Centre of Excellence for Nuclear Materials

Workshop

Materials Innovation for Nuclear Optimized Systems

December 5-7, 2012, CEA – INSTN Saclay, France

Laurent CHAFFRON et al.
CEA (France)

Innovative SiC/SiC Composite for Nuclear Applications

Workshop organized by:
Christophe GALLÉ, CEA/MINOS, Saclay – christophe.galle@cea.fr
Constantin MEIS, CEA/INSTN, Saclay – constantin.meis@cea.fr

Article available at http://www.epj-conferences.org or http://dx.doi.org/10.1051/epjconf/20135101003
Innovative SiC/SiC Composite for Nuclear Applications

Laurent CHAFFRON¹, Cédric SAUDER¹, Christophe LORRETTE¹, Laurent BRIOTTET², Aurore MICHAUX¹, Lionel GÉLÉBART¹, Aurélie COUPÉ¹, Maxime ZABIEGO³, Marion LE FLEM¹, Jean-Louis SÉRAN¹

¹CEA-DEN-DMN, Service de Recherche Métallurgiques Appliquées, SRMA (Saclay, France)
²CEA-DRT, Laboratoires d’Innovation pour les Technologies des Energies, LITEN (Grenoble, France)
³CEA-DEN-DEC, Service d’Etudes et de Simulation du Comportement des Combustibles, SESC (Cadarache, France)

Among various refractory materials, SiC/SiC ceramic matrix composites (CMC) are of prime interest for fusion and advanced fission energy applications, due to their excellent irradiation tolerance and safety features (low activation, low tritium permeability,…). Initially developed as fuel cladding materials for the Fourth generation Gas cooled Fast Reactor (GFR), this material has been recently envisaged by CEA for different core structures of Sodium Fast Reactor (SFR) which combines fast neutrons and high temperature (500°C). Regarding fuel cladding generic application, in the case of GFR, the first challenge facing this project is to demonstrate the feasibility of a fuel operating under very harsh conditions that are (i) temperatures of structures up to 700°C in nominal and over 1600°C in accidental conditions, (ii) irradiation damage higher than 60 dpa_SiC, (iii) neutronic transparency, which disqualifies conventional refractory metals as structural core materials, (iv) mechanical behavior that guarantees in most circumstances the integrity of the first barrier (e.g.: ε > 0.5%), which excludes monolithic ceramics and therefore encourages the development of new types of fibrous composites SiC/SiC adapted to the fast reactor conditions. No existing material being capable to match all these requirements, CEA has launched an ambitious program of development of an advanced material satisfying the specifications [1]. This project, that implies many laboratories, inside and outside CEA, has permitted to obtain a very high quality compound that meets most of the challenging requirements. We present hereinafter few recent results obtained regarding the development of the composite. One of the most relevant challenges was to make a gastight composite up to the ultimate rupture. Indeed, multicraking of the matrix is the counterpart of the damageable behavior observed in these amazing compounds. Among different solutions envisaged, an innovative one has been successful. It consists of inserting a metallic layer between two tubes of CMC [2]. The concept, illustrated in figure 1, guaranties a perfect helium tightness up to fracture of the CMC.

Fig. 1: Sandwich cladding concept: tightness is ensured up to CMC failure thanks to the elastic metallic layer.

Fig. 2: Sandwich cladding Cross section (metal is in white).
Another challenge was to prepare a representative cladding with very strict geometrical tolerances. Revisiting the fabrication of the entire breading process has allowed to ensure a perfect geometry of the final tube. Thanks to the high quality of manufacture and the high level of purity of composite materials manufactured at CEA, few tens of CMC objects (tubes, disks and plates) have been prepared in order to be irradiated in the Russian reactor “BOR 60”. For the first time, composite materials will be submitted to swift neutrons at very high damaging doses (up to 80 dpa\text{SiC}) between 400 and 520°C. Post irradiation examinations expected for 2015 should give reliable results on the behavior of this multi-materials component. In parallel, other basic researches are conducted to improve the properties of the CMC and round off the understanding \cite{3, 4, 5}. Some new results allowed to extend the field of use of the CMC through an optimization of the interphase of the composite. The figure 4 shows the relative elongation of a CMC after a two hours dwell time annealing in argon at different temperatures: optimized composite can sustain very high temperature without drastic drop of its mechanical properties.

![Fig. 3: CMC specimen prepared for BOR60 irradiation](image1)

![Fig. 4: Evolution of the relative elongation of two composites with the annealing temperature: optimized CVI conditions to improve mechanical properties.](image2)

References


\cite{3} C. Sauder, J. Lamon, Influence of fiber surface roughness on mechanical behaviour of SiC/SiC minicomposites with Hi-Nicalon S and SA3 reinforcement. 35\textsuperscript{ème} International Congress on Advanced Ceramic and Composites, Daytona beach 25 Janvier 2011.


