Synthesis and Property Evaluations of Silicon Carbide Nanotube Reinforced Ceramic Matrix Composites

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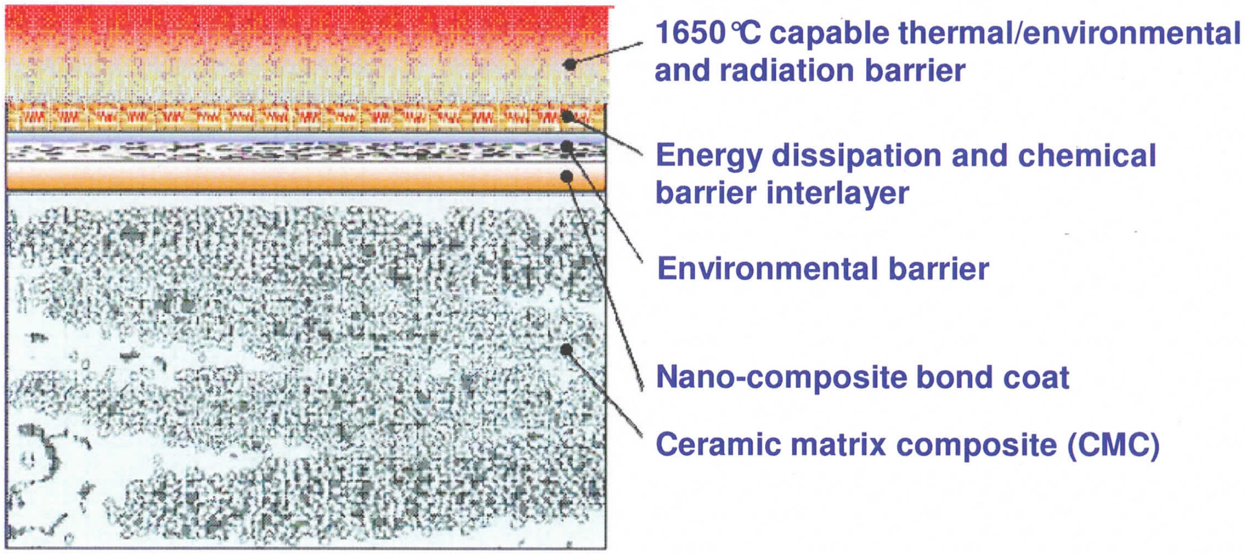
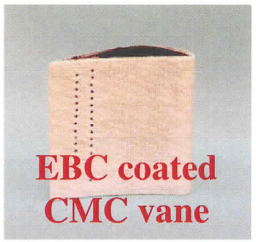
Motivation

- Environmental barrier coating (EBC) systems are critical for protecting Si-based ceramic hot-section components, e.g., SiC/SiC combustors and vanes
- Nanotube composites, potentially having high strength and functional properties, are currently being considered for environmental barrier coatings to improve the coating overall performance
- SiC nanotubes (SiCNTs) are being incorporated into EBC bond coats to help increase coating high temperature strength and toughness





Outline

- Synthesis of Silicon Carbide Nanotubes (SiCNT)
  - Process optimization
  - Nanotube annealing removing extra carbon
- Thermogravimetric Analysis (TGA) stability study in O_2 and air
- Nanotube Composite systems, HfO_2- and $Yb_2Si_2O_7$-based nanotube systems
  - Furnace phase stability testing of hot-processed composite systems
  - Strength comparisons
- Thermal Conductivity of HfO_2-Si, HfO_2-SiCNT and $Yb_2Si_2O_7$ systems
- Cyclic Durability of advanced coating-CMC systems
- Summary

Experimental

- SiC nanotubes synthesized by Si reaction with multiwall carbon nanotubes (CNTs, Pyrograf III® Carbon Fiber, HHT Grade) at 1400℃ in Ar + H_2

- Composite Materials/Specimens (hot-press) for property studies
  - 1" diameter x 2~3 mm thick disc SiCNT, composite specimens or coatings for HfO_2+Si and HfO_2+SiCNT, $Yb_2Si_2O_7$+Si, $Yb_2Si_2O_7$+SiCNT, and coated CMC specimens

- Thermogravimetric Analysis (TGA) in O_2 and Air, and furnace stability testing in air and

- X-ray diffraction and SEM characterizations

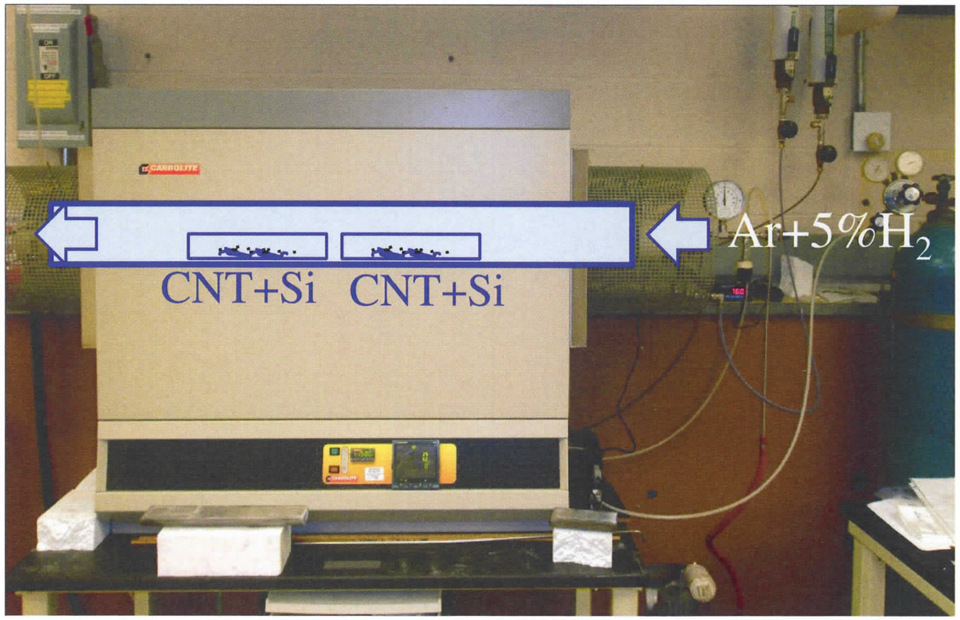
- Laser-heat-flux ball-on-ring test for mechanical property characterizations

- 3500 W continuous wave (cw) CO_2 laser (10.6 micron wavelength) used for high temperature thermal conductivity testing and high heat flux cyclic durability testing

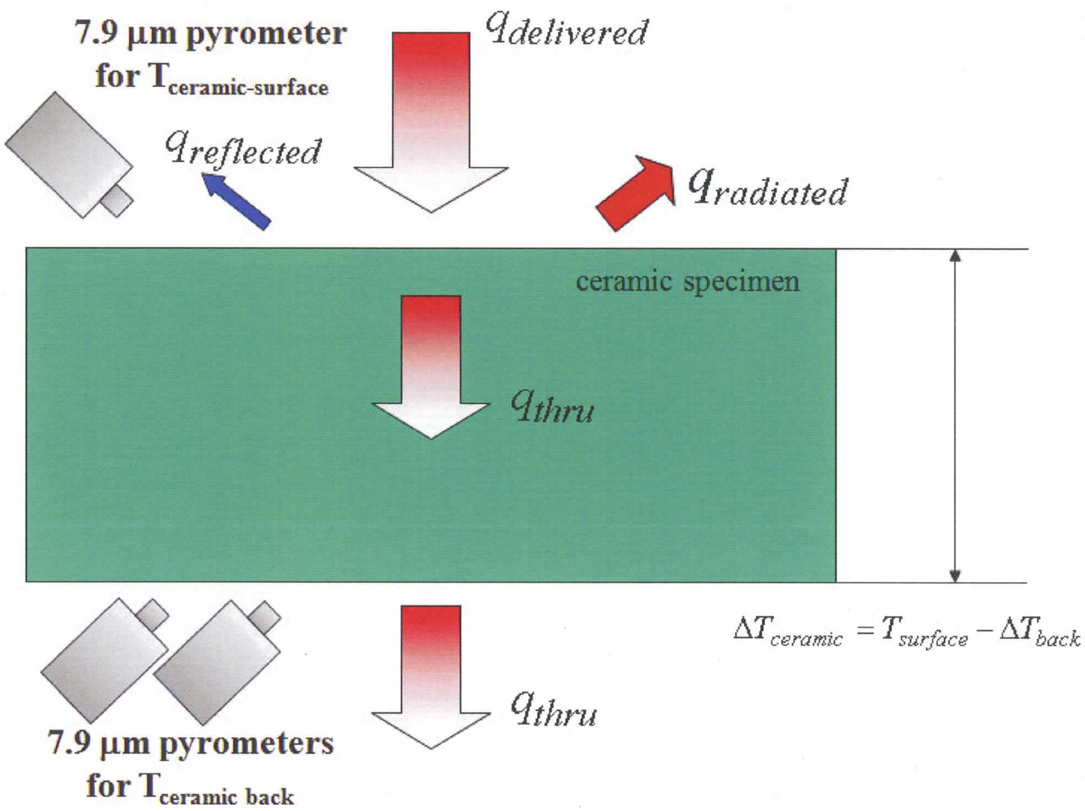
SiCNT Processing and Process Optimization

