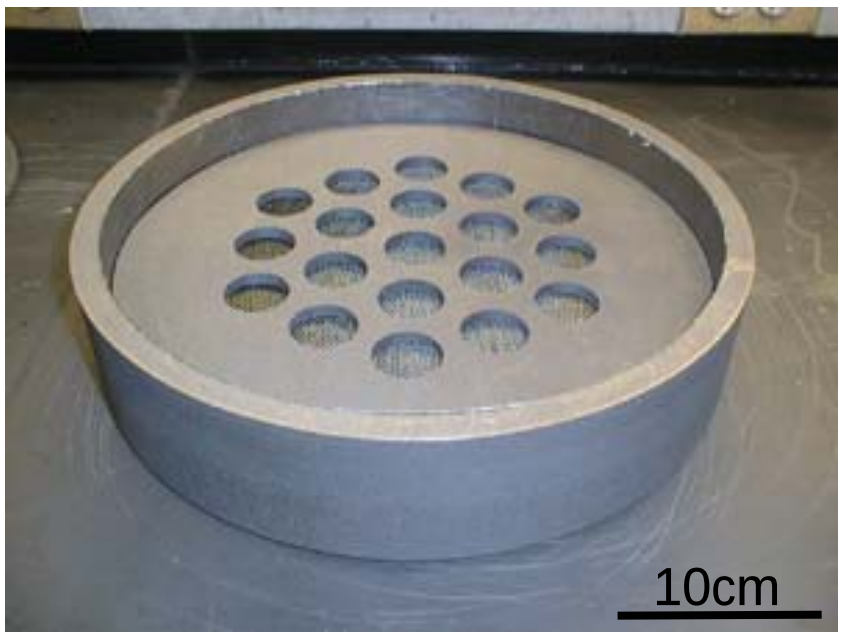


Forced-Flow, Thermal-Gradient CVI Was Developed to Reduce Processing Time

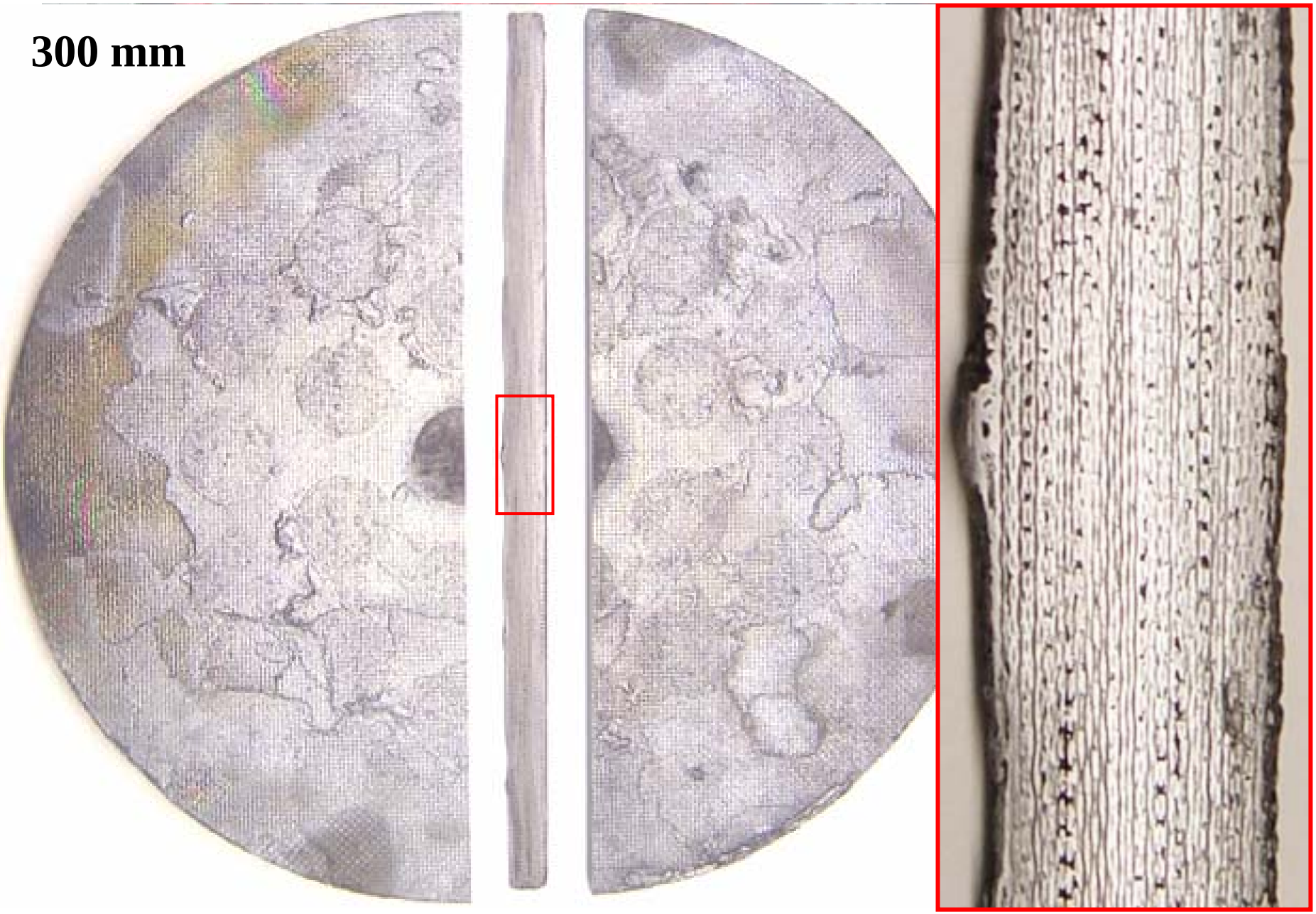


Large F-CVI Furnace and Fixtures

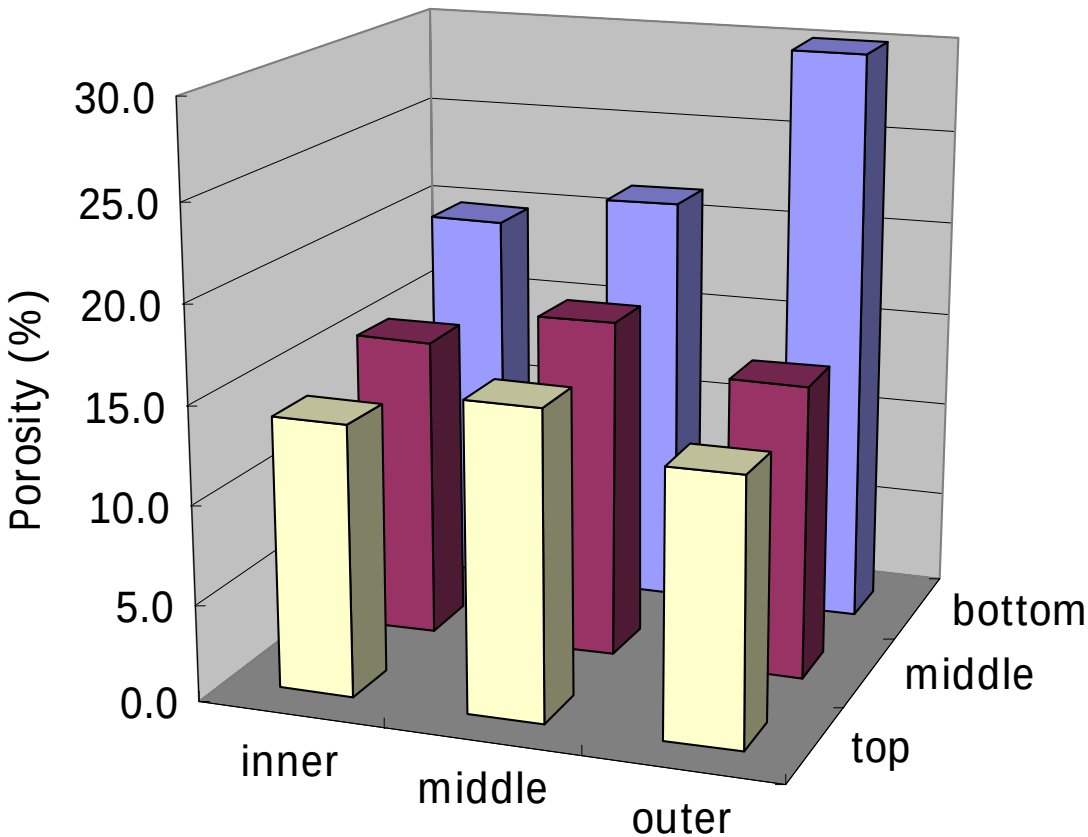


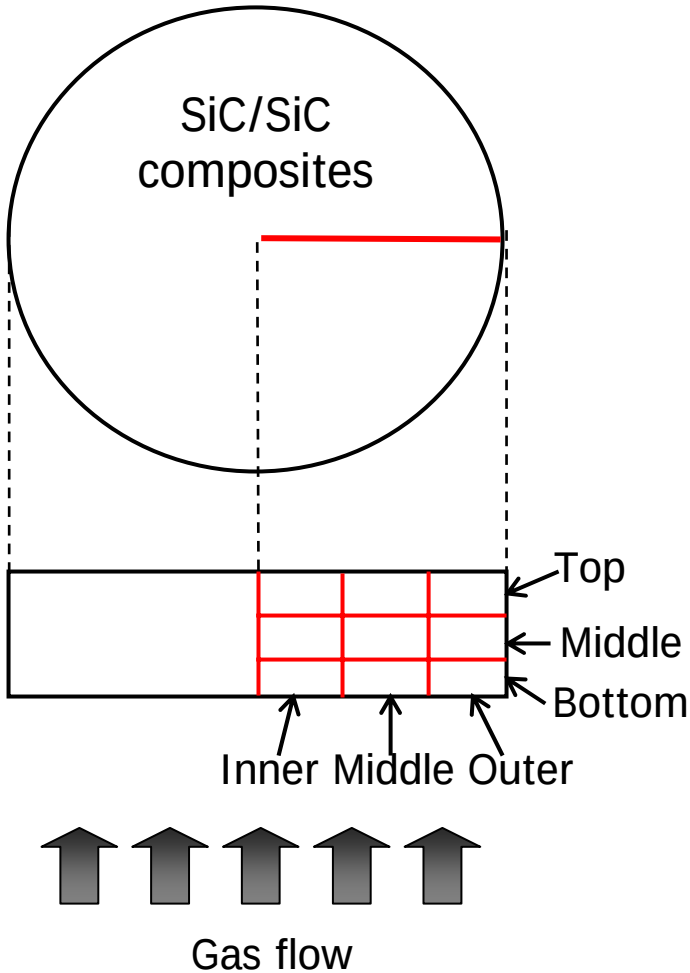


SiC/SiC Composites fabricated by F-CVI



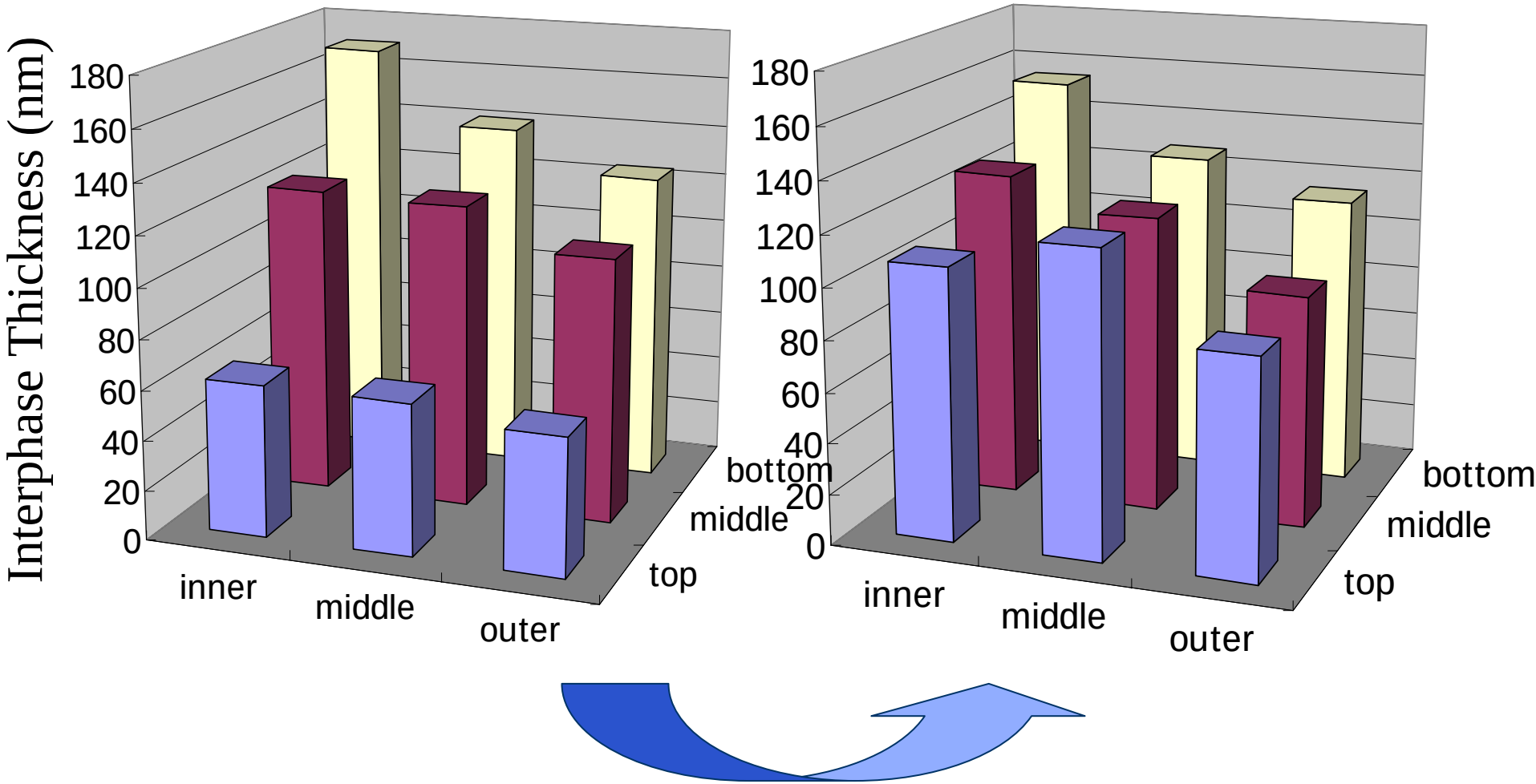
Distribution of Porosity in Composite 1266 (early part)





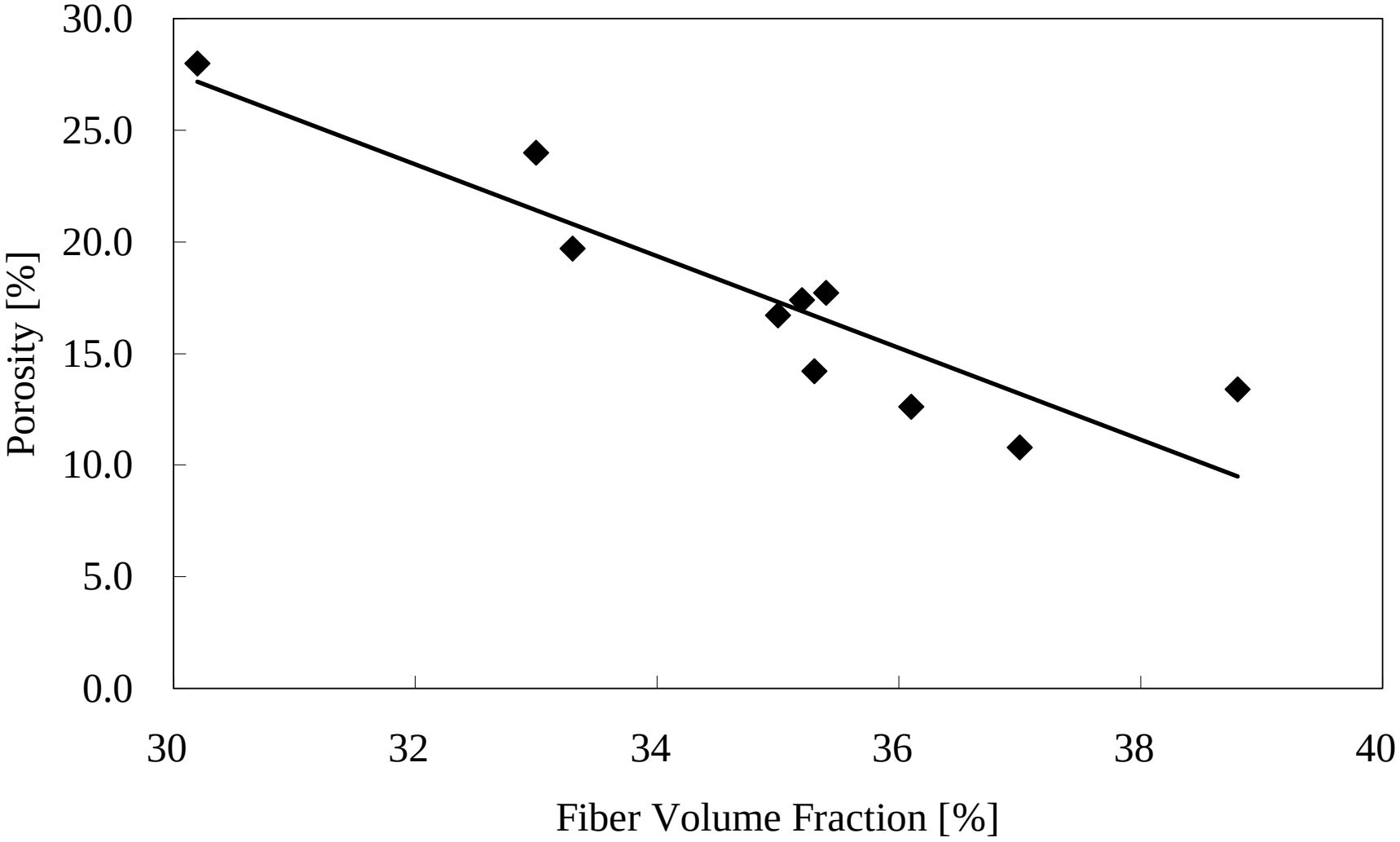
Tyranno SA Plain Weave
PyC ; 75 nm

Improvement of Scatter of F/M Interphase Thickness

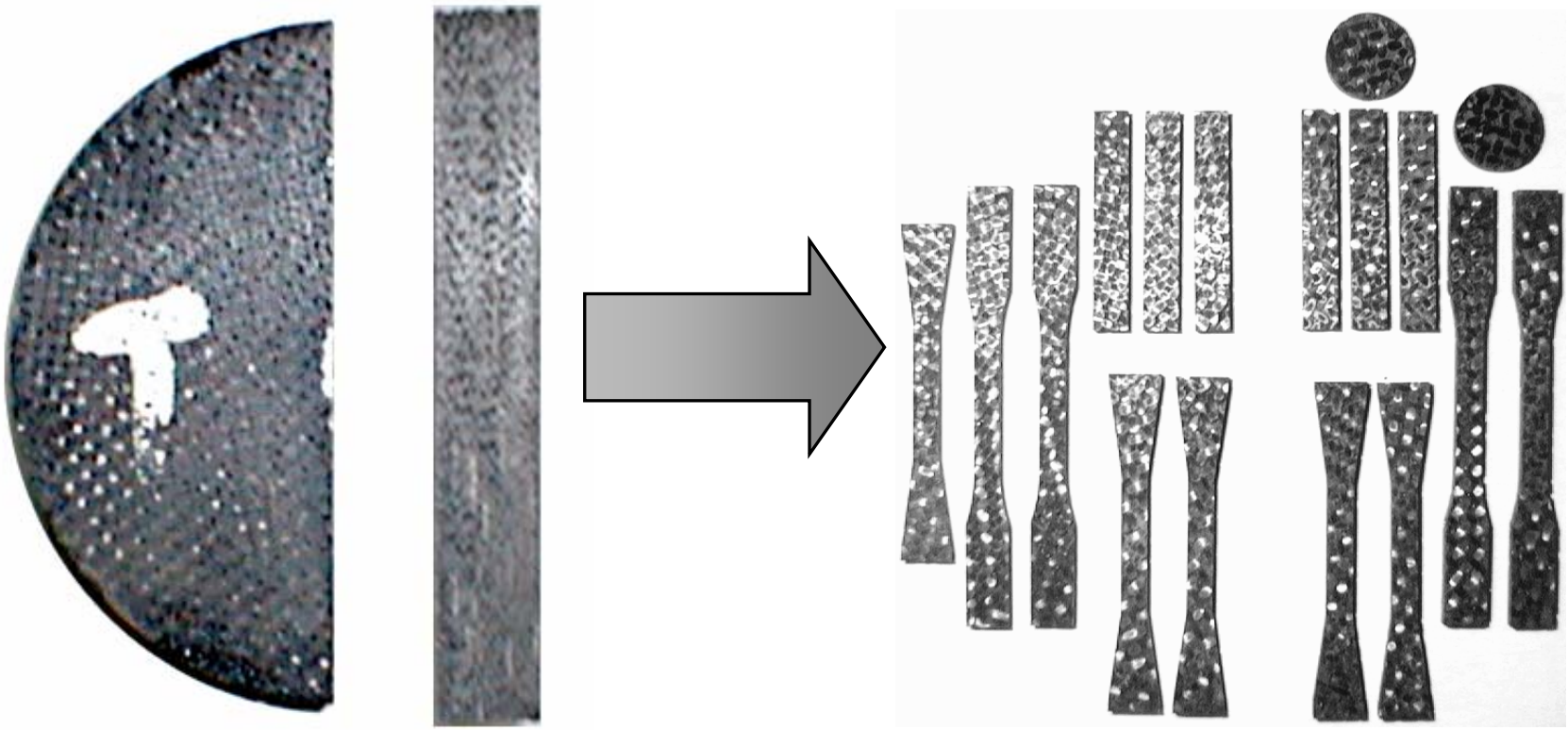


Reverse upstream side and downstream side in middle of deposition

Effect of Fiber Volume Fraction on Porosity



Composites fabricated by F-CVI and machined specimens (75mm diameter)

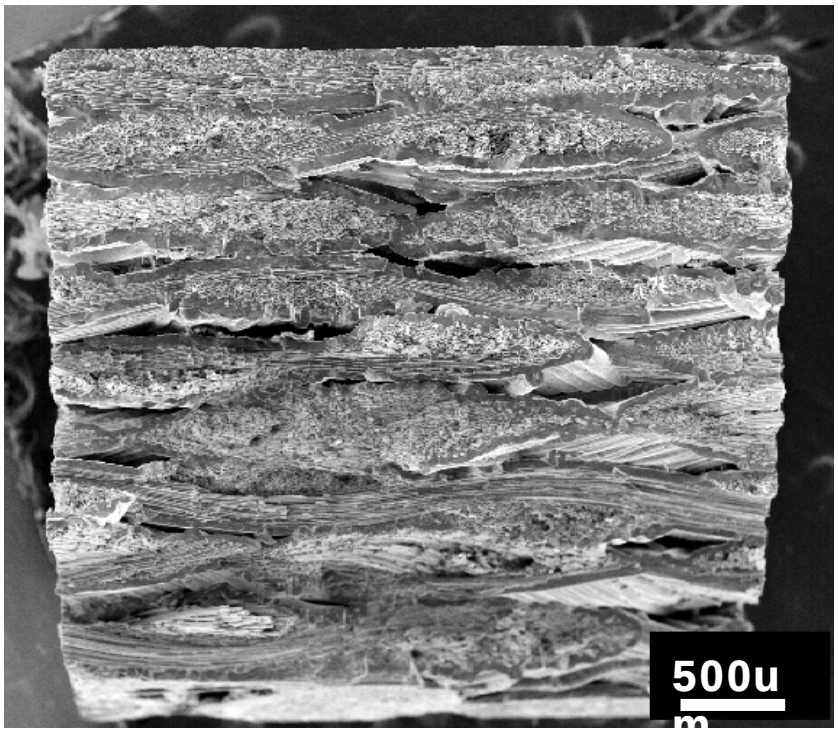


Top view Cross section

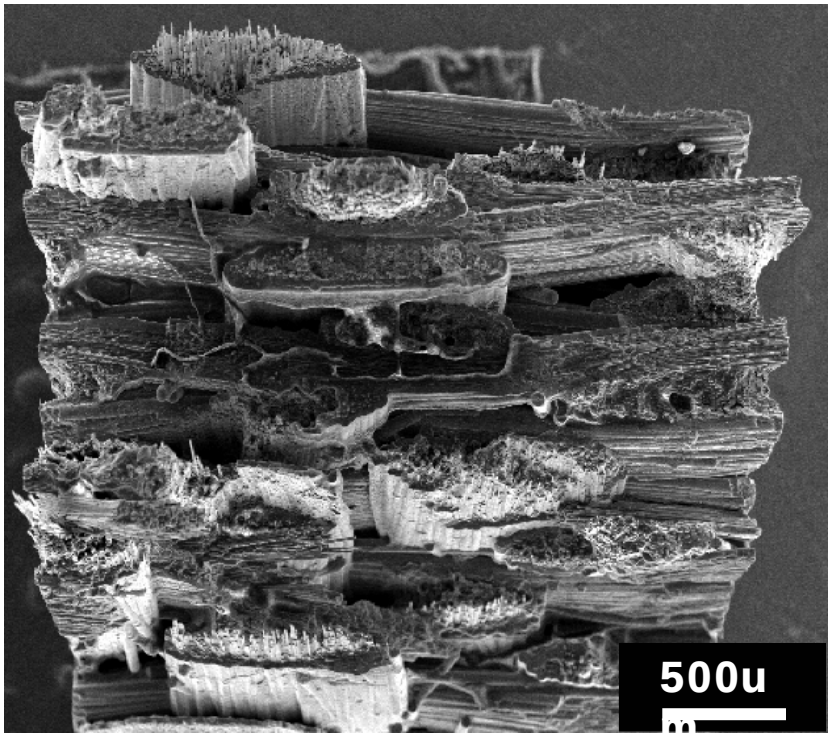
1cm

Effect of Fiber Orientation on Fracture Surface

[-30°/0°/30°]



[0°/90°]

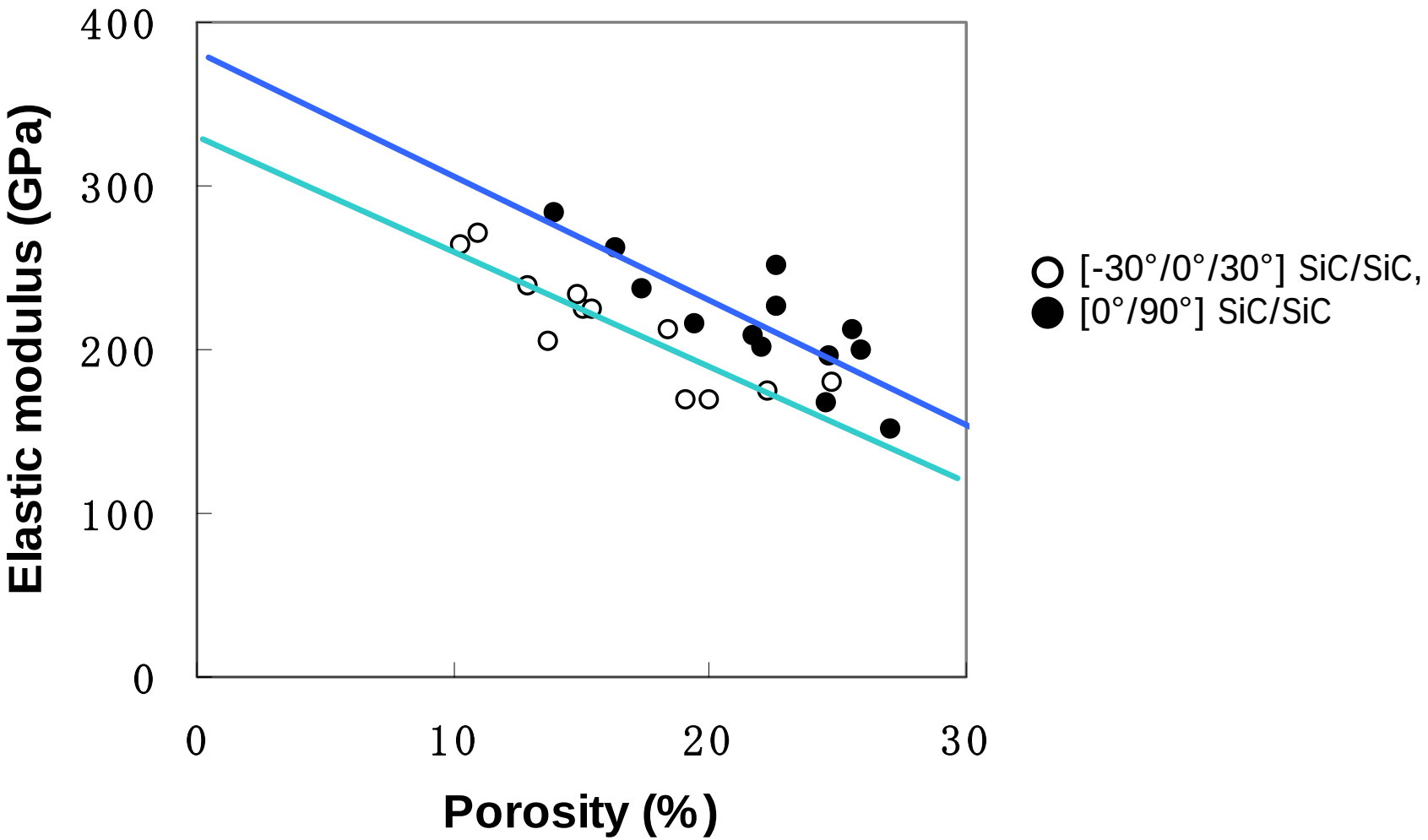


- Short Fiber pull-outs were observed in 0° bundles in both materials
- Individual fiber pull-outs could not be observed in oriented bundles

