Fission Energy Workshop: Opportunities for Fundamental Research and Breakthrough in Fission
Global Climate & Energy Project
Massachusetts Institute of Technology, Cambridge, MA,
November 29-30, 2007

**Advances in Ceramic Materials**
-SiC/SiC Composite-

**Akira Kohyama**
Institute of Advanced Energy,
Kyoto University,
Kyoto, Japan

http://akweb.iae.kyoto-u.ac.jp
SiC/SiC for Nuclear Applications

- SiC/SiC composites are considered as advanced structural materials in fission and fusion energy systems
  - Heat resistance
  - Intrinsic safety features

- VHTR / NGNP
  - Control rods
  - Control rod supports
  - HX

- GFR
  - Core structures
  - Fuel pins
  - HX

- Fusion
  - Blanket structures
  - Blanket channel liners

Japanese new programs, INERI, GNEP, GIF, BA and many other programs include SiC/SiC applications in LWR, SFR, VHTR, GFR and Fusion
Gen IV GFR
Choice of Materials

- Ceramics and Ceramic-Matrix Composites
  Advantages: capability of high temperature use, neutron properties
  Critical issues: toughness, data bank, knowledge of irradiation effects

  - SiC/SiC composites (reference “ceramic” solution for nuclear use)
    - Current Estimated Possible Operating Range 550-1050°C
    - Status: some development in fusion programs with many outstanding issues
      - Porosity mastering => thermal conductivity & gas permeability (fission products)
      - Thermal conductivity degradation under irradiation
      - Irradiation embrittlement (matrix, fiber & interface) and fiber debonding
      - Manufacturing/joining (many different fiber types under evaluation)
    - Codes & standards must be established
    - Cost-SiC/SiC still about an order of magnitude higher in cost than austenitic steels

  - Other Carbides (ZrC, TiC, NbC), nitrides (Si$_3$N$_4$, TiN, ZrN, AlN), oxides (MgO, Zr(Y)O$_2$), and silicides (Zr$_3$Si$_2$)
    - ZrC considered as alternative solution to SiC to reach higher temperatures
    - Thermal conductivity, toughness/embrittlement, joining could be critical
      - AlN-good thermal conductivity
      - Si$_3$N$_4$, good strength
    - Nitrides may require enriched nitrogen to minimize C-14
    - Cost may be prohibitive
    - No irradiation data
    - No design codes

Borrowed from Todd Allen
Candidate GFR in-core structures with SiC/SiC
- material requirements -

1: Shield SiC/SiC Pin Type Fuel
   a) The SiC/SiC has to be compatible with He, FP Gas and Fuel at high temperature
   b) SiC/SiC should keep high thermal conductivity and very low FP gas release. “sealing layers” is an option
      a) the degradation of thermal conductivity is critical from heat flow point of view
      b) Strength requirement is realistic level, but should keep it under high neutron fluence.

2: Coated Particle Fuel with SiC/SiC Compartment
   a) The SiC/SiC inserts have to be compatible with He at very high temperature
   b) SiC/SiC should keep high thermal conductivity and low helium leakage rate (for vertical cooling) or high helium leakage rate (for horizontal cooling). “Porosity control” is a challenge
   c) Strength requirement is mild, but should keep it under high neutron fluence.

3: Composite Type Block Fuel with SiC Matrix
   a) SiC matrix should keep high thermal conductivity and low helium leakage rate
   b) Particle fuel with SIC coating should be uniformly embedded without damage
By using SiC/SiC fuel pin, Gas Plenum can be minimized drastically.
GFR using Coated Particle Fuel and SiC/SiC Compartment

*(Horizontal flow cooling concept with directly cooling system)*

Ref.: M. Konomura et al., Grobal2003
**R & D of Fuel Compartment for GFR**
*Horizontal Cooling Core*

**Requirements:**
- High Thermal Conductivity
- High Temperature Strength and Ductility
- Stability Under Reactor Core Environment
- Uniform Porosity Distribution (Well Controlled)