- The SiCNT processing using Silicon + Carbon Nanotube (CNT) mixtures in $Ar+5\%H_2$ 1400℃, with two 8 hr processing reaction cycles

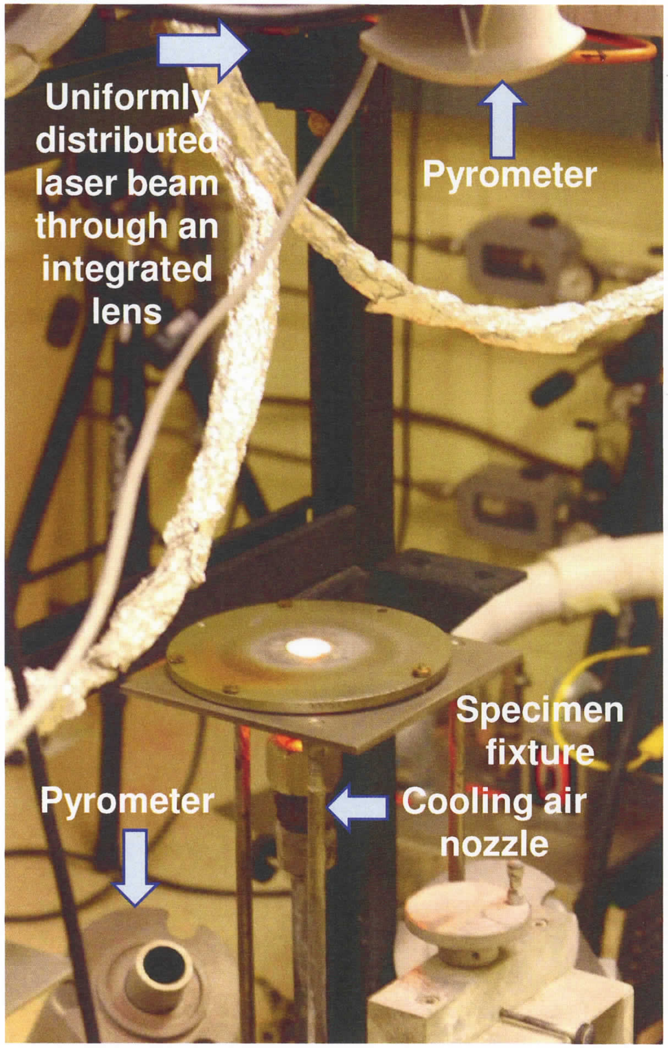
- CNT vs. silicon weight ratios studied: 50:50, 55:45, 60:40, and 70:30 for environmental barrier coating composite applications



Laser Steady-State Heat Flux Thermal Conductivity Testing Approach



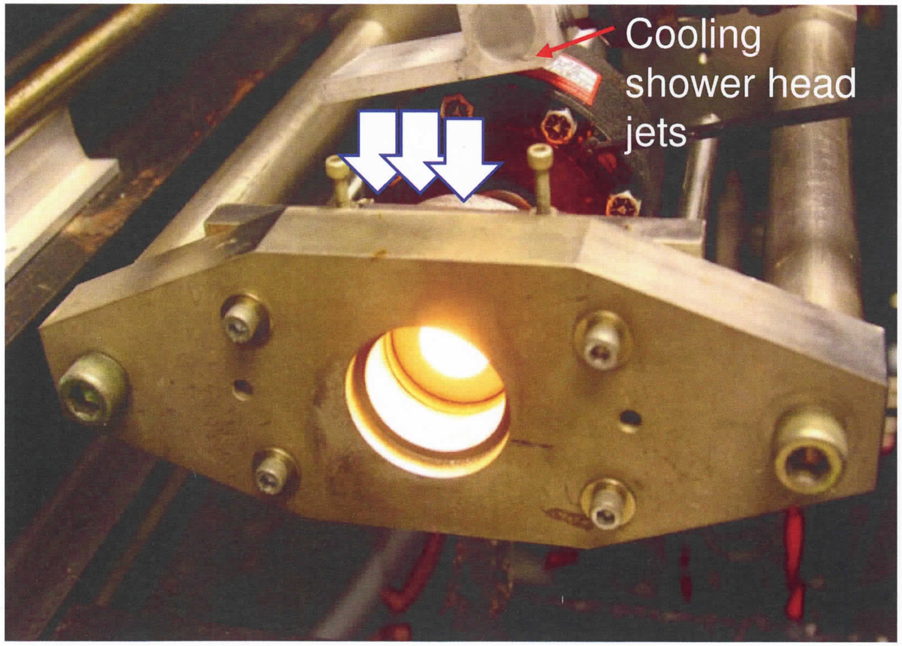
Schematic of the laser heat flux test principles

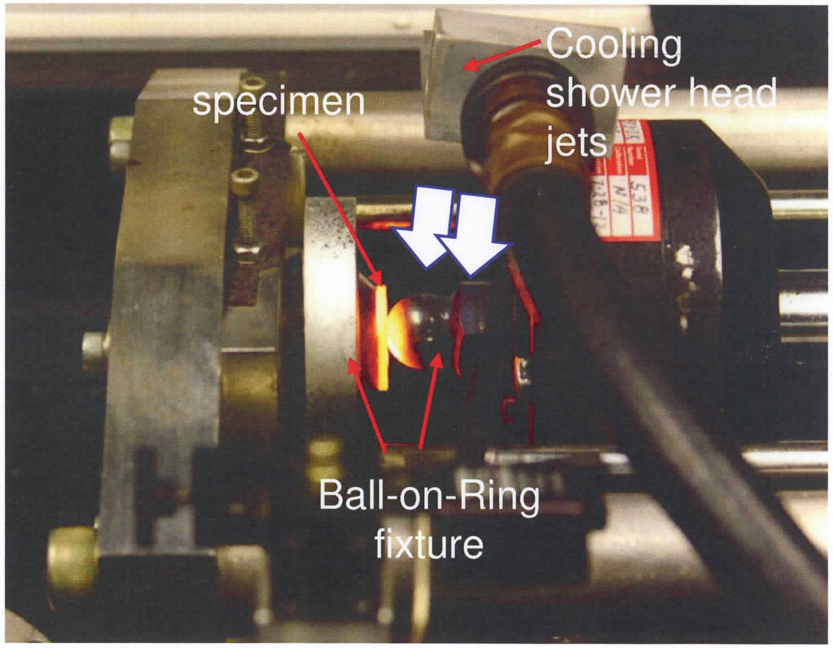


Laser Heat Flux Biaxial Strength Test Rig

Integrated high power CO_2 laser and mechanical Ring-on-Ring or Ball-on-Ring test rig

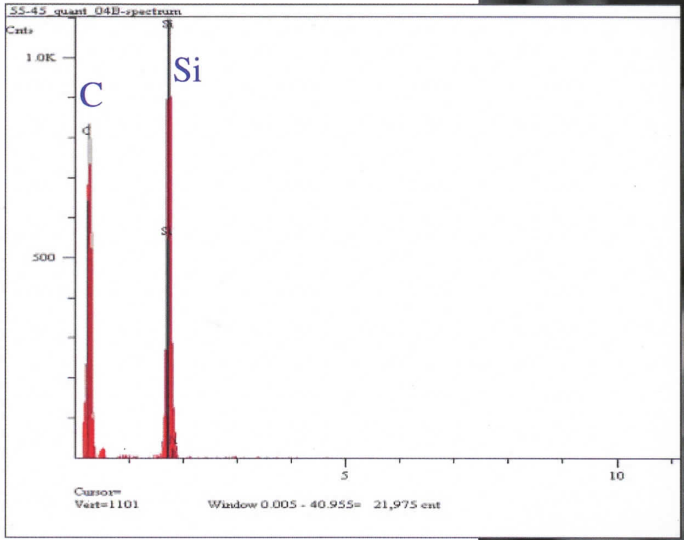
- Accommodates 1” diameter, or 2” diameter disc test specimens and also various configuration subelements
- Used for nanotube composite specimen fracture strength testing

