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# PROCESSING AND PROPERTIES OF SIC/SIC COMPOSITES FOR NUCLEAR POWER PLANT APPLICATIONS

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DEN/DANS/DMN/SRMA

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- **SiC and SiC/SiC composites for nuclear applications**
  - SiC advantages and drawbacks
  - SiC/SiC requirements for cladding applications
- **Processing of SiC/SiC composites for nuclear application**
- **Properties of fabricated SiC/SiC composites**
  - Mechanical
  - Thermal
  - Thermochemical compatibility
- **Conclusion**

## **Nuclear applications requirements for core materials**

### **Stability under neutron irradiation up to high doses (in dpa)**

- Few dpa for thermal neutron applications (LWR,(V)HTR)
- 100 dpa for fast neutron applications (GFR, SFR)
- Requirements:
  - Dimensional stability (reduced swelling)
  - Stability of thermal and mechanical behavior
  - Low irradiation creep

### **Gas tightness for cladding applications**

### **Low neutron absorption (function of incidental energy)**

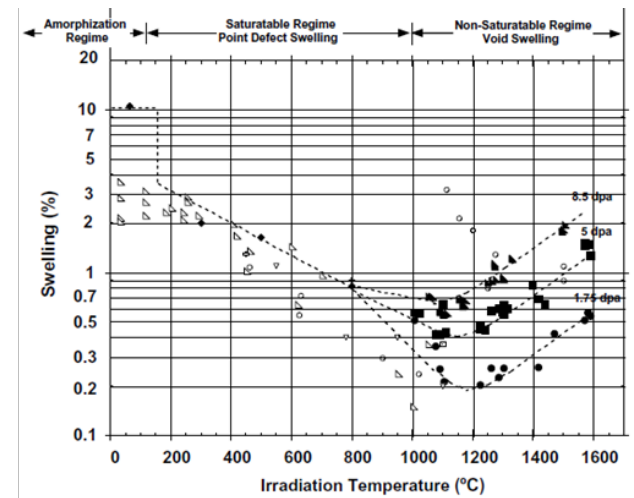
### **Resistance in accidental situations (very high temperatures)**

### **Compatibility with waster reprocessing**

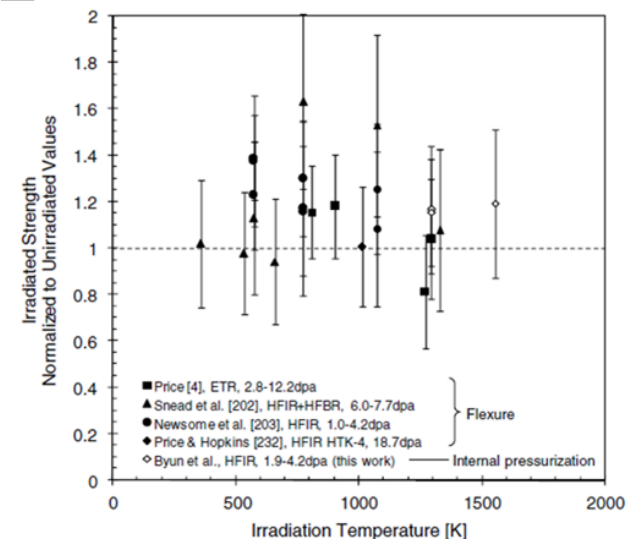
### **Low activation materials (ideally)**

## SiC (high purity CVD) for nuclear reactors

- High decomposition temperature of SiC (over 2000°C)
- Swelling under irradiation:
  - Low (< 3%) for  $T > 200^{\circ}\text{C}$
  - Independent of the dose in the 200 – 800°C range
- Mechanical properties (Young modulus, failure strain) are only a little affected by irradiation up to 1200°C
- Low creep under irradiation in the 200 – 1000°C temperature range
- Low residual activity
- Good neutronic behavior
- Good air oxidation resistance up to 1500°C

