Innovative SiC/SiC composites for nuclear applications

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
WHAT IS A SIC/SIC COMPOSITE?

Fibre: ensures the mechanical strength

Interphase: bonding between fiber and matrix

Matrix: protects the fiber and displays load transfer

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

Choice of the fiber:

Stability under irradiation ⇒ Hi-Nicalon S ou 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>

TSA is the target!

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

Thermal exchange = High $\lambda$
$\lambda_{\text{SiC}}$ is lowered under irradiation (highly lowered at low temperatures)

Irradiation mechanical behavior
Strain to failure $\varepsilon_R > 0.5$

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

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

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

Goal: Development of a gastight component prepared from HNS SiC/SiC composite
PROCESSING : INFLUENCE OF BRAIDING AND GRINDING

- Properties can be tailored thanks to appropriate braiding
- Grinding has no significant effect on CMC

Filament Winding
2D braiding
3D braiding

With and without grinding
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 - 200 MPa 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

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm at)</th>
<th>Concentration (ppm at)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>51.7</td>
<td>50.7</td>
</tr>
<tr>
<td>N</td>
<td>0.089</td>
<td>&lt; 0.0007</td>
</tr>
<tr>
<td>O</td>
<td>0.35</td>
<td>0.043</td>
</tr>
<tr>
<td>S</td>
<td>0.032</td>
<td>0.026</td>
</tr>
</tbody>
</table>

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

- Fe: < 0.01
- S: 15.60
- N: 0.34
- O: 0.35
- H: 0.032
- C: matrix
- Al: 0.52
- Si: matrix
- P: 0.22
- Cl: 2.86
- K: 0.0560
- Ca: 1.50
- Ti: < 0.04
- Cr: < 0.1
- Fe: 5.36
- Co: 0.01
- Ni: 0.04
- Cu: < 0.01
- As: < 0.01
- Zr: 0.02
- Nb: < 0.01
- Mo: < 0.01
- Sn: < 0.008
- Hf: < 0.005
- Ta: < 1
- W: < 0.001
- Pt: < 0.005
**Liquid Phase Process:**

→ Hybrid Process **CVI + EPI + PIP**

**Objective:** Increase thermal conductivity of SiC/SiC

by lowering porosity

![Diagram of processing steps](attachment:image)

**Raw material**

- SiC nanopowder
- LTMEx pyrolysis
- C_f/PyC/SiC nano
- C_f/PyC/SiC nano + SiC Polymer
- C_f/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

CEA – DEN

MINOS Workshop - December 5-7, 2012, CEA – INSTN Saclay, France
PROCESSING: « SANDWICH » CONCEPT

Sandwich concept (CEA Patent)

All stages of process are done in CEA

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

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

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

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

outer
Liner
inner

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