*He permeability should be precisely controlled*

**Potential Concepts:**
- **Type A**
  - Connecting Random Pores
- **Type B**
  - Through Thickness Channels
### R & D of Multi-Functional Porous SiC

<table>
<thead>
<tr>
<th>Method</th>
<th>NITE</th>
<th>NITE</th>
<th>NITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>β-SiC</td>
<td>β-SiC</td>
<td>β-SiC</td>
</tr>
<tr>
<td>Type of Pore</td>
<td>Connecting open pore</td>
<td>Through thickness cylindrical pore</td>
<td>Through thickness cylindrical pore</td>
</tr>
<tr>
<td>Potential Applications</td>
<td>Separation foil, Thermal insulation panel, Vibration/Sound absorber</td>
<td>Filter, Separation Foil, Micro Heat Exchanger</td>
<td>Stud hole, bearing hole, composite fuels, flow channel</td>
</tr>
<tr>
<td>Example</td>
<td><img src="1mu.png" alt="Image" /></td>
<td><img src="10mu.png" alt="Image" /></td>
<td><img src="1000mu.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Example Images**

- **1μm**: Shows the structure of porous material at a microscopic level.
- **10μm**: Displays a detailed view of the pores and their uniformity.
- **1000μm**: Illustrates the overall size and scale of the porous material.
Development of Environmentally Tolerant CMC; Directions

◆ SiC fiber
   - Oriented to high crystallinity and stoichiometry – two products have been commercialized (Tyranno™-SA, Hi-Nicalon™ Typs-S: Cef-NITE is becoming available)
   - Issues in further activation reduction and creep resistance

◆ Interphase (fiber-matrix interfacial phase)
   - Oriented for radiation resistance – presumably determines high-fluence (100dpa~) irradiation properties
   - Pyrolytic carbon (PyC) – experience in non-nuclear applications, high-fluence property is an issue

◆ SiC-based interphase – recent trend for nuclear applications, e.g., multilayered (SiC/C)$_n$ pseudo-porous SiC

◆ SiC Matrix
   - Controllability in density (full dense to porous)
   - Oriented to high crystallinity and stoichiometry
Comparison of state of the art SiC/SiC composites
- NITE Composite as the breakthrough -

- Process Cost: (0.1 MV/kg)
- UTS: (300 MPa)
- PLS: (150 MPa)
- Max. App. Temperature: (1300°C)
- Thermal Conductivity: (15W/mK)
- Density: (3.0 g/cm³)

R&D Target for Fusion Reactor

- Dupont Enhanced SiC/SiC
- Snecma Cerasep N3-1
- Stoich PIP+MI SiC/SiC (2000)

Cera-NITE

Memo:
*1 Chart axes are expressed by linear scale except process cost
*2 Rough estimates (fiber cost not included, Labor cost + matrix raw materials):
Progress in SiC Fibers

Improvements in high temperature properties open wider capabilities in production process options.
Representing Advanced SiC Fibers
- 7-10μm dia., 50-100nm grain size -

<table>
<thead>
<tr>
<th></th>
<th>Fiber Cross-section</th>
<th>Center Close-up</th>
<th>Peripheral Close-up</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cef-NITE</strong></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>(pilot-F1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tyrano-SA</strong></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>(grade-3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### SiC(-based) Fibers Used for Composites

<table>
<thead>
<tr>
<th>SiC Fiber</th>
<th>C/Si Atomic Ratio</th>
<th>Oxygen Content (wt%)</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation (%)</th>
<th>Density (g/cm³)</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tyranno SA Gr.3</td>
<td>1.07</td>
<td>&lt;0.5</td>
<td>2.6</td>
<td>400</td>
<td>0.6</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>Hi-Nicalon Type-S</td>
<td>1.05</td>
<td>0.2</td>
<td>2.6</td>
<td>420</td>
<td>0.6</td>
<td>3.1</td>
<td>11</td>
</tr>
<tr>
<td>Hi-Nicalon</td>
<td>1.39</td>
<td>0.5</td>
<td>2.8</td>
<td>270</td>
<td>1.0</td>
<td>2.74</td>
<td>14</td>
</tr>
</tbody>
</table>