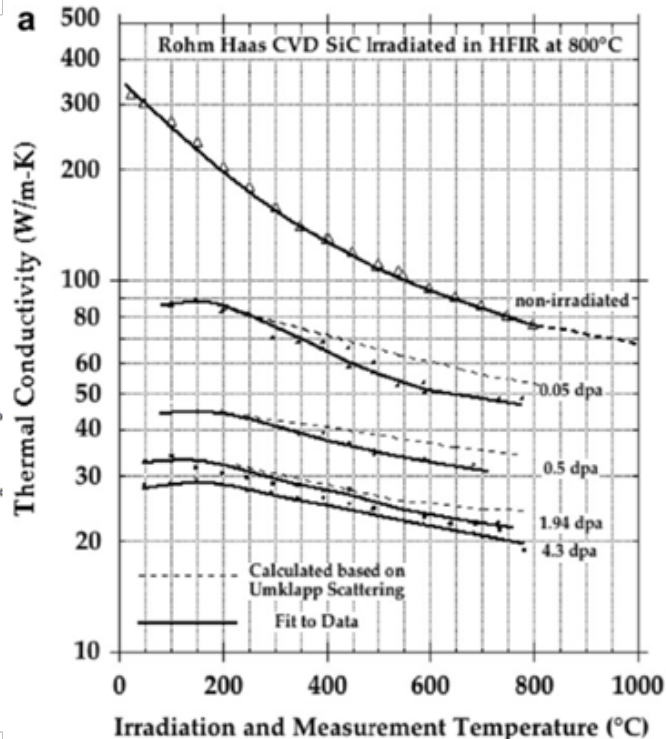
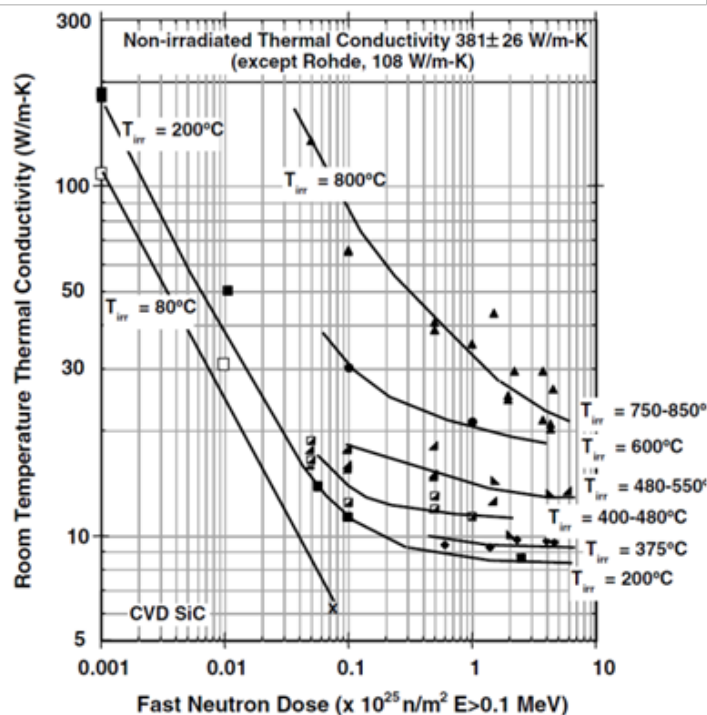


L.L. Snead et al. / Journal of Nuclear Materials 371 (2007) 329–377



## SiC and SiC/SiC main drawbacks

- SiC = brittle behavior → SiC/SiC composites
- Strong decrease of the thermal conductivity under irradiation  
Temperature gradients → Strong thermal stresses → Failure ?



