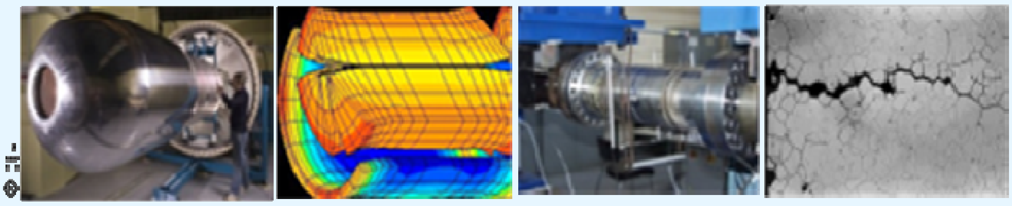
# MINOS

## Centre of Excellence for Nuclear Materials

# Workshop

## Materials Innovation for Nuclear Optimized Systems



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

**Patrick DAVID et al.**

CEA (France)

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

**Workshop organized by:**

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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 [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 [2]. During the last decade, intensive investigations on 4$^{th}$ generation fission reactor applications have been conducted [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 [4] or closed tubular braids [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 [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.

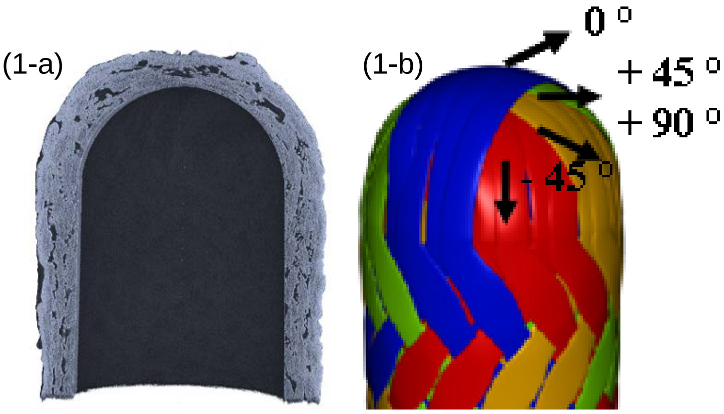


**Fig. 1: The closed extremity of the SiC/SiC densified braid (1-a) and a representation (simulation) of the position of the yarns (1-b).**

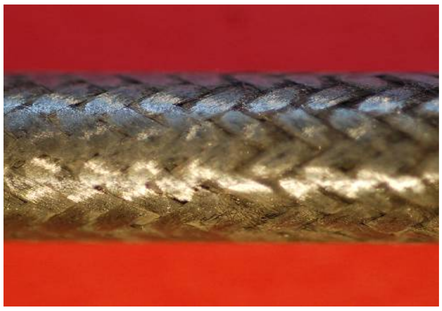

**Fig. 2: A view of the surface of the SiC/SiC densified braid, after machining (Ra ~ 10 μm).**

**Fig. 3: A view of the film-boiling reactor. The fibrous structure is immersed in a liquid precursor and brought to about 1000°C through radio-frequency heating.**

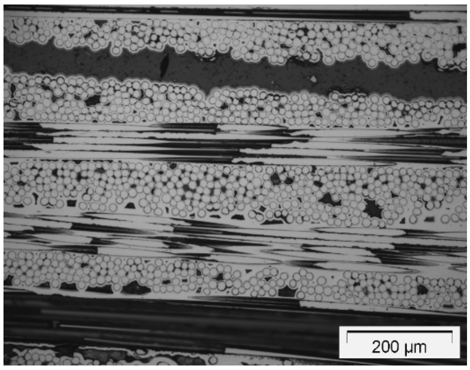


**Fig. 4: The microstucture of a SiC/SiC composite (hexagonal tube application) densified with the film-boiling technique.**

**Table 1: Accuracies obtained for the geometrical dimensions of a 10-cm long, 4-layered bi-axial braid.**

| External Diameter (mm) | General straightness (mm) | Local straightness (mm) |
|---|---|---|
| [8.96, 8.99] | < 0.03 | 0.04 |

### References

[1] L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, Status of silicon carbide composites for fusion. J. Nucl. Mater. 233–237, 26 (1996).
[2] H. Feinroth, B. Hao, L. Fehrenbacher, Progress in developing an impermeable, high temperature ceramic composite for advanced reactor clad and structural applications. ICAPP Proceedings (2002).
[3] W. Corwin, The Gas Fast Reactor (GFR) Survey of Material Experience and R&D Needs to Assess Viability. Ref: ONRL/TM-2004/99 (2004).
[4] CEA Patent, CEA Patent, Method for producing a cellular fibrous structure, P. David. WO 2009/0065794, 28/05/2009.
[5] CEA Patent, Architecture fibreuse tubulaire fermée et procédé de fabrication, P. David, JL Bonnand, B. Bompard, PCT/EP2010/067736, 18/11/2010.
[6] CEA Patent, Joint d'interface solide à porosité ouverte pour crayon de combustible nucléaire et pour barre de commande nucléaire. M. Zabiego, P. David, A. Ravenet, D. Rochais, PCT/EP2011/060001, 16/06/2011.