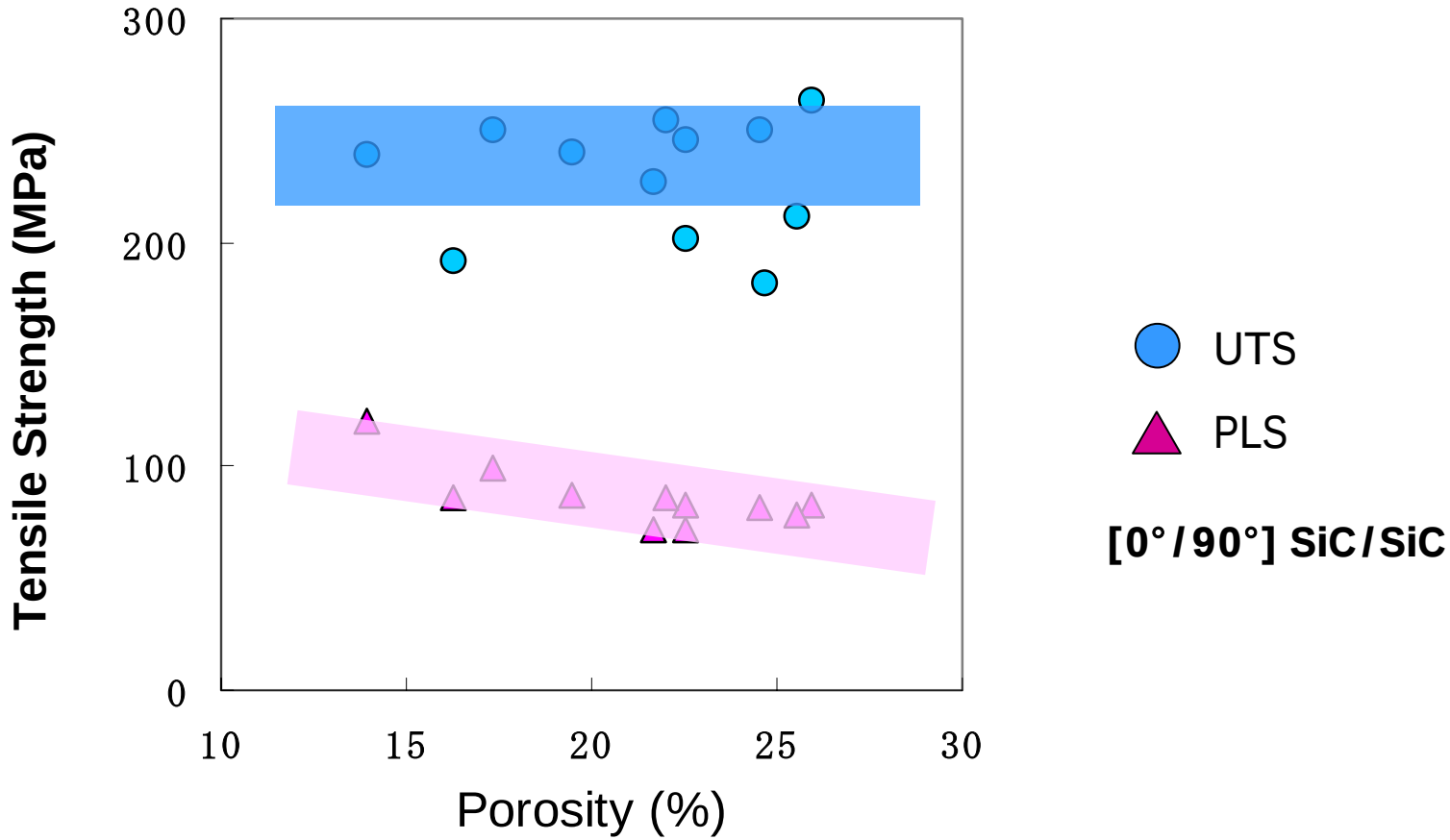
→Bundle fracture was characteristic in oriented fiber bundles

→Different fracture mode (tension, shear)

Porosity dependence of Elastic Modulus

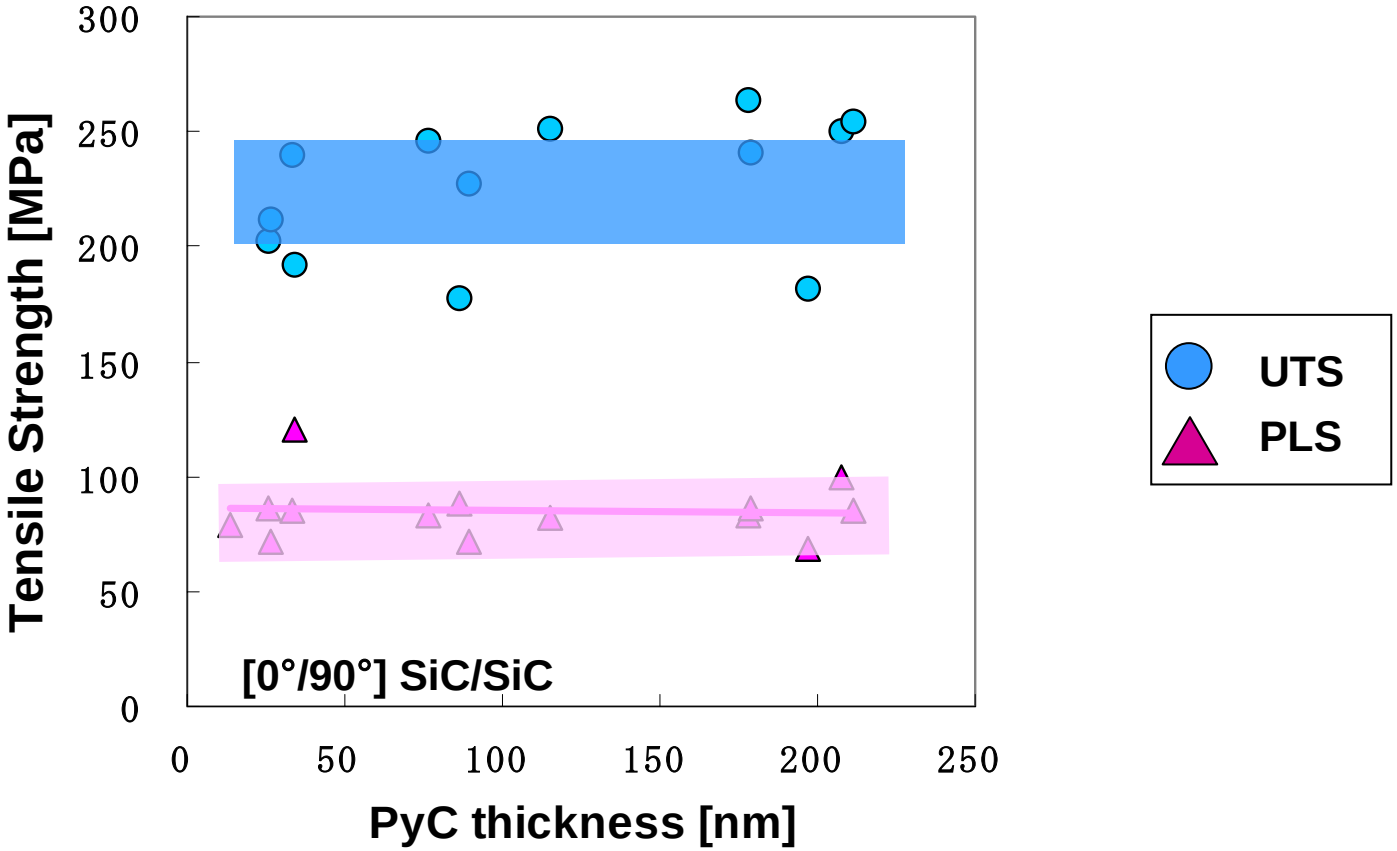


Dependence of Porosity on Tensile Properties



- Tensile strength (UTS) was nearly independent of porosity
- Proportional Limit Stress (PLS) was reduced with increased porosity

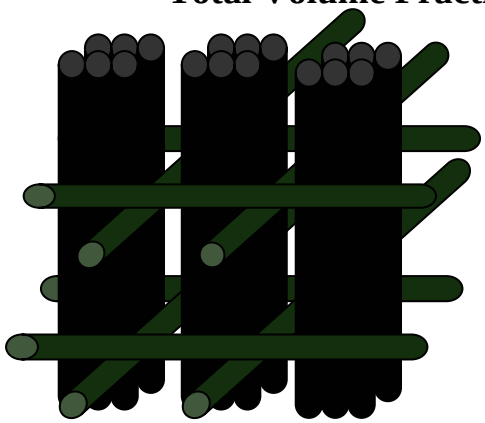
Dependence of Carbon Interphase Thickness



· **Dependence of carbon interphase thickness on UTS and PLS was small**

Engineered High Thermal Conductivity, low T-3 retention SiC/G Composite

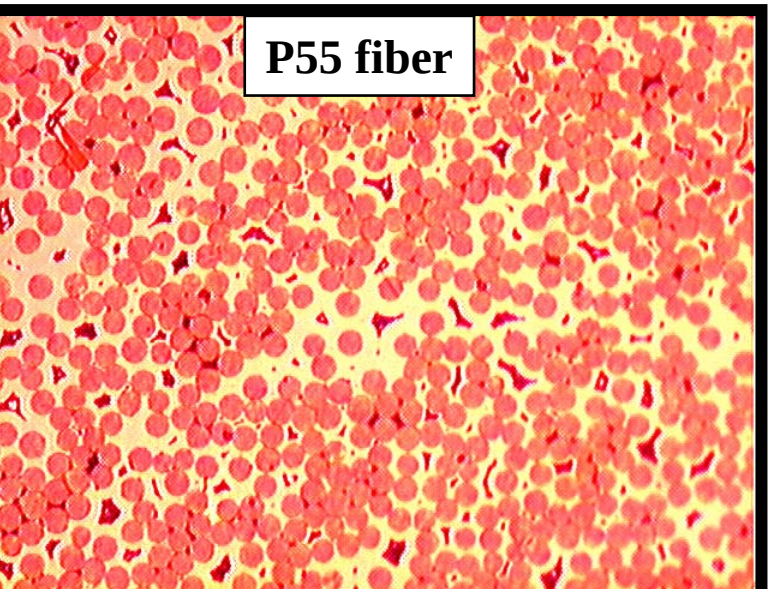
- Matrix : CVI SiC , no interphase
- Fibers : Z-direction either Amoco P55
  or Thornel K-1100 fiber
  X-Y direction Amoco P-55 fiber.
  Total Volume Fraction 44%.

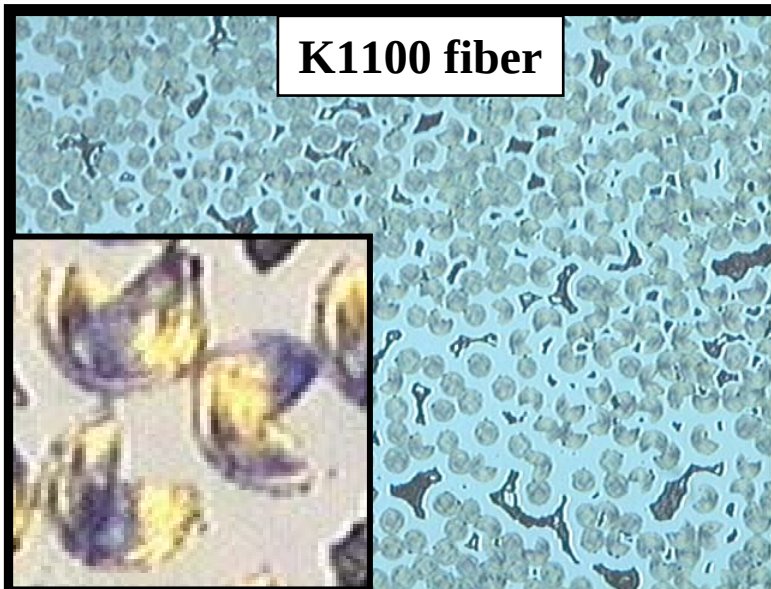


High TC

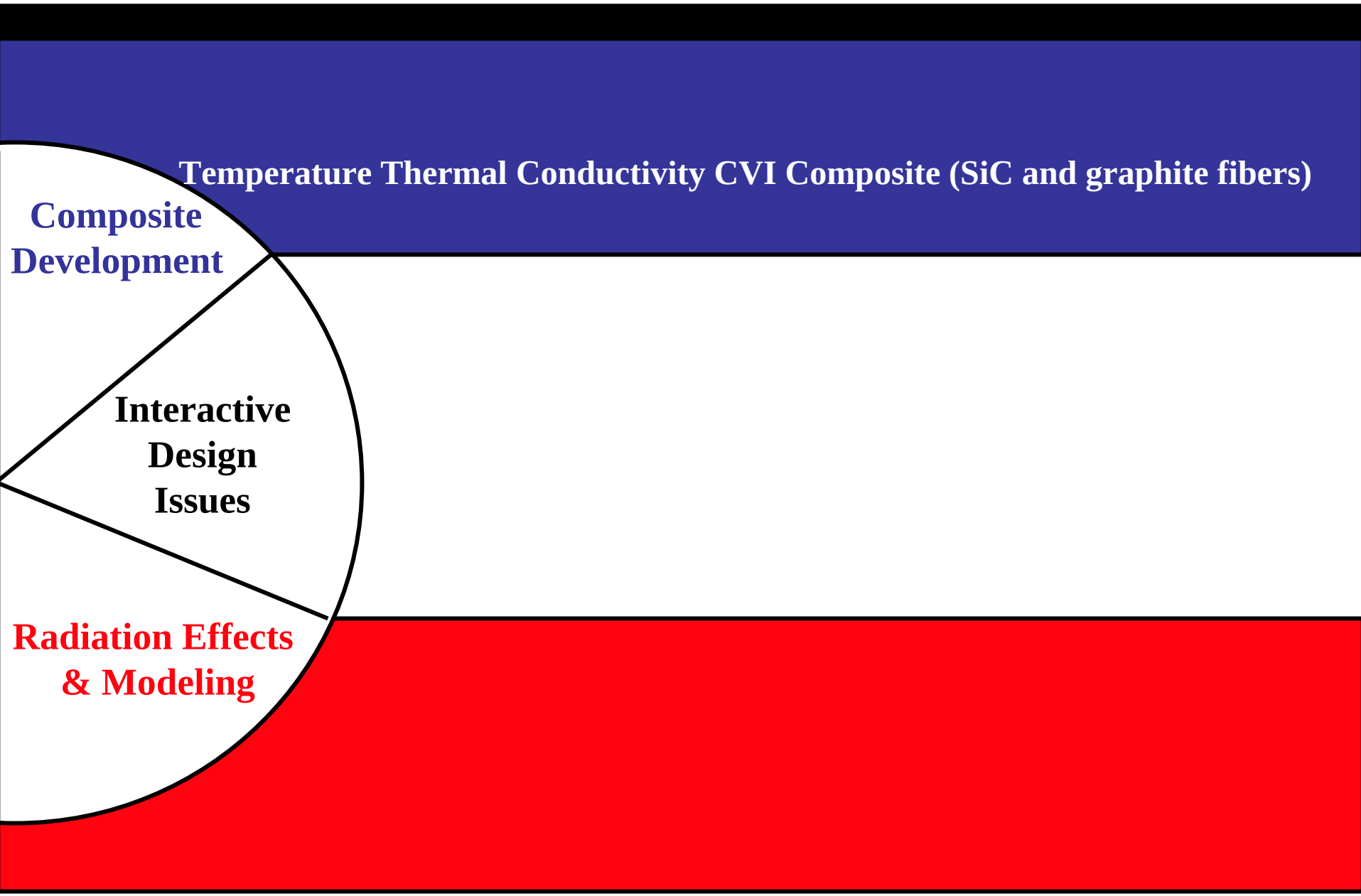
- Architecture :
  Unbalanced 1-1-6 weave.

Fiber	K-1100	P-55	Nicalon Type-S
Kth (W/m-K@RT)	~950	120	15
Diameter (micron)	10	10	13
Tensile Strength (GPa)	3.1	1.9	2.6
Tensile Modulus (GPa)	965	379	420
Density (g/cc)	2.2	2.0	3.2





Summary of Planned Ceramic Composite Program



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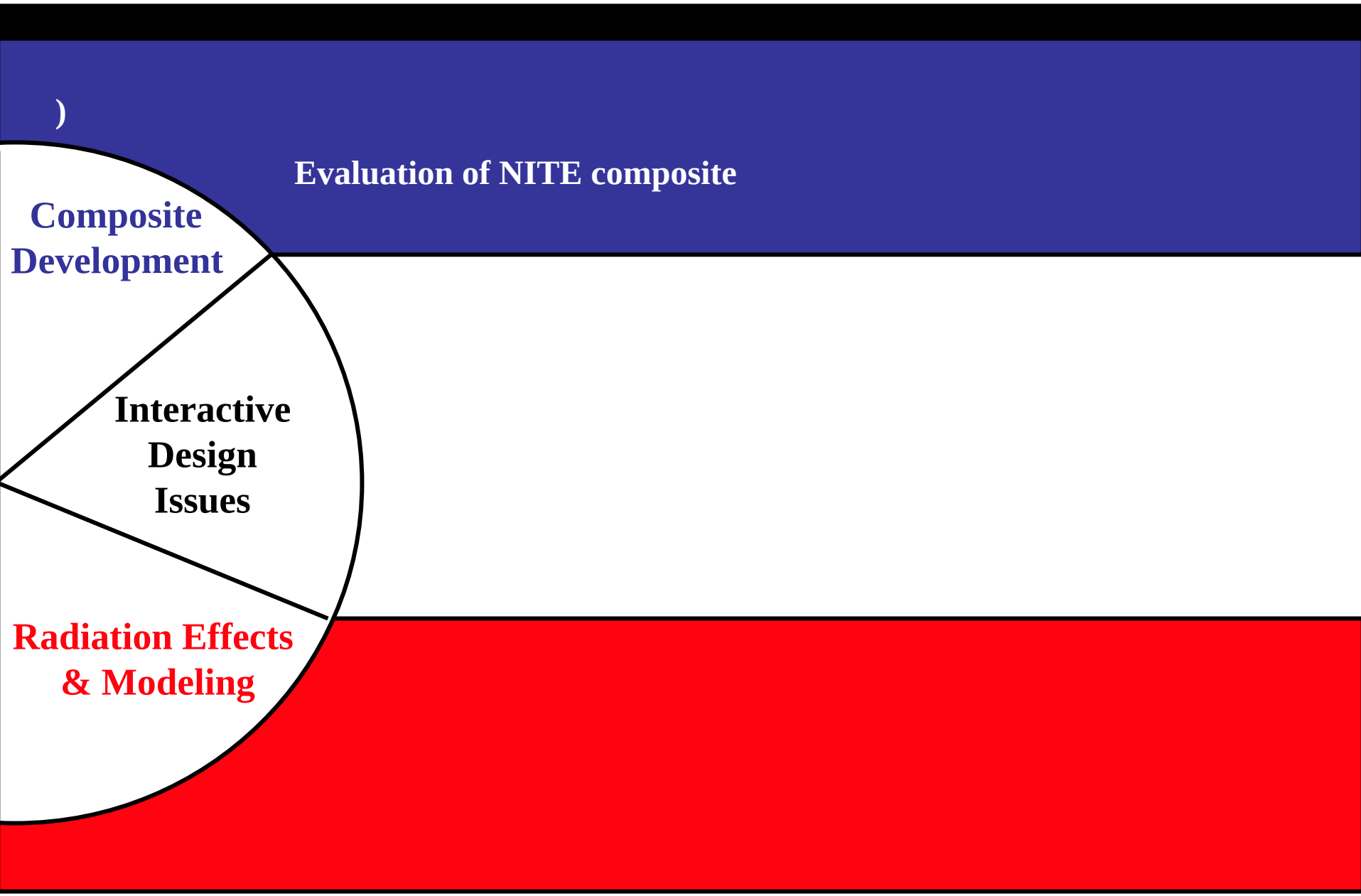
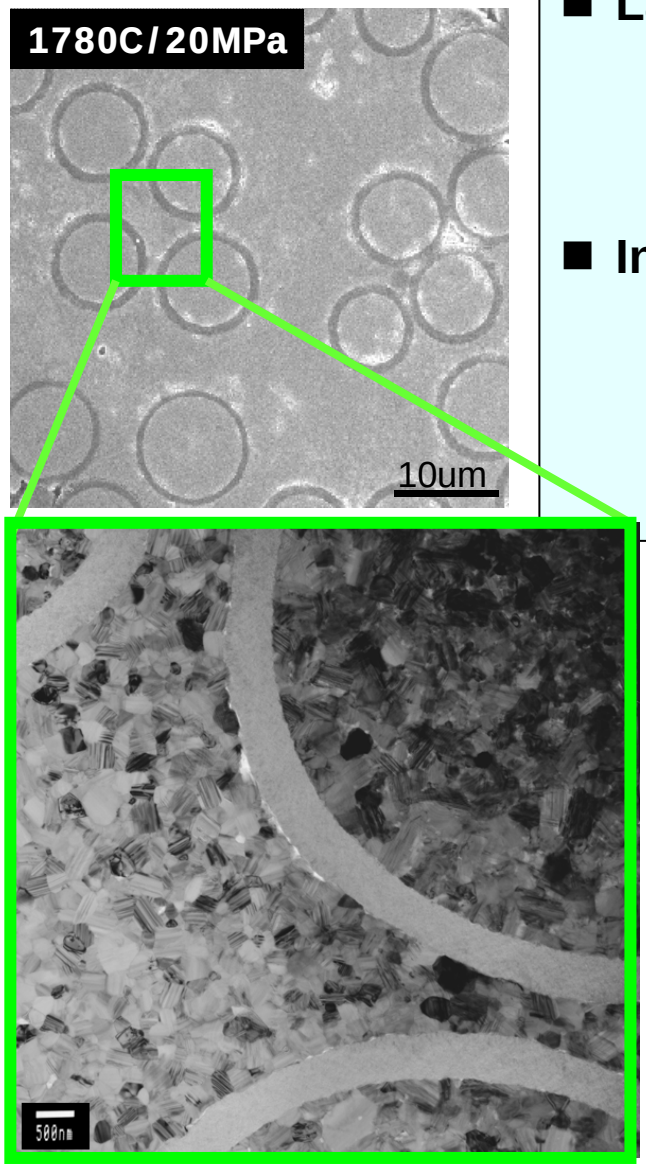
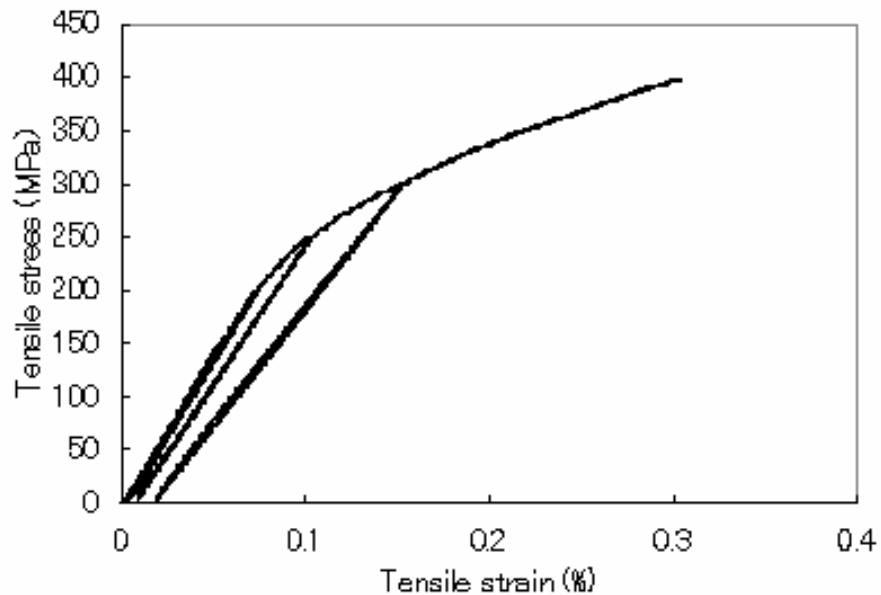


Advanced SiC/SiC by LPS/NITE Process

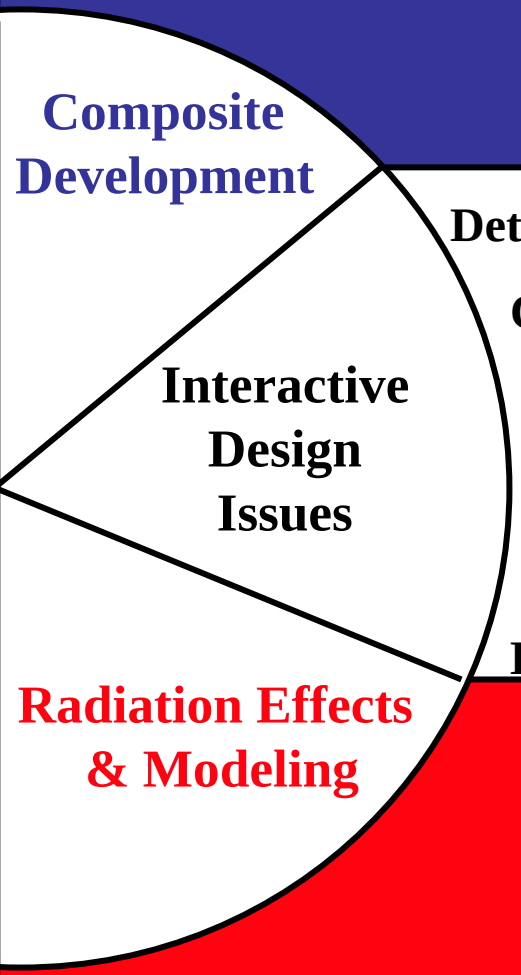
NITE: Nano-Infiltration and Transient Eutectic Phase Process



- **Lab-scale materials demonstrated:**
  - **Promising mechanical/fracture properties**
  - **High thermal conductivity**
  - **Hermeticity / helium-tightness**
- **Industrial production:**
  - **Demonstrated complex shaping and thin-wall/thick brick production**
  - **Licensed medium-scale production in preparation**



Summary of Planned Ceramic Composite Program



Determine high temperature corrosion of SiC in LiPb and water vapor

Crack extension in water vapor containing environment

Continue surface coatings (glassy, ductile and refractory metals)

Begin generation of comprehensive data-set on 2D CVI SiC/SiC

Joining with preceramic polymers

Determine design space for electrical resistivity of SiC composite

SiC/SiC: Chemical Compatibility

- **Pb-17Li coolant**

  - Reaction: 2 SiC + 2 Li = Li_2C_2 + 2 Si

  - Fenici: 800 C/1500 h: CVI SiC/SiC stable

  - Terai: 300-500 C/ 666 h: SiC stable
- **Li: SiC very unstable**
- **Helium + impurity O_2**

  - SiC forms a protective SiO_2 layer.

  - Carbon interface reacts with O_2 to reduce strength, increase da/dt, creep

  - 0.1 ppm O_2 should lead to 30 yr life, model calculations.

  - Transmutation of Li ceramic breeding material will release O_2 that will react with T to form T_2O: H_2O reacts with SiC to form SiOH (g), significant issue for turbine applications but no information on lower concentrations of H_2O.
- **On-going work: da/dt in Ar+H_2O at 800 to 1100 C, Type S SiC/SiC composite**

SiC/SiC: Coatings

- **Candidate materials**

  - Ductile metals such as V

  - Glasses that can flow to relax stresses

  - SiC seal coat

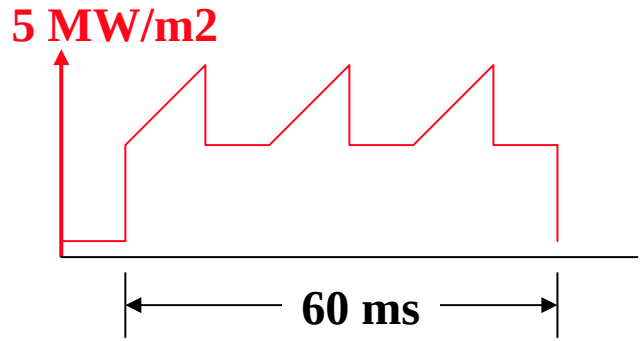
  - Advanced composite coatings: Ti_3SiC_2 + SiC, thermal fatigue
- **Status**

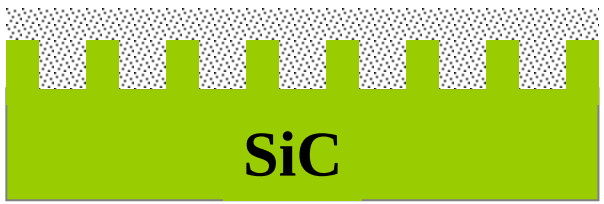
  - European work with glass coatings

  - SiC: not likely to work because it will microcrack
- **On-going work:**

  - Proposal to evaluate ductile metal coatings: in situ creep tube will provide coating, irradiation creep and burst strength data.

Infrared Rapid Melt Processing and Thermal Shock
--> Rapid melting of surface refractory, leaving substrate cool





QuickTime™ and a
decompressor
are needed to see this picture.