## SiC/SiC main drawbacks

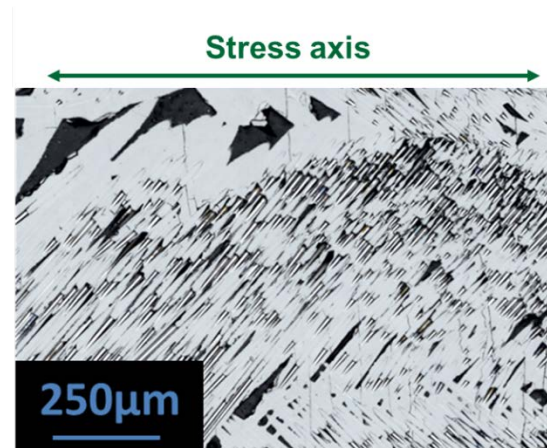
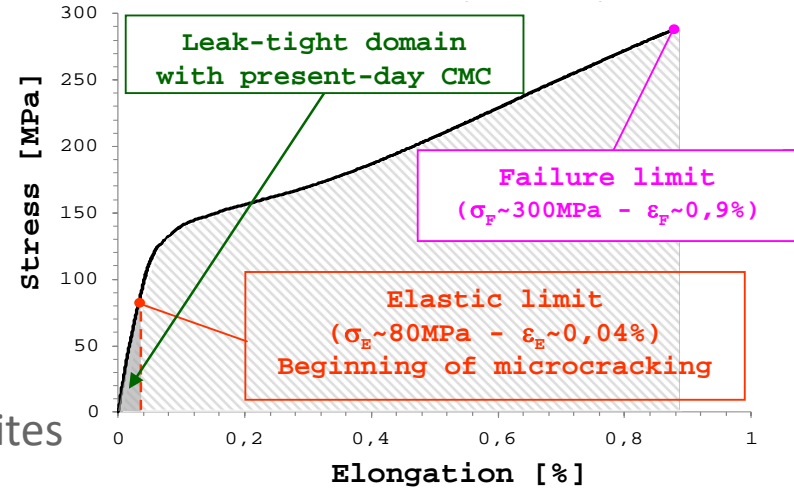
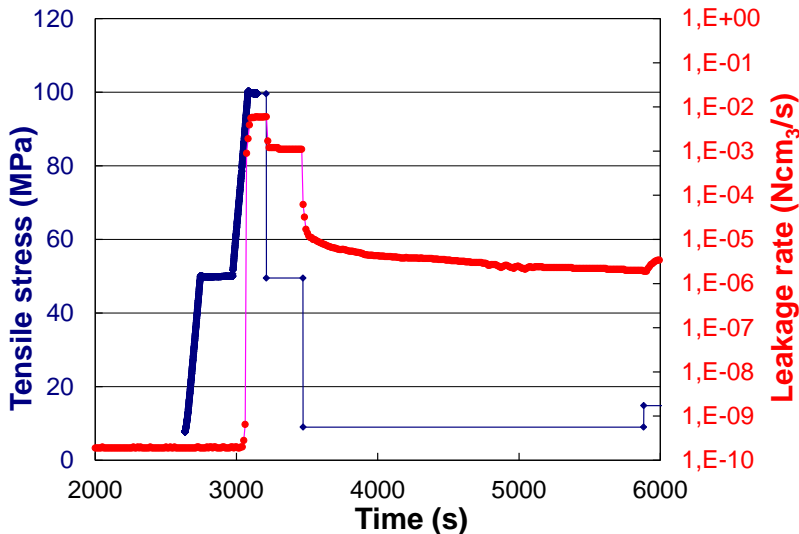
Lower thermal conductivity of CVI processed SiC/SiC composites (porosities)

Anisotropic mechanical behavior

**Hermeticity** of SiC/SiC composites:

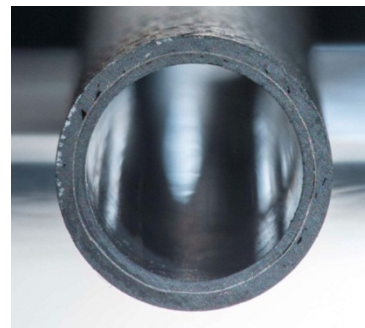
- Porosities
- Pseudo-ductility of the SiC/SiC composites  
→ microcracks (matrix multicracking) generated over the elastic limit of the composites

- **Loss of gas-tightness**



## GFR and LWR: Cladding

→ Sandwich cladding concept (Patent WO 2013/017621 A1)



GFR: Need of material capable to **withstand** the :