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

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*Studies supervised by CEA/DEN*

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# PRESENTATION OUTLINE

1- Generalities

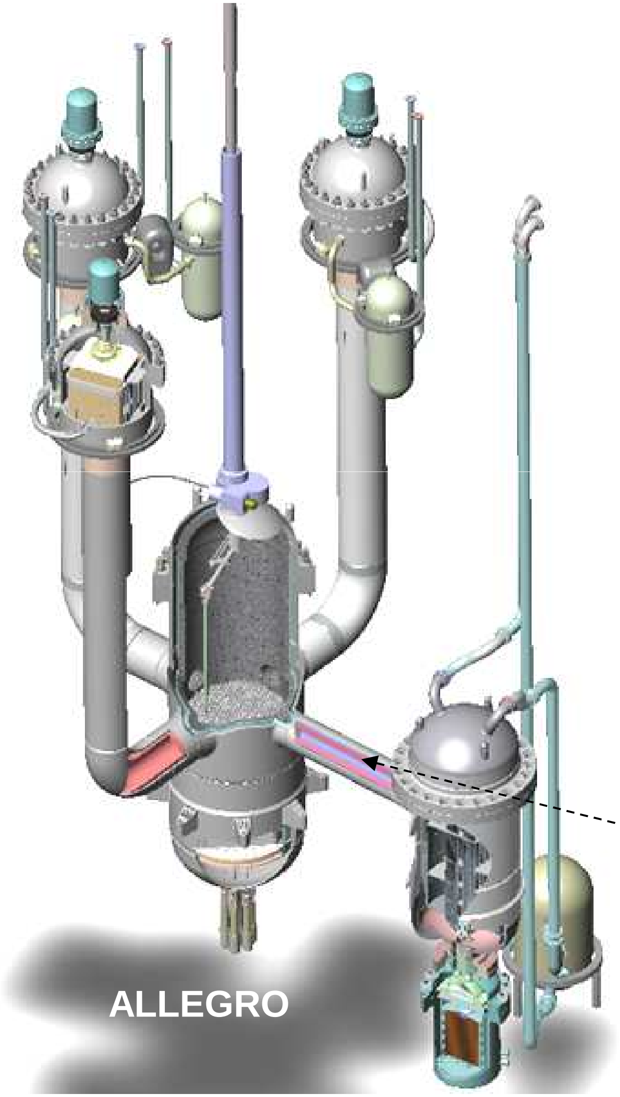
2- Honeycomb

3- Pin, buffer

4- Hexagonal Tube (Film-Boiling densification)

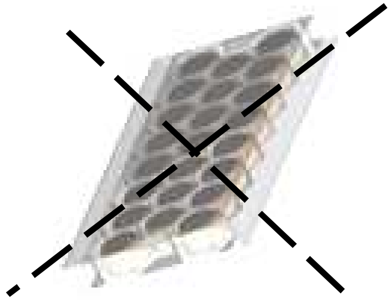
5- Insulators

6- Conclusion

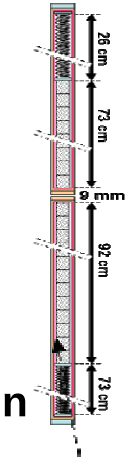



## 1- GFR Fuel claddings

T ~ 900°C, $P_{He}$ ~ 70 bar
2 concepts



Honey Comb

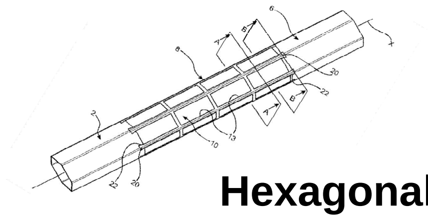



Pin

Buffer

## 2- SFR Hexagonal tube

T ~ 700°C



Hexagonal tube

## 3- GFR Hot Gas Duct

T ~ 450°C / 850°C, $P_{He}$ ~ 70 bar, $v_{He}$ ~ 40-70 m/s
**Insulators**

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

# GENERALITIES : MATERIALS SPECIFICATIONS (Claddings)

. Irradiation behaviour

. Mechanical behaviour 900°C

} → SiC/SiC

$\sigma$ : as high as possible, $\varepsilon$ > 0,5-1 %

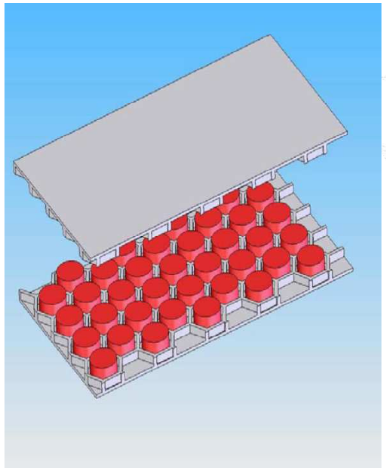
. Thermal conductivity: as high as possible (> 10 W/mK)

. Gas tightness (liner)

. Dimensional accuracy : better than 0.1 mm

. Surface smoothness : Ra < 50 µm

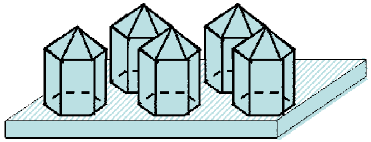
. Closure system (two half pin concept)

