New Textile Structures and Film-Boiling Densification for SiC/SiC Components

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New Textile Structures and Film-Boiling Densification for SiC/SiC Components

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Among all ceramic candidates, silicon carbide (SiC) materials present the best properties for use in very harsh nuclear environments. Indeed, they possess an excellent behavior under high neutron irradiation, high thermal conductivity and mechanical properties at high temperature in addition to a chemical inertness. Meanwhile, as monolithic ceramics are too brittle, it is necessary to use SiC in the form of SiC/SiC materials, which exhibit a high fracture toughness and allow the manufacturing of both very thin and large pieces. Principal studies of nuclear applications have been conducted since the middle of the 1990’s, for blanket of wall fusion reactors \cite{1}. SiC/SiC composites have also been recently envisaged as alternatives to zircaloy fuel claddings in order to cope with core overheating accidents of Light Water Reactors \cite{2}. During the last decade, intensive investigations on 4\textsuperscript{th} generation fission reactor applications have been conducted \cite{3}, mainly for fuel claddings, and also, more recently, for other components, such as the Hexagonal Tube (HT) for pin assembling, control rods, heat exchangers or thermal barriers for the Hot Gas Duct.

Several developments and optimizations are necessary to meet the specifications of structural components in nuclear systems which differ strongly from those of common aeronautical and spatial applications. The performed studies have addressed several technological points that were considered as bottlenecks. For Gas cooled Fast Reactor claddings, new textile processes have been developed for manufacturing of honeycomb structures \cite{4} or closed tubular braids \cite{5} (Figure 1), used as fibrous reinforcement structures. Control of the geometry can be improved using graphite tools, during densification, and by addition of a sacrificial layer that is machined away after densification (Table 1), (Figure 2). The internal surface smoothness has been increased through an initial Chemical Vapor Deposition step on the graphite rod used as a mandrel for pin braiding. As SiC/SiC materials possess a limited tolerance when it comes to the set deformation, a flexible ceramic porous bond, constituted of a ceramic textile structure, has been proposed \cite{6} and characterized to improve the fuel pellet-clad interaction.

Concerning the Hexagonal Tube, studies have been performed on the very particular film-boiling process (Figures 3 and 4). The aim was to reduce the important densification time and cost, due to the quite large dimensions and thickness of this component. Depending on the chemical precursors used, the main difficulty consisted in controlling either the matrix composition, which can contain excess carbon, or the microstructure, which can be less ordered and conductive than CVI deposits. A few investigations have also been initiated on SiC/SiC with low density and conductivity, to manufacture a thermal barrier for the Hot Gas Duct.

Owing to the stringent specifications set for nuclear components, the development of SiC/SiC materials, and more particularly for cladding applications, is an ambitious target, both from technological and scientific standpoints. Complementary tests and characterizations are still necessary to prove that these materials are consistent with the targeted performance. All the knowledge and knowhow developed during these studies should be useful to obtain technological solutions for tailored and reliable SiC/SiC components for high-temperature (nuclear) applications.
Table 1: Accuracies obtained for the geometrical dimensions of a 10-cm long, 4-layered bi-axial braid.

<table>
<thead>
<tr>
<th>External Diameter (mm)</th>
<th>General straightness (mm)</th>
<th>Local straightness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[8.96, 8.99]</td>
<td>&lt; 0.03</td>
<td>0.04</td>
</tr>
</tbody>
</table>

References

NEW TEXTILE STRUCTURES
AND FILM-BOILING DENSIFICATION
FOR SIC/SIC COMPONENTS (IV Gen.)