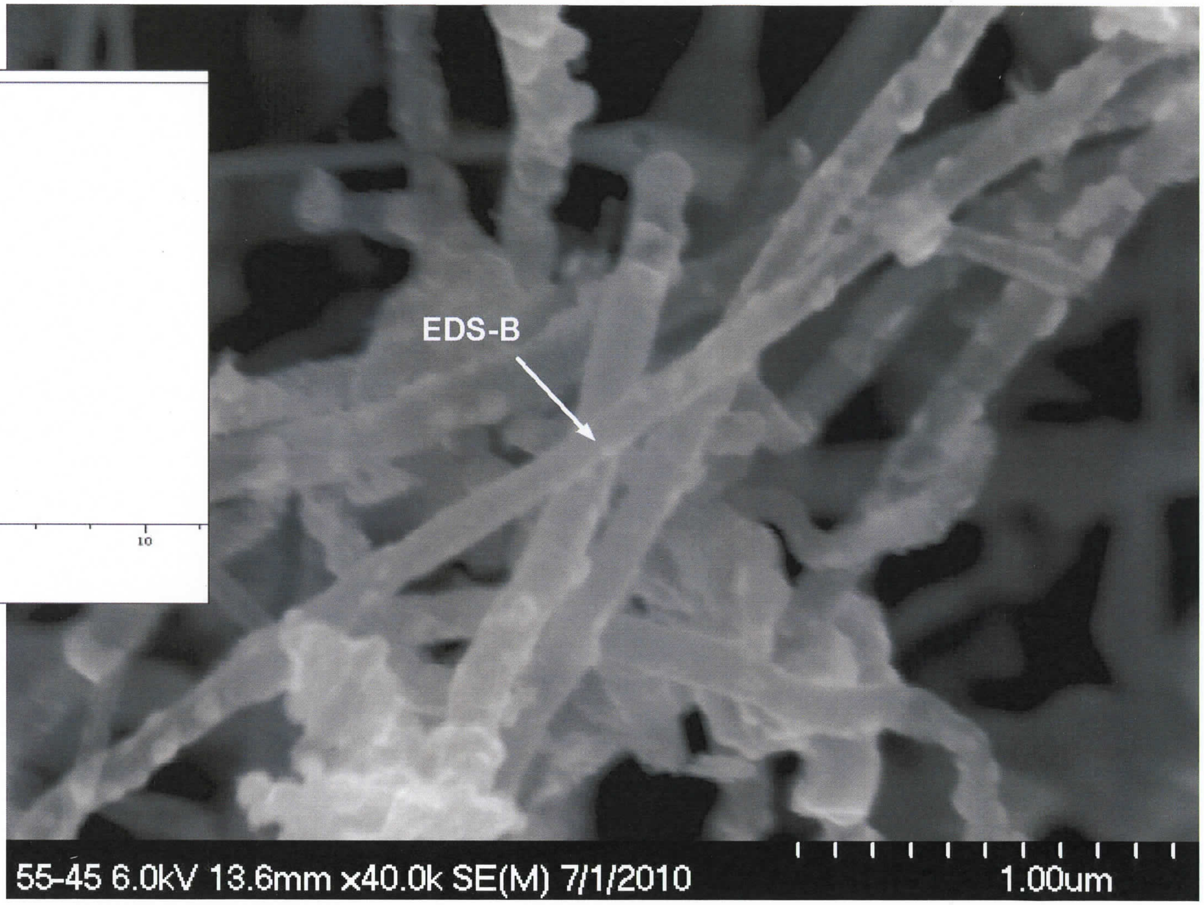




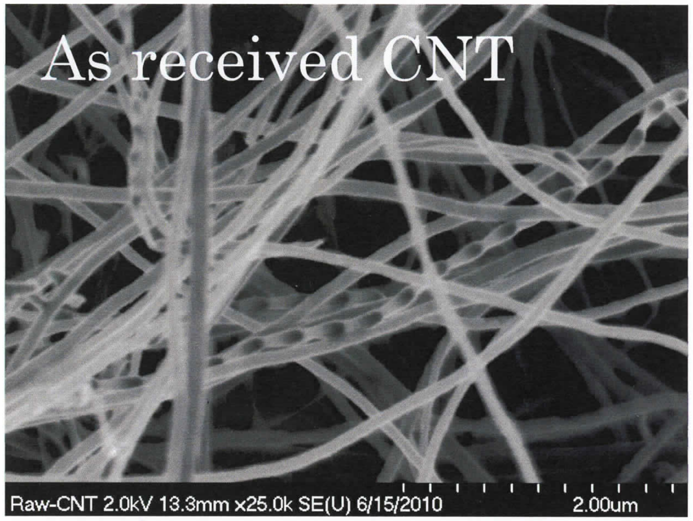
SiCNT Processing and Process Optimization

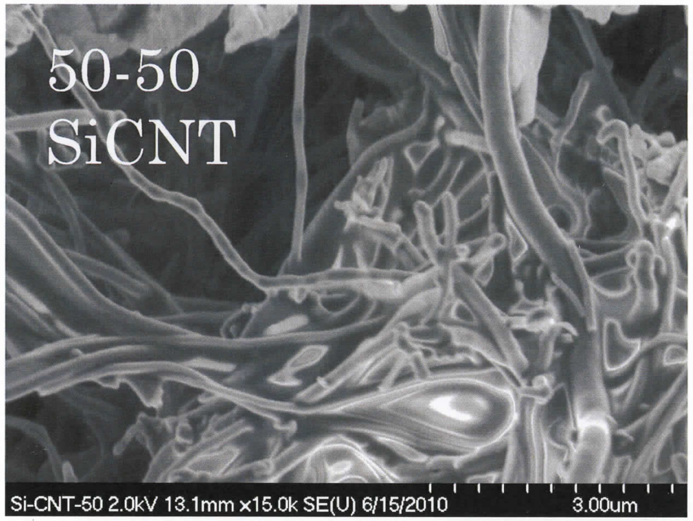
- Optimized CNT/Si ratio found to be 55:45 with SiCNT content quality and nanotube morphology retention
- Obtained almost full β-SiC phase for the SiCNT based on X-ray diffraction analysis

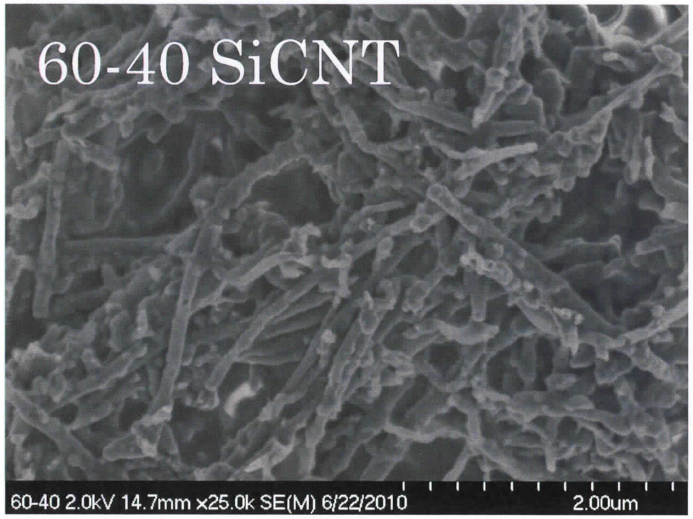


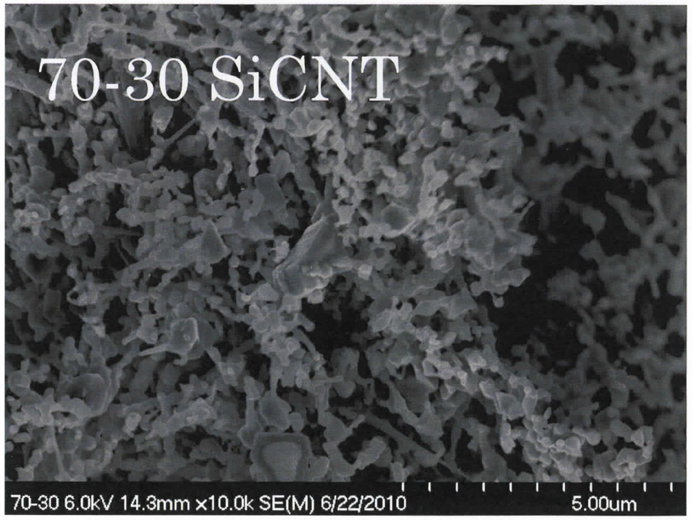


Less Optimized SiCNTs Showing Larger Amount of Either Incomplete CNT Conversion or Damaged Nanotubes