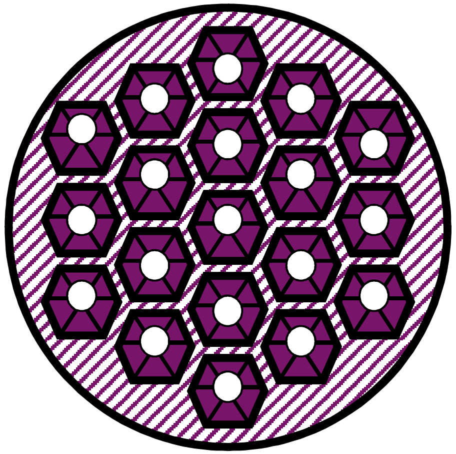


Ext. Across flat : 13 mm
e (wall) : 1.3 mm
H : ~ 3-10 mm

$\Phi_{unt}$ : 7 ; 8 mm
e : 1 mm
L : ~ 1.5 or 3 m

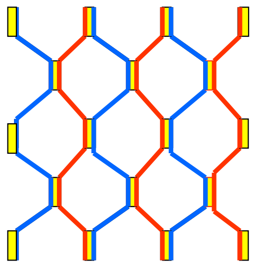
# 2- NEW PROCESS FOR HONEYCOMBS

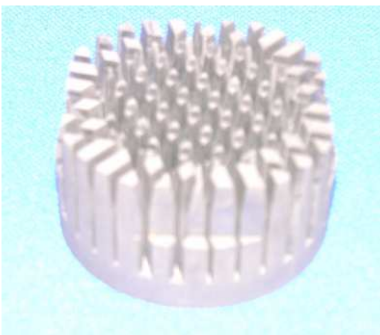




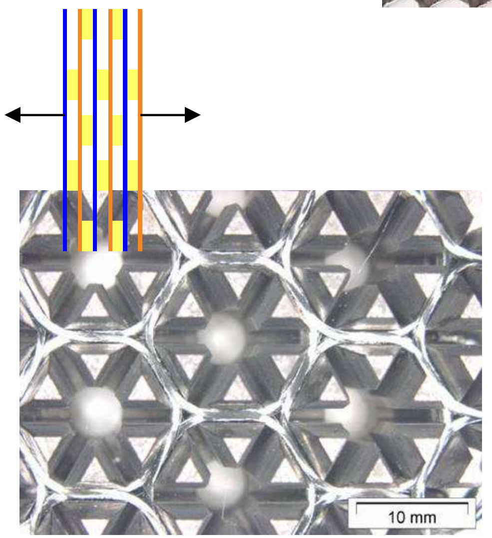
Main drawbacks (HC walls) of existing process

- thickness : not  constant or not accurate
- fibres % : not constant
- continuity of the fibers between the cells : none or partial



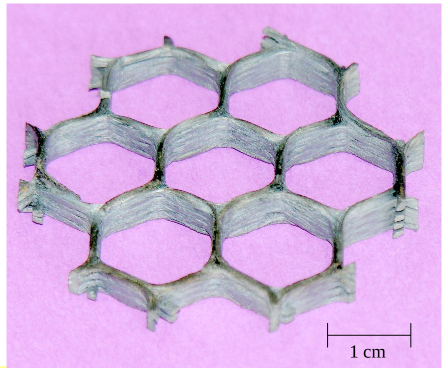


Graphite tool



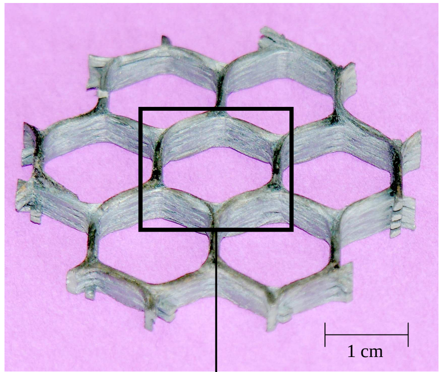

SiC fibers (TSA3) placement

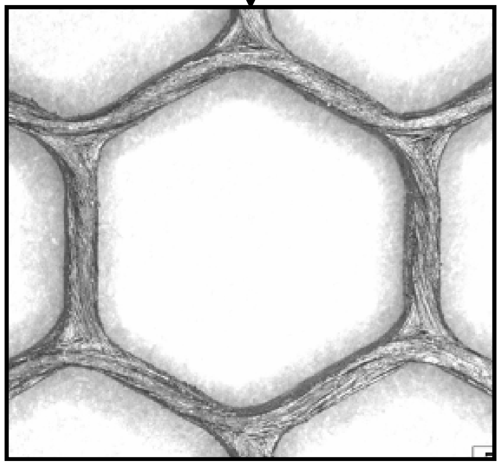
PyC deposit
and SiC CVI

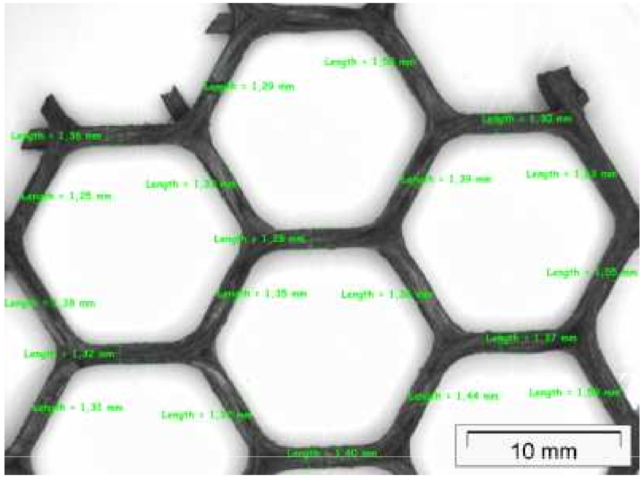



CEA Patent (WO 2009/065794)