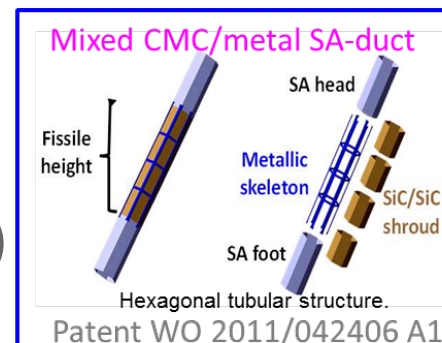
- **Nominal** temperature:  $\approx 600 - 1000^{\circ}\text{C}$  for the cladding
- **Accident** temperature: maintenance of the gas-tightness (up to  $1600^{\circ}\text{C}$ ) and preservation of the geometry (up to  $2000^{\circ}\text{C}$ )

LWR: **Potential gain** in accidental situations (**in the framework of the ATF**)

## SFR: Structural material

→ Hexagonal tube:

- avoid steel issues (**swelling** under irradiation, **creep** at high temperature)
- resistance to **fusion**





## Which fiber ?

### Stability under irradiation:

- Ideally boron-less (activation under irradiation)



- Non-stoichiometric fibers (Nicalon and Hi-Nicalon)

→ Shrinkage → Poor mechanical behavior

- Stoichiometric fibers ≈ CVD SiC: **Moderate swelling**

→ **Hi-Nicalon S and Tyranno SA3 fibers**

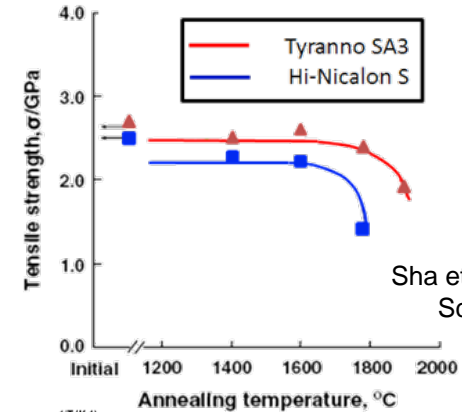
### Thermal conductivity (without irradiation):

**TSA3** (65W/m/K) > **HNS** (18 W/m/K)

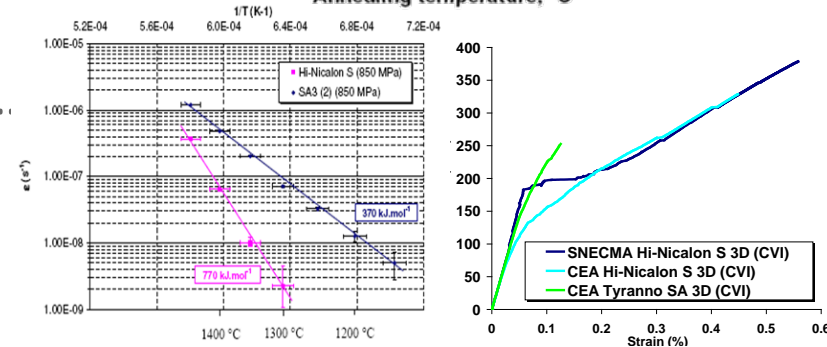
### Stability at high temperatures: **TSA3 > HNS**

### Creep at high temperature: **TSA3 < HNS**

Chem. elem.	HNS	TSA3	Chem. elem.	HNS	TSA3
C (% at.)	50.0	53.0	K (ppm)	0.12	0.77
Si (% at.)	49.1	46.4	Ca (ppm)	1.9	16
C/Si	1.02	1.14	Ti (ppm)	0.05	46
N (ppm)	170	630	Cr (ppm)	7.7	0.54
O (ppm)	8500	770	Fe (ppm)	50	1,1
H (ppm)	300	460	Co (ppm)	0.04	< 0.02
B (ppm)	2.0	3000	Ni (ppm)	0.41	0.19
Na (ppm)	0.31	2.2	Cu (ppm)	0.08	0.03
Mg (ppm)	0.17	0.99	As (ppm)	0.53	0.35
Al (ppm)	2.8	1250	Zr (ppm)	0.05	0.12
P (ppm)	1.7	0.43	Ta (ppm)	< 1	< 1
S (ppm)	57	2.8	W (ppm)	0.23	0.02
Cl (ppm)	44	10	Nb, Mo, ... (ppm)	< 0.01	< 0.01



Sha et al, J. Mater. Sci (2007).