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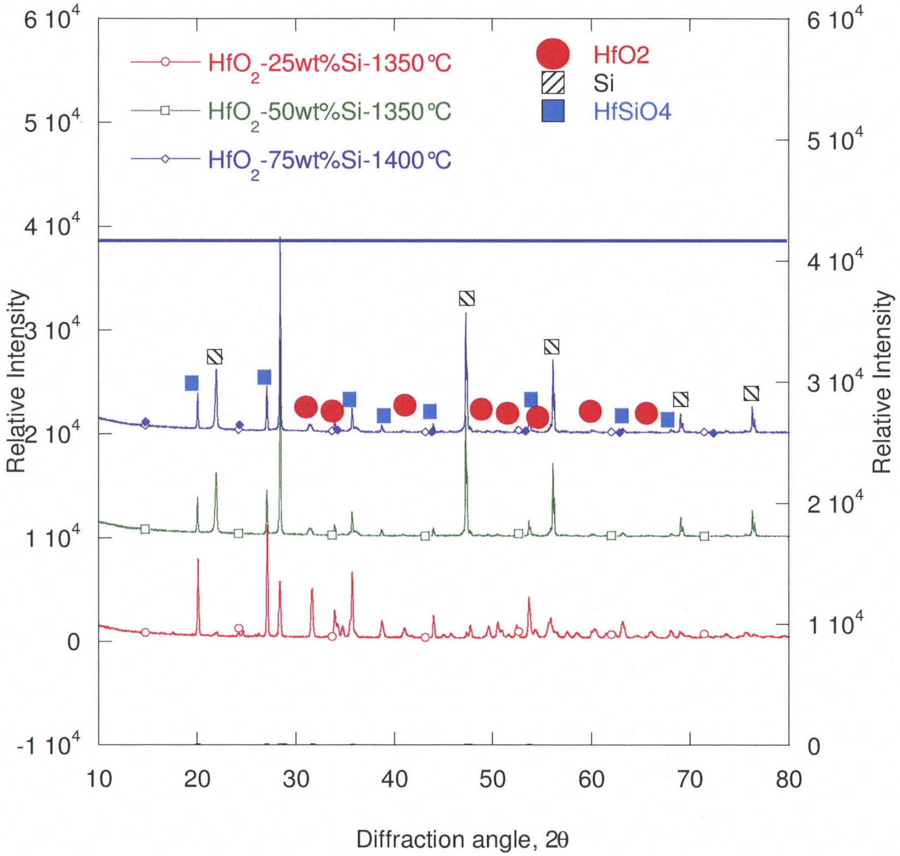
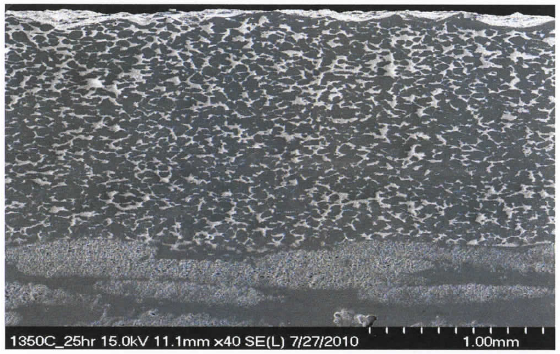
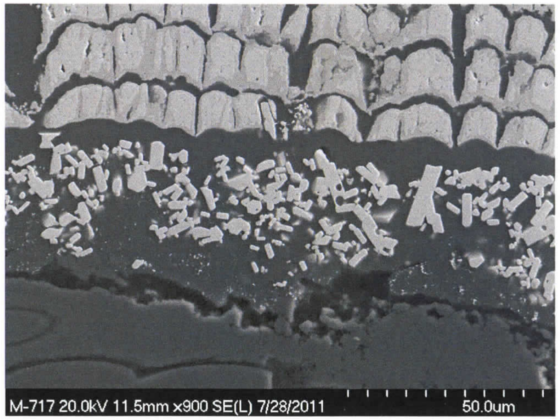
The HfO_2+Si Bond Coats Showed Significantly Improved Temperature Capability as Compared to Si bond Coats

- Higher stability observed even after 1450ºC+ temperature testing





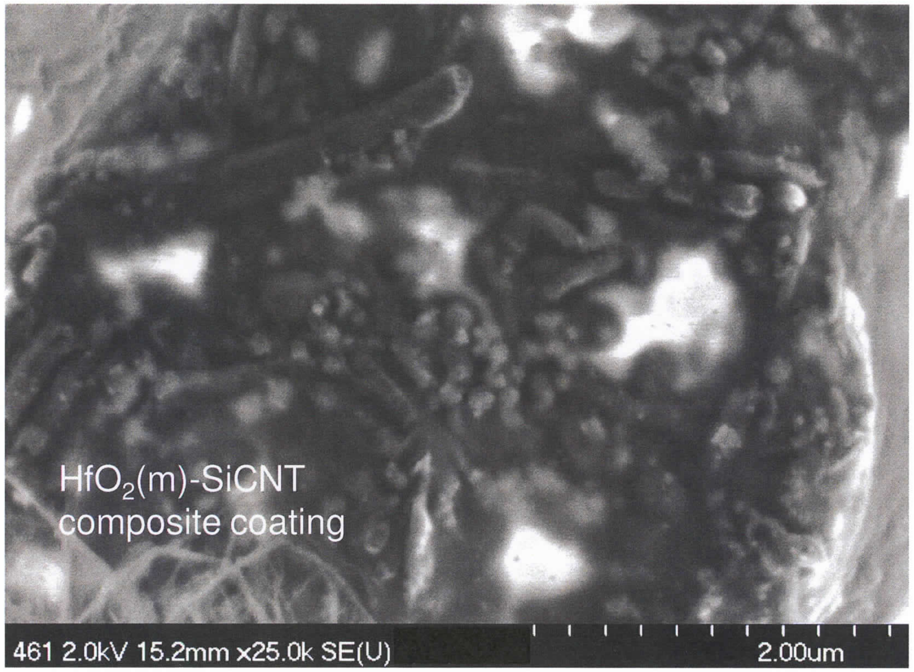
Cross-section, Hot-pressed HfO_2-50wt%Si on CMC, 1350°C tested



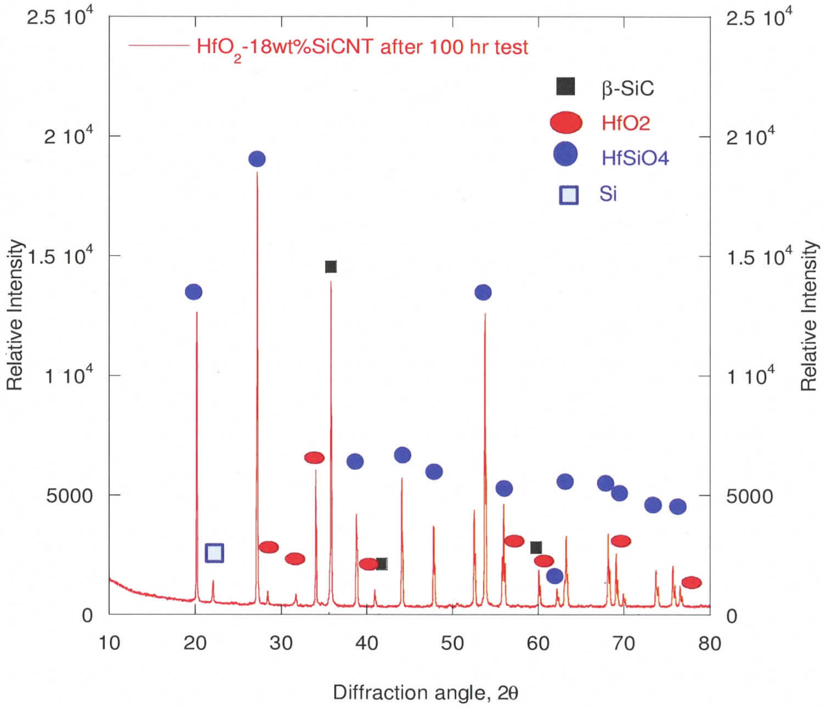
Cross-section, EB-PVD HfO_2-Si, 1500°C tested

The HfO_2+SiCNT(Si) Bond Coats Showed High Temperature Stability in Oxidizing Environments

- HfO_2, SiCNT and HfO_2 silicate are major phases after the 100hr testing up to 1450℃
- Further stability improvements can be achieved in the nanotube composite systems by alloying approaches