Specifications: **Argon plasma (up to 1MW)**

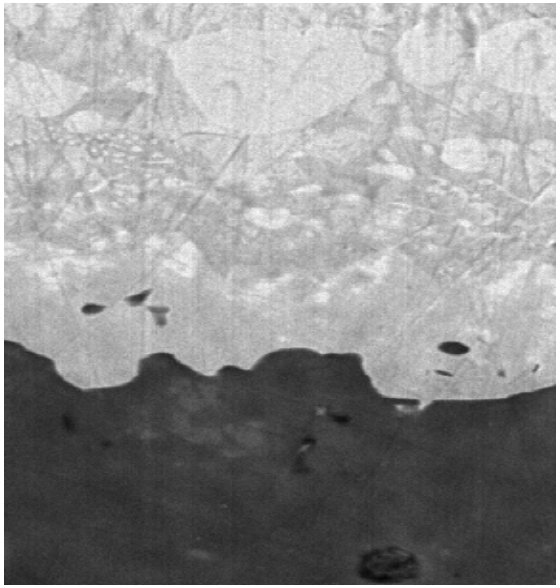
Pulse length : 10 ms (no shuttering)

Rep Rate : 5-10 Hz

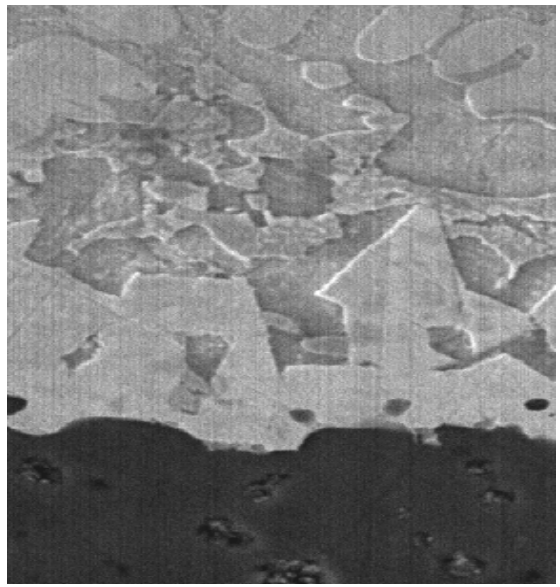
Maximum heat flux at maximum area : 5 MW/m2 at 2.5 x 35 cm

Maximum heat flux attainable :12. 5 MW/m2 at 2.5 x 20 cm

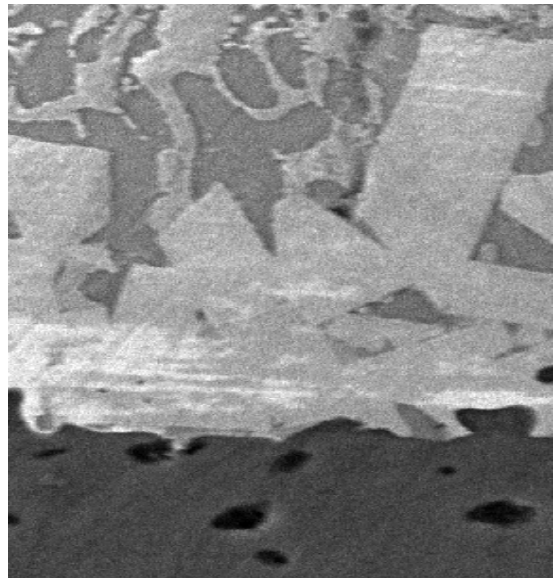
Example : Infrared Processed Hexaloy SA / W powder



W powder



W deposition +
W powder



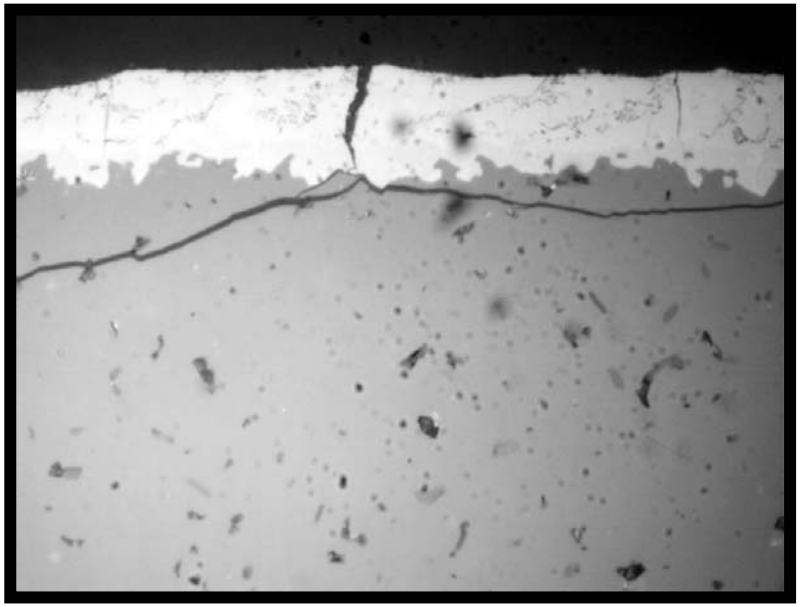
W deposition +
annealing+ W
powder

5μm

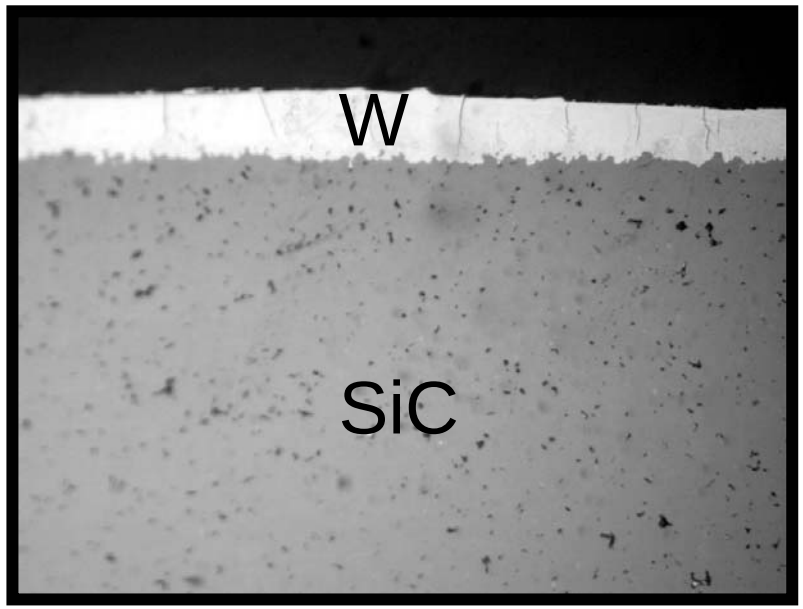
Process variable included: W powder alone
Deposition of thin layer of tungsten + powder
Deposition of W and annealing to bond thin interface

TEM of interface revealed essentially no difference in processes, but the interfaces were very clean

Crack formation



No preheating



Preheating

Initial processing resulted in cracking in tungsten which propagated across interface into substrate. This would cause spalling during fatigue loading. This has been controlled by preheating of the substrate prior to Infrared Processing.

SiC/SiC: Joining

- **Preceramic polymer: allylhydridopolysilane (aHPCS) + SiC powder**

  - 85 MPa average 4-point bend strength, RT
- **ARCJointT: NASA developed, reaction formed SiC + other phases, applied in air with a torch- field application**

  - 134 MPa average 4-point bend strength, RT

  - 247 MPa after anneal at 1100 C in air
- **High-temperature brazes: Si-22%Ti: eutectic**

  - 60 MPa shear strength, RT
- **Displacement reaction composite: Ti_xSi_yC + SiC**

  - 187 MPa 4-point bend strength, RT
- **On-going work: PNNL working with aHPCS + SiC powder, preparation for irradiation in HFIR.**

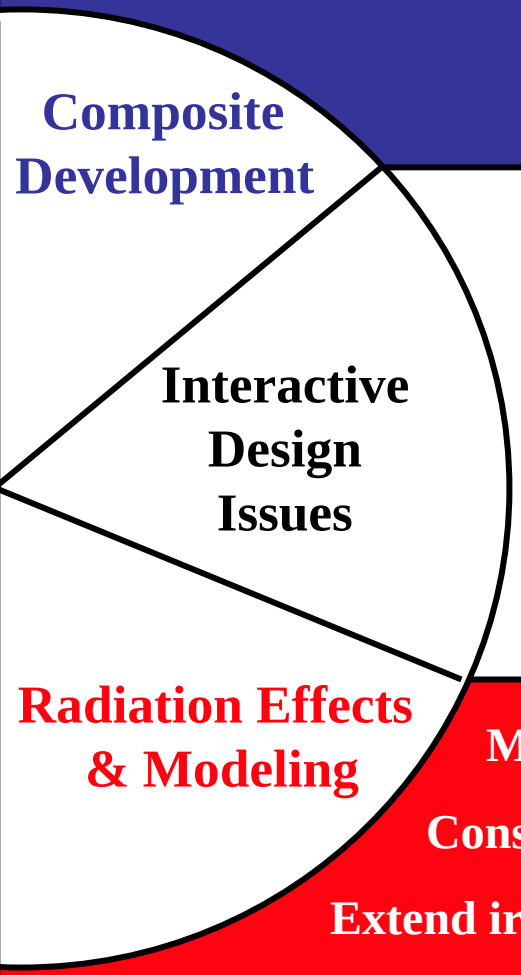
Electrical Resistivity

- The electrical resiststivity of SiC is assumed > 100 ohm-m for MHD pressure loss considerations. Currently, non-irradiated and neutron irradiated composites are being evaluated (different fibers, matrices and interfaces) to map design space for electrical resistivity. Preliminary data reveals a problem with low resistivity.

Comprehensive Data Set

- Design community is advocating a comprehensive handbook of SiC/SiC properties. We are now in a position to fabricate materials for round-robin testing and relevant property information. This talk is being fed by mechanical property and materials development areas.

Summary of Planned Ceramic Composite Program



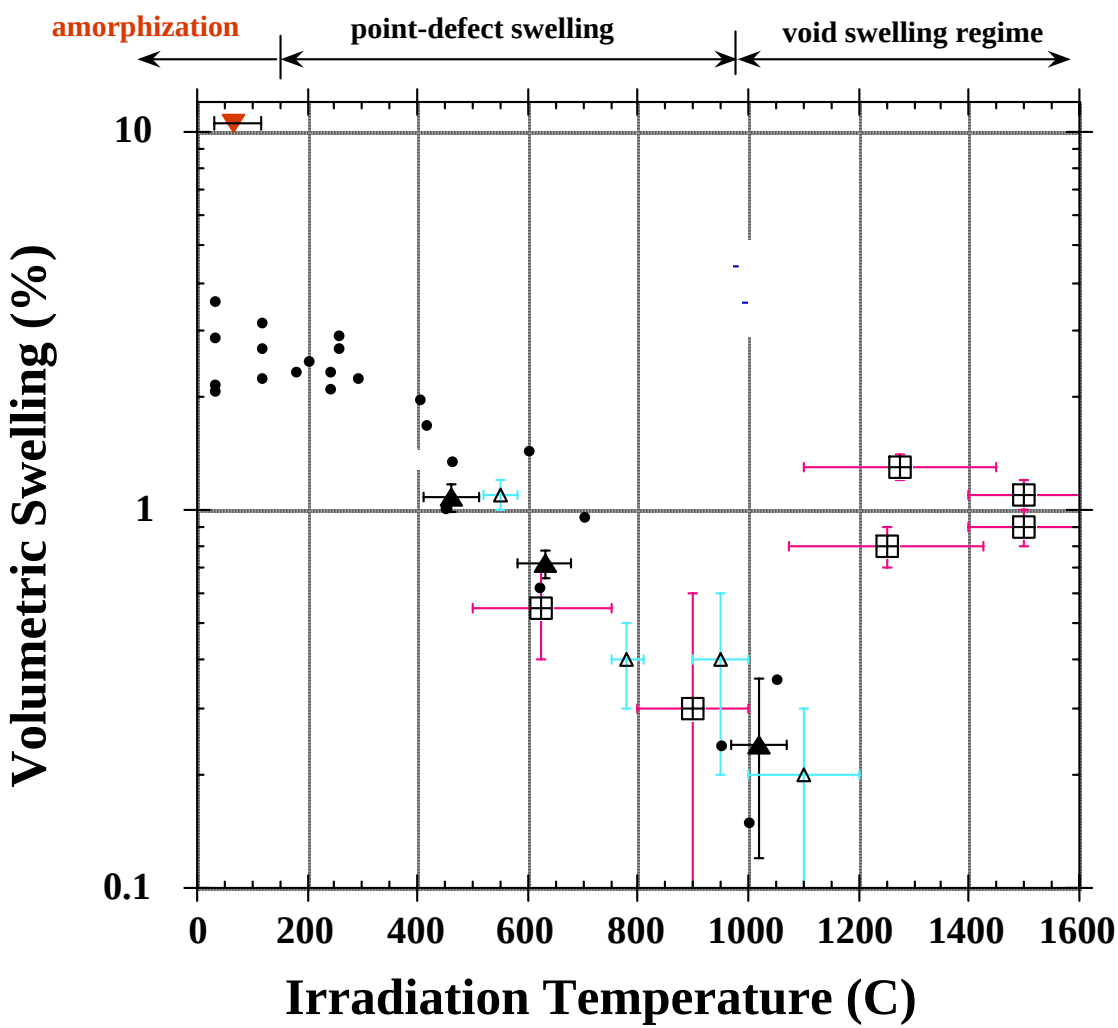
Mapping of swelling and microstructure of SiC at high T

Constitutive modeling of composite fracture under irradiation

Extend irradiation effects database on SiC and SiC/SiC to higher dose

Thermal conductivity modeling and development of practical algorithm

Irradiation Induced Strain and Amorphization



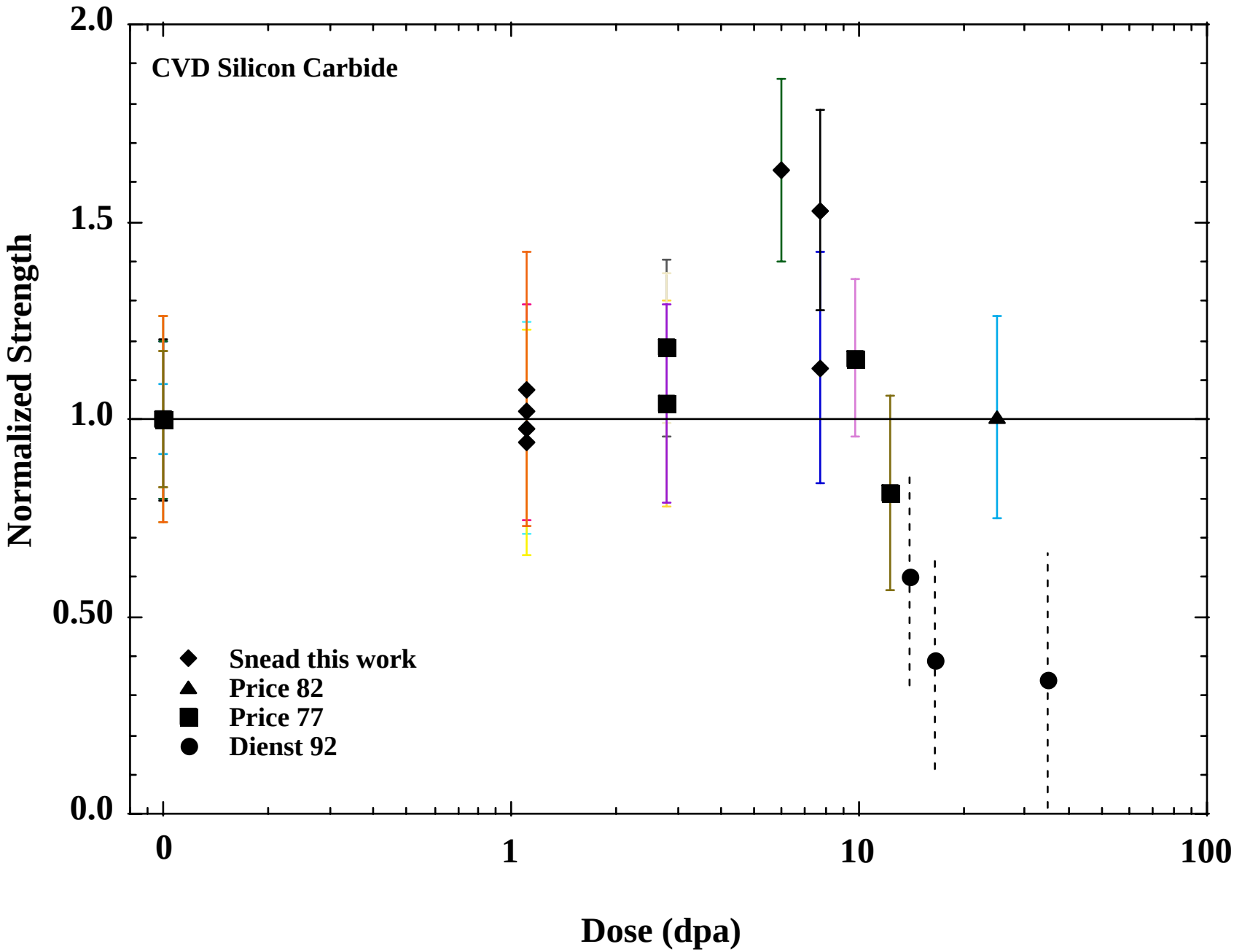
- Ceramics undergo swelling due to radiation-induced interstitial strain

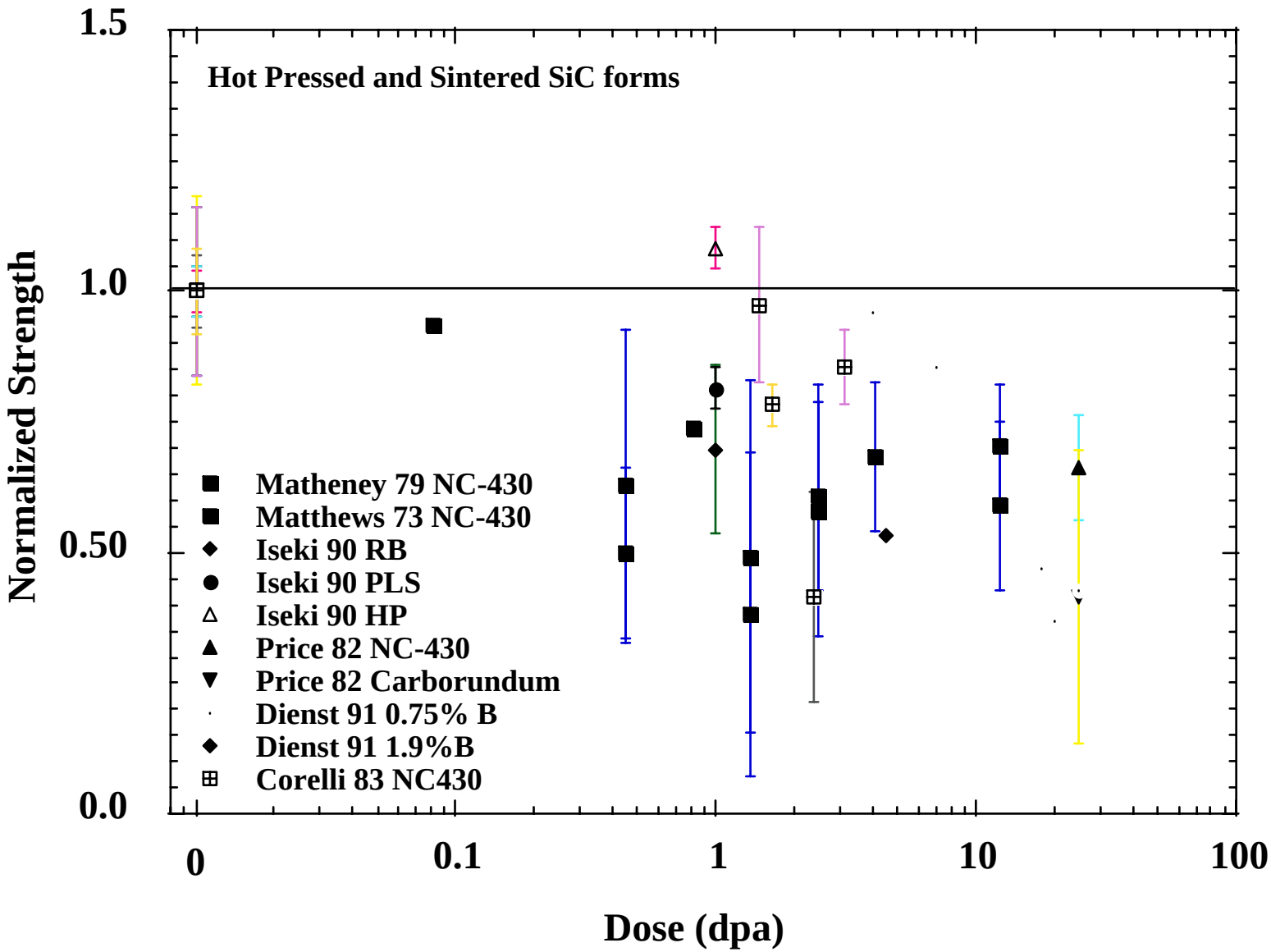
- SiC swelling regimes:
  - Amorphization (T< 150°C)
  - Point Defect Swelling (<1000°C)
  - Void Swelling (?)

- Upper temperature swelling is being mapped by ion beams (Kyoto) and will be mapped (600-1500°C) using HFIR irradiation (METS.)

Radiation-hard SiC composites

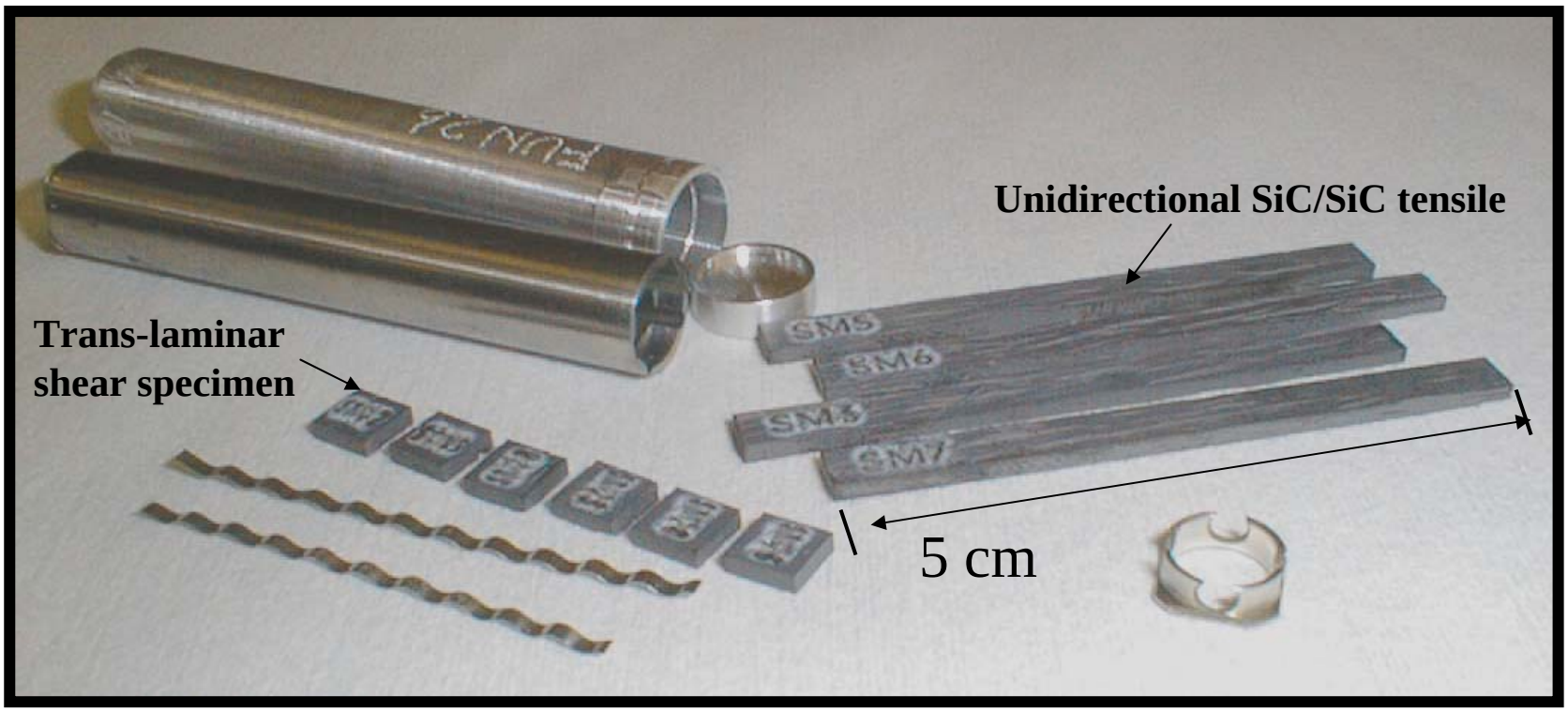
Nicalon™ Fiber Type	C/Si Atomic Ratio	Oxygen Content (wt/%)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Density (g/cm3)	Diameter (μm)
Ceramic Grade	1.31	11.7	3.0	220	2.97	2.55
Hi	1.39	0.5	2.8	270	7.77	2.74
Type-S	1.05	0.8	2.6	410	24.1	3.1


CVD Silicon Carbide
Normalized Strength
2.0
1.5
1.0
0.50
0.0
0
1
10
100
Dose (dpa)
Snead this work
Price 82
Price 77
Dienst 92


Hot Pressed and Sintered SiC forms
Normalized Strength
1.5
1.0
0.50
0.0
0
0.1
1
10
100
Dose (dpa)
Matheney 79 NC-430
Matthews 73 NC-430
Iseki 90 RB
Iseki 90 PLS
Iseki 90 HP
Price 82 NC-430
Price 82 Carborundum
Dienst 91 0.75% B
Dienst 91 1.9%B
Corelli 83 NC430

FUN (Fusion Unidirectional) Rabbit Program

- Study of composite systems under irradiation through constitutive modeling of ideal unidirectional systems.