# HONEYCOMBS CHARACTERIZATION



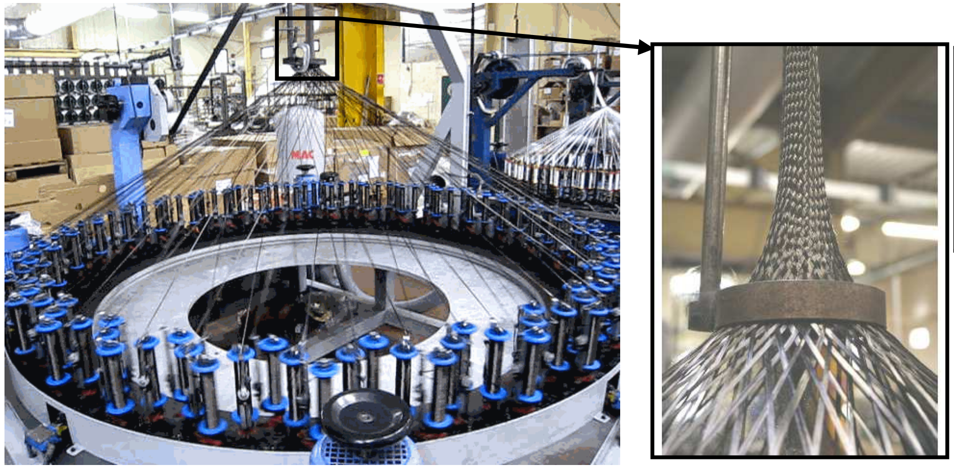





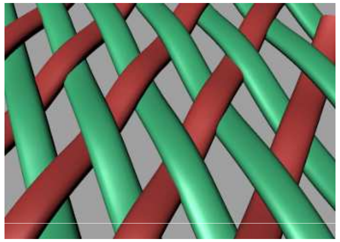

Results
. density ~ 2.4
. fibers (V%) ~ 30

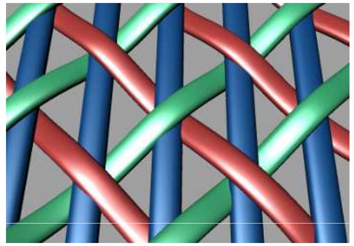
| Wall thickness | Target: 1.3 mm |
|---|---|
| . minimum | 1.25 |
| . maximum | 1.63 |
| . average | **1.39** |
| . standard deviation | 0.1 |
| | |
| **Distance between 2 // walls** | Target: 12.7 mm |
| . minimum | 12.57 |
| . maximum | 12.95 |
| . average | **12.84** |
| . standard deviation | 0.12 |
| | |

# 3- PIN / GENERAL MANUFACTURING



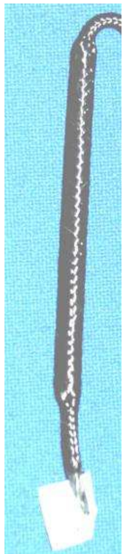
| 2 D braiding main parameters | |
|---|---|
| Braiding type | Bi-axial, tri-axial (2,2) |
| Angle (°) | 30 ;45 ; 62 |
| Number of layers | 3 ; 4 |