## Conclusion: Both fibers seem interesting but...

... there is some issues with the mechanical behavior of TSA3 composites

## HNS fibers have been chosen

## Densification ?

### Reference process: CVI

- **High purity**
- Crystalline SiC ( $\beta$ ) matrix phase
- Relatively **low temperature process** ( $\approx 1000^\circ\text{C}$ )
- Along with the deposition of an **interphase**

### Drawbacks:

- Time consuming  $\rightarrow$  **High costs**
- **Porosities** in the final material ( $< 10\%$ )

### Other processes (SITE, NITE, PIP)

- Less data on the viability/advantages of those processes for nuclear applications
- Cladding application  $\rightarrow$  Thin tubes  $\rightarrow$  Processes might not be suited

## Conclusion: CVI has been chosen

## Interphase

- Necessity of an interphase between at the fiber/matrix interphase otherwise **brittle behavior**
- Which choice ?

For now on, Carbon and BN are “mastered”... but BN contains boron...

→ **Pyrocarbon is the only suitable material**

- Pyrocarbon properties:

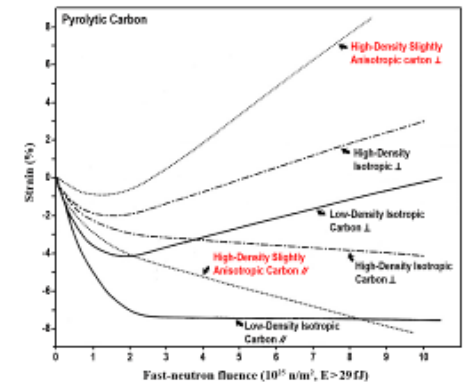
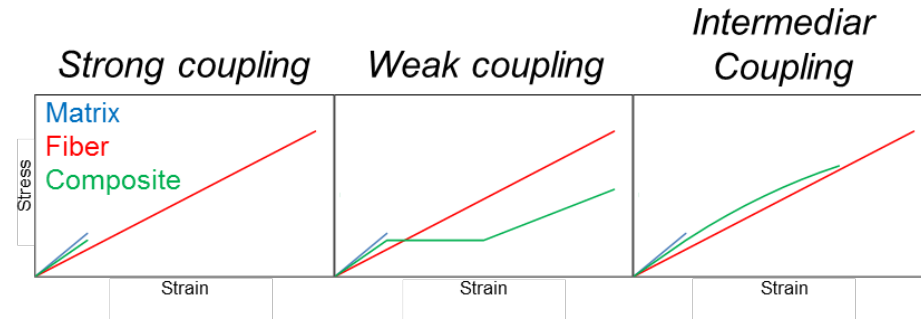
- Influence of irradiation:

- Shrinkage parallel to deposition planes
- Shrinkage → swelling perpendicular to deposition planes
- Ideally: PyC has a specific texture → anisotropic dimensional changes

- Mechanical properties:

- **Degradation** of SiC/PyC/SiC if  $e(\text{PyC}) \geq 300$  nm
- **Stability** if  $e(\text{PyC}) \leq 150$  nm

- CEA PyC properties (**confidential**)



Référence

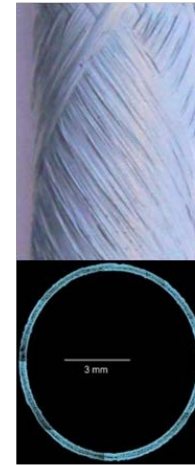
## Texture ?