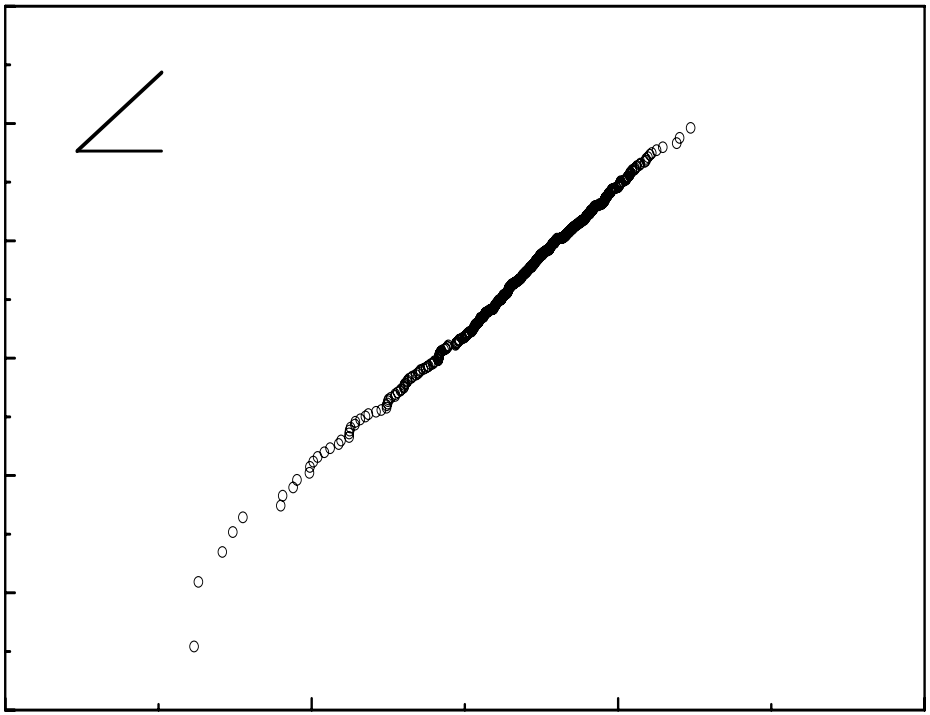


- **Fibers : Nicalon Type-S, Tyranno SA, AVCO SCS-0**
- **Interphases : Carbon, Multilayer SiC, Pseudo Porous SiC**
- **Matrix : ICVI SiC**
- **Current Irradiation : HFIR, 200-800°C, 1 to 10 dpa, 26 capsules.**

ORNL/JUPITER

Background

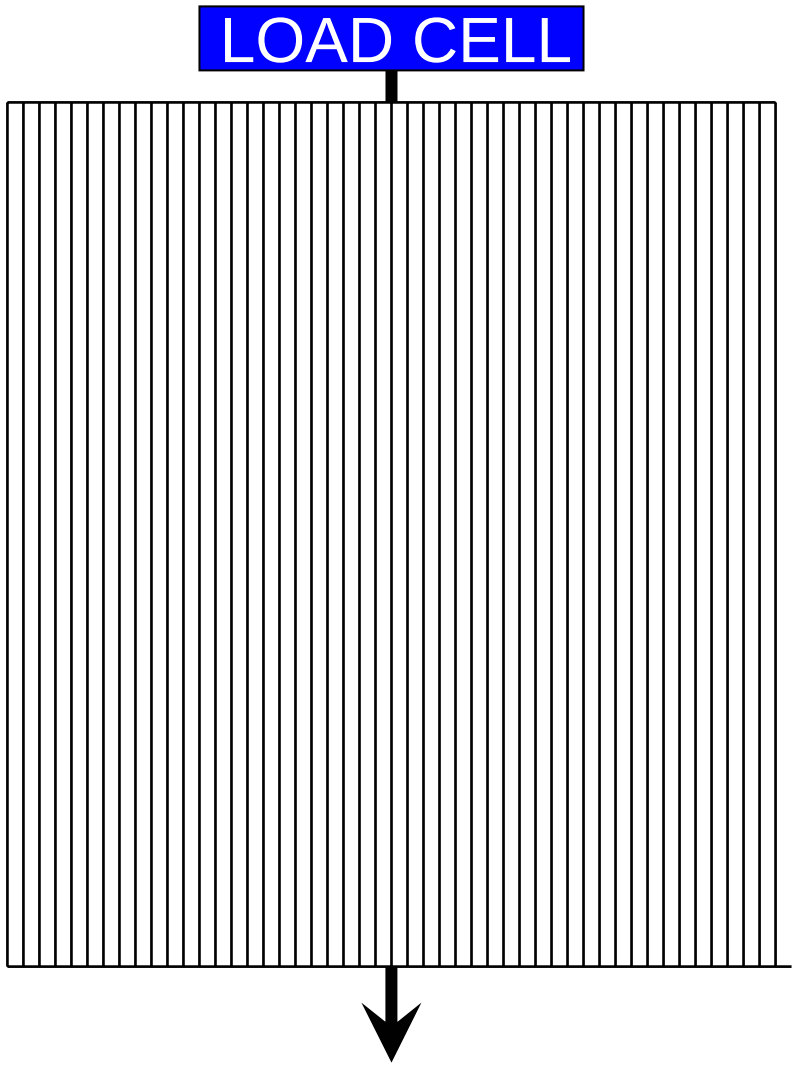
- *The strength of most ceramic fibers are distributed according to a two-parameter Weibull distribution.*

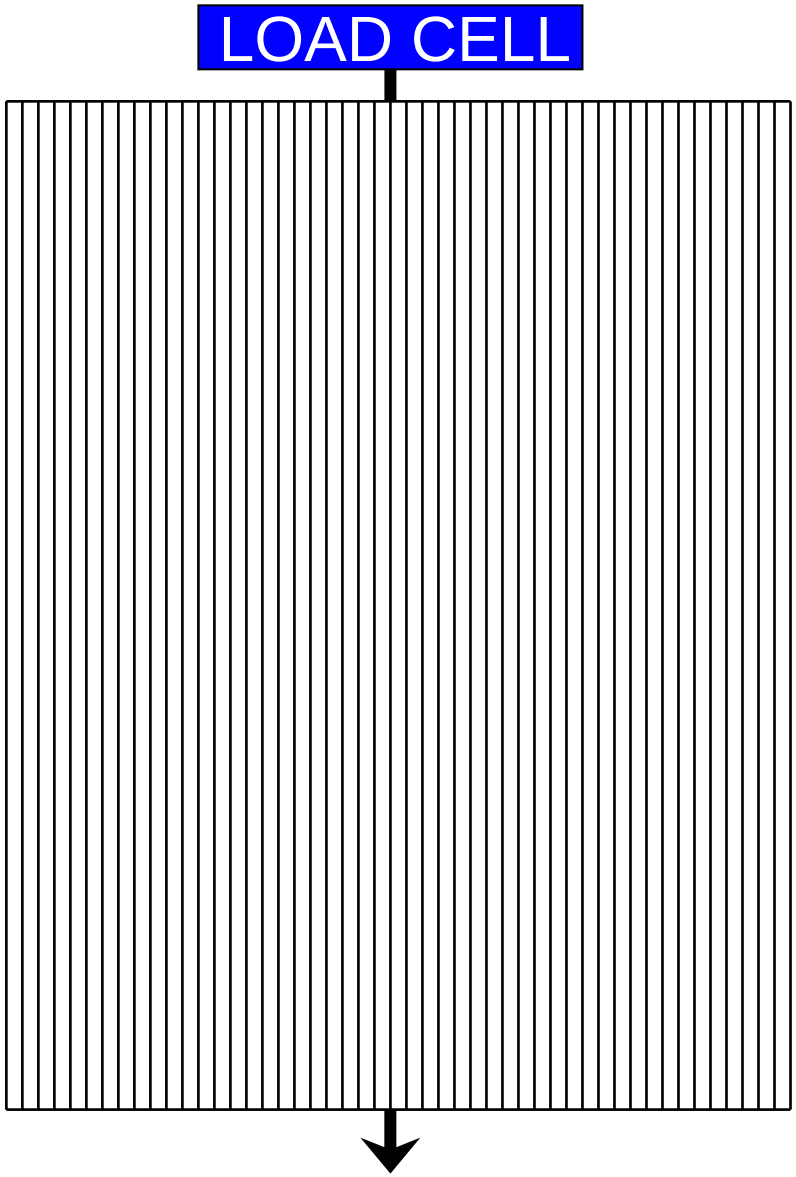


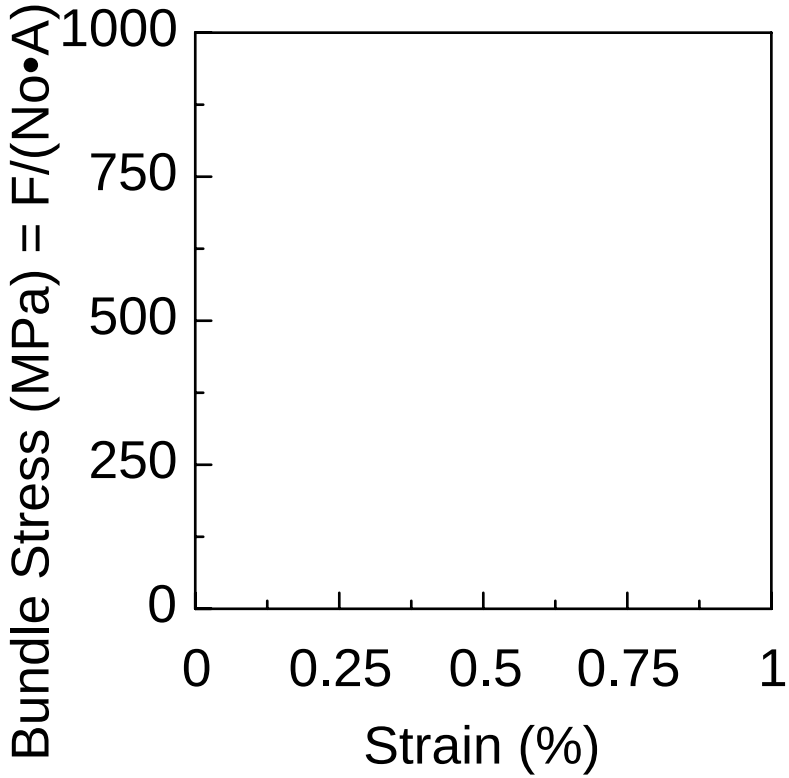
Question : What is the effect of Weibull modulus of fiber and its relation to fracture in the composite?

Model : Assuming a bundle containing N_o fibers with Weibull modulus m, and characteristic strength s_o , to a constant displacement rate.

Exercise

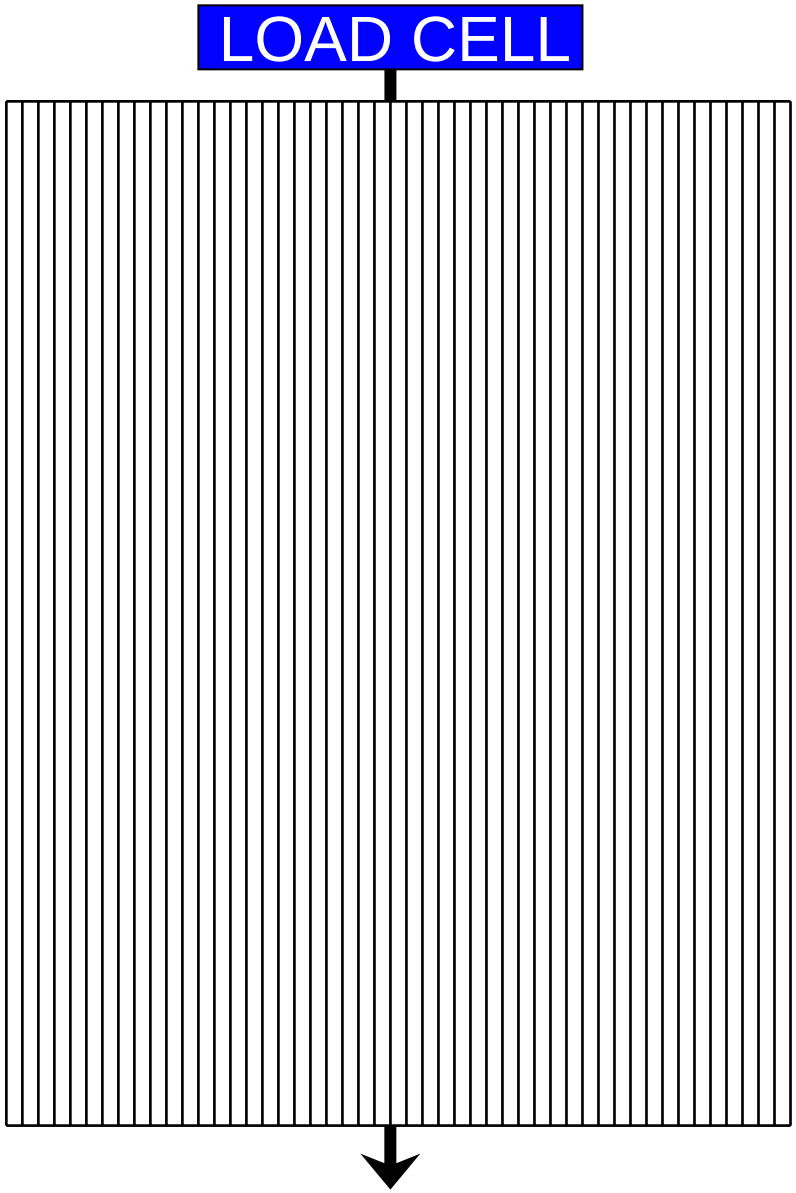


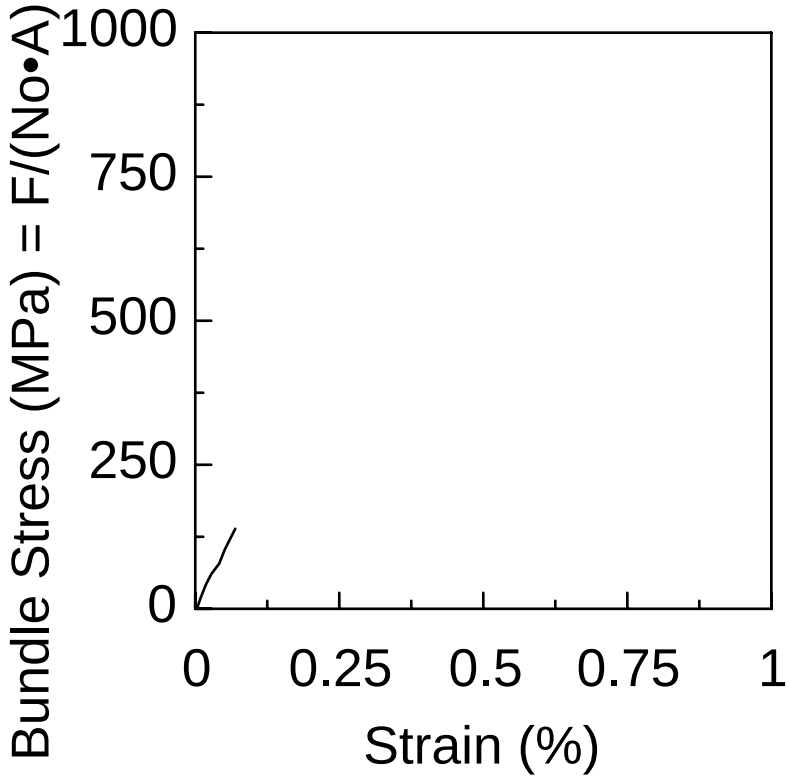




CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

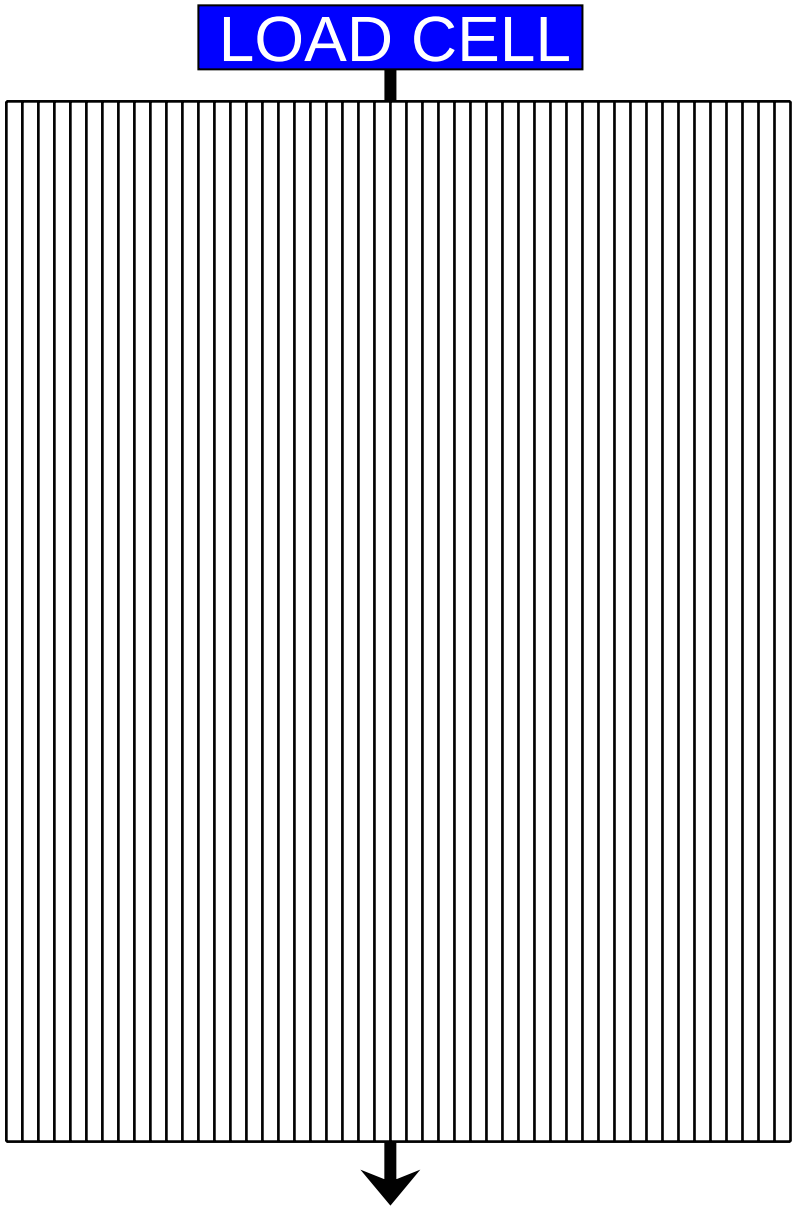
ornl

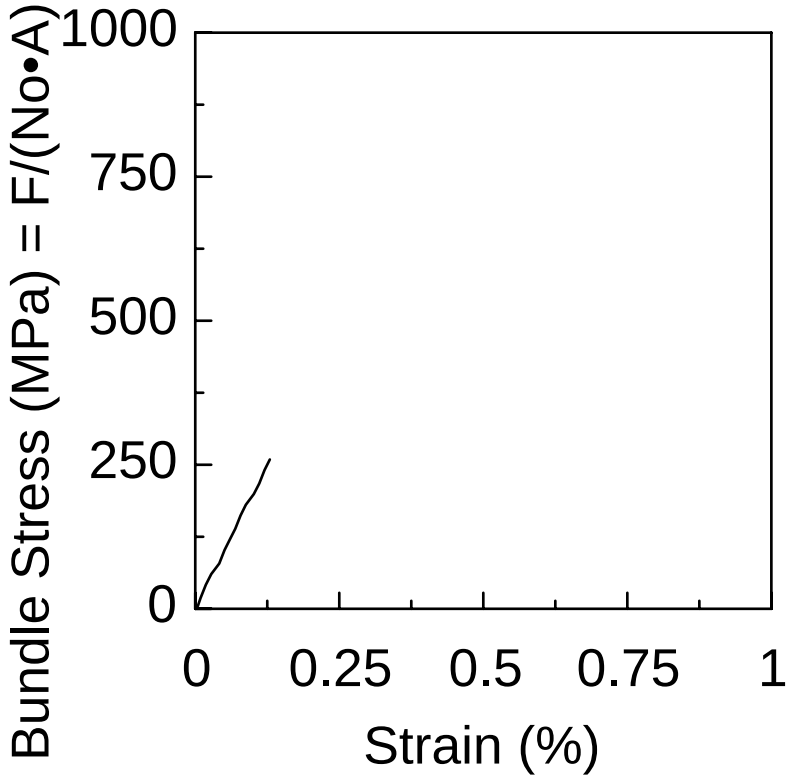




CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

ornl





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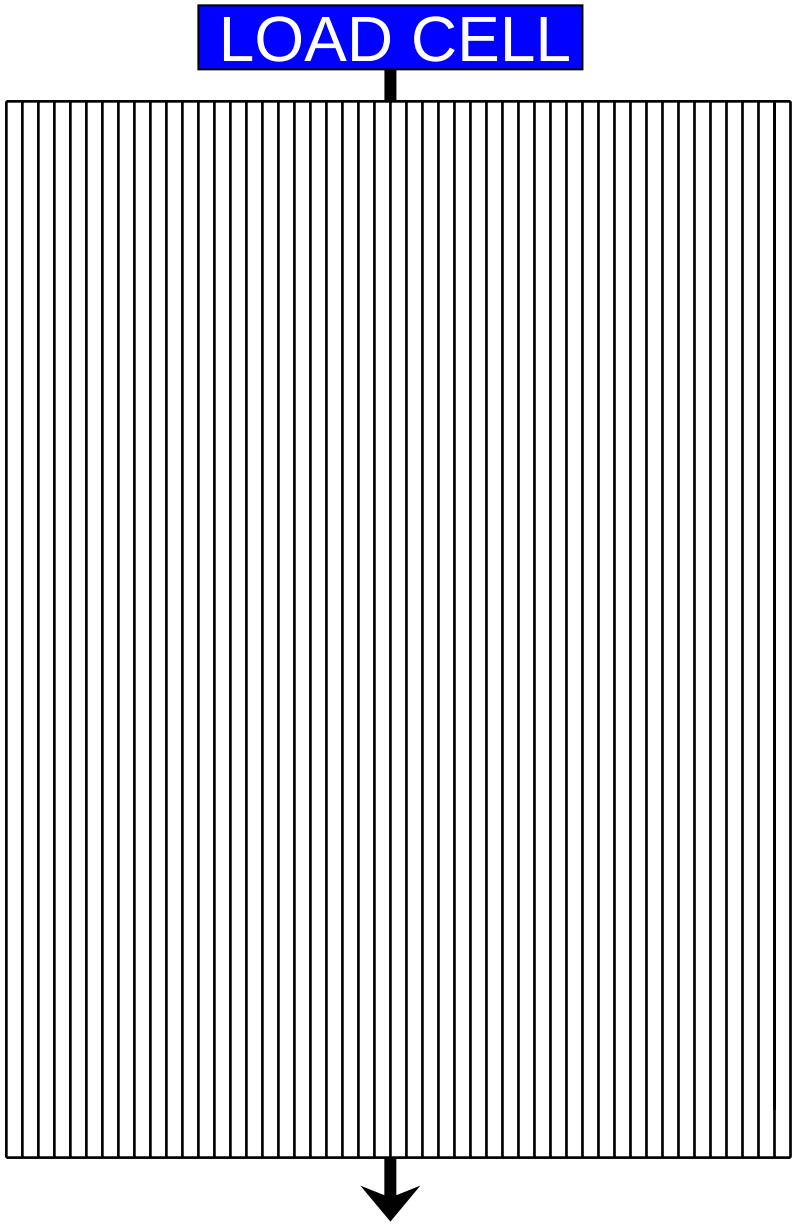

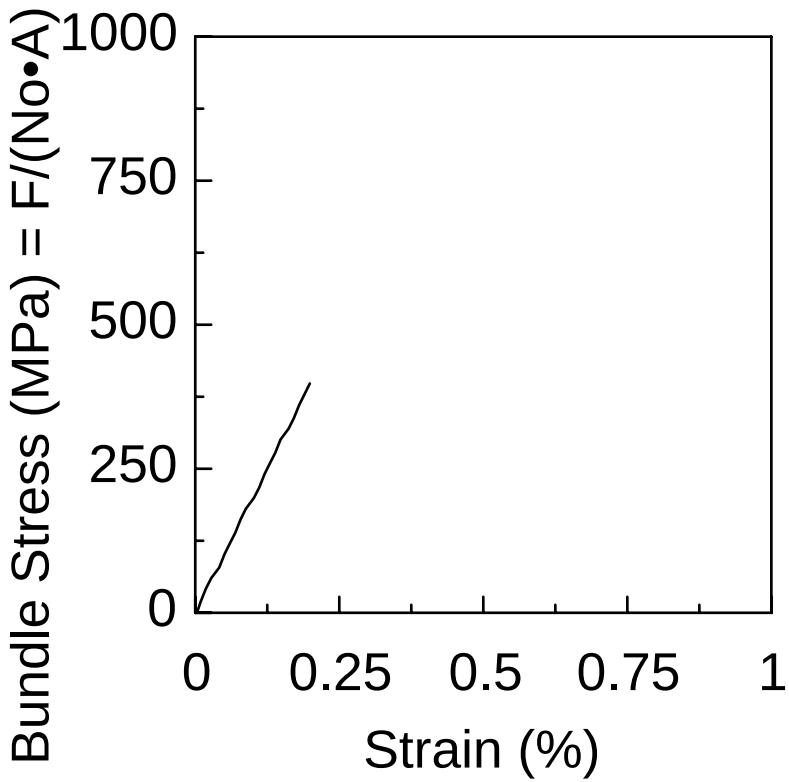

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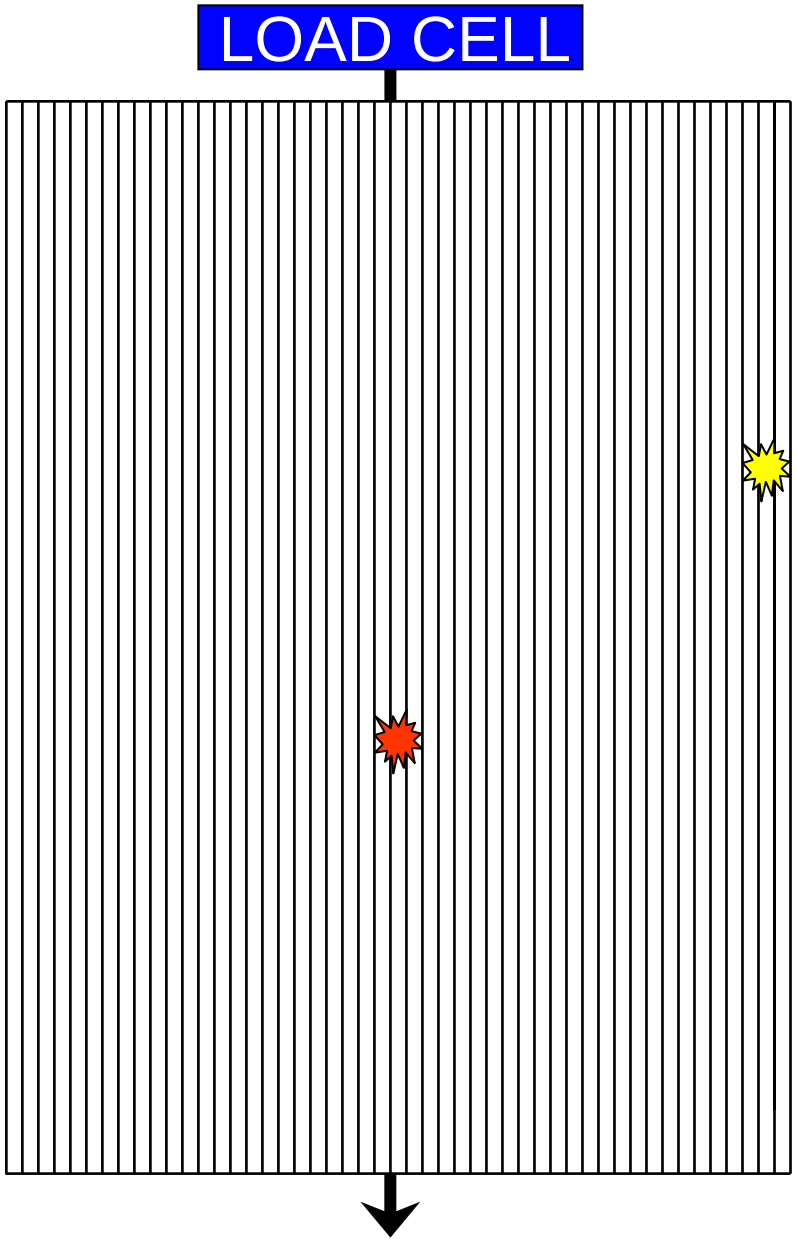

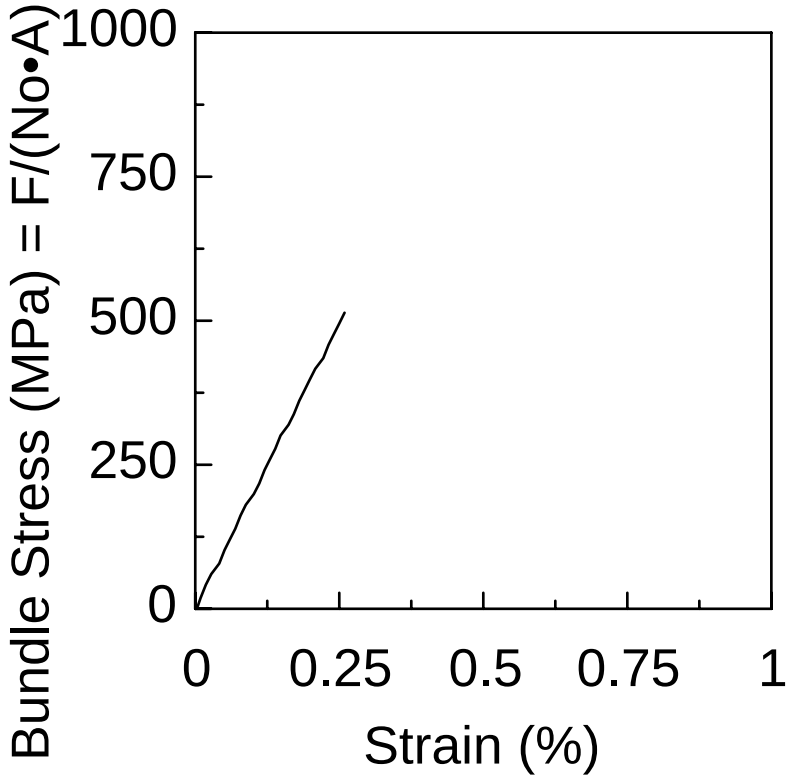

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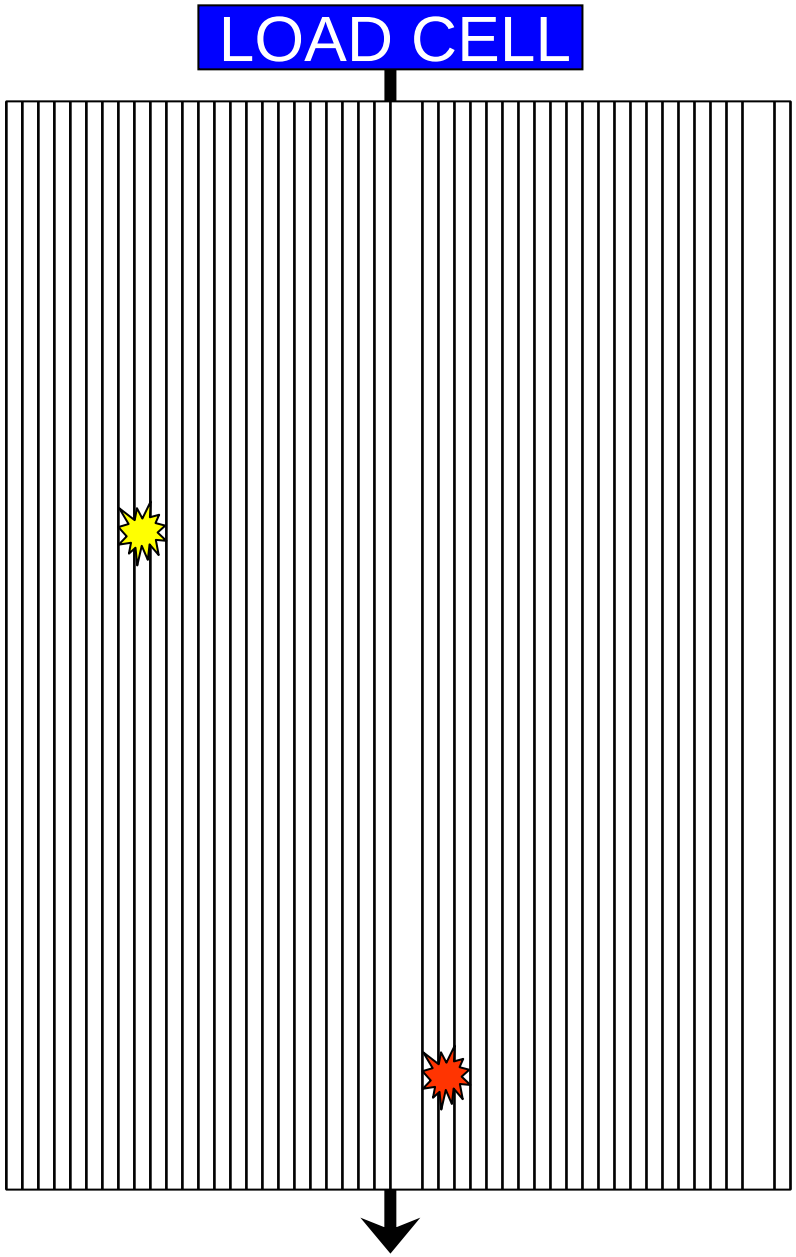