SiC fibers

Braiding
on a substrate

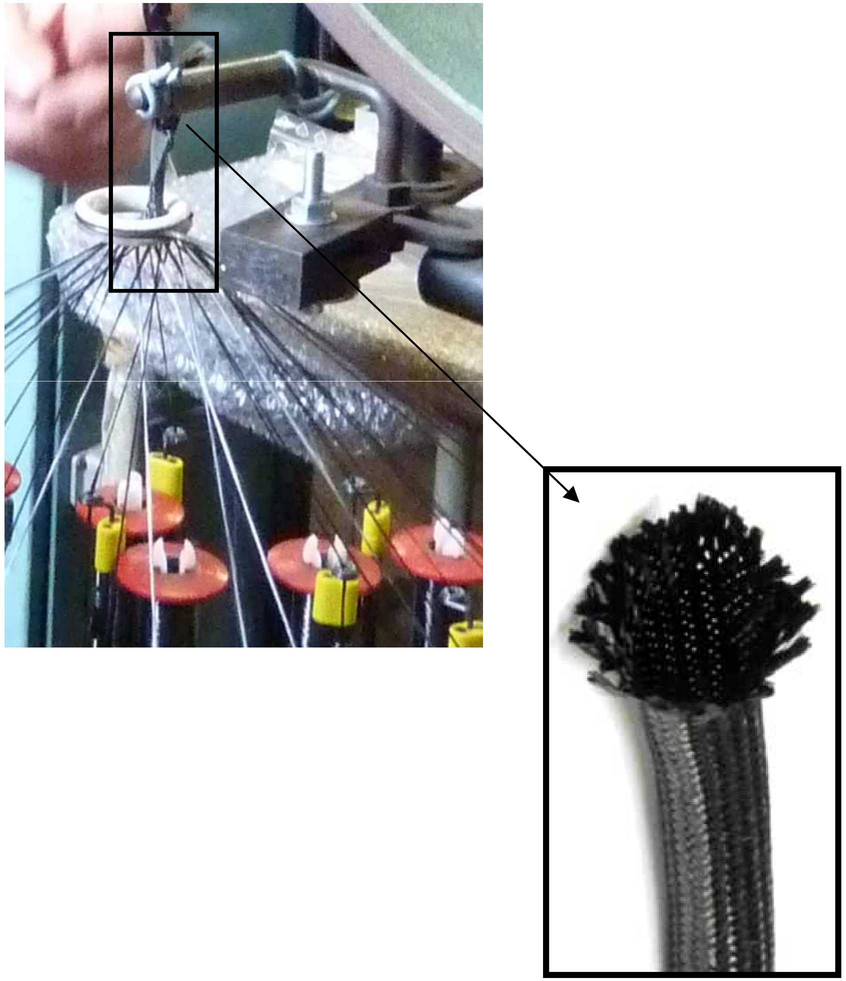


Insertion in a
carbon tool

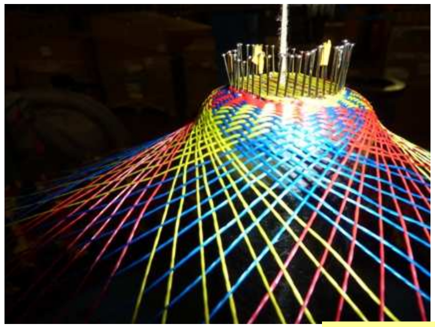
CVI ; removing
the substrate

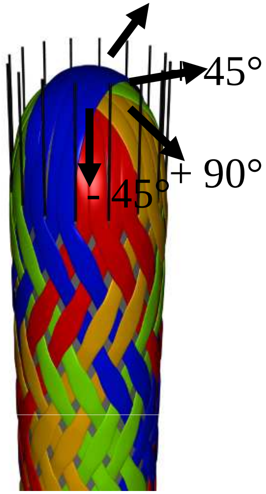
# NEW PROCESS FOR PIN CLOSURE

## Regular braiding



## Braiding with a closed extremity

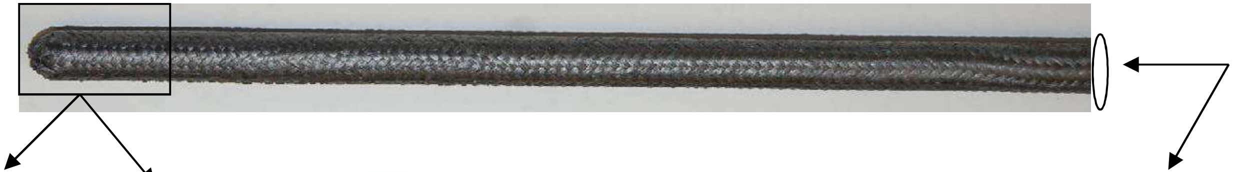





CEA Patent EP2010/067736

# PIN CLOSURE RESULTS

Tomography

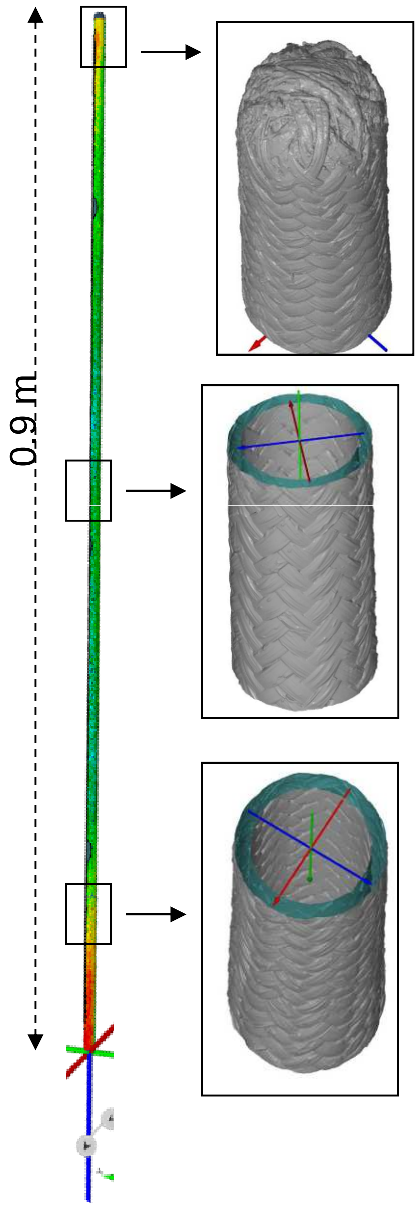


External view

Longitudinal section view

Internal view

# PIN CHARACTERISTICS / Internal part



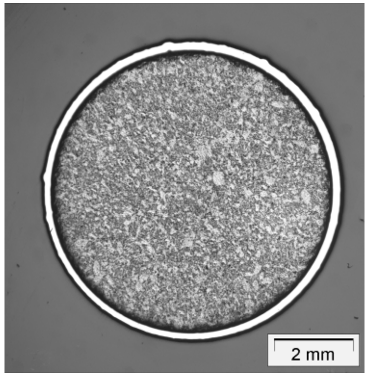

Internal diameters (mm)

| Circle_Section2 | |
|---|---|
| | Actual |
| X | -0.00 |
| Y | +9.00 |
| Z | +0.00 |
| Ø | +8.12 |

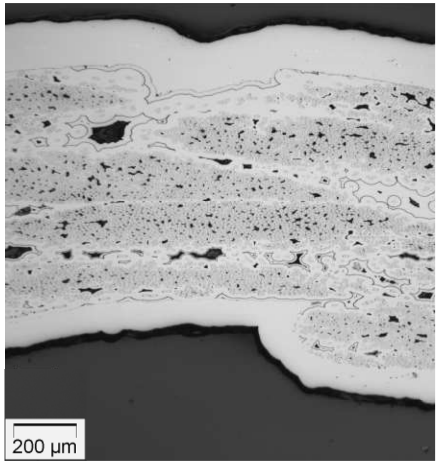
| Circle_Section2 | |
|---|---|
| | Actual |
| X | +0.00 |
| Y | +10.00 |
| Z | +0.00 |
| Ø | +8.16 |

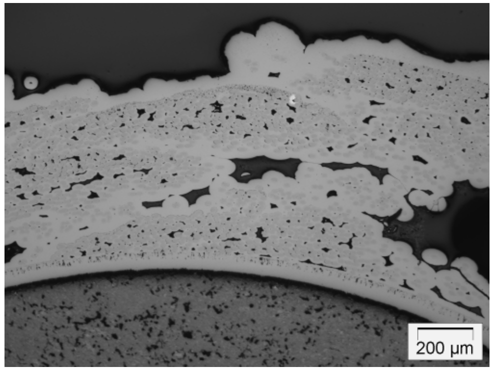
| Circle_Inter_Section2 | |
|---|---|
| | Actual |
| X | +0.01 |
| Y | +10.00 |
| Z | +0.00 |
| Ø | +8.14 |

SiC CVD on C rod




Braiding, densification



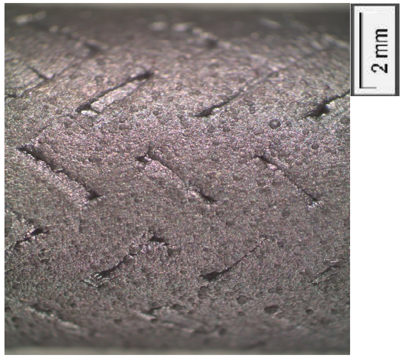

Internal roughness

Ra = 26 µm

# PIN CHARACTERISTICS/External surface

Samples: 10 cm length pin (inner diameter : 7.0 mm ; external : 9.0 mm)

Pin machining




Machining + CVD

Smoothness step + machining

Control of the diameter

| Φ external (mm) | Before machining | After machining | | | | |
|---|---|---|---|---|---|---|
| | | Plane A | Plane B | Plane C | Plane D | Plane E |
| HNS, 4 L bi-axial, 45 ° | 10,1+-0,1 | 8,98 | 8,99 | 8,98 | 8,97 | 8,99 |
| SA3, 3 L bi-axial, 62 ° | 10,1+-0,1 | 8,96 | 8,93 | 8,96 | 8,96 | 8,96 |