Fiber: 3D orthogonal weave (1:1:1)  
X, Y fibers: Tyranno SA, Z fibers: P120  
Cef-NITE Woven Fabrics (1.5m w)
Advanced Matrix Densification Methods

- Oriented to high crystallinity and stoichiometry
- **CVI method**: technically most established, high crystallinity, high purity, stoichiometry; *limitations in shape/geometry and porosity*
- **PIP method**: issues in baseline properties, crystallinity and stoichiometry; process technique improvement and near-stoichiometry polymer development in progress; *limitations in shape/geometry and porosity*
- **MI method**: issues in phase control; needs process improvement
- **Novel techniques (NITE-process)**: extensive progress and outstanding performance have been confirmed
What is NITE method

- **Nano-Infiltration Transient Eutectic Phase Process**
  - High Density and Excellent Hermeticity
  - High thermal conductivity, Chemical stability
  - Flexibility in size and shape
  - Applicability of existing near net-shaping techniques
Matrix-Fiber-Interface Integrity

SiC(matrix) SiC(fiber) Carbon layer

1780°C/20MPa
CVI SiC/SiC VS. NITE SiC/SiC

CVI-SiC/SiC (PW)

Cross-section
Surface

Density: 2.4Mg/m³
Porosity: 18%

NITE-SiC/SiC (PW)

Cross-section
Surface

Density: 3.1Mg/m³
Porosity: 1.3%

Introducing The Breakthrough of SiC Materials!!

NITE Method ▶ Nano-Infiltration and Transient Eutectic Phase Method
Cef-NITE ▶ SiC Fiber (Tyranno-SA Grade)
Cera-NITE ▶ SiC/SiC Composite with Cef-NITE by NITE

Cef-NITE® and Cera-NITE® to the NITE for the NITE by the NITE

Patents: Japan, US, EU
Licensed to IEST
High Ductility Type
(Highly-dense Composites)

Polished cross section

Density: 2.98Mg/m³
Porosity: 1.93%

Fracture surface

Tensile fracture behavior

UTS ≈ 400MPa
PLS ≈ 210MPa

$E' \approx E_f V_f$

$E$

$E_0$

$UTS$
High Strength Type
(Highly-dense Composites)

Polished cross section

Density: 3.11Mg/m³
Porosity: 0.59%

Tensile fracture behavior

$E' \approx E_f V_f$

Fracture surface
High Thermal Conductivity Type

Polished cross section
Density: 3.15Mg/m³
Porosity: 0.6%

50 μm

Tensile fracture behavior

High Ductility (highly dense) Type
High Ductility (porous) Type
High strength (highly dense) Type
High thermal conductivity (highly dense) Type

Thermal conductivity / W/mK

Tensile stress / MPa

Tensile strain / %
Shape & Machine Flexibility of NITE-SiC/SiC

- Thick Block: 97 x 97 x 70 mm
- Combustor Liner
- Thin Plate: 195 x 195 x 2.0 mm
- Tube: Φ31-33*60 mm

10 mm
Burst test by pressurized water was done by MHI-Nagoya
Li-Pb Loop test at 600 C was successful -S. Konishi Program on IHX for GFR
Excellence in Thermal Stress Resistance
- Thermal stress figure of merit: \( M \) -

\[
M = \frac{\sigma_U k_{th} (1-v)}{\alpha_{th} E}
\]

- Cera-NITE
- SiC/SiC (CREST-ACE CVI)
- SiC/SiC (SNECMA Cerasep N3-1)
- V-alloy (V-4Cr-4Ti)
- Steel (Fe-8Cr-2W)
- Pure Aluminum
- Titanium 318
Improvement in Hermeticity
- Permeability of Helium -

He gas permeability, $K (m^2/s)$

Pressure of high pressure chamber, $P_H$ (Pa)

- PIP
- HP
- PIP+MI
- PG#1 NITE-SiC/SiC
- PG#2 NITE-SiC/SiC
- Cera-NITE
- Monolithic SiC by NITE
Neutron Irradiation Effect on Dimensional Stability
- CVI SiC/SiC with different SiC fibers -