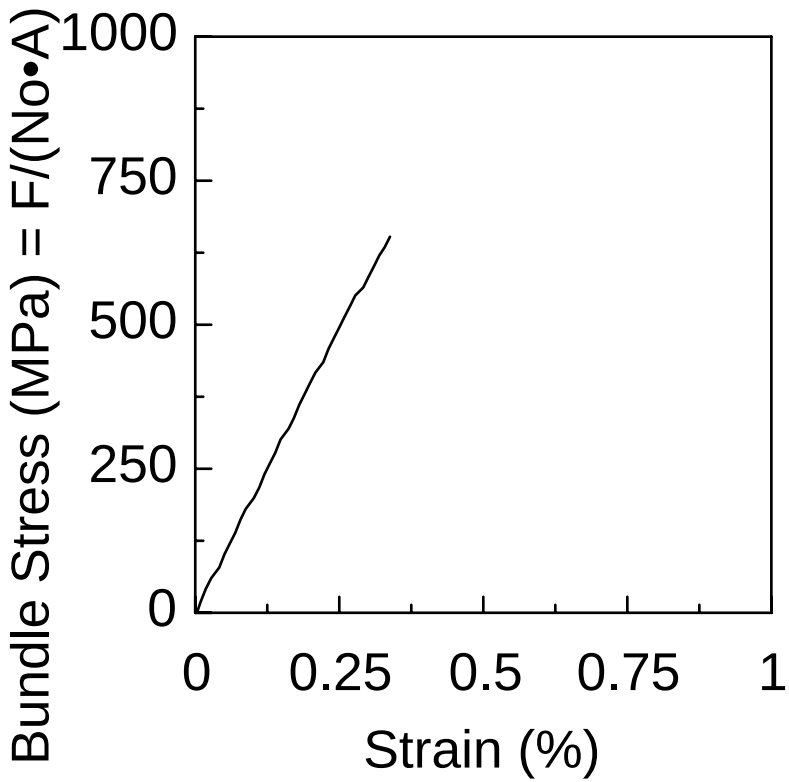

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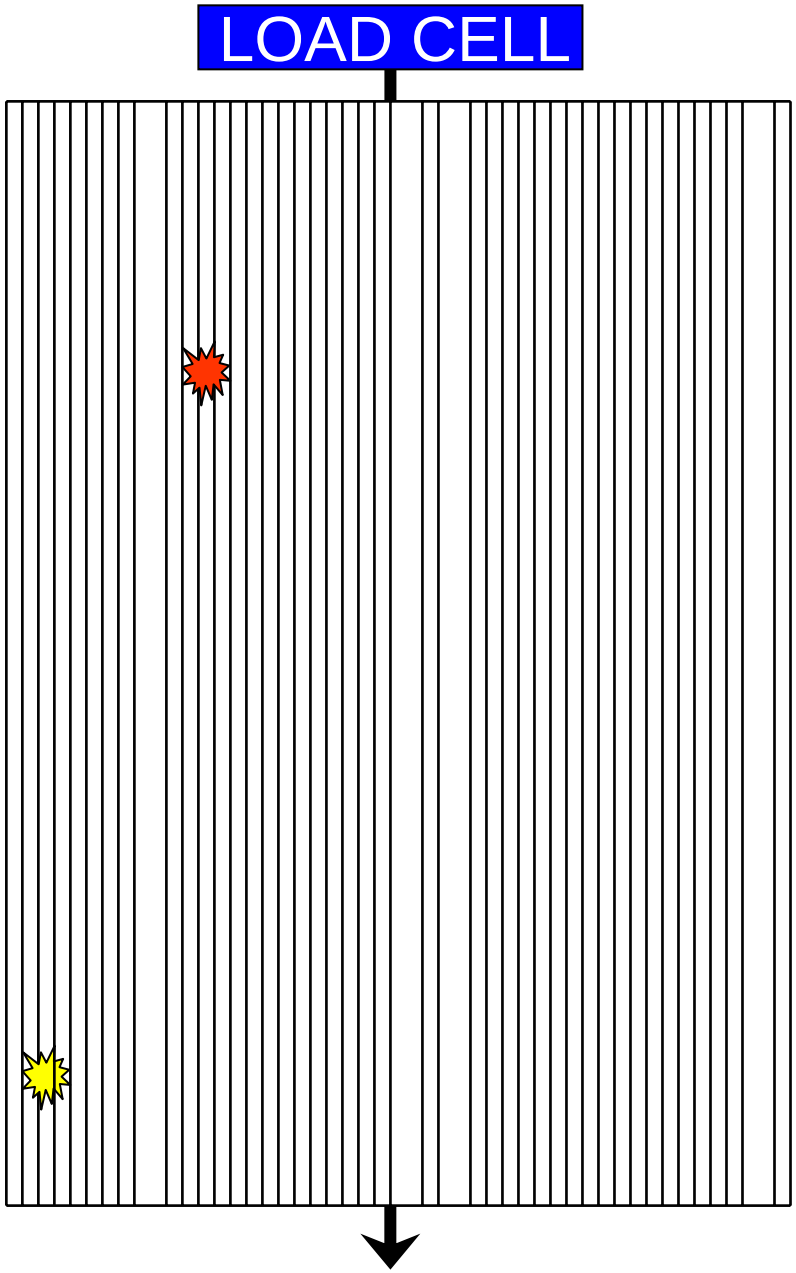

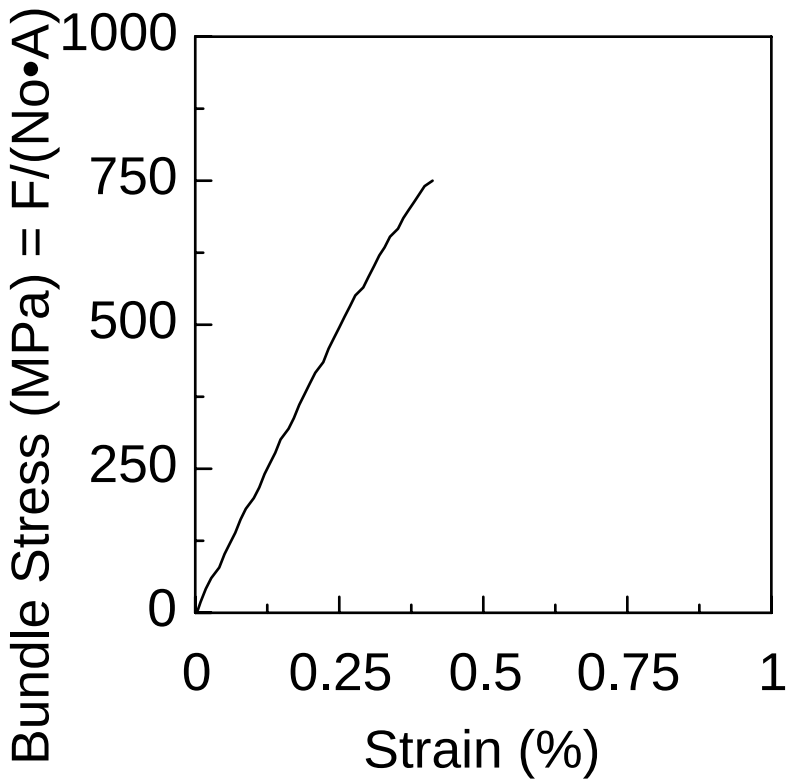

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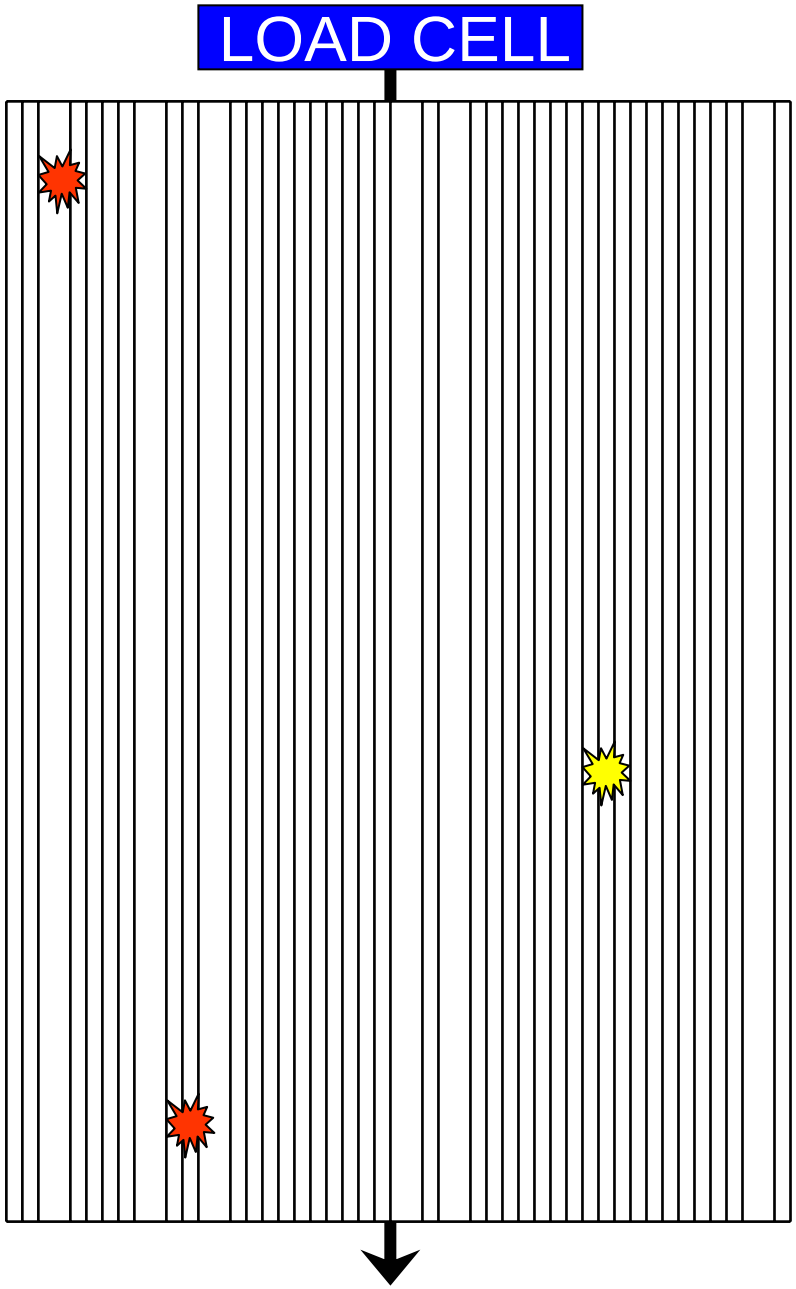

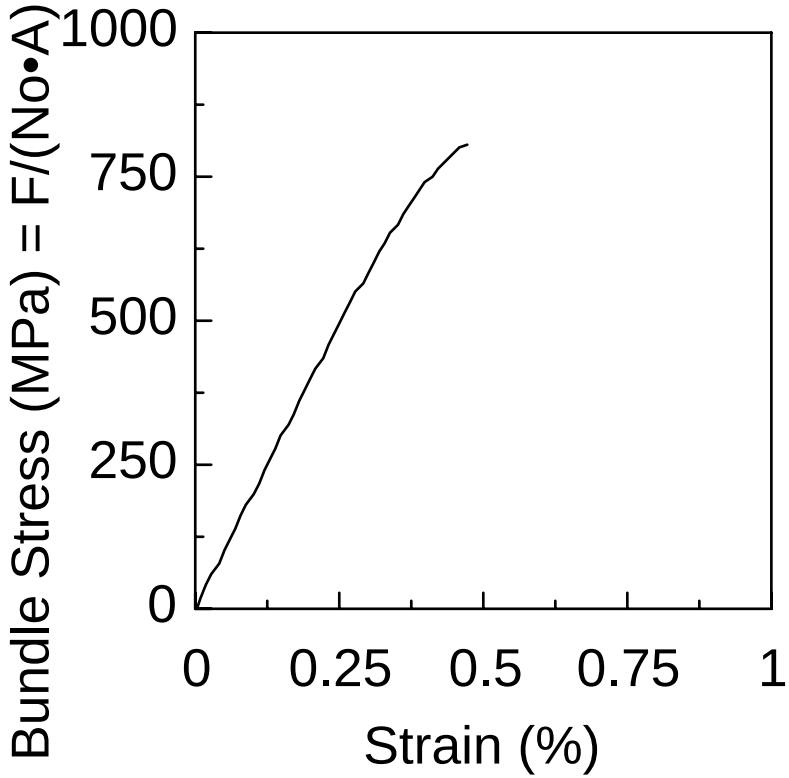

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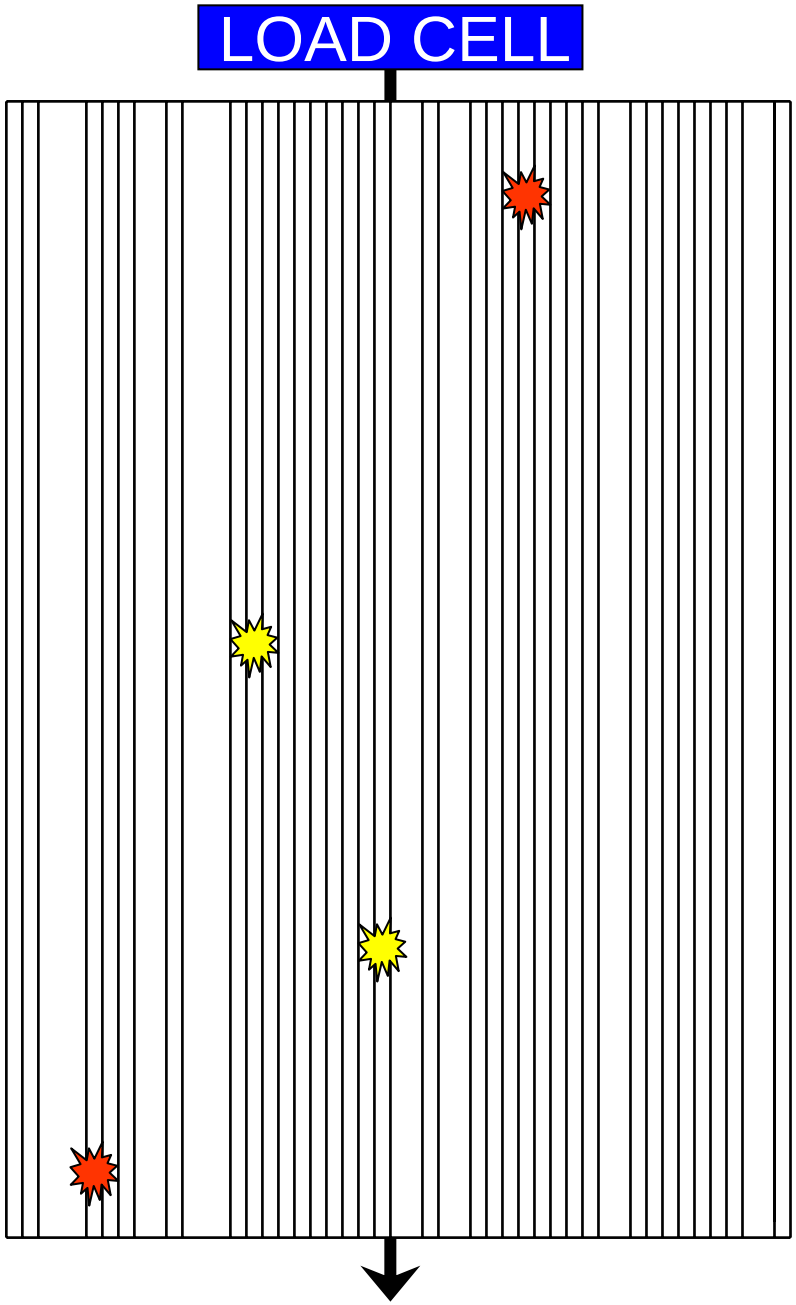

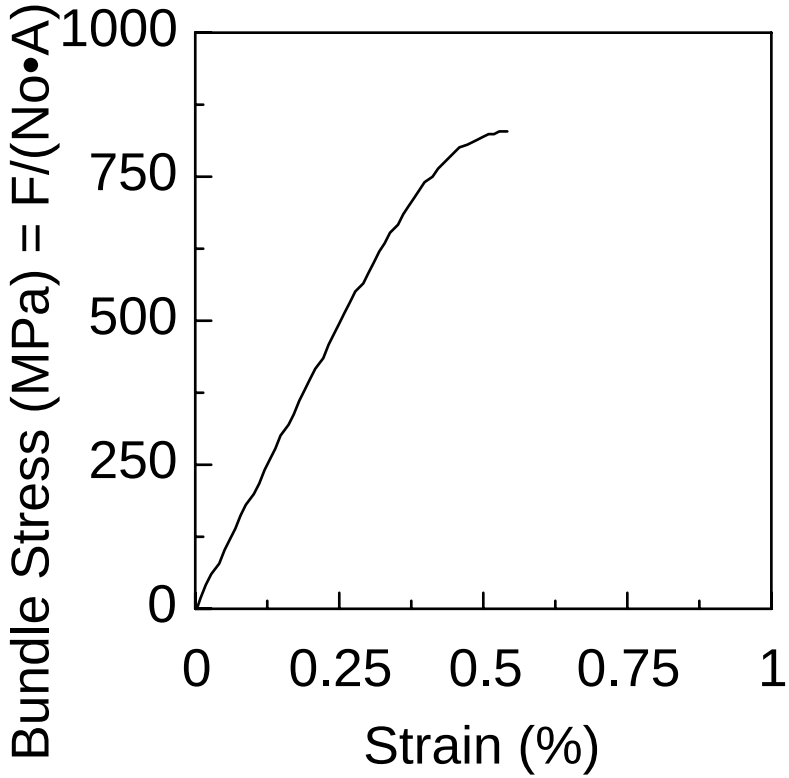

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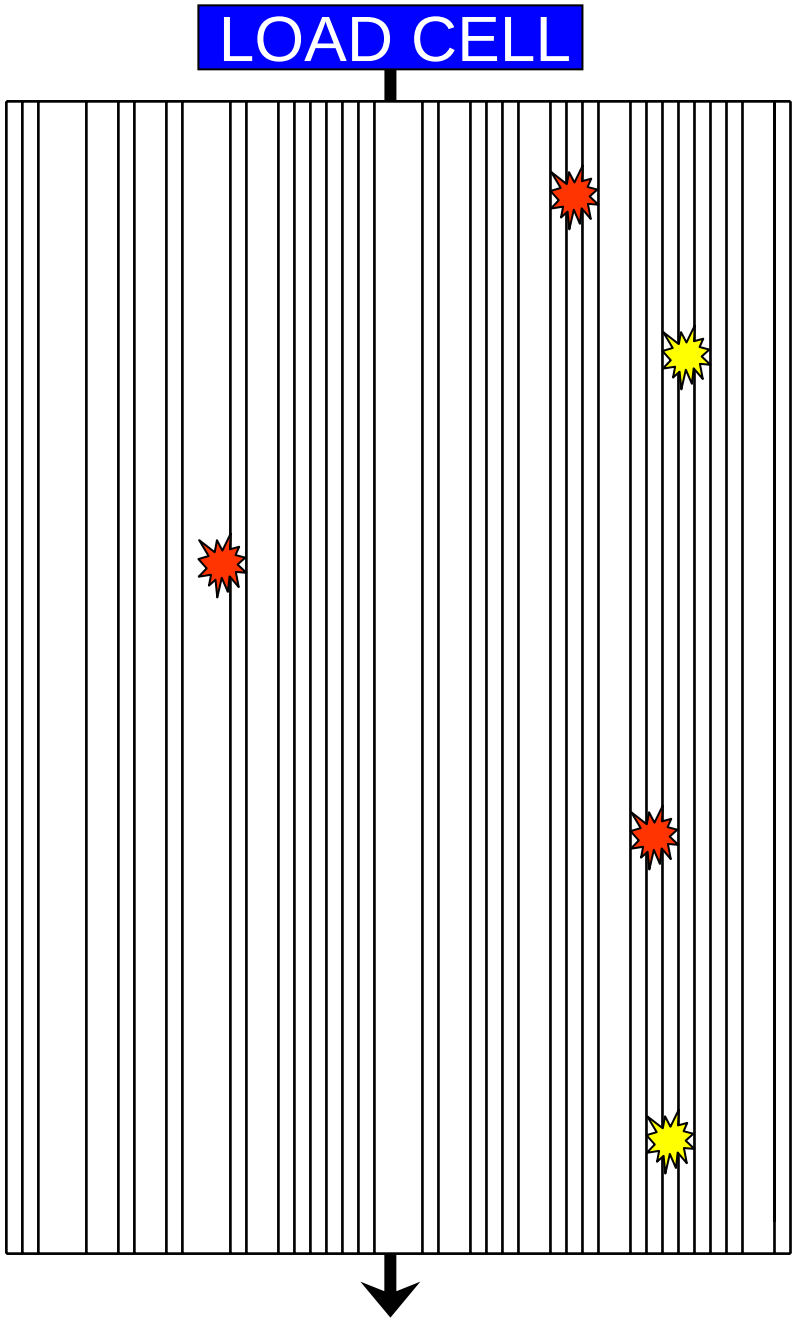

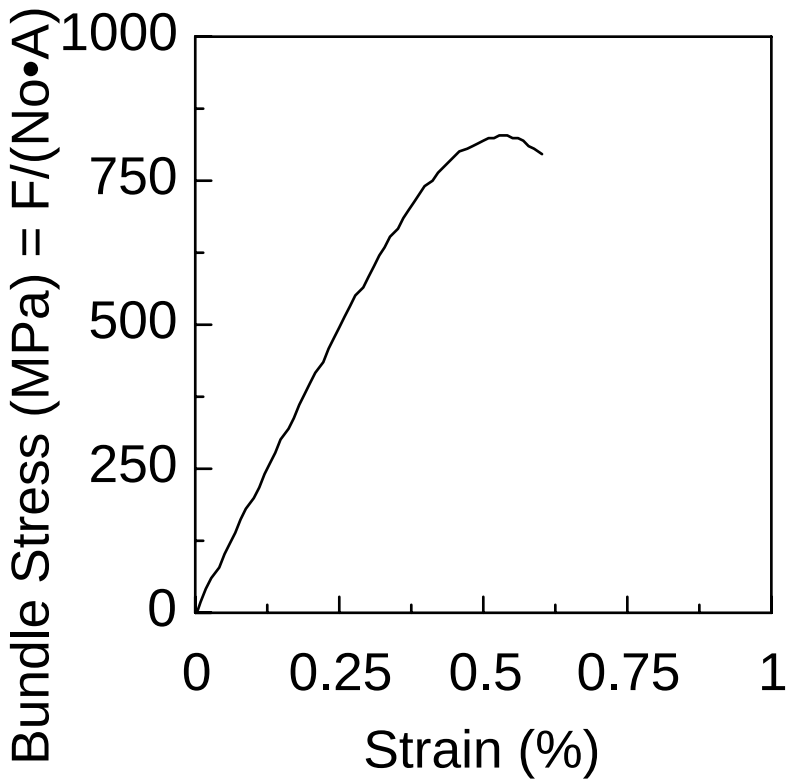

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CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

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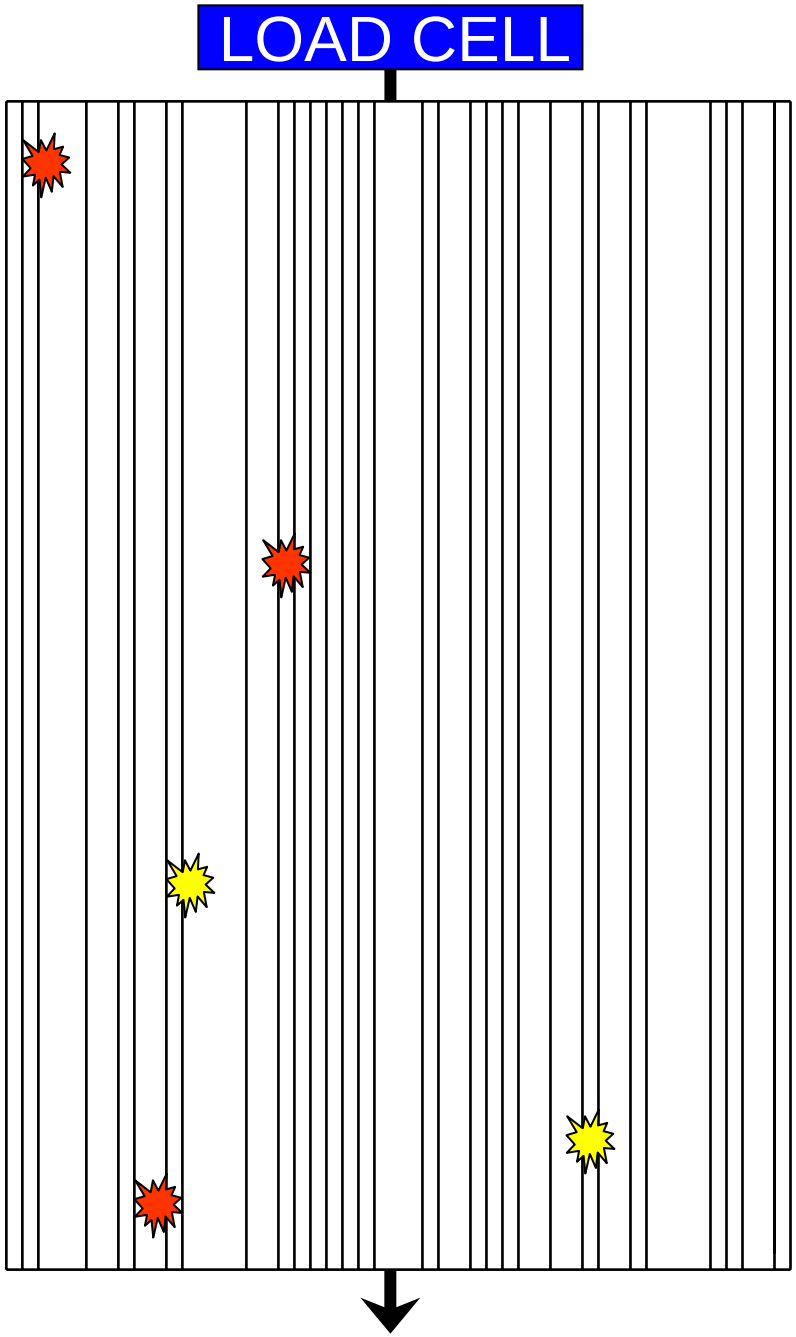