Straightness (along a line)

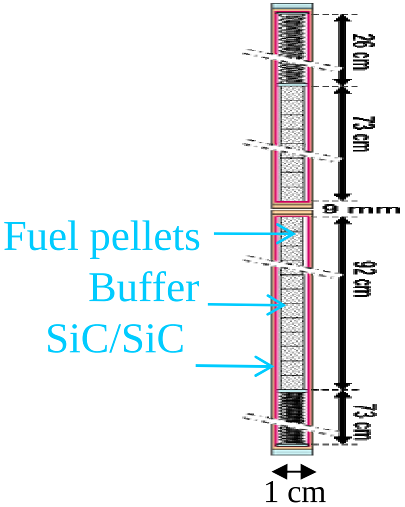
| Tube (after machining) | General straightness (mm) | Local straightness (mm) |
|---|---|---|
| HNS, 4 L bi-axial, 45 ° | < 0,03 | 0,04 |
| SA3, 3 L bi-axial, 62 ° | < 0,04 | 0,08 |

**Straightness has to be improved for 0.9 m long pin**

Roughness

| Ra (µm) | Rz (µm) |
|---|---|
| 10 | 60 |

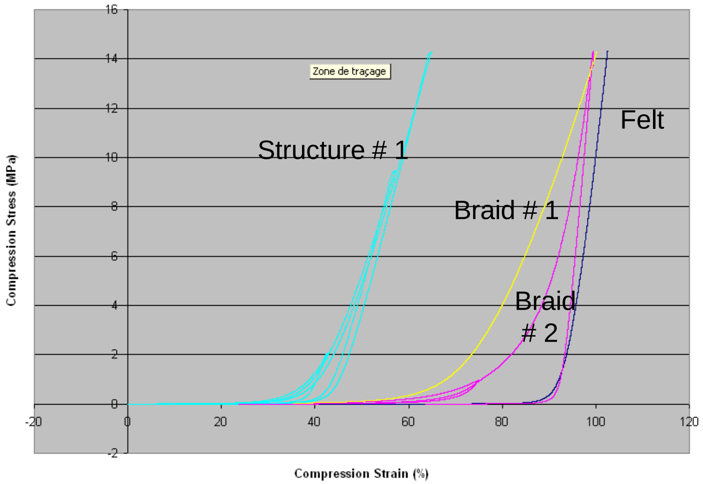
# PIN BUFFER CONCEPTION




Pellet/clad porous-solid (“buffer”) bond

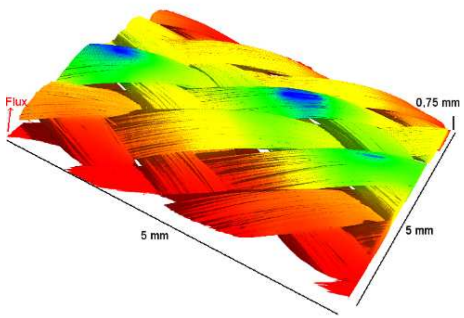
- Thermal conductivity, at high T
- Mechanical protection (PCMI, chips…)
- Pellet/clad centering, FP diffusion barrier

Material: ceramic (C, SiC) porous structure



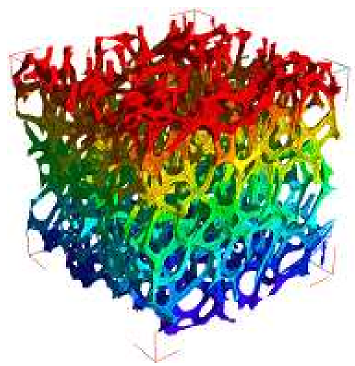

Excellent compressibility up to $\sigma$ = 10 MPa

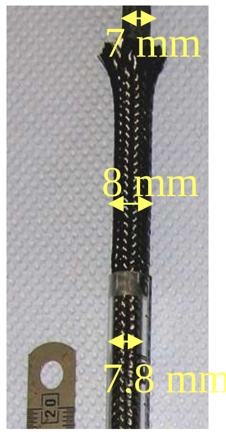
Braid




$\lambda_{radial}$ 1.1 W/m.K (1000°C, 1-70 b He)

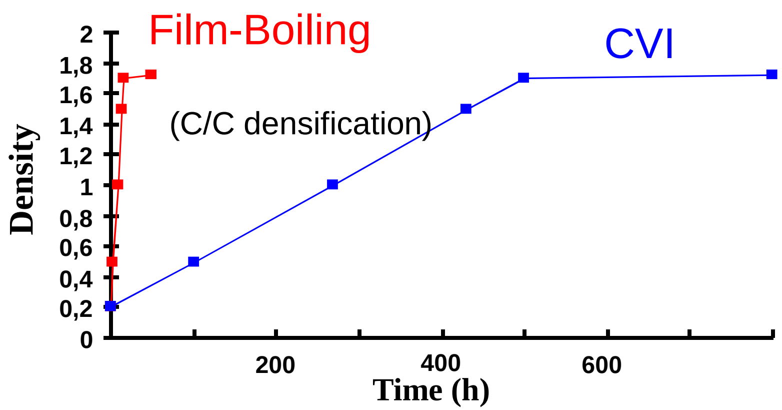
Foam





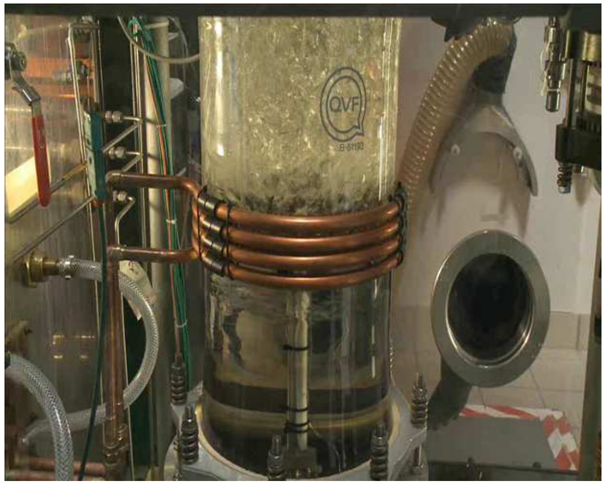

Patent CEA (Cadarache, Le Ripault) 2010 (Claddings, control rods)