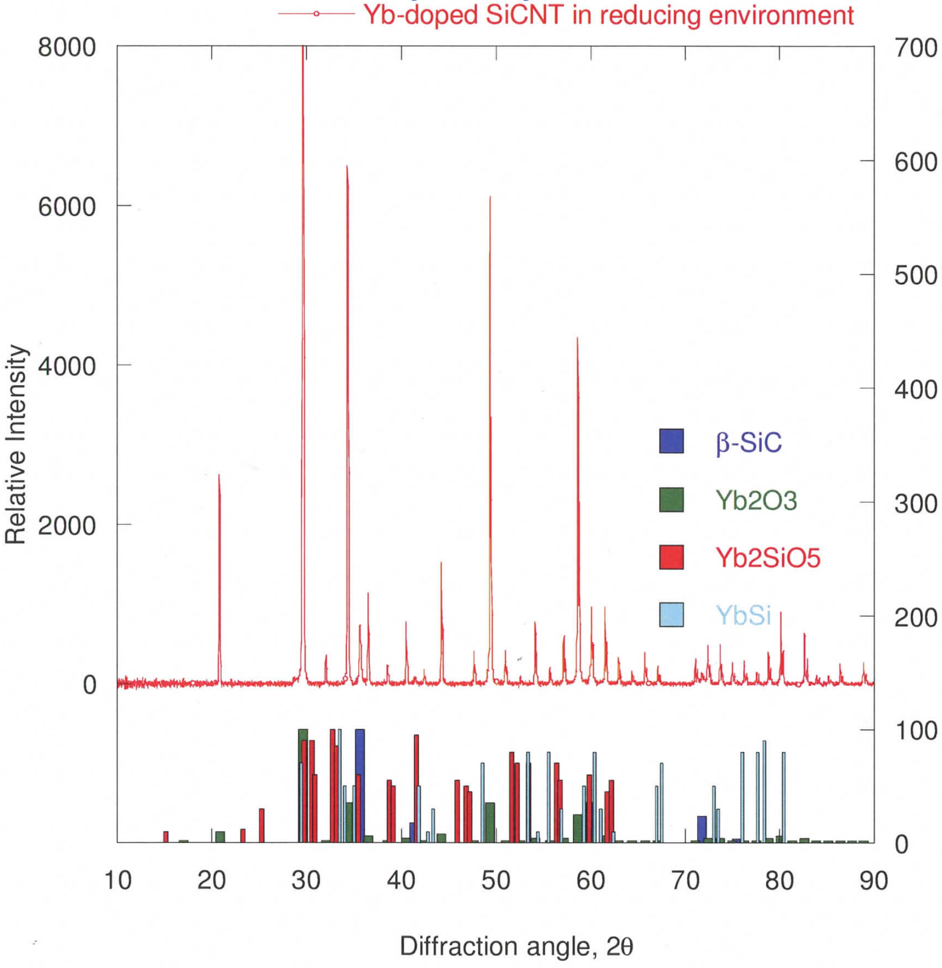
SiC nanotube (SiCNT) and HfO_2-based nanotube composite coatings

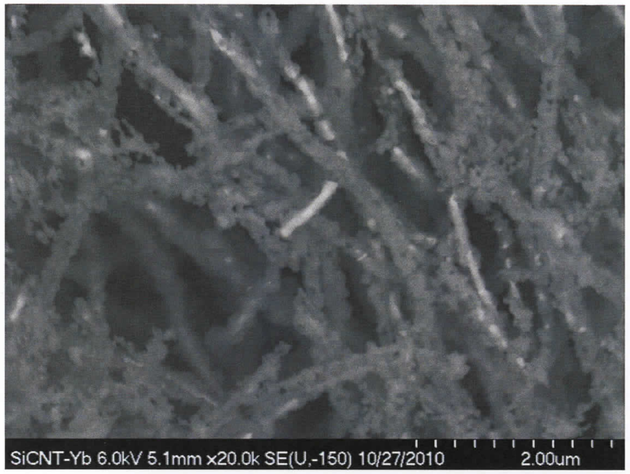


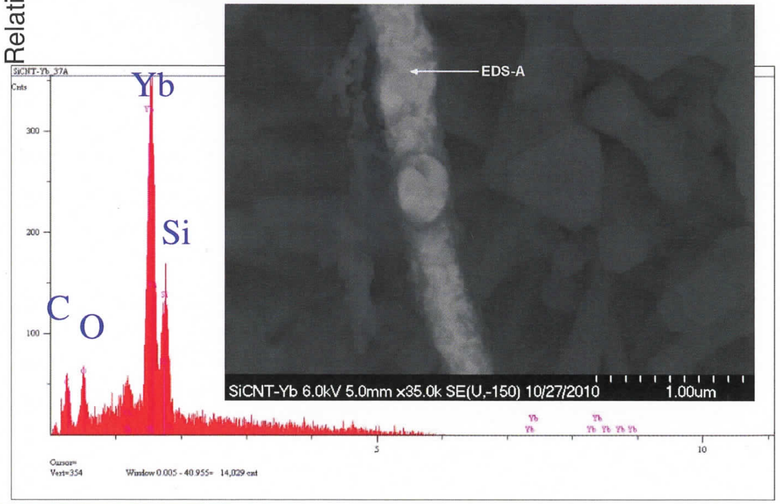
X-ray diffraction analysis

Yb-Doped SiCNTs Processed to Improve the Nanotube and Composite Stability

- Ytterbium alloying by SiCNT reacting with fine Yb_2O_3 powders in $Ar+H_2$
- EDS and X-ray Analysis used to confirm the Yb incorporation of the SiCNTs

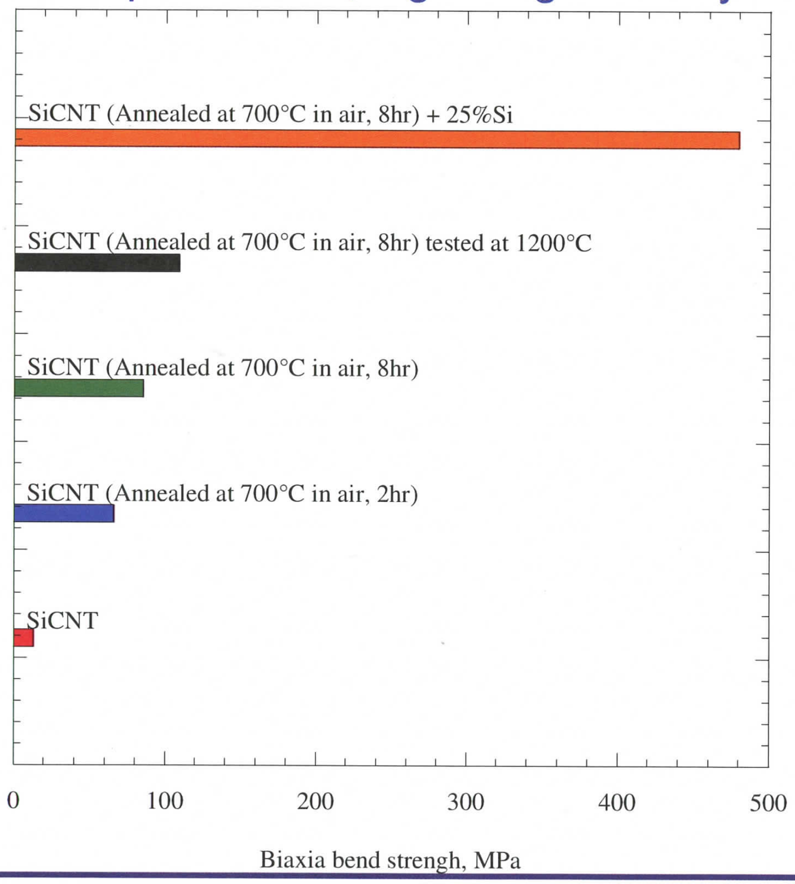


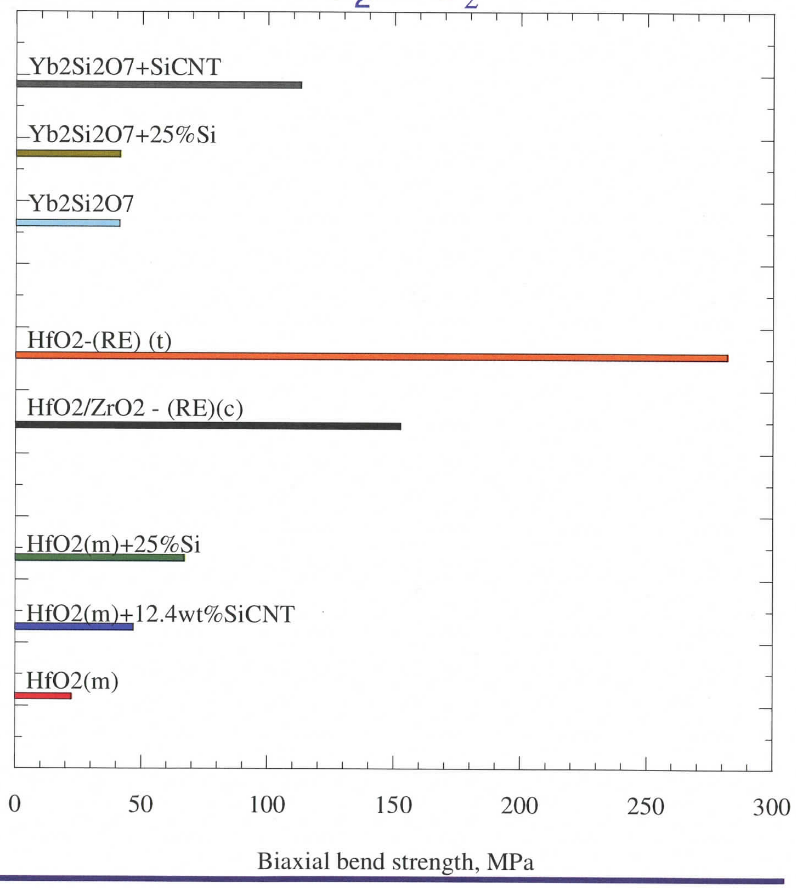




Strength Improvements in the Nanotubes and Banotube Composite Systems

- Annealing and Si addition improved the SiCNT strength
- 2 ~ 3 X improvements were observed compared to the baselines
- Further stability and strength improvements my be achieved with more sophisticated, high toughness systems, such as with t' HfO_2/ZrO_2