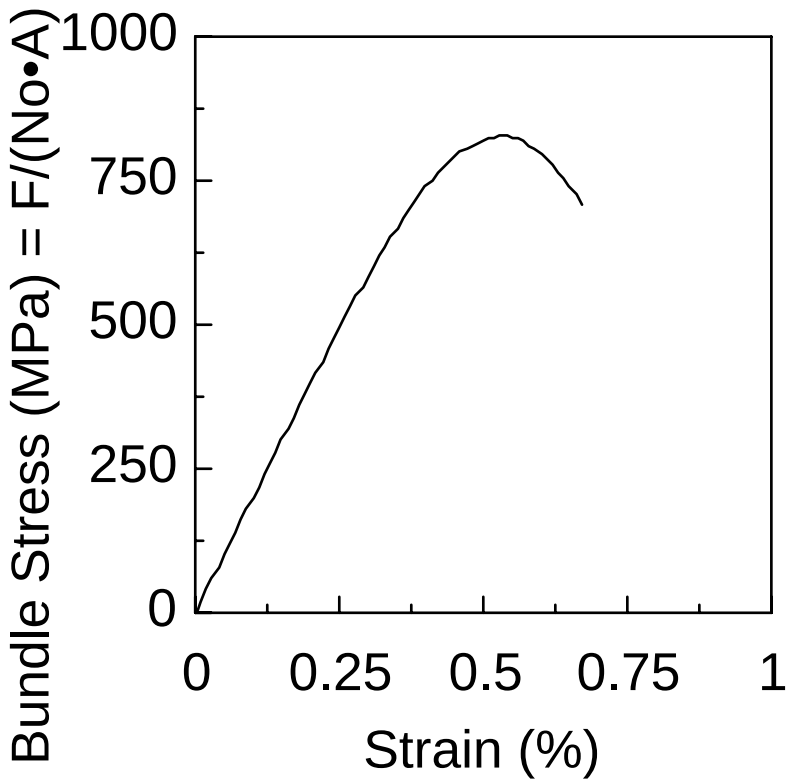

CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

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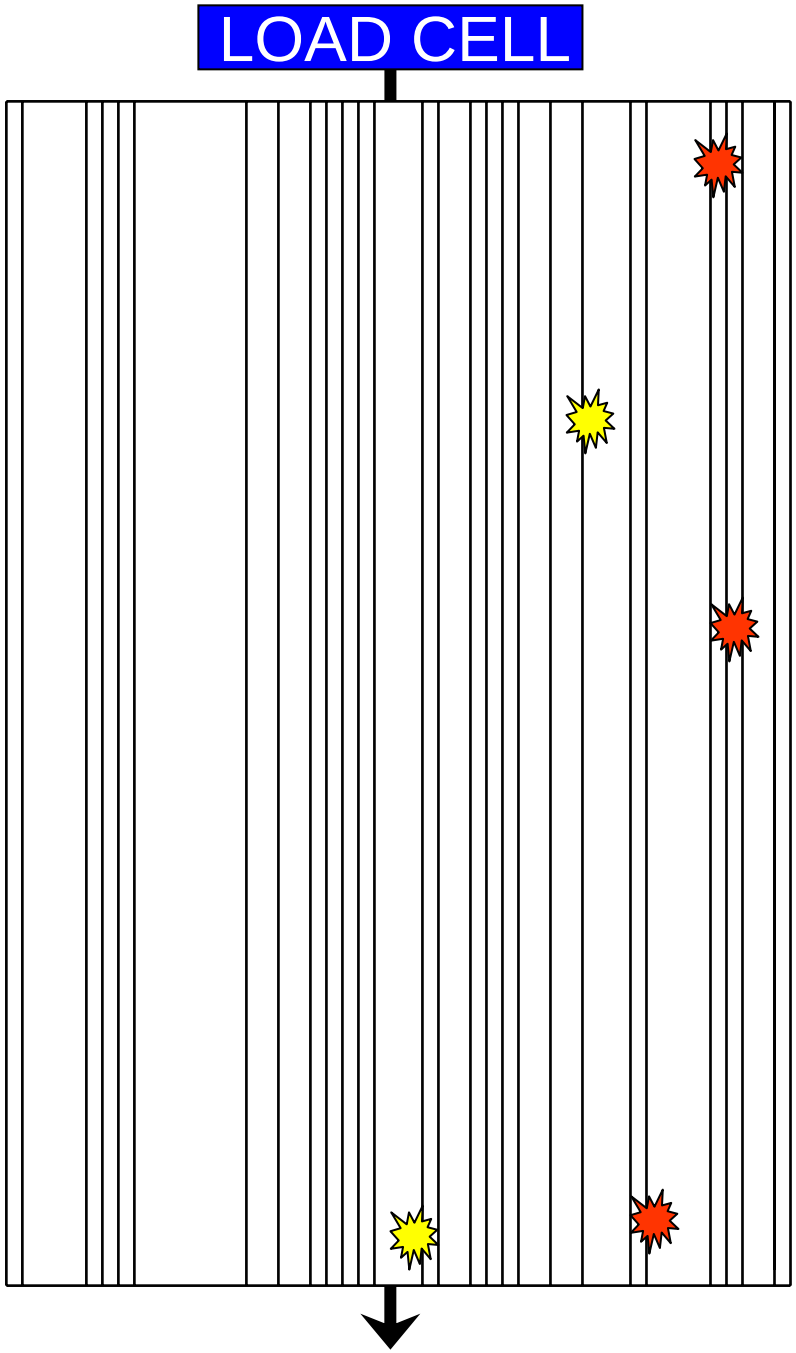
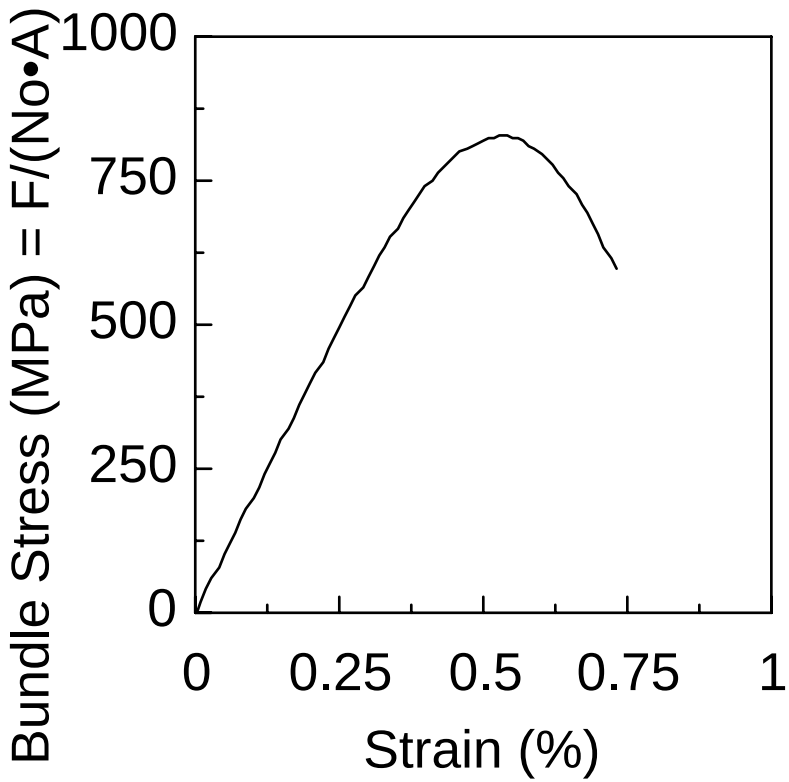
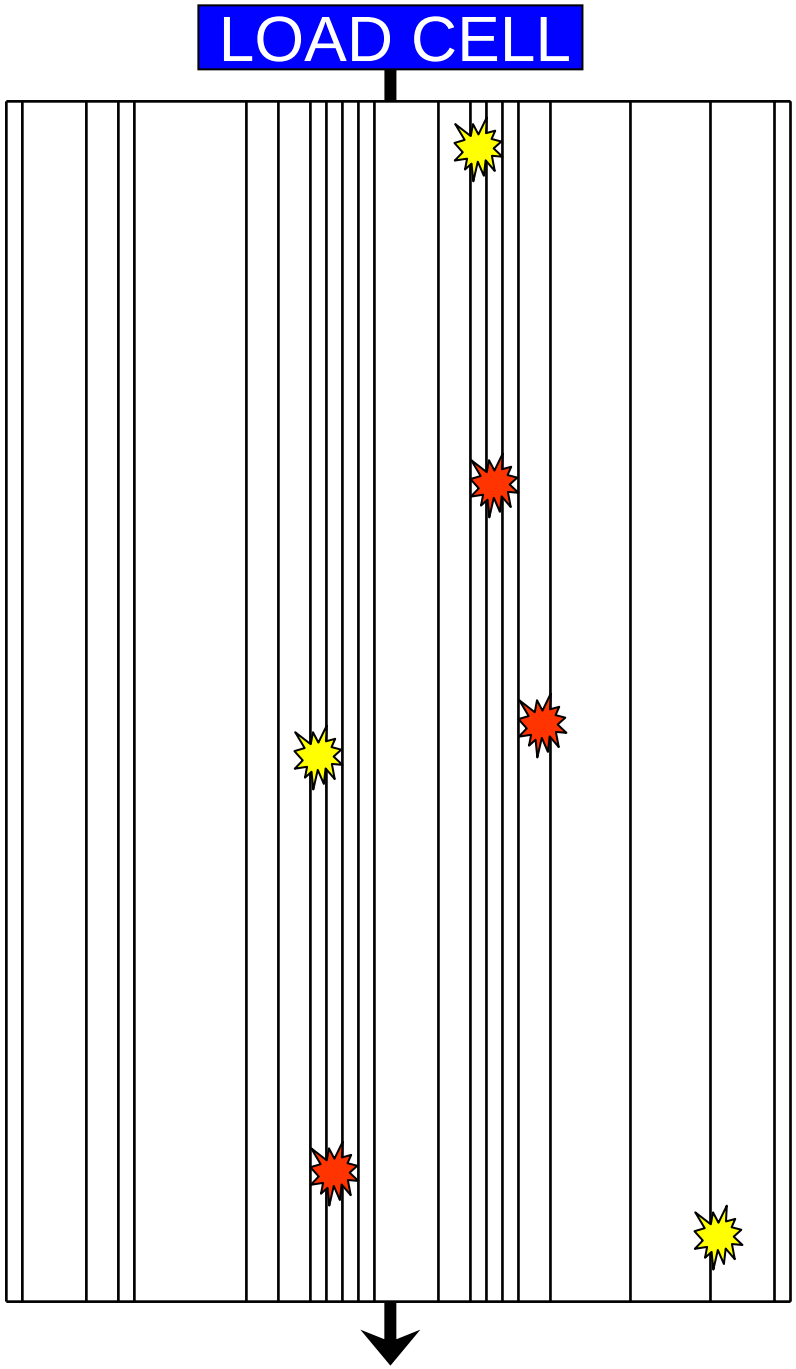
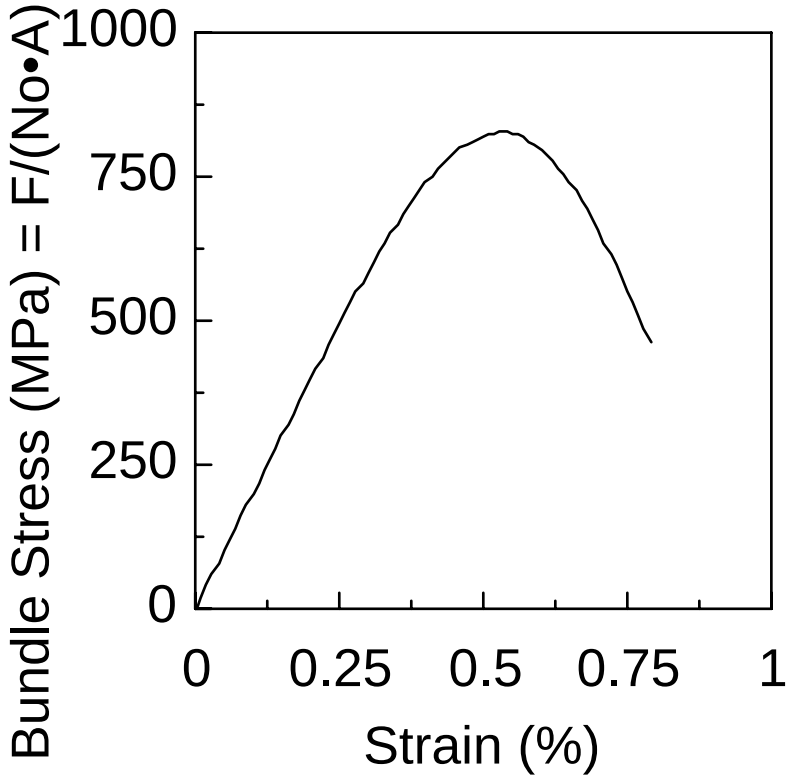

LOAD CELL


Bundle Stress (MPa) = F/(No•A)
1000
750
500
250
0
0
0.25
0.5
0.75
1
Strain (%)





CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

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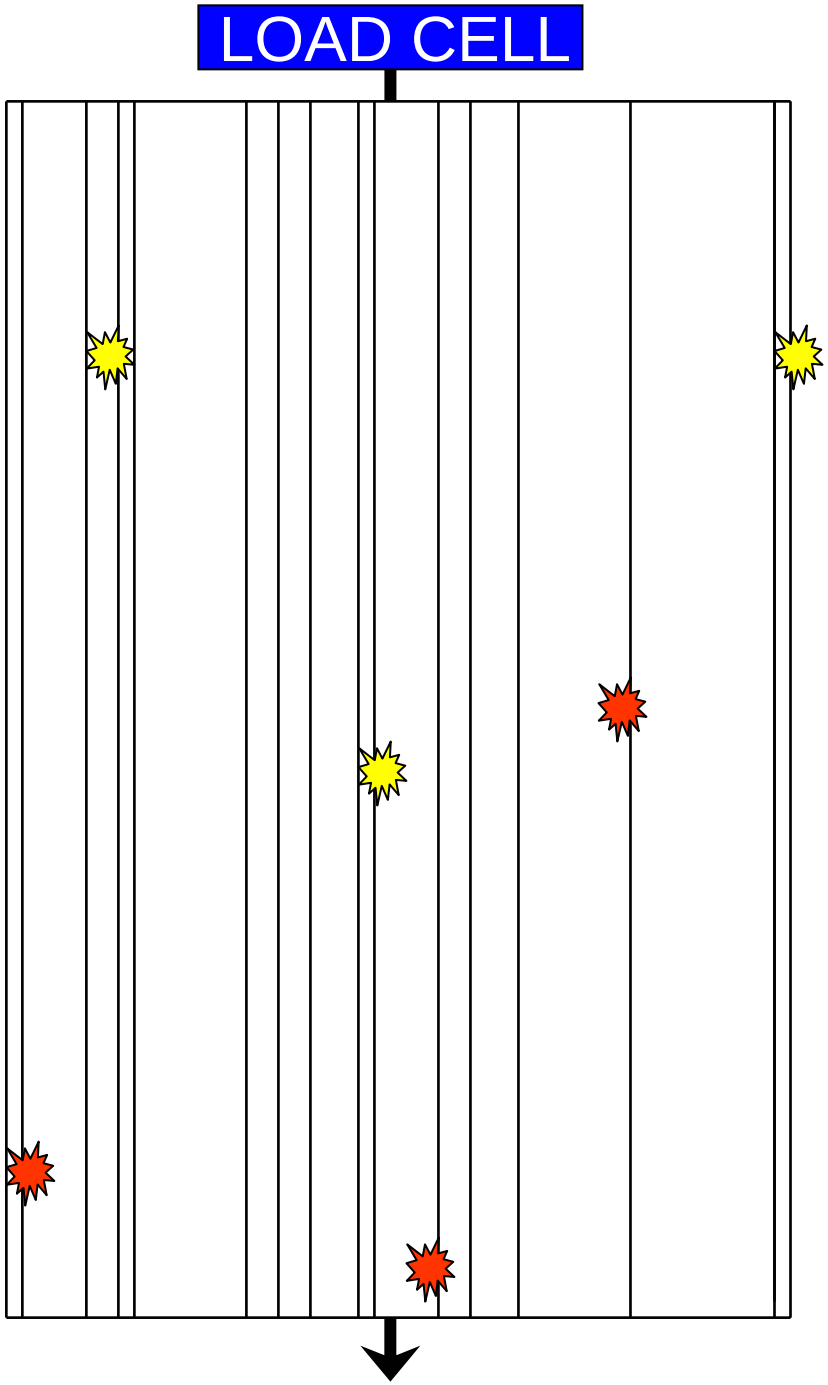

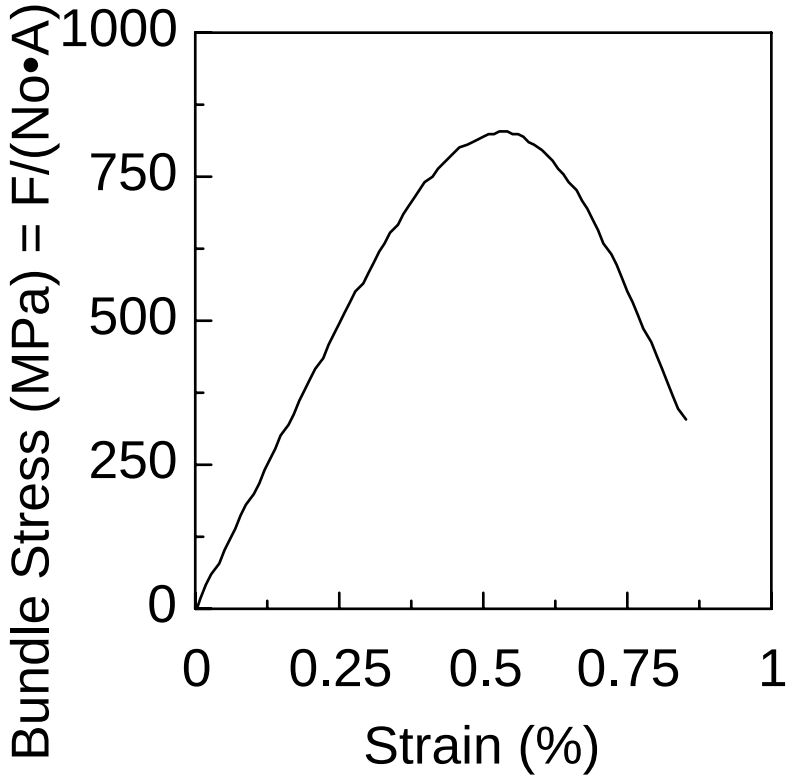

CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

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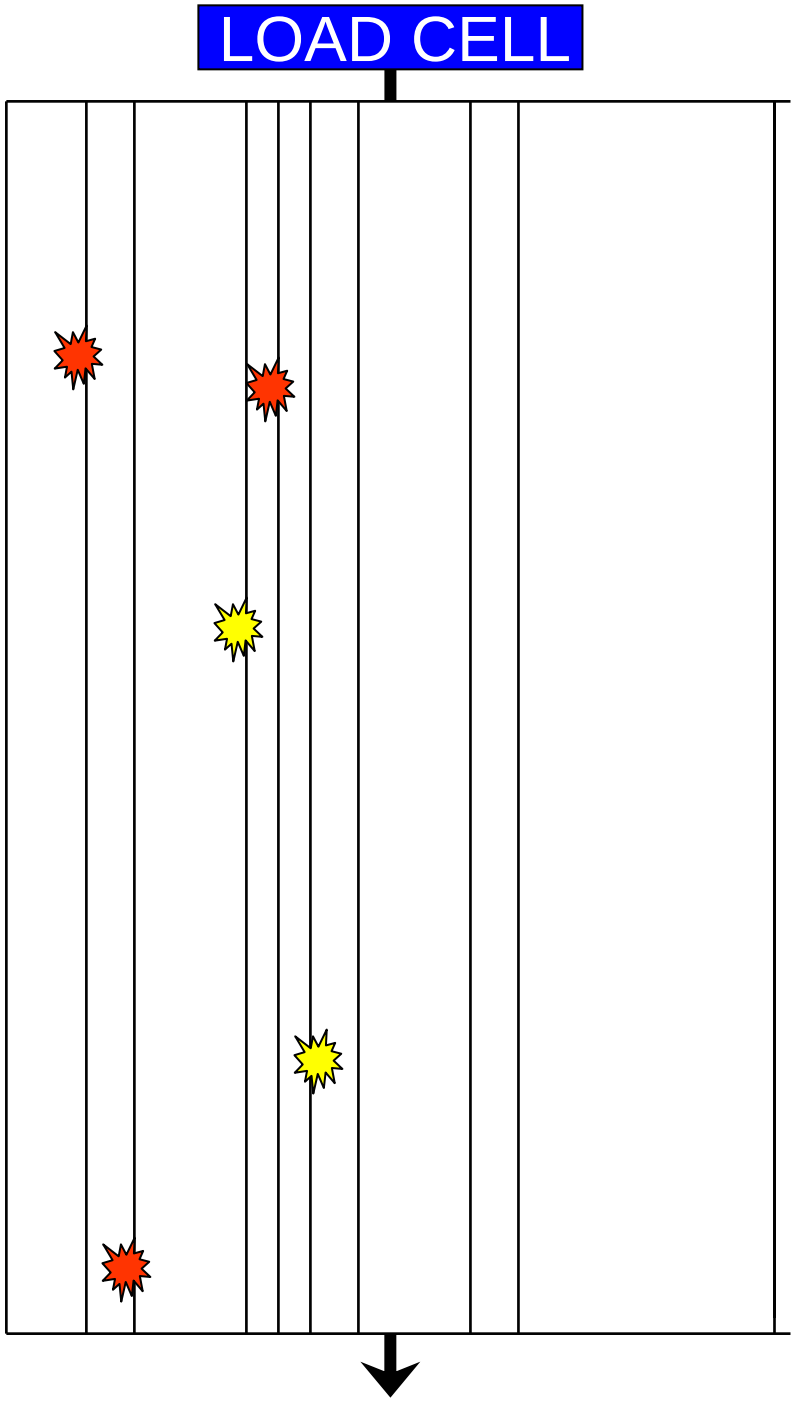

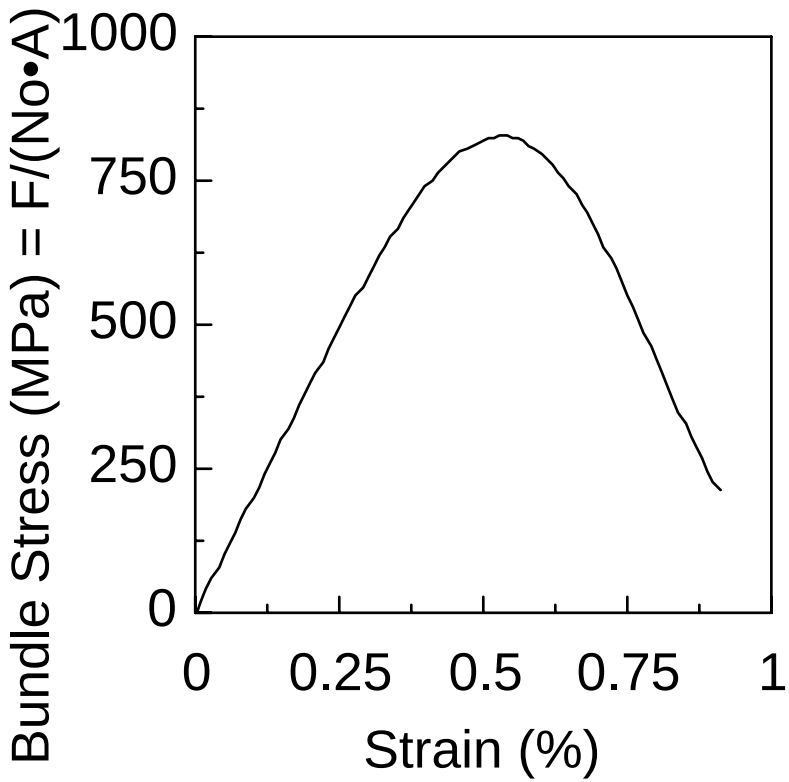

CFCC
CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

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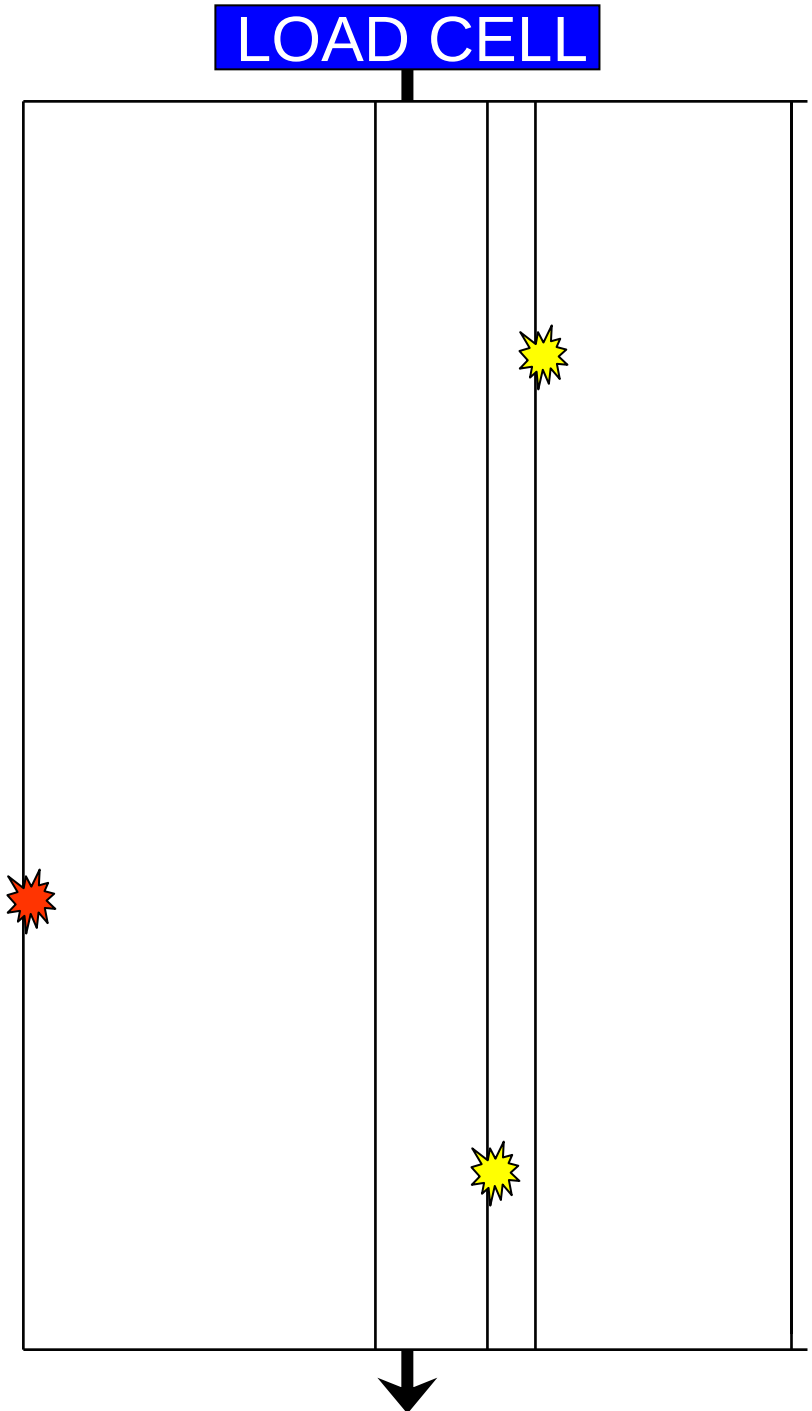

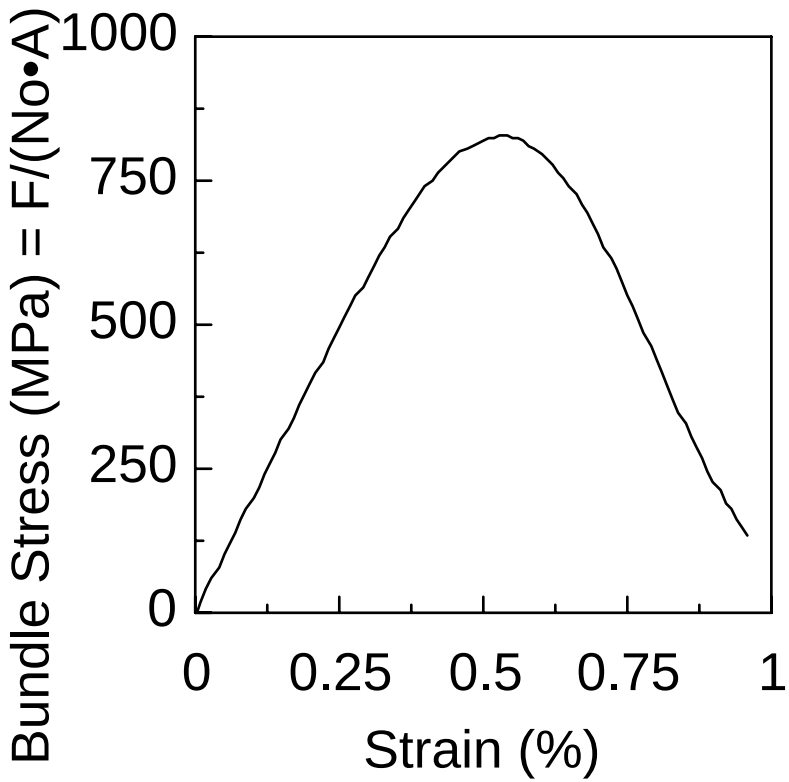

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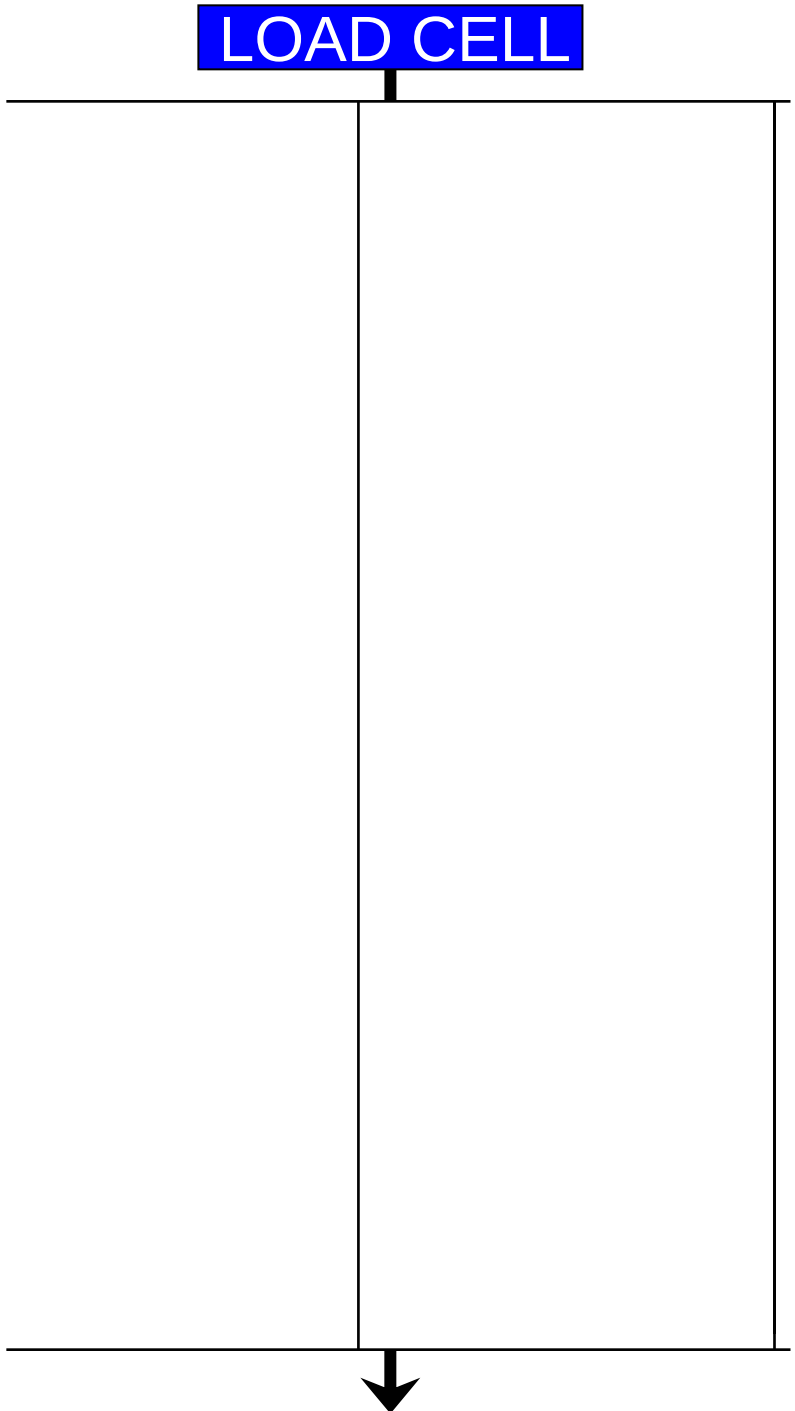