- Tubular geometry: ~~Weaving~~
- 2 suitable techniques:
  - **Filament winding**: ensure really good circular shape for internal surface but...it is time consuming
  - **2D braiding**: low level of porosities
  - **3D braiding**: **high level of porosities**
  - Along with the deposition of an **interphase**
- 3 layers of filament winding or 2D braiding to reach a final thickness of 1mm
- Mechanical properties:
  - 2D braiding gives better mechanical properties for a given angle
  - Despite its high porosity, 3D braiding offers great mechanical properties

## Choice:

- **1 layer of filament winding** (smooth internal face)
- **2 layers of 2D braiding**
- **45°** for behavior in tension and internal pressure

Filament winding



porosity ~ 5-10%

2D braiding

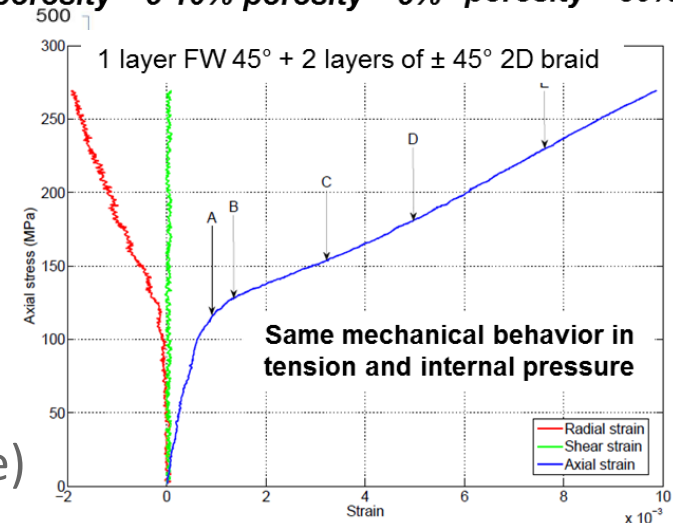


porosity ~ 5%

3D braiding



porosity ~ 30%



## Influence of the surface roughness

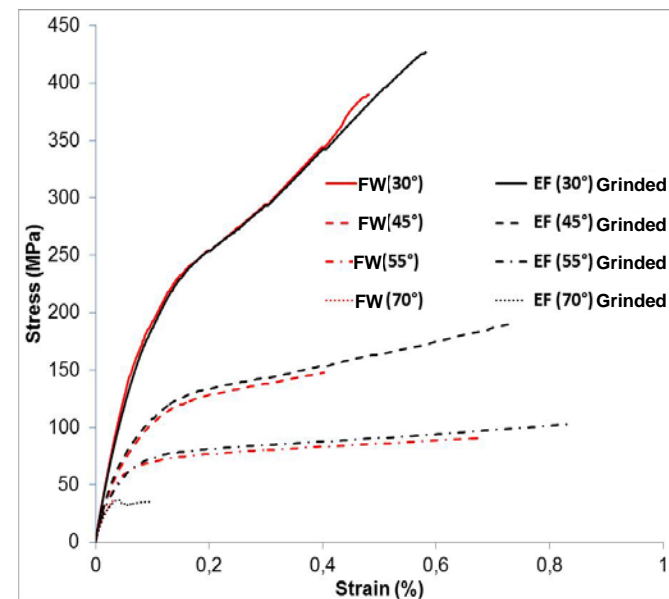
- Original surface (70°C 2D braiding)
- Grinding of the inside and the outside
- Influence on the mechanical properties ?



- Properties of the grinding:
  - External and internal cylindricalities < 0.05 mm
  - Concentricity < 0.05 mm
  - Straightness on the interior and exterior < 0.04 mm
  - $R_a < 5 \mu\text{m}$  ;  $R_z < 30 \mu\text{m}$

## Conclusion:

- No effect of grinding on the mechanical properties**
- Very good surface roughness (tolerance)**
- Necessity for the “sandwich” cladding**



## The “sandwich” pin cladding: GFR and LWR

- At first, developed for GFR cladding
- To solve the **leak-tightness** issues (over the elastic limit of the SiC/SiC composites) → **Liner**  
SiC/SiC provide the **mechanical resistance**  
Liner ensure the **gas-tightness up to failure**