Innovative SiC/SiC Composites for Nuclear Applications


MINOS Workshop, Materials Innovation for Nuclear Optimized Systems
December 5-7, 2012, CEA – INSTN Saclay, France
Development of refractory materials for pin cladding of 4th generation reactors

- R&D mostly driven by GFR fuel objectives (2004-2010)
- Recently extended to other applications: SFR & PWR

Focus on SiC/SiC composites:

- Refractory material (>> 1000°C)
- Irradiation resistance
- Low activation
- Neutron transparency
- Corrosion resistance

Issues: gastightness + mechanical properties + thermal properties
Matrix: protects the fiber and displays load transfer

Interphase: bonding between fiber and matrix

Fibre: ensures the mechanical strength

WHAT IS A SiC/SiC COMPOSITE?

→ SiC/SiC is a non brittle ceramic
WHICH SIC/SIC FOR NUCLEAR APPLICATION?

**Choice of the fiber:**

- **Stability under irradiation** ⇒ Hi-Nicalon S or Tyranno SA3 fibers only
- **Stability at high temperature** ⇒ Tyranno SA3 fibers looks better
- **Thermal conductivity** ⇒ Tyranno SA3 fibers looks better
- **Cost** ⇒ Tyranno SA3 fiber is cheaper (30%)

<table>
<thead>
<tr>
<th></th>
<th>HNS</th>
<th>TSA3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal stability</td>
<td>🎓</td>
<td>🎓</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>🎓</td>
<td>🎓</td>
</tr>
<tr>
<td>Cost</td>
<td>🎓</td>
<td>🎓</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>🎓</td>
<td>🎓</td>
</tr>
</tbody>
</table>

**Choice of the interphase:** PyC

**Choice of the matrix:** SiC CVI

CEA – DEN

MINOS Workshop - December 5-7, 2012, CEA – INSTN Saclay, France
THE MAIN CONCERNS FOR PIN CLADDING

FP retention = gas-thightness

SiC/SiC is not gastight upon its linear elastic domain.

Introduction of a liner for gas-tightness = CEA sandwich concept

Thermal exchange = High $\lambda$

$\lambda_{SiC}$ is lowered under irradiation (highly lowered at low temperatures)

- **Deal with it !**
  - Use of SA3 reinforcement
  - Process a specific matrix for composites $\Rightarrow$ very long term work

Irradiation mechanical behavior

Strain to failure $\varepsilon_R > 0.5$

- **Ok with HNS**
  - No solutions with SA3
  - Look for high dose irradiated mechanical behavior.

Goal: $\rightarrow$ Development of a gastight component prepared from HNS SiC/SiC composite
Properties can be tailored thanks to appropriate braiding.

Grinding has no significant effect on CMC.
Influence of a thermal treatment (2h in Ar) on mechanical properties

CVI SiC/SiC tube is not sensitive to very high temperature in inert atmosphere
Reference SiC/SiC material for Pin cladding:

FW (45°) 1 layer + 2D braiding (45°) 2 layers

Mechanical behavior is the same for traction or internal swelling

Fatigue tests:
20 -200MPa at 5 Hz
No failure after 500 000 cycles!
3 Patents:

⇒ Control of dimensions and tolerances of CMC composites

CEA/LTMEx Products

External and internal dimensions within 0.01mm tolerance

- external and internal dimensions: ±0.01 mm
- external cylindricity < 0.03mm with mean value of 0.02 mm.
- internal cylindricity < 0.05mm with mean value of 0.04 mm.
- concentricity < 0.05mm with mean value of 0.04 mm
- external Straightness < 0.02mm with mean value of 0.005 mm
- internal Straightness < 0.04mm with mean value of 0.02 mm
- $R_a$ (mean roughness) < 5µm and $R_z$ (max roughness) < 30µm

Very good dimensional accuracies (could be improved for internal part)
### Purity of CEA SiC/SiC composites