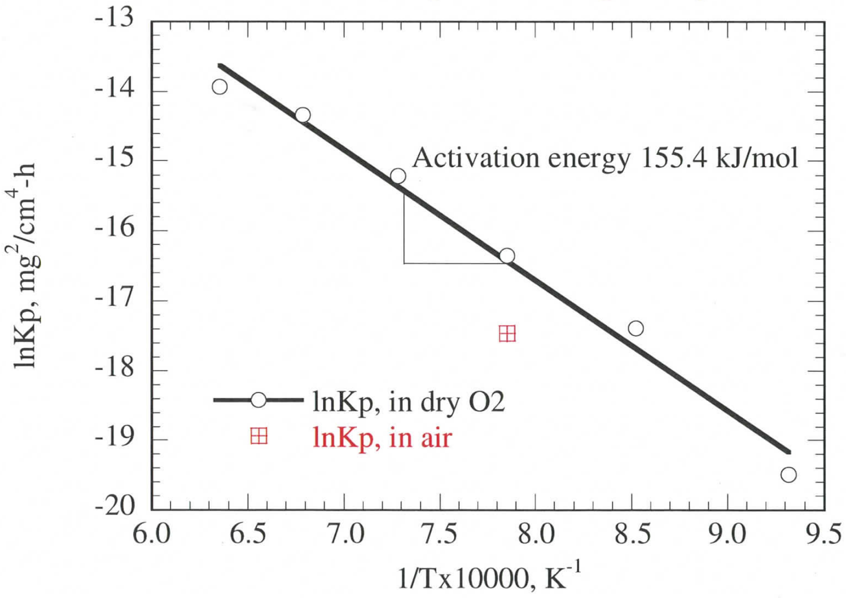




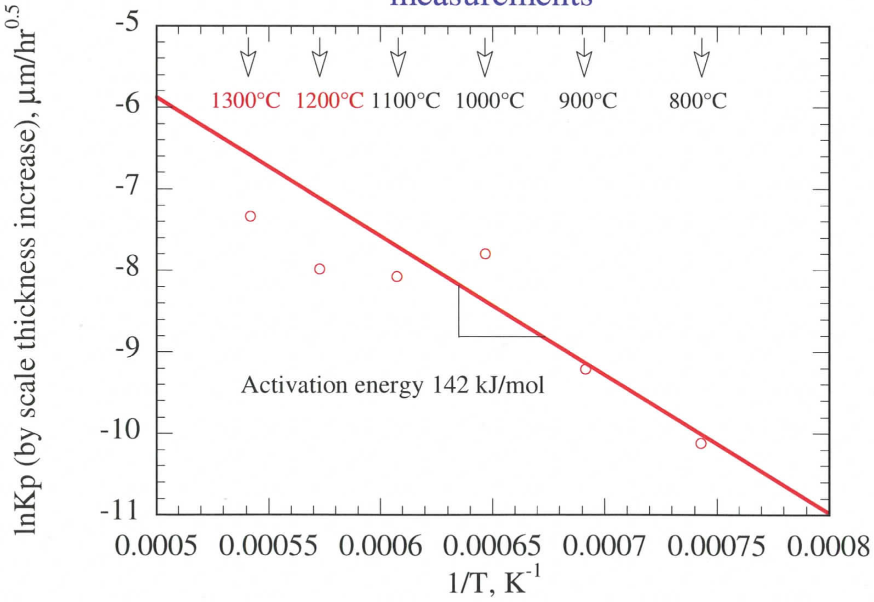
Oxidation Kinetics of SiCNTs

- Silica scale growth on SiCNTs follows pseudo-parabolic behavior
- Upper temperature limit found ~ 1100°C in O_2 environment
- Slower oxidation rate observed in air as compared to oxygen environment tests
- Effective protection barrier layer expected to improve the SiCNT composite stability
- Activation energy determined and good agreement between TGA and scale thickness measurement results

Based on TGA parabolic region Kp

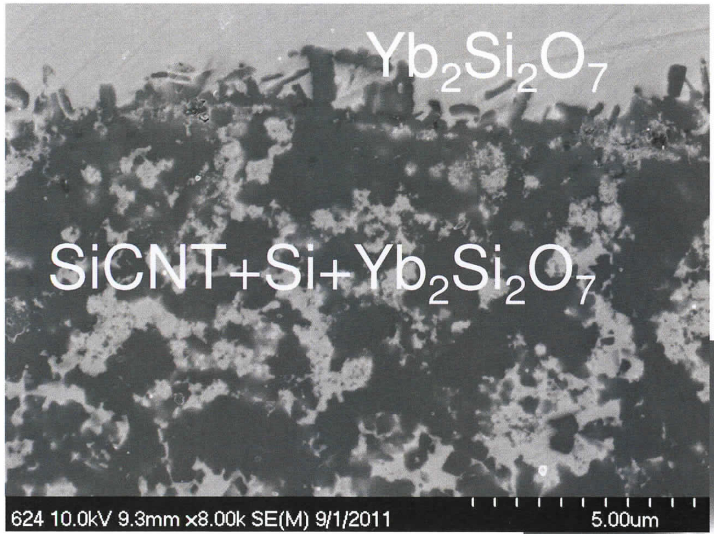


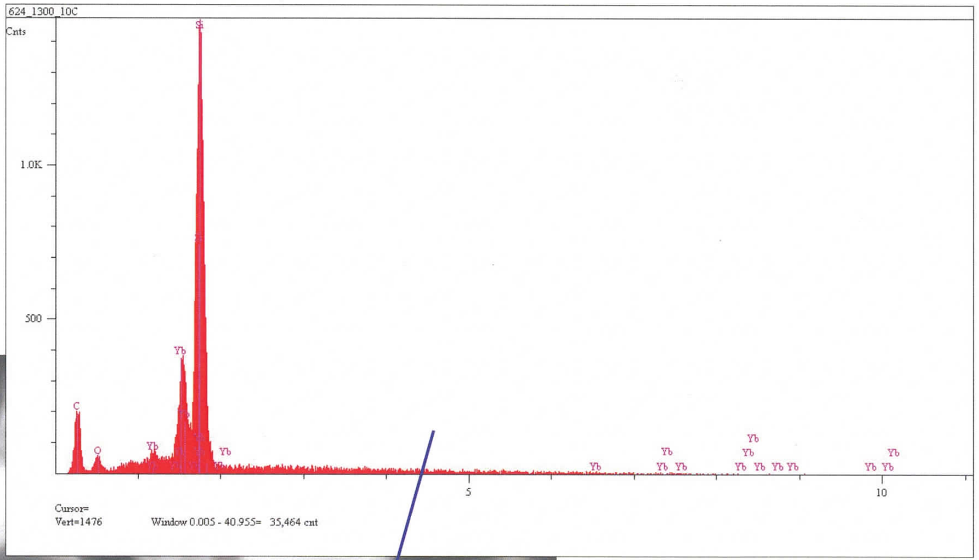
Based on SiCNT scale thickening measurements