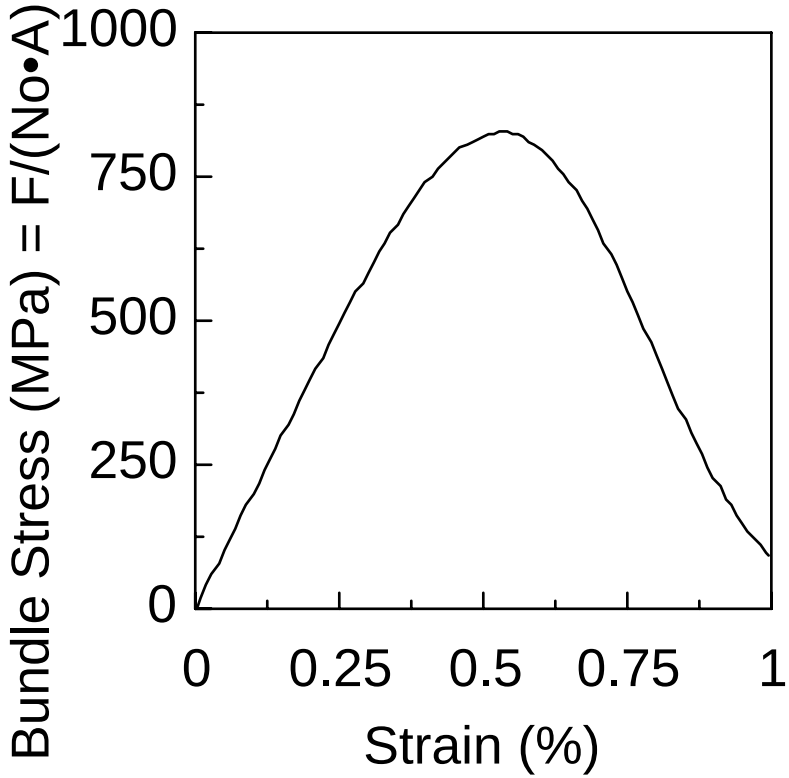

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CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

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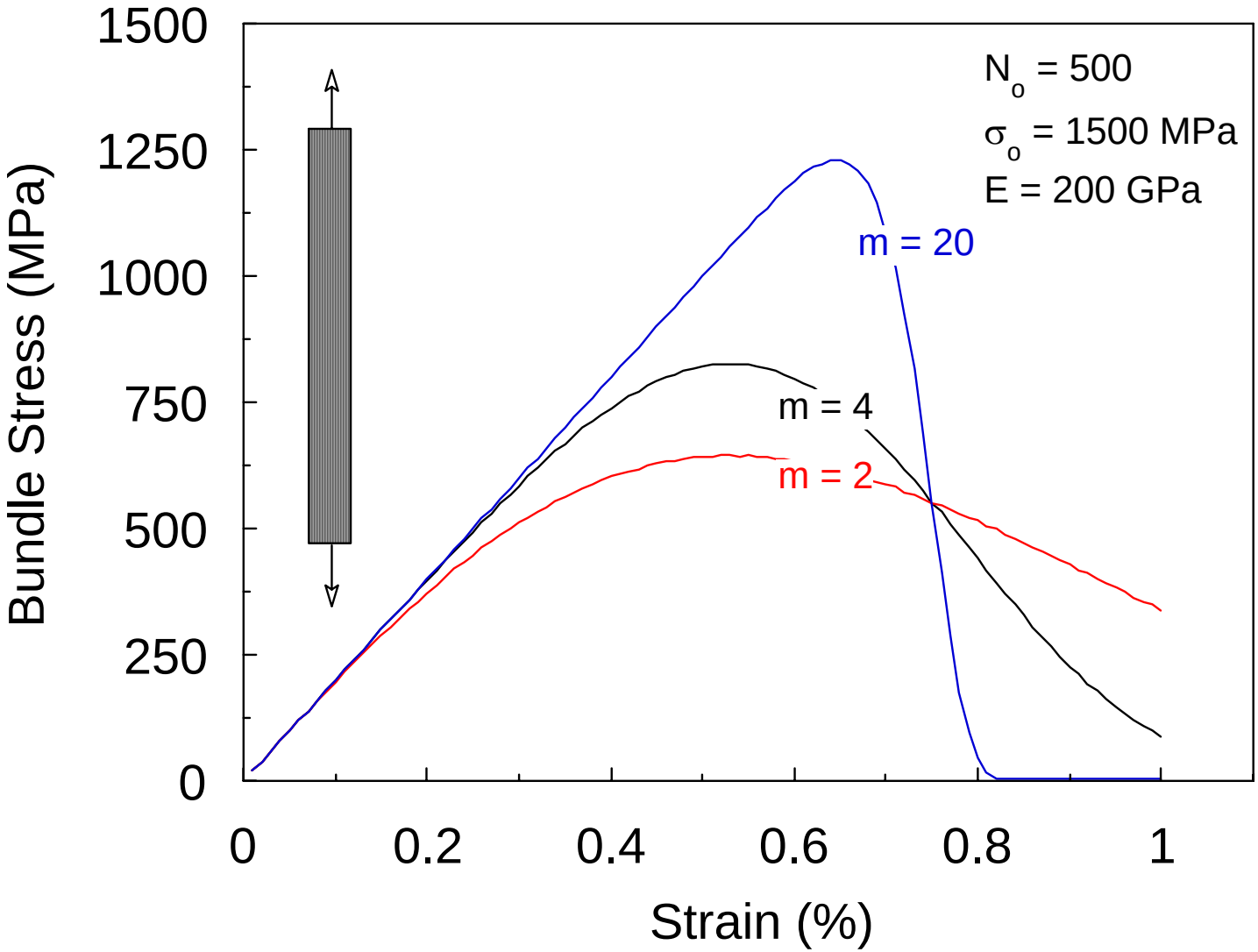
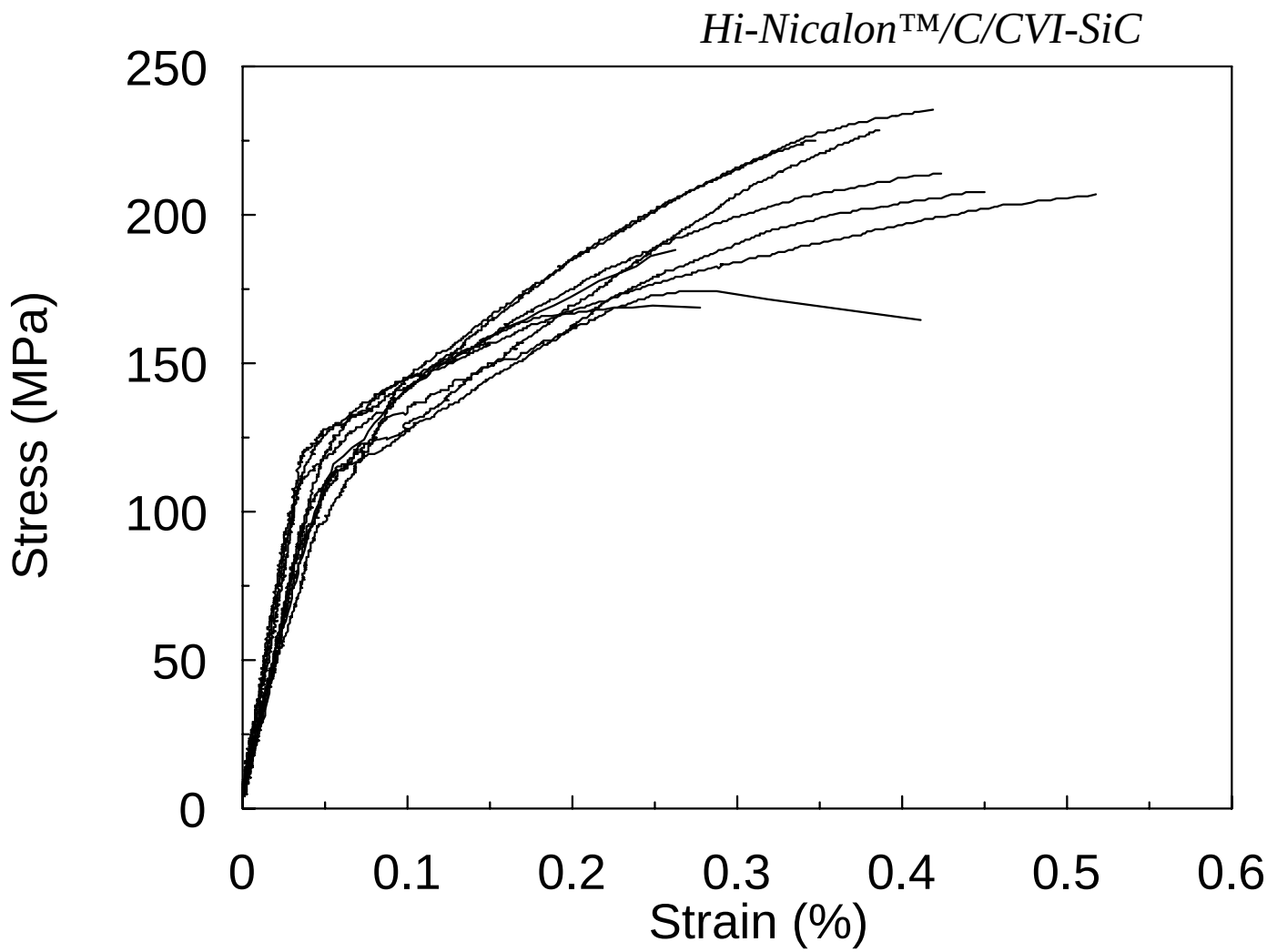


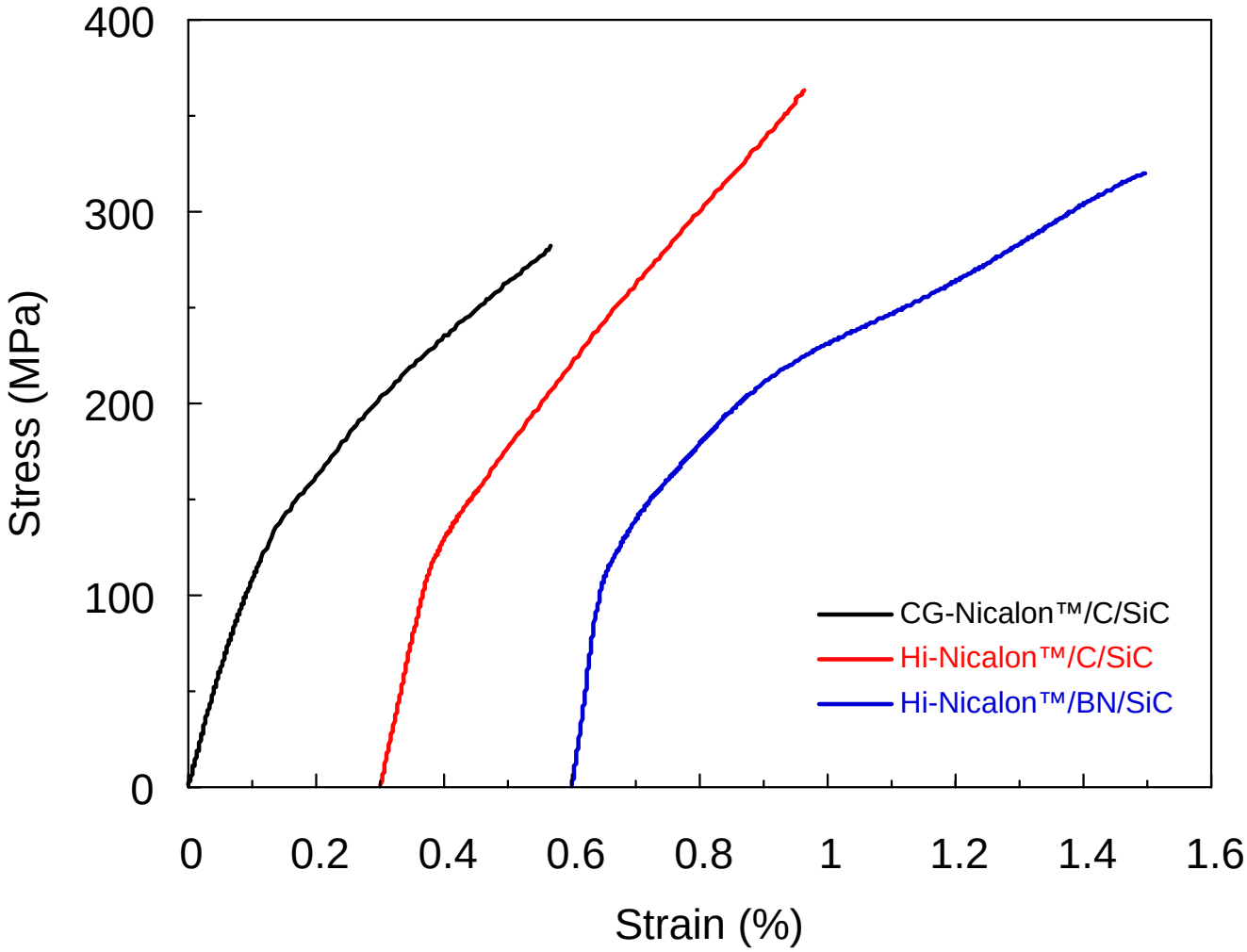
The distribution of fiber strengths is responsible for the "graceful" mode of failure of CFCCs. <u>Therefore, we want strong fibers with low Weibull modulus!</u>

Reproducibility of Tensile Behavior



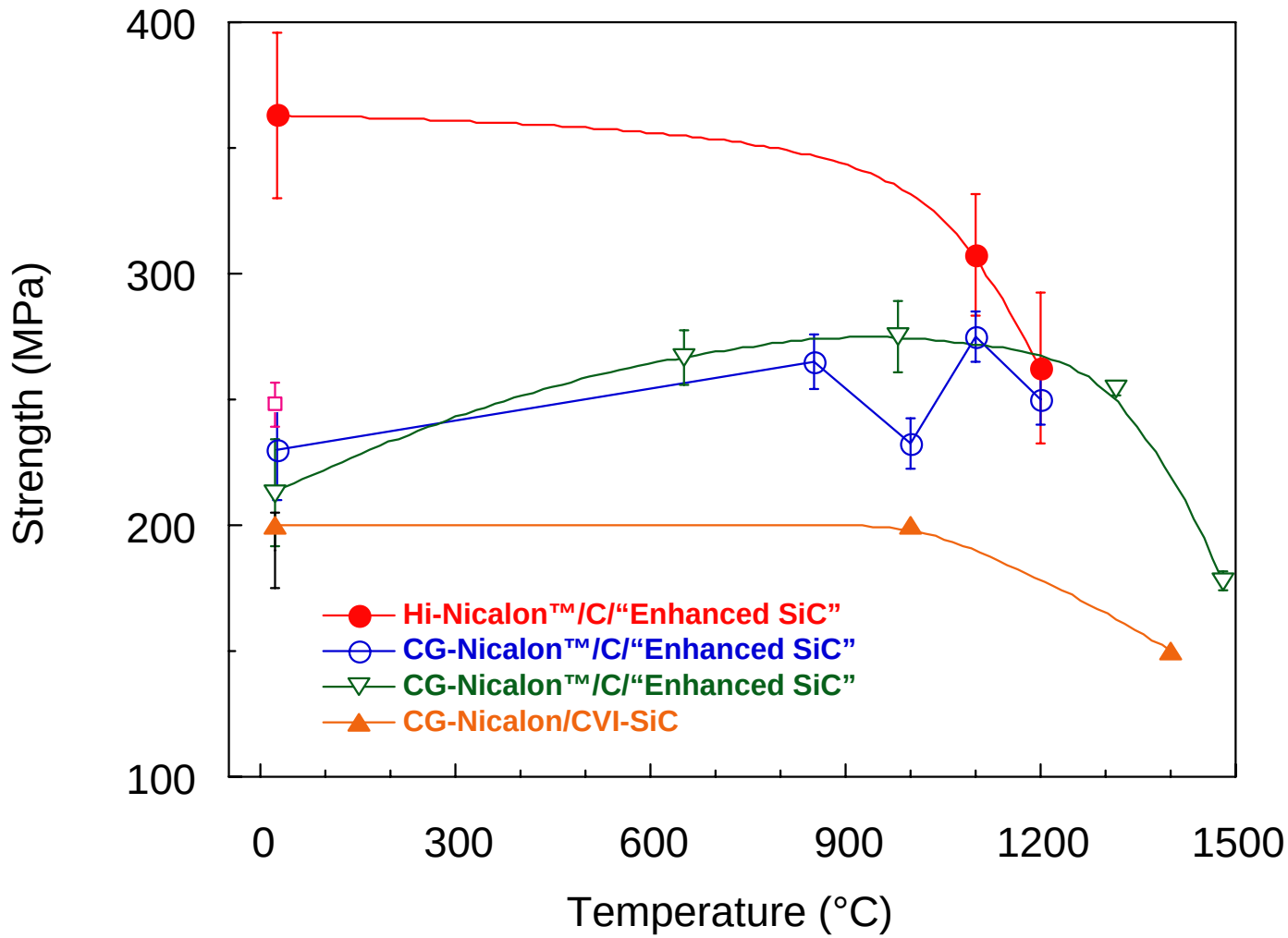
E. Lara-Curzio (2000)

Effect of fiber or interphase on tensile response



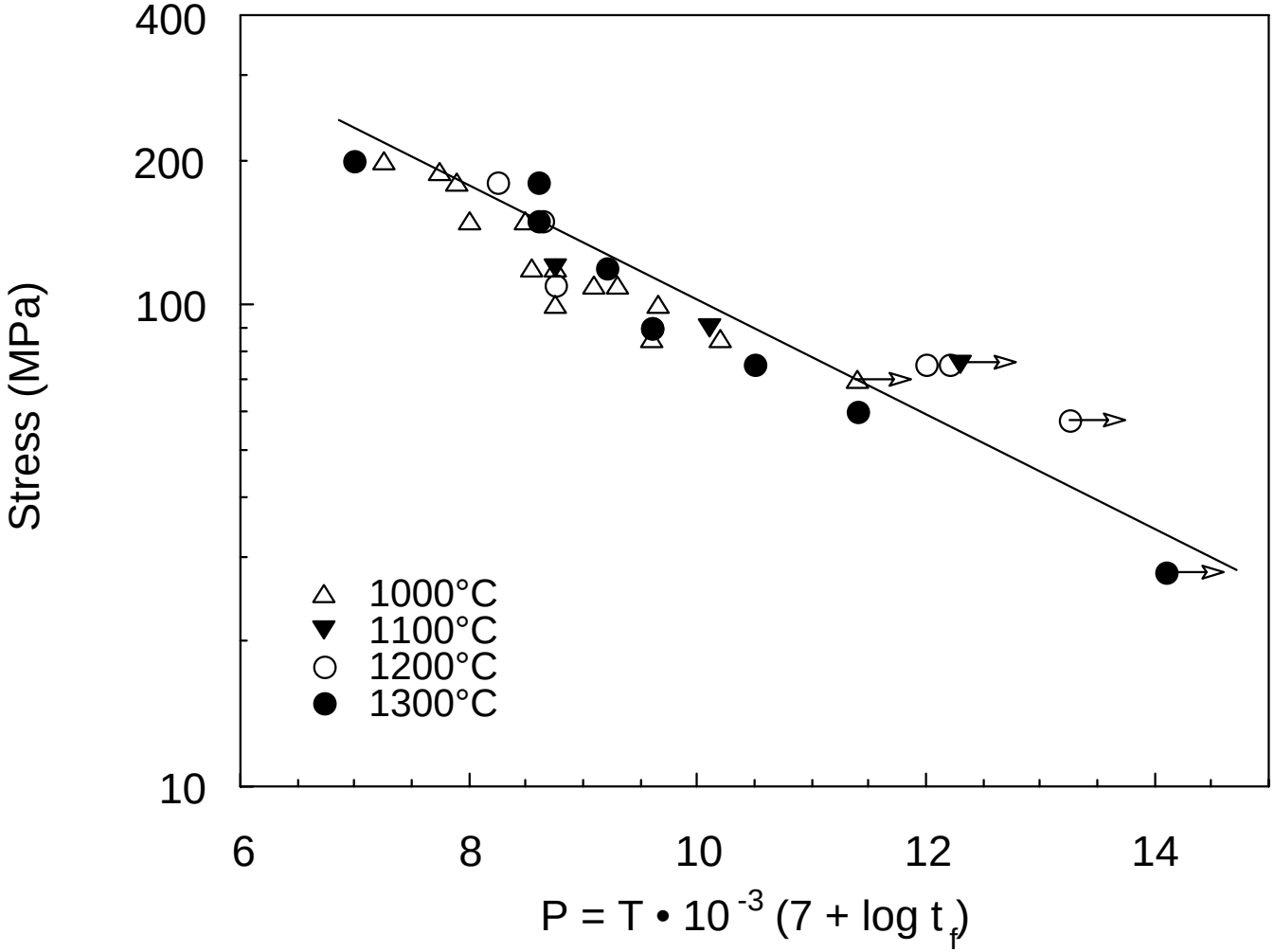
E. Lara-Curzio (2000)

Effect of Temperature on Tensile Strength



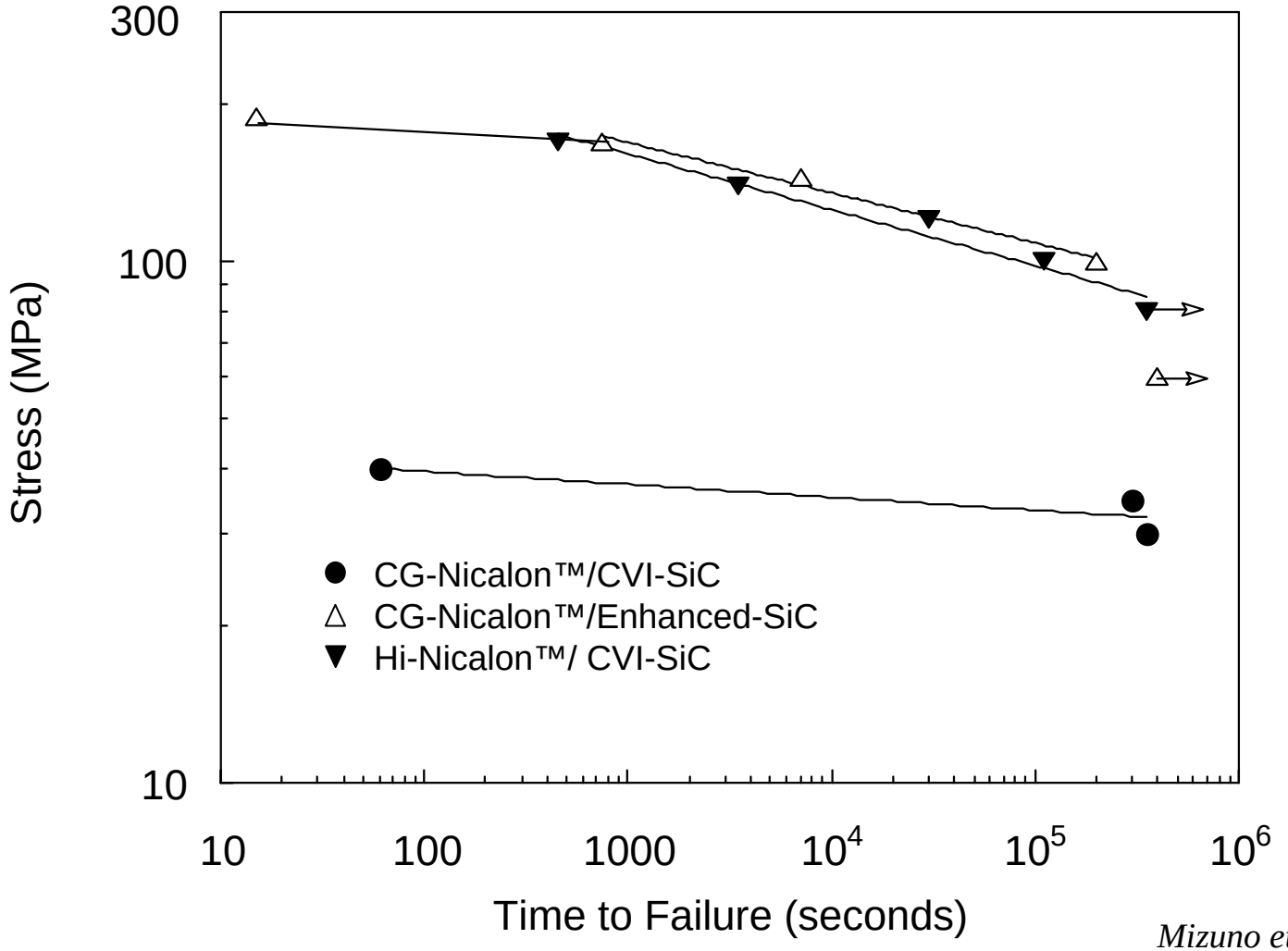
E. Lara-Curzio (2000)

Larson-Miller Plot for CG-Nicalon™/CVI-SiC



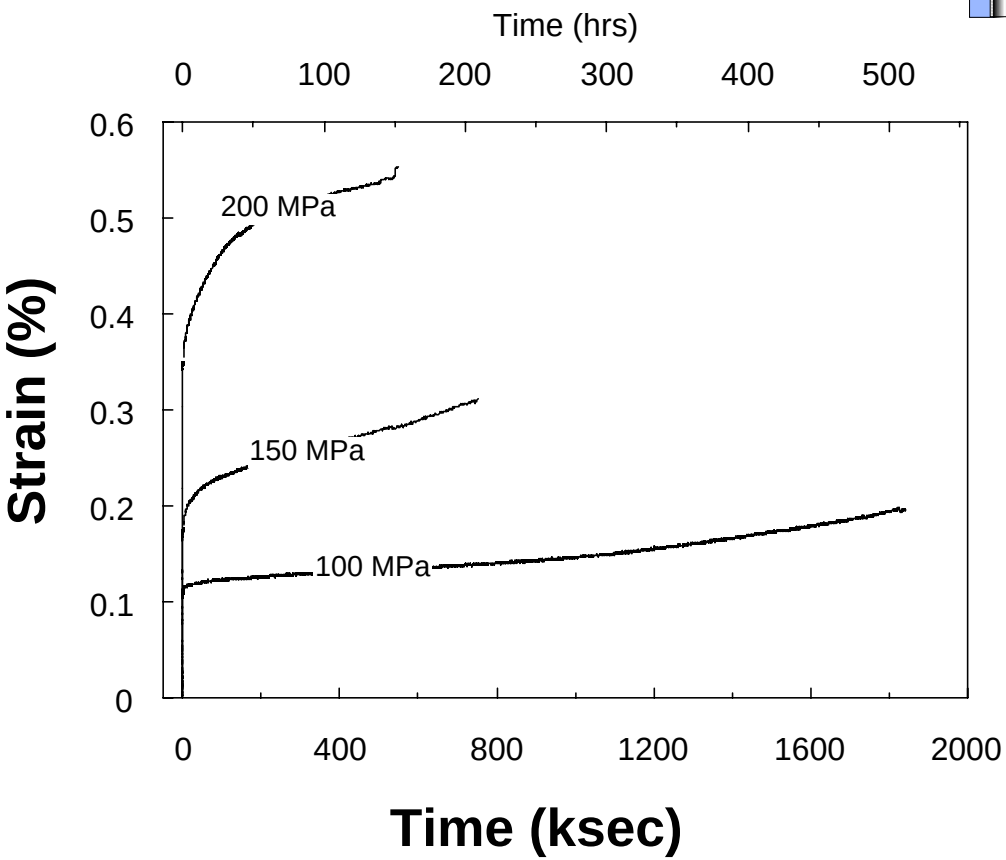
Zhu et al. (1999)

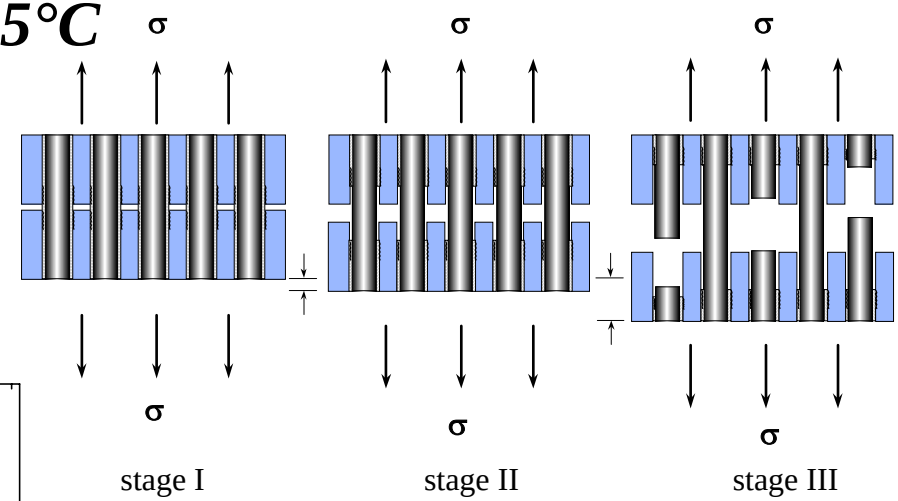
Stress-Rupture: Air/ 1300°C
CVI-SiC Matrix Composites



Mizuno et al. (1998)