**Very few impurities**

Residual Impurities (Fe, S, N, O, H) belong to Hi-Nicalon S fibers

### Residual Impurities Concentration

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm at) SiC/SiC CEA</th>
<th>Concentration (ppm at) SiC CVD (R&amp;H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0,2200</td>
<td>2,54</td>
</tr>
<tr>
<td>C</td>
<td>matrix</td>
<td>matrix</td>
</tr>
<tr>
<td>Na</td>
<td>&lt; 0,04</td>
<td>&lt; 0,04</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt; 0,04</td>
<td>&lt; 0,04</td>
</tr>
<tr>
<td>Al</td>
<td>0,52</td>
<td>&lt; 0,007</td>
</tr>
<tr>
<td>Si</td>
<td>matrix</td>
<td>matrix</td>
</tr>
<tr>
<td>P</td>
<td>0,22</td>
<td>0,058</td>
</tr>
<tr>
<td>S</td>
<td>15,60</td>
<td>4,4</td>
</tr>
<tr>
<td>Cl</td>
<td>2,86</td>
<td>0,12</td>
</tr>
<tr>
<td>K</td>
<td>0,0560</td>
<td>&lt; 0,03</td>
</tr>
<tr>
<td>Ca</td>
<td>1,50</td>
<td>0,15</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt; 0,04</td>
<td>&lt; 0,04</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>Fe</td>
<td>5,36</td>
<td>&lt; 0,02</td>
</tr>
<tr>
<td>Co</td>
<td>&lt; 0,01</td>
<td>&lt; 0,01</td>
</tr>
<tr>
<td>Ni</td>
<td>0,34</td>
<td>0,03</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt; 0,01</td>
<td>&lt; 0,01</td>
</tr>
<tr>
<td>As</td>
<td>&lt; 0,01</td>
<td>&lt; 0,01</td>
</tr>
<tr>
<td>Zr</td>
<td>0,02</td>
<td>&lt; 0,002</td>
</tr>
<tr>
<td>Nb</td>
<td>&lt; 0,01</td>
<td>&lt; 0,01</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt; 0,01</td>
<td>&lt; 0,01</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 0,008</td>
<td>&lt; 0,008</td>
</tr>
<tr>
<td>Hf</td>
<td>&lt; 0,005</td>
<td>&lt; 0,005</td>
</tr>
<tr>
<td>Ta</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>W</td>
<td>&lt; 0,001</td>
<td>&lt; 0,001</td>
</tr>
<tr>
<td>Pt</td>
<td>&lt; 0,005</td>
<td>&lt; 0,005</td>
</tr>
</tbody>
</table>
**Liquid Phase Process:**

→ Hybrid Process **CVI + EPI + PIP**

**Objective:** Increase thermal conductivity of SiC/SiC by lowering porosity

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVI</td>
<td>Interphase PyC + SiC Pre-densification</td>
</tr>
<tr>
<td>EPI + PIP</td>
<td>SiC green Matrix</td>
</tr>
</tbody>
</table>

**Raw material**

- SiC nanopowder
- C/PyC/SiC nano
- C/PyC/SiC nano + SiC Polymer
- C/PyC/SiC nano + SiC Polymer

**Processing of a SiC layer on composites**

**Objectives:** Densification and smoothing of SiC/SiC composites

This alternative process could be used for densification of hexagonal tubes (cf P David oral) for which requirements are less harsh
PROCESSING : « SANDWICH » CONCEPT

Sandwich concept (CEA Patent)

Leak-tight domain with present-day CMC

Failure limit
(σ_f~300MPa - ε_f~0,9%)

Elastic limit
(σ_e~80MPa - ε_e~0,04%)
Beginning of microcracking

- Metallic liner only ensures tightness (processing in LTMEX)
- Composite ensures mechanical resistance
- Process is simple and reproducible

All stages of process are done in CEA

This type of cladding is supposed to be tight up to failure of the pin

Internal tube SiC/SiC: e~0.3mm
liner Ta: e<0.1mm
External tube SiC/SiC: e~0.6mm
Tantalum and Niobium are the best candidates for GFR. Is it still true for PWR or BWR?
Sandwich Concept – tightness during tensile test

Detection limit

« sandwich » concept allows to keep tightness up to failure of SiC/SiC pin cladding
3. SANDWICH CHARACTERIZATION

**Sandwich Nb – 1000h – 1200°C – Sandwich Ta**

- Very encouraging results with Ta
- Reaction zones are not symmetric (not observed with plates)
- Further characterization needed

CEA – DEN

MINOS Workshop - December 5-7, 2012, CEA – INSTN Saclay, France
Very encouraging results have been obtained with CVI minicomposite (CROCUS irradiation performed in OSIRIS).

**NEXT STEP:**

⇒ Irradiation in BOR60 (sodium, 550°C up to 105-120 dpa SiC)

First irradiation of SiC/SiC composites at such doses (Including sandwich specimens)

**Irradiation should start on december 19, 2012**

⇒ PIE are expected for 2015
CONCLUSION AND PROSPECTS

• **CMC: Tailoring materials**

• **Current work focused on fabrication of gastight closed for fast reactor applications (and hexagonal tube)**

• **Development of high skills in CMC manufacturing process at CEA**

• **Robust program of characterization: assessment of the high quality of the composites made at CEA**

• **Pursuit of Investment for CMC development: delivery of a winding machine in the next days and investment of a braiding machine in 2013**

• **Collaborative work with french universities through Matinex and NEEDs networks (Bordeaux, Mulhouse, Caen, Grenoble) and industrial partners**