Old Fiber
Amorphous Si-Ti-C-O Fiber (Tyranno™-TE)

New Fiber
Stoichiometry Si-C Fiber (Hi-Nicalon™-Type-S)

Excellent Stabilities in; Dimension, Strength

JMTR Irradiation: at (573K +) 773 K, - 1 dpa-SiC
Influence of Neutron Irradiation on Flexural Strength of CVI-SiC Composites with Nicalon™-Family SiC Fibers

![Graph showing the influence of neutron irradiation on flexural strength. The graph plots the ratio of irradiated to unirradiated flexural strength against neutron dose (dpa-SiC) on a logarithmic scale. The graph includes data points for different irradiation conditions and fiber types, with annotations for different experimental sets.](attachment:graph.png)
Dual-ion Irradiation to SiC at MUSTER Facility, Kyoto University
Significant Advancement in Mapping
- Microstructural Development -

- Black spots are probably small loops or SIA cluster as local embryo.
- Perfect loops develop into dislocation network at high and high doses.
- Microstructural development in the high dose regime is similar to some of fcc metals.

Mid-temperature range may suggest little concern about swelling/degradation.
Crack Propagation in SiC with/without Ion Bombardment

Un-irradiated  Irradiated

Dual-ion, 800°C, 3dpa

Complex crack path
Microstructure after indentation test
Dual-ion irradiated at 800°C, 1dpa (16g)
Fabrication of C/C, SiC/SiC Control Rod Components

- Simple braiding processes sufficient (modest strength required)
  - 60° braid angle
  - Orthotropic material properties
  - Liquid or vapor infiltration
    - C/C - Liquid & vapor mesophase pitch infiltration
    - SiC/SiC – CVI process

Borrowed from L. Snead (ORNL)
### Potential Areas of SiC/SiC Application in VHTR

<table>
<thead>
<tr>
<th>Component</th>
<th>HTTR</th>
<th>R&amp;D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel block Reflector</td>
<td>Isotropic reactor grade graphite (IG-110)</td>
<td>Irradiation data Life extension (Non-destructive method)</td>
</tr>
<tr>
<td>Control rod cladding</td>
<td>Alloy 800H</td>
<td>Irradiation data Design code</td>
</tr>
<tr>
<td>Upper shield Core barrel</td>
<td>Graphite Metals</td>
<td>Irradiation data Design code</td>
</tr>
</tbody>
</table>

GTHTR-300 (by JAERI)
Core restraint mechanism of VHTR

The specified minimum ultimate compressive strength; $Su=61\text{MPa}$

[The graphite structural design code for the HTTR] **Stress limit of reflector block**; $1/4Su=15\text{MPa}$

Thickness of C/C composite should be less than 50mm

Ref.: S. Hanawa et al., SMiRT18-C06-1 (2005).
Industrialization of SiC/SiC for Energy Applications

Large-scale and Stable Supply of Industrialized Materials;
+ Fibers; Cef-NITE production is aiming over 1 ton/year from 2008 by the first continuous production line at Ube with the capability of 4 tons/year (in Japan)
+ Woven fabrics production trials (1.5m width) have been started with the variations of architecture. (in Japan)
+ Coatings; Continuous and large-scale process R & D is almost finished. New process facility in Japan is under preparation. (in USA and Japan)
+ Nano-Powders; Pilot plant construction is ready to go. (in France)
+ SiC/SiC Composites; Cera-NITE is becoming commercially available. (in Japan)
SUMMARY

SiC/SiC R & D activities for nuclear applications are leading contributions to advanced SiC/SiC development. Those progresses are based on the understandings of materials behavior under nuclear environments. Element improvements for fiber, interphase and matrix bring extensive progresses in the decade.

Recent development of novel composite processes enhances the promises of SiC/SiC composites. Now entering production phase.

There have been many breakthroughs in these years, which satisfy basic requirements for fusion and advanced fission application and give us confidence that SiC/SiC can be low risk/high return materials.