### Which material ?

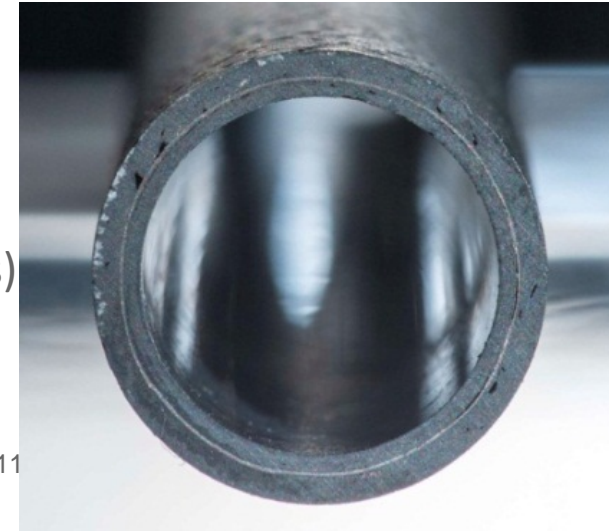
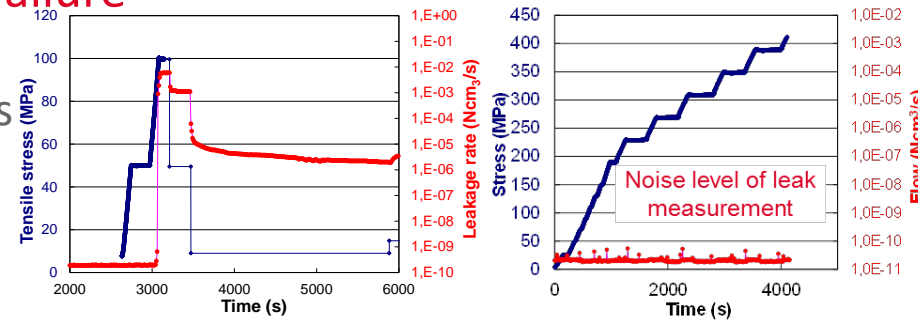
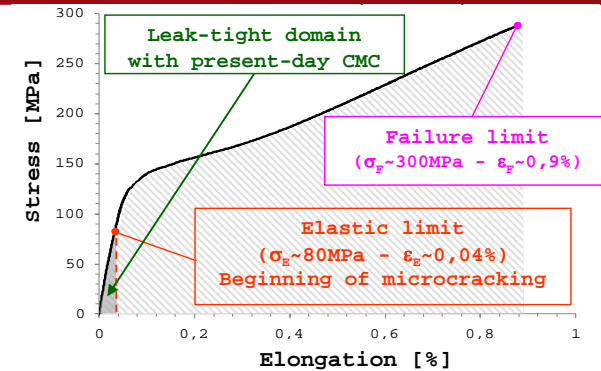
- SiC/SiC = to solve high temperature issues  
→ **Refractory materials**
- Has to be ductile to be manufactured  
+ end-plugs → **Refractory metals**
- **Welding** practicable (end-plugs)
- **Thermochemical compatibility** with SiC/fuel
- Necessity to **grind** the composite surface

### Properties:

- Inner SiC/SiC  $\approx$  0.3 mm
- Liner  $\approx$  0.1 mm (limited because of neutronic calculations)
- Outer SiC/SiC  $\approx$  0.6 mm

- Tantalum has been chosen for GFR

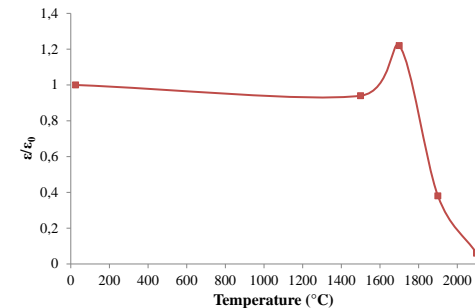
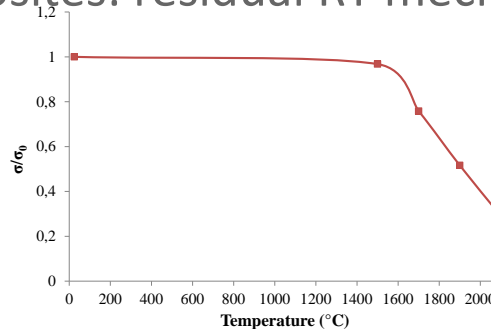
- On-going investigation** to determine the most suited metal for **LWR**



## Mechanical behavior (1/2)