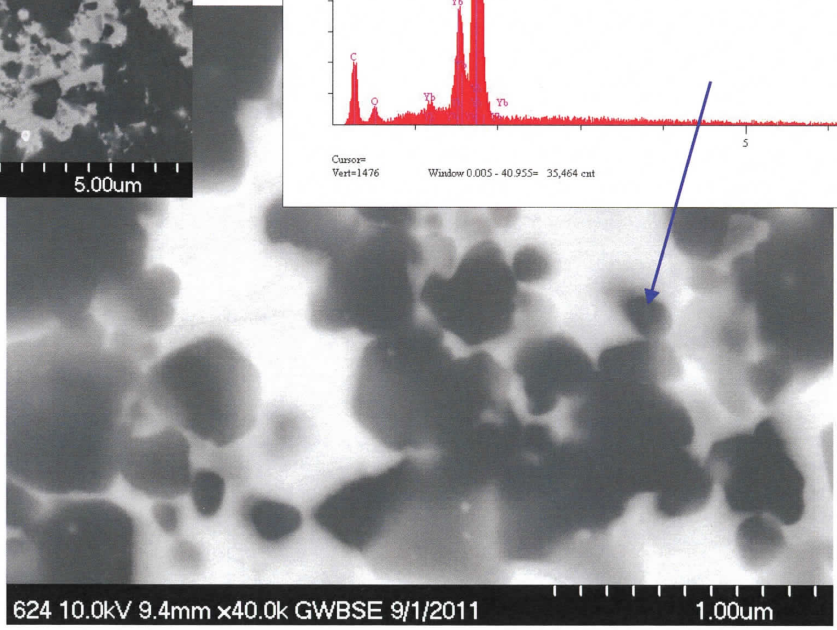


SiCNTs Stability in Protective Coatings

- SiCNTs survived in furnace testing at 1300℃ for 50 hours

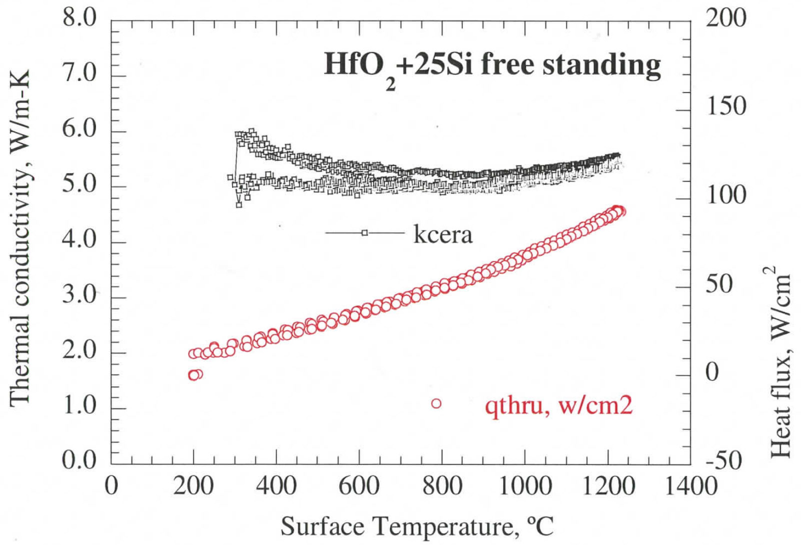


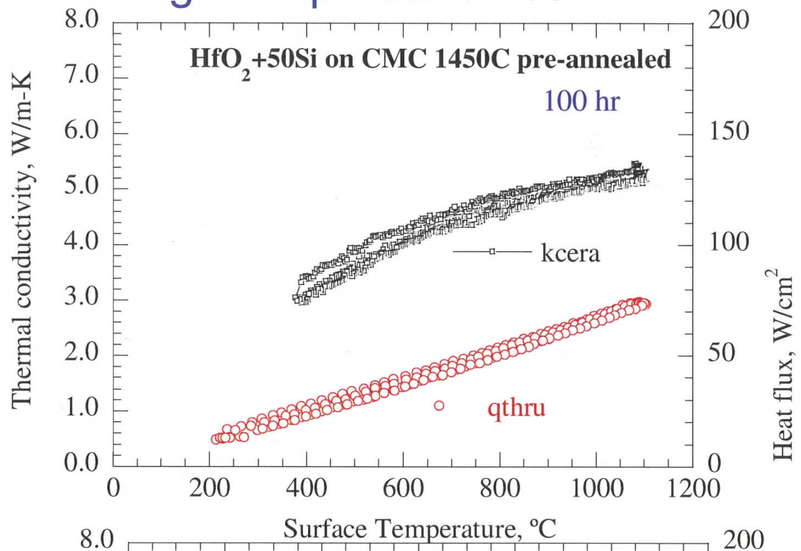


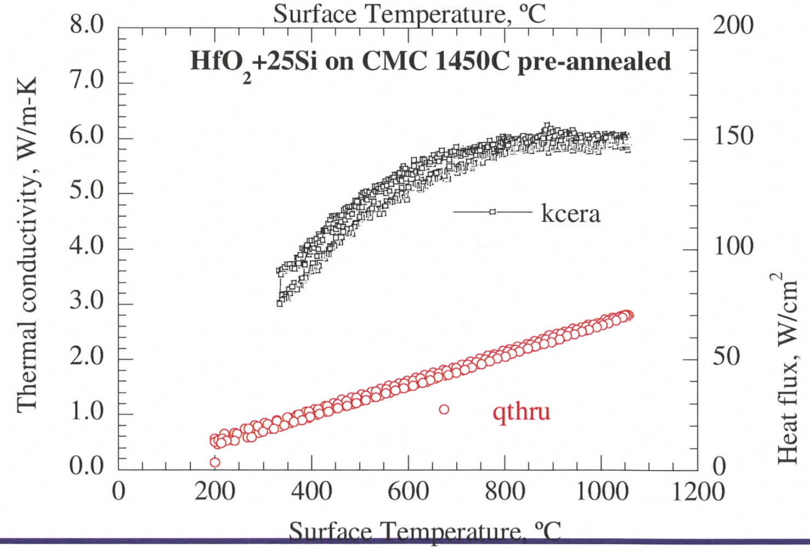


Thermal Conductivity of HfO_2-Si Systems

- Thermal conductivity maintained stable after high temperature 100 hr annealing

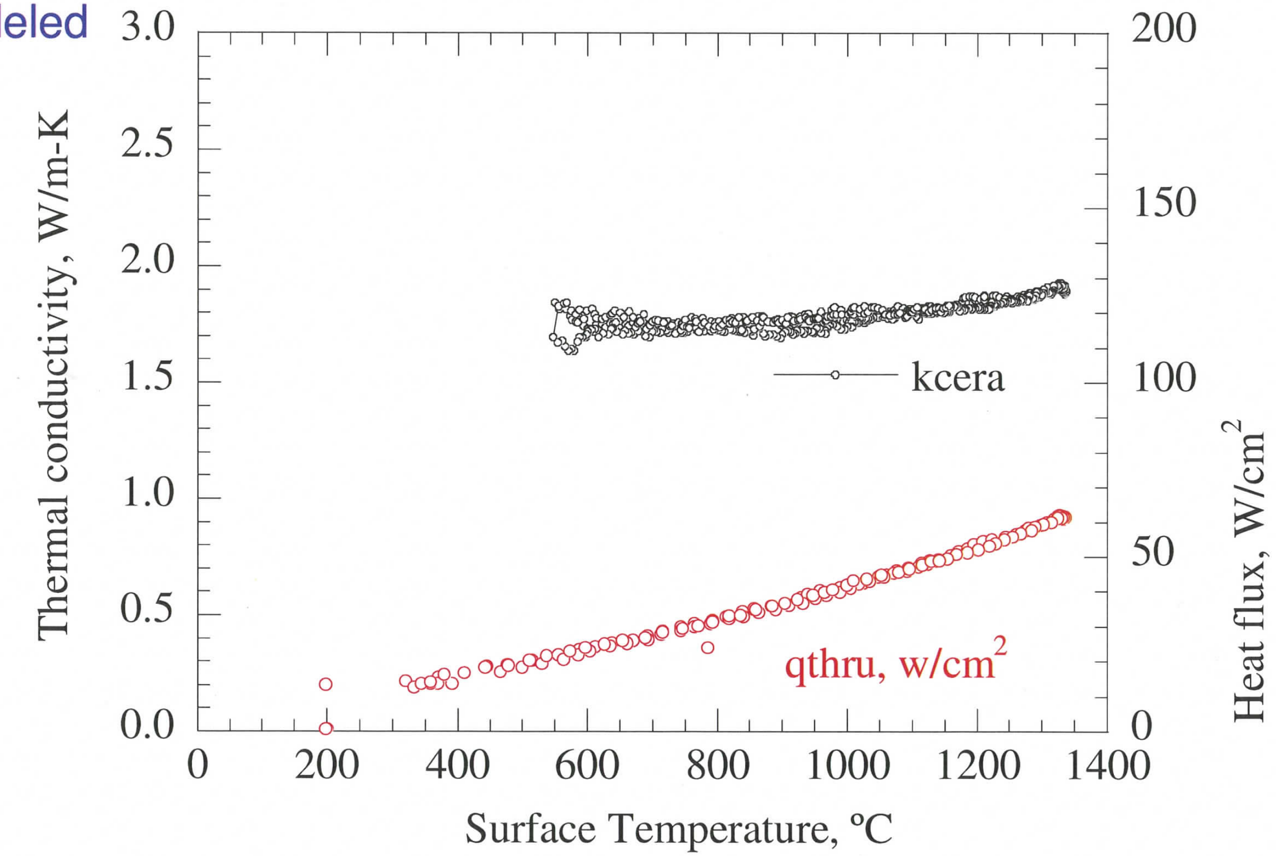






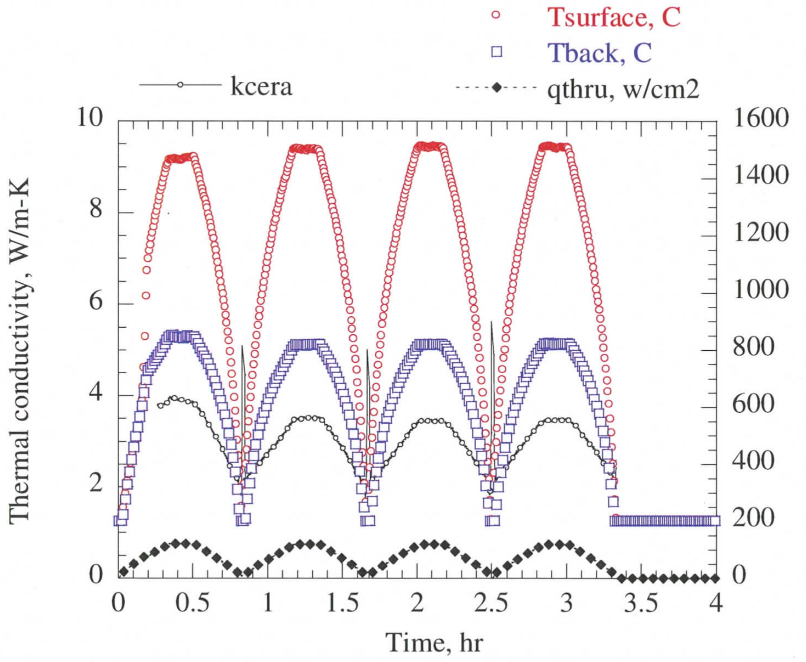
Thermal Conductivity of HfO_2-12.4wt%SiCNT

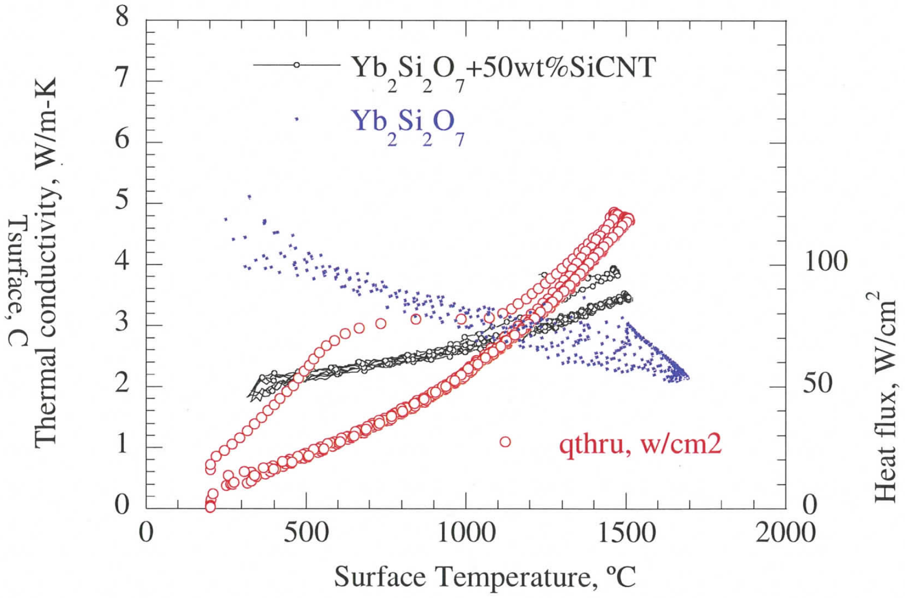
- Relatively low thermal conductivity, possibly due to high interface areas and interface phase thermal resistance
- Effect of nanotube fractions on thermal conductivity is being evaluated and modeled



Thermal Conductivity of $Yb_2Si_2O_7$-50wt%SiCNT

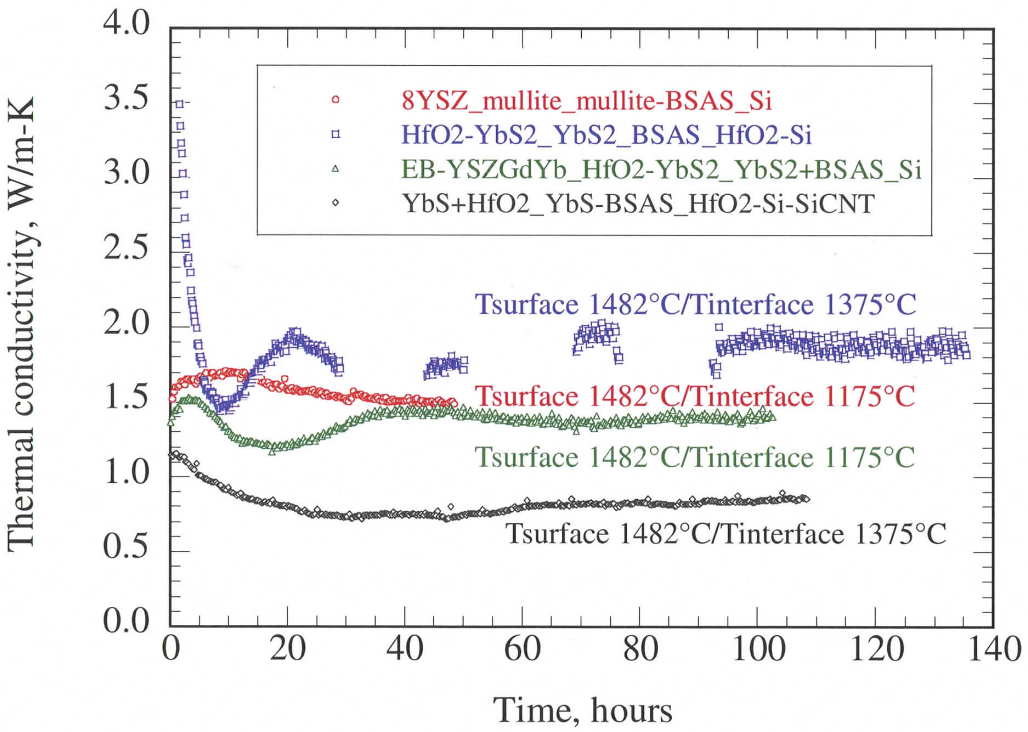
- Slightly enhanced thermal conductivity at high temperature as compared to the bulk $Yb_2Si_2O_2$ due to the SiCNT addition

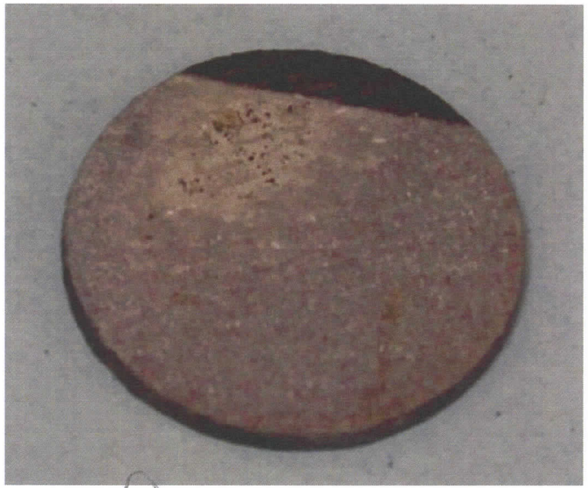




High Heat Flux Thermal Gradient Cyclic Durability Evaluation of Environmental Barrier Coating and Bond Coat Systems

- Laser high heat flux rig thermal gradient thermal cyclic testing at surface temperature of 1482°C (2700°F)
- Advanced bond coats tested at up to 1375°C





HfO_2-yttrebia silicate coating with HfO_2-Si and HfO_2-Si/SiCNT bond coat, after 100hr testing at Tsurface 1482°C/Tinterface 1375°C

Summary

- SiCNT processing has been optimized for EBC bond coat applications, with the optimum Si:CNT weight ratio being 55:45.
- SiCNT annealing or purafication treatment improved strength by removing residual carbon
- Composite HfO_2-SiCNT-Si and $Yb_2Si_2O_7$-SiCNT-Si bond coats synthesized for high temperature environmental barrier coating applications, showed significantly improved strength and high temperature stability
- SiCNT demonstrated the strength and further enhanced with alloy doping systems
- Thermal conductivity of HfO_2+SiCNT and $Yb_2Si_2O_7$+SiCNT bond coats evaluated
- Advanced alloyed nanotubes were synthesized for more advanced system applications

Summary

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