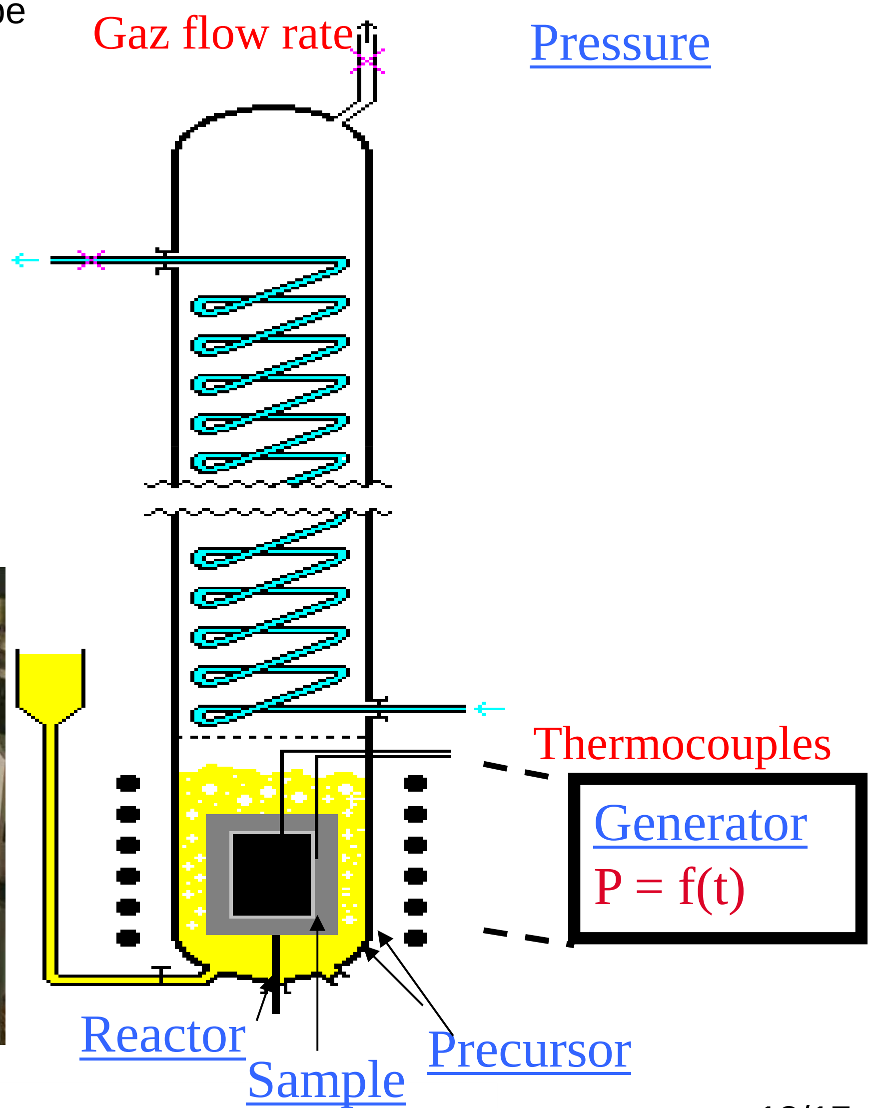
CEA process: . high densification rate → Hex.Tube
. thick part





C/C brake



# STUDIES FOR HEXAGONAL TUBE DENSIFICATION

<u>Parameters</u>

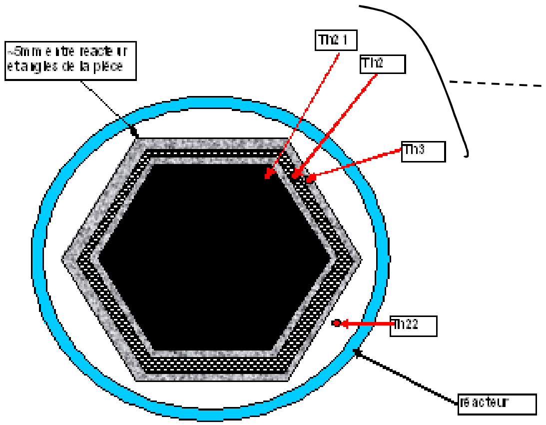
- chemical precursors (MTS, CVD 4000, …)

$$SiCl_3CH_3 \longrightarrow (3 - x)\ SiC + x\ C + x\ SiCl_4 + (3 - 4\ x)\ HCl + 2\ x\ H_2$$

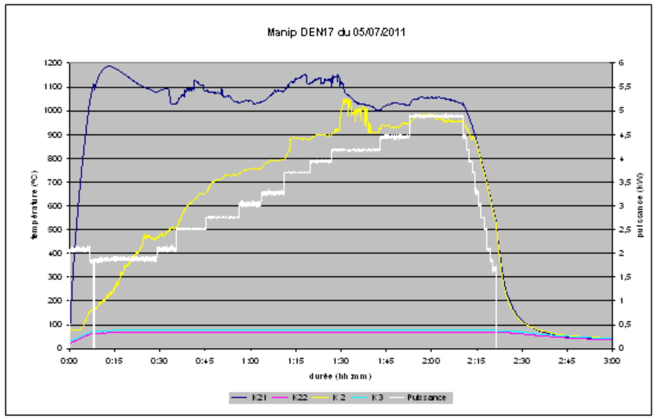
V densification : 0.1 - 1 mm/h (T < 1000 °C)