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Studies supervised by CEA/DEN

MINOS
Materials Innovation for Nuclear Optimized Systems
Workshop
December 5-7, 2012, CEA - IRSTN, Saint-Paul, France
1- Generalities

2- Honeycomb

3- Pin, buffer

4- Hexagonal Tube (Film-Boiling densification)

5- Insulators

6- Conclusion
1- GENERALITIES: SiC/SiC APPLICATIONS

1- GFR Fuel claddings
   T ~ 900°C, P_{He} ~ 70 bar
   2 concepts

2- SFR Hexagonal tube
   T ~ 700°C

3- GFR Hot Gas Duct
   T ~ 450°C / 850°C, P_{He} ~ 70 bar, v_{He} ~ 40-70 m/s

Other potential applications:
- WPR components with improved safety
- control rods, …
. Irradiation behaviour

. Mechanical behaviour 900°C

\[ \sigma : \text{as high as possible, } \varepsilon > 0.5-1\% \]

. Thermal conductivity: as high as possible (> 10 W/mK)

. Gas tightness (liner)

. Dimensional accuracy: better than 0.1 mm

. Surface smoothness: Ra < 50 \(\mu m\)

. Closure system (two half pin concept)

\[ \text{Ext. Across flat: 13 mm} \]
\[ e \text{ (wall): 1.3 mm} \]
\[ H : \sim 3-10 \text{ mm} \]

\[ \Phi_{\text{int}} : 7 ; 8 \text{ mm} \]
\[ e : 1 \text{ mm} \]
\[ L : \sim 1.5 \text{ or } 3 \text{ m} \]
2- NEW PROCESS FOR HONEYCOMBS

Main drawbacks (HC walls) of existing process
- thickness: not constant or not accurate
- fibres %: not constant
- continuity of the fibers between the cells: none or partial

Graphite tool

SiC fibers (TSA3) placement

PyC deposit and SiC CVI

CEA Patent (WO 2009/065794)
HONEYCOMBS CHARACTERIZATION

Results
- density ~ 2.4
- fibers (V%) ~ 30

<table>
<thead>
<tr>
<th>Wall thickness</th>
<th>Target: 1.3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimum</td>
<td>1.25</td>
</tr>
<tr>
<td>maximum</td>
<td>1.63</td>
</tr>
<tr>
<td>average</td>
<td>1.39</td>
</tr>
<tr>
<td>standard deviation</td>
<td>0.1</td>
</tr>
</tbody>
</table>

| Distance between 2 || walls | Target: 12.7 mm |
|-------------------|-----------------|
| minimum           | 12.57           |
| maximum           | 12.95           |
| average           | 12.84           |
| standard deviation | 0.12            |
2 D braiding main parameters

<table>
<thead>
<tr>
<th>Braiding type</th>
<th>Bi-axial, tri-axial (2,2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle (°)</td>
<td>30 ; 45 ; 62</td>
</tr>
<tr>
<td>Number of layers</td>
<td>3 ; 4</td>
</tr>
</tbody>
</table>

SiC fibers

Braiding on a substrate

Insertion in a carbon tool

CVI; removing the substrate
NEW PROCESS FOR PIN CLOSURE

Regular braiding

Braiding with a closed extremity

0°

45°

45° + 90°
PIN CLOSURE RESULTS

Tomography

External view

Longitudinal section view

Internal view
PIN CHARACTERISTICS / Internal part

Internal diameters (mm)

SiC CVD on C rod

Braiding, densification

Internal roughness

Ra = 26 µm
Samples: 10 cm length pin (inner diameter : 7.0 mm ; external : 9.0 mm)

Control of the diameter

<table>
<thead>
<tr>
<th>Control parameter</th>
<th>Plane A</th>
<th>Plane B</th>
<th>Plane C</th>
<th>Plane D</th>
<th>Plane E</th>
</tr>
</thead>
<tbody>
<tr>
<td>After machining</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNS, 4 L bi-axial, 45 °</td>
<td>8.98</td>
<td>8.98</td>
<td>8.97</td>
<td>8.99</td>
<td></td>
</tr>
<tr>
<td>SA3, 3 L bi-axial, 62 °</td>
<td>8.96</td>
<td>8.93</td>
<td>8.96</td>
<td>8.96</td>
<td>8.96</td>
</tr>
</tbody>
</table>

Straightness has to be improved for 0.9 m long pin

Straightness (along a line)

<table>
<thead>
<tr>
<th>Straightness parameter</th>
<th>General straightness (mm)</th>
<th>Local straightness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube (after machining)</td>
<td>&lt; 0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>HNS, 4 L bi-axial, 45 °</td>
<td>&lt; 0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>SA3, 3 L bi-axial, 62 °</td>
<td>&lt; 0.04</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Roughness

<table>
<thead>
<tr>
<th>Roughness</th>
<th>$R_a$ ($\mu m$)</th>
<th>$R_z$ ($\mu m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane 10°</td>
<td>10°</td>
<td>60°</td>
</tr>
<tr>
<td>Plane 60°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PIN BUFFER CONCEPTION

Pellet/clad porous-solid (“buffer”) bond
- Thermal conductivity, at high T
- Mechanical protection (PCMI, chips…)
- Pellet/clad centering, FP diffusion barrier

Material: ceramic (C, SiC) porous structure

Excellent compressibility up to $\sigma = 10$ MPa

Patent CEA (Cadarache, Le Ripault) 2010 (Claddings, control rods)
5- FILM-BOILING FOR HEX. TUBE DENSIF./ GENERALITIES

CEA process:  
- high densification rate
- thick part

Film-Boiling

<table>
<thead>
<tr>
<th>Gaz flow rate</th>
<th>Pressure</th>
</tr>
</thead>
</table>

Density

CVI

Hex.Tube

200 400 600

Time (h)

25 cm

C/C brake

2

1,8

1,6

1,4

1,2

1

0,8

0,6

0,4

0,2

0

0

0,2

0,4

0,6

0,8

1

1,2

1,4

1,6

1,8

2

(C/C densification)

Thermocouples

Generator

P = f(t)

Precursor

Sample

Reactor

Sample

Thermocouples

Generator

P = f(t)
STUDIES FOR HEXAGONAL TUBE DENSIFICATION

Parameters

➤ chemical precursors (MTS, CVD 4000, …)

\[
\text{SiCl}_3\text{CH}_3 \rightarrow (3 - x) \text{SiC} + x \text{C} + x \text{SiCl}_4 + (3 - 4 x) \text{HCl} + 2 x \text{H}_2
\]

V densification : 0.1 - 1 mm/h (T < 1000 °C)

➤ structures, samples configuration, T cycles, …

Film boiling apparatus

Localization of the thermocouples

Thermal cycle
H.T DENSIFICATION RESULTS

Felts (\(\rho \sim 2.9\))

Non crimp fabric (fibers placement)

Macroscopic view

Microstructure view (optical microscopy)

Braids

Densification

. C excess : 1 - 15 % at.
Specifications: \( \lambda < 0.5 \) W/m.K, for \( 450°C < T < 850°C \) and \( P \sim 70 \) bar

1- Low conductivity matrix

<table>
<thead>
<tr>
<th>Material</th>
<th>Diffusivity ( (10^{-5} \text{ m}^2\cdot\text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tyranno SA3</td>
<td>0.9</td>
</tr>
<tr>
<td>CVI matrix</td>
<td>1.3</td>
</tr>
<tr>
<td>Film Boil. matrix (b)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Thermal diffusivity of SiC fibres and SiC matrices

2- Low density composite

<table>
<thead>
<tr>
<th>SiC/SiC density ( (\text{g/cm}^3) )</th>
<th>Diffusivity ( (10^{-7} \text{ m}^2\cdot\text{s}^{-1}) )</th>
<th>Transversal conductivity ( \text{(W/m.K)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26</td>
<td>1.5</td>
<td>0.03</td>
</tr>
<tr>
<td>0.53</td>
<td>3.1</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Thermal diffusivity and conductivities of low density SiC/SiC

Simulated T in a low density SiC/SiC

\( T \) (Normalized)
6- CONCLUSION

- New materials and processes
- Characterization and simulation of the fibrous architectures and composites
- Continuation
  - film-boiling, for hexagonal tube
  - characterizations (thermal, mechanical)

Transposition of the knowledge to other fields: aeronautic, spatial, energy
Thank you for your attention