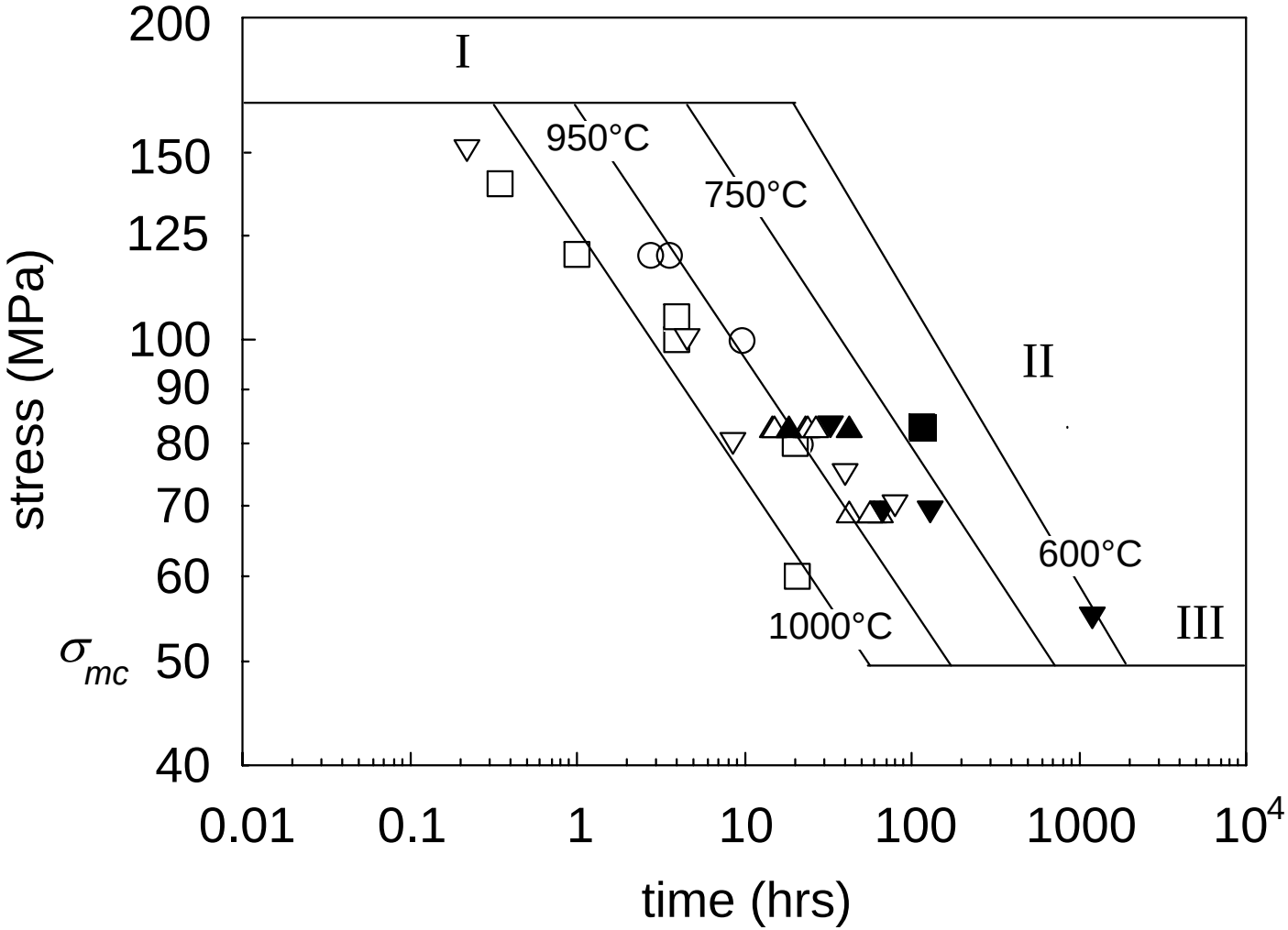
Stress-Rupture Nicalon™/ C /CVI-SiC
Air / 425°C





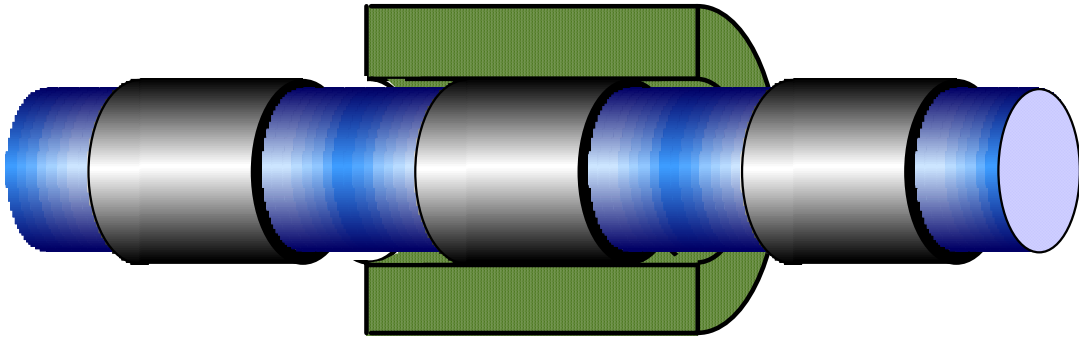
E. Lara-Curzio (1998)

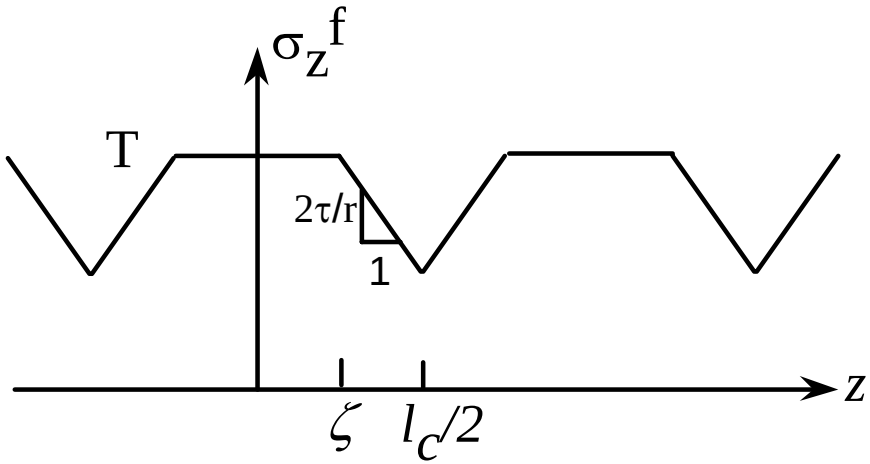
Stress-Rupture in Air
CG-Nicalon™/CVI-SiC



E. Lara-Curzio (2000)

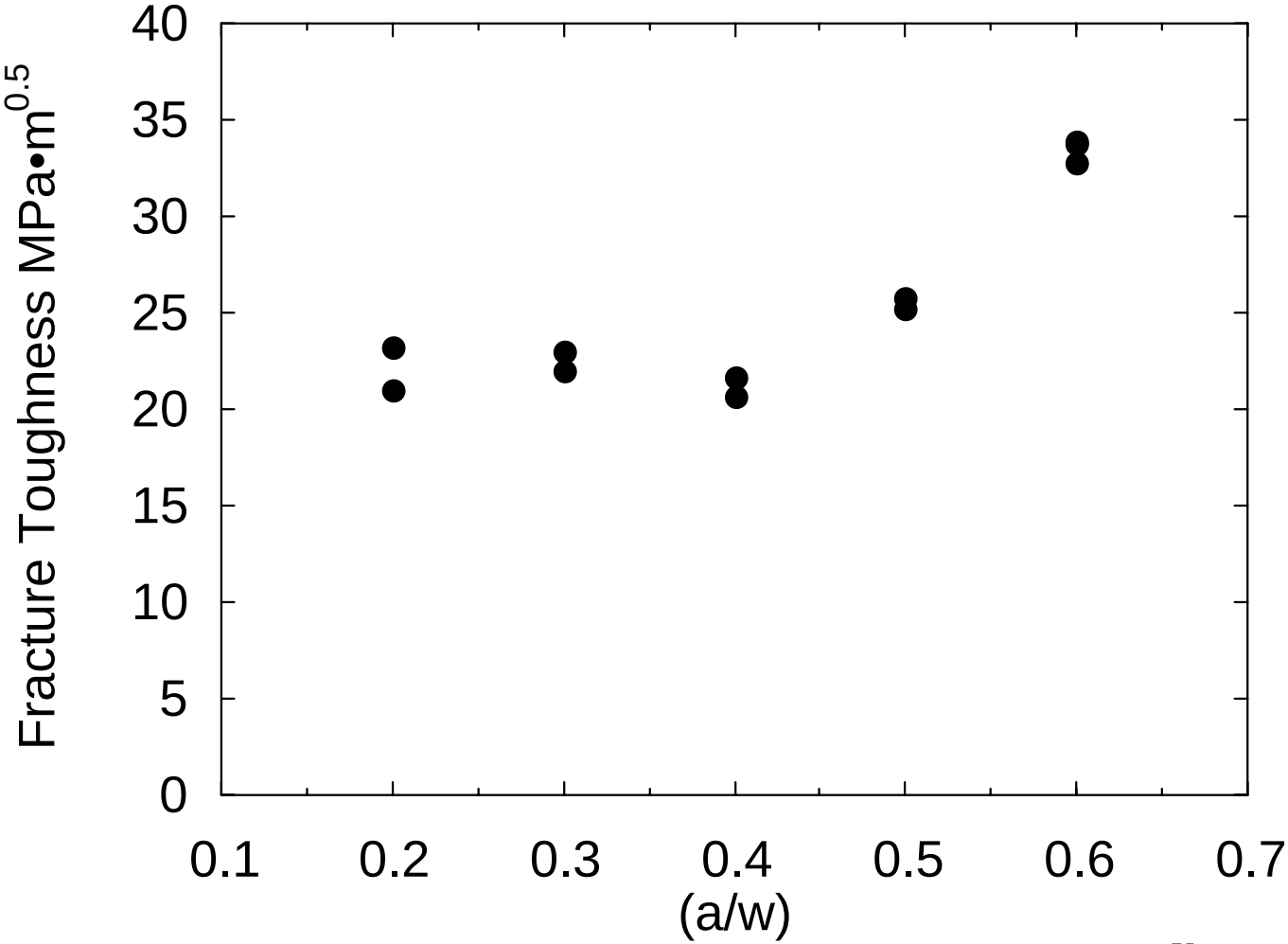
Micromechanical model of stress-rupture incorporating kinetics of oxidation (fiber, interphase), fracture mechanics and stochastic nature of fiber strength





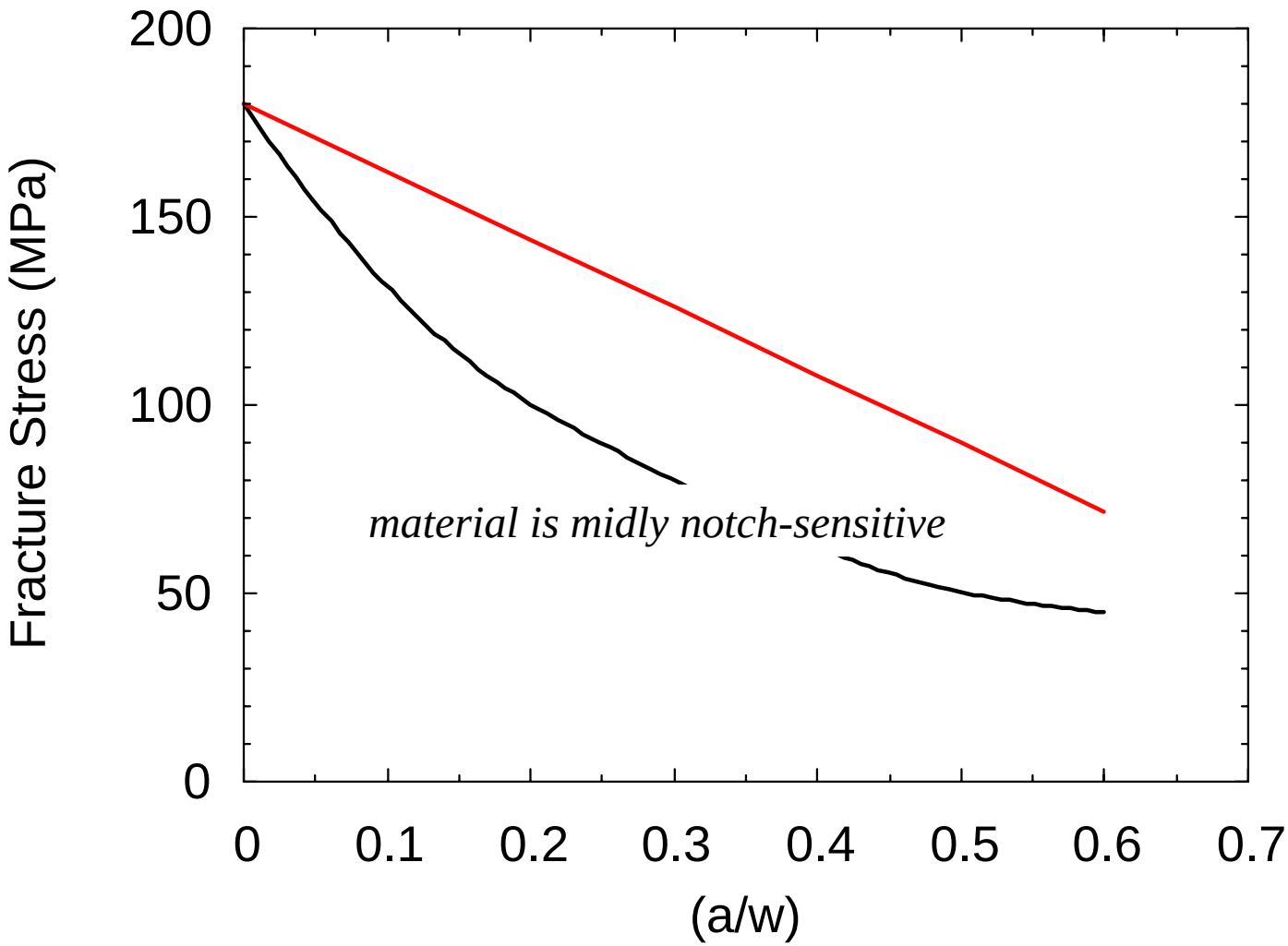
E. Lara-Curzio (2000)

Fracture Toughness: CG-Nicalon™/CVI-SiC

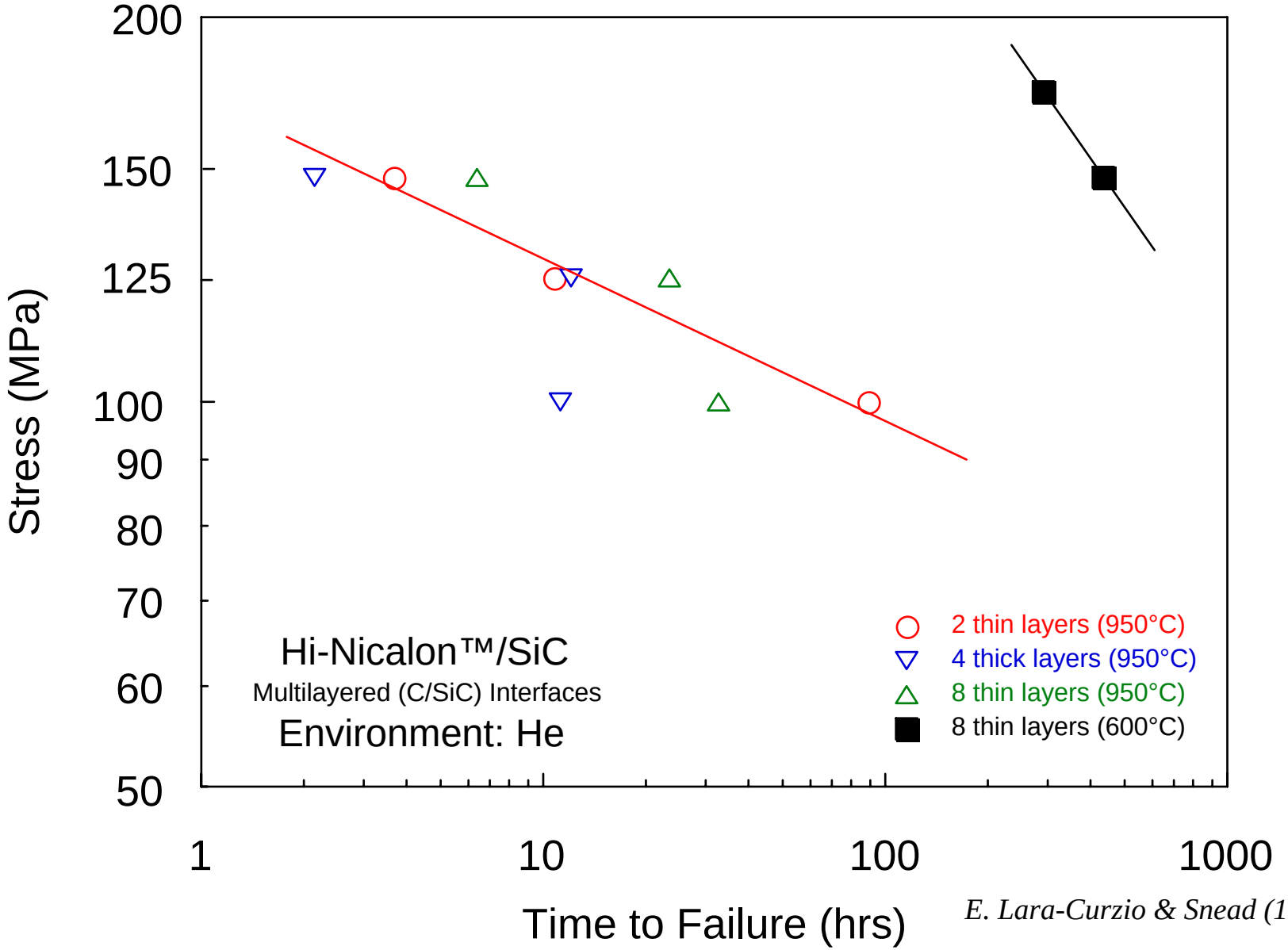


Kagawa (1998)

Notch Sensitivity: CG-Nicalon™/CVI-SiC

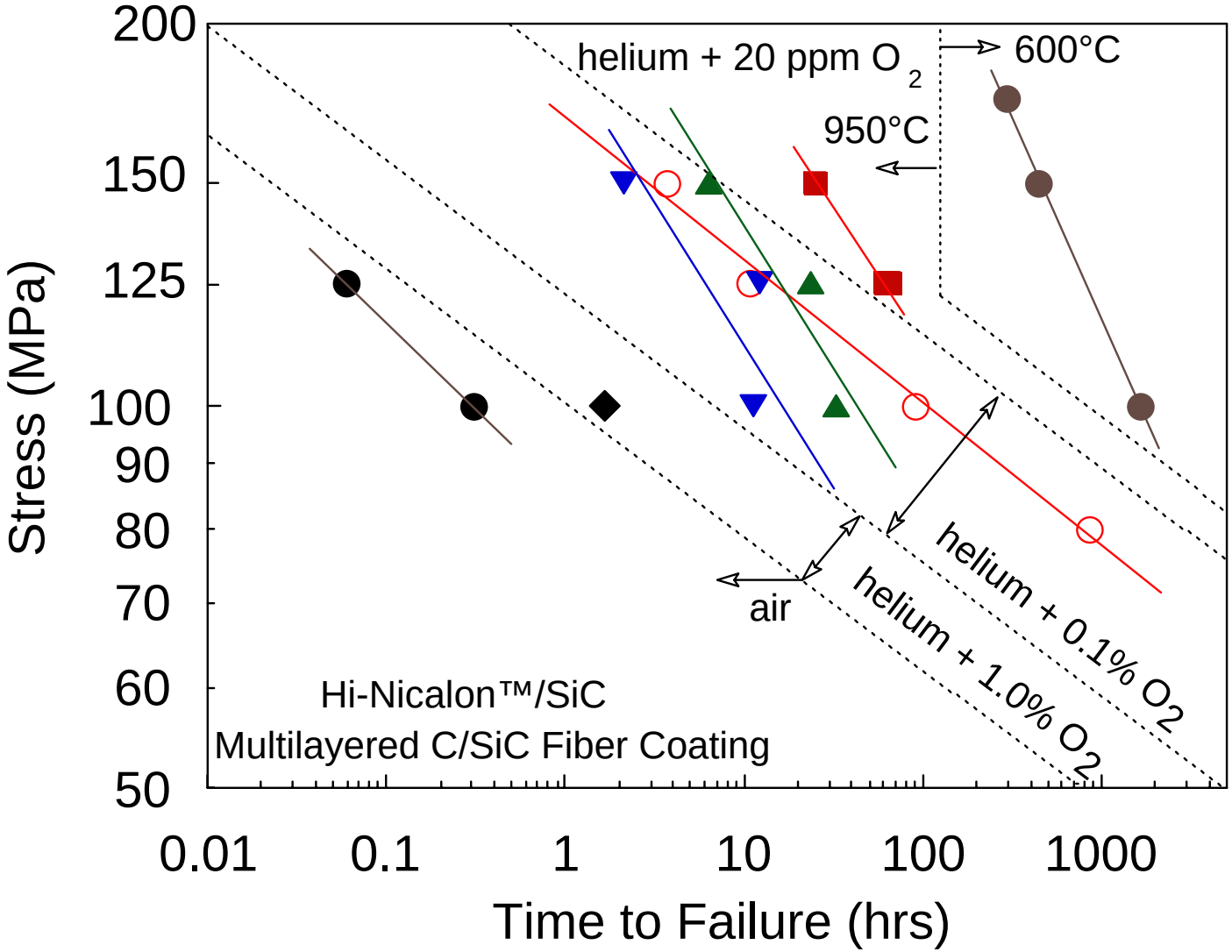


Stress-Rupture in "inert" environment



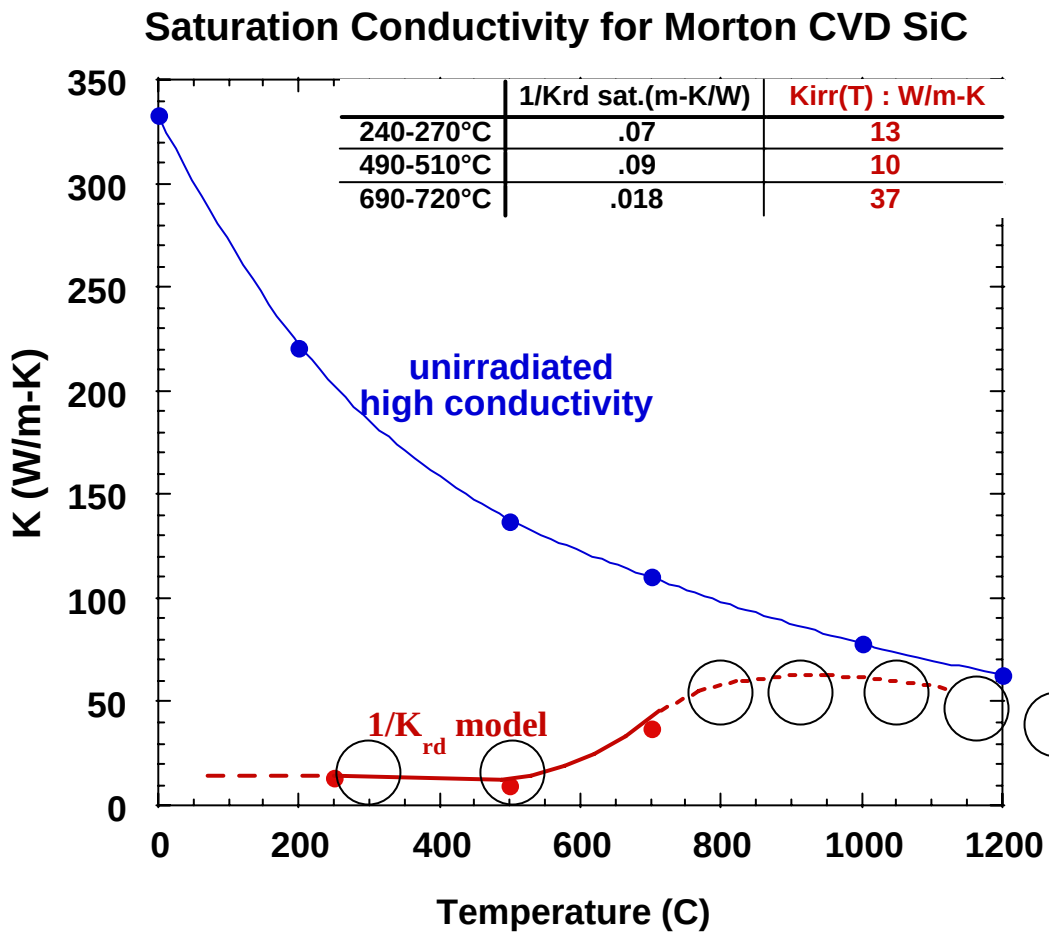
E. Lara-Curzio & Snead (1998)

Stress-Rupture in "inert" environment



E. Lara-Curzio & Snead (1998)

Thermal Defect Resistance for Predicting Conductivity



	1/Krd sat.(m-K/W)	Kirr(T) : W/m-K
240-270°C	.07	13
490-510°C	.09	10
690-720°C	.018	37

$$\frac{1}{K_{irr}(T)} = \frac{1}{K_{unirr}(T)} + \frac{1}{K_{rd}(T)}$$

For composites, add resistance of cracks and interfaces

14J
METS
Others

- Maximum thermal conductivity can be estimated for any material based on $1/K_{rd}$ measured from an "ideal" material.

- Maximum irradiated thermal conductivity for SiC is estimated to be ~ 10 W/m-K at 500°C, ~37 W/m-K at 700°C.

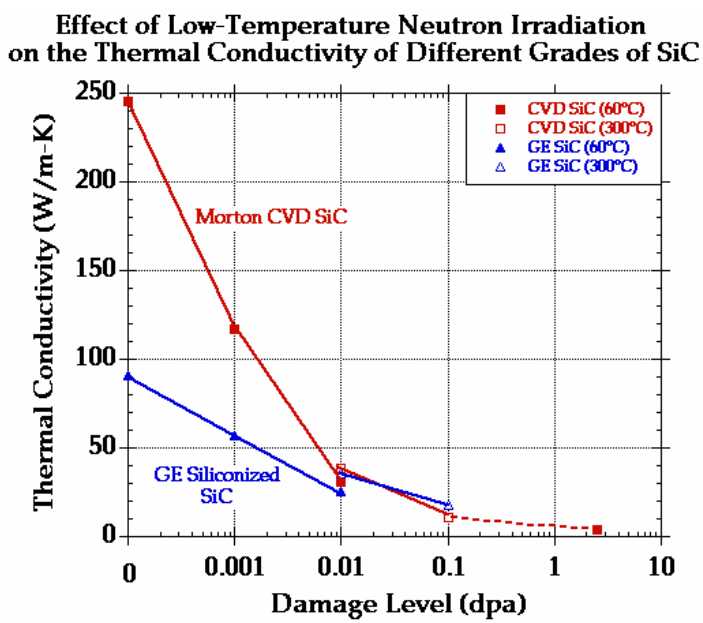
Physics of phonon transport & scattering are being investigated in neutron-irradiated ceramics (ORNL and Merrimack College)

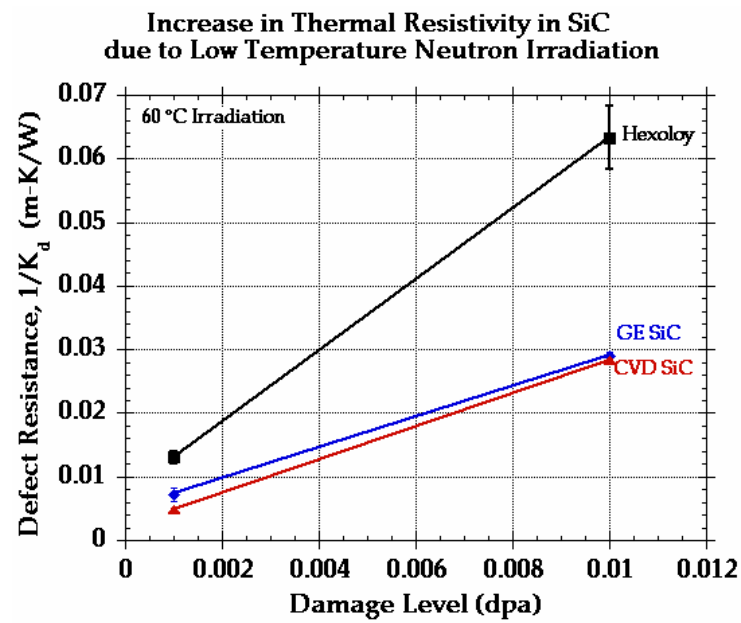
$$[K(T)]^{-1} = \left[\frac{1}{K_u(T)} + \frac{1}{K_{gb}(T)} + \frac{1}{K_{d0}} + \frac{1}{K_{rd}}\right]$$

Thermal resistance of different phonon scattering centers can be simply added if their characteristic phonon interaction frequencies are well-separated from one another

$$\frac{K_{irr}}{K_{unirr}} = \left(\frac{2h\upsilon^2}{18\pi^2\Omega\Theta_D K_{unirr} C_v}\right)^{1/2} \tan^{-1}\left(\frac{2h\upsilon^2}{18\pi^2\Omega\Theta_D K_{unirr} C_v}\right)^{-1/2}$$

Thermal resistance due to radiation-induced defects (vacancies, dislocation loops, etc.) is proportional to their concentration





SiC/SiC: Thermal Conductivity

- **Status:**
  - **- Models developed that accurately predict behavior**
  - **- Latest SiC/SiC with Type S: 26 W/m-K, highest to date for CVI matl.**
  - **- Efforts to engineer higher thermal conductivity in progress:**
    34 W/m-K achieved.
  - **- Irradiation will reduce value to 1/2 at 1000 C, goal is 20 W/m-K.**

- **On-going work:**
  - **- Continue to measure thermal conductivity of advanced materials and check against models.**

- **Issues: effect of transmutants**