- structures, samples configuration, T cycles, …

Film boiling apparatus




Localization of the thermocouples




Thermal cycle

# H.T DENSIFICATION RESULTS

## Felts

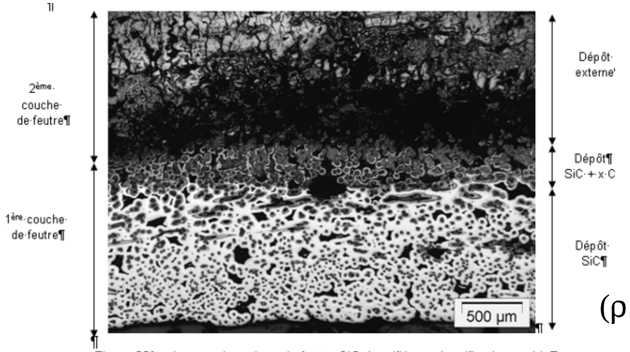
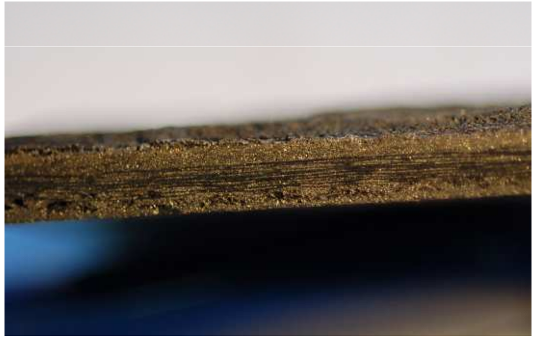



Figure 23° : microscopie optique du feutre SiC densifié par densification rapide (grossissement x 50).

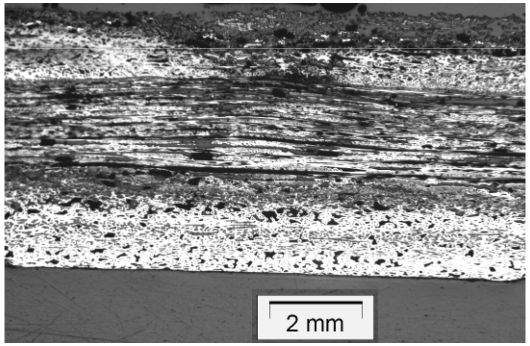
(ρ ~2,9)

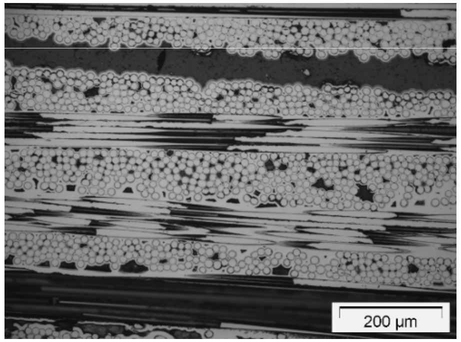
## Braids

## Non crimp fabric (fibers placement)



Macroscopic view




Microstructure view (optical microscopy)

**Densification**

. C excess : 1 - 15 % at.

# 5- INSULATING SiC COMPOSITES
## (HTR Hot gas duct application)

Specifications : $\lambda < 0.5$ W/m.K, for 450°C < T < 850°C and P ~ 70 bar

### 1- Low conductivity matrix

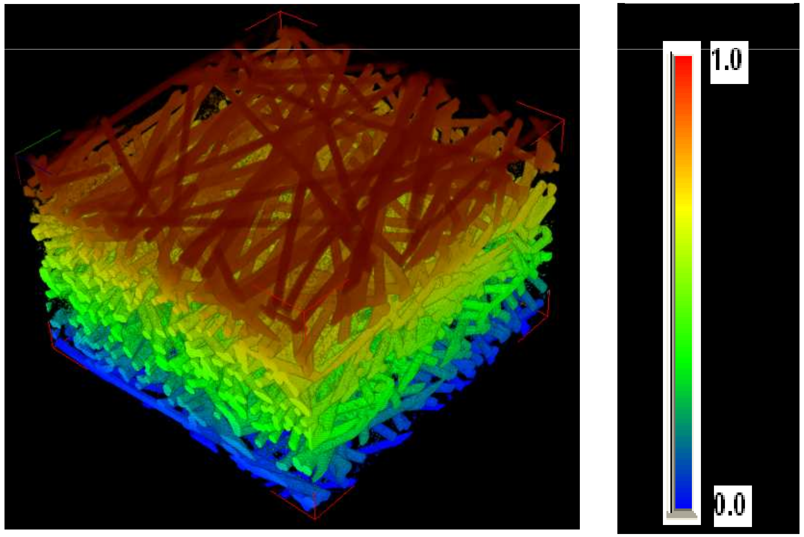
| Material | Diffusivity ($10^{-5}$ $m^2.s^{-1}$) |
|---|---|
| Tyranno SA3 | 0.9 |
| CVI matrix | 1.3 |
| Film Boil. matrix (b) | 0.1 |

Thermal diffusivity of SiC fibres and SiC matrices

### 2- Low density composite

| SiC/SiC density ($g/cm^3$) | Diffusivity ($10^{-7}$ $m^2.s^{-1}$) | Transversal conductivity (W/m.K) |
|---|---|---|
| 0.26 | 1.5 | 0.03 |
| 0.53 | 3.1 | 0.12 |

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

→ Transposition of the knowledge to other fields :

aeronautic, spatial, energy

- Continuation

. film-boiling, for hexagonal tube
. characterizations (thermal, mechanical)

# Thank you
# for your attention

Commissariat à l'énergie atomique et aux énergies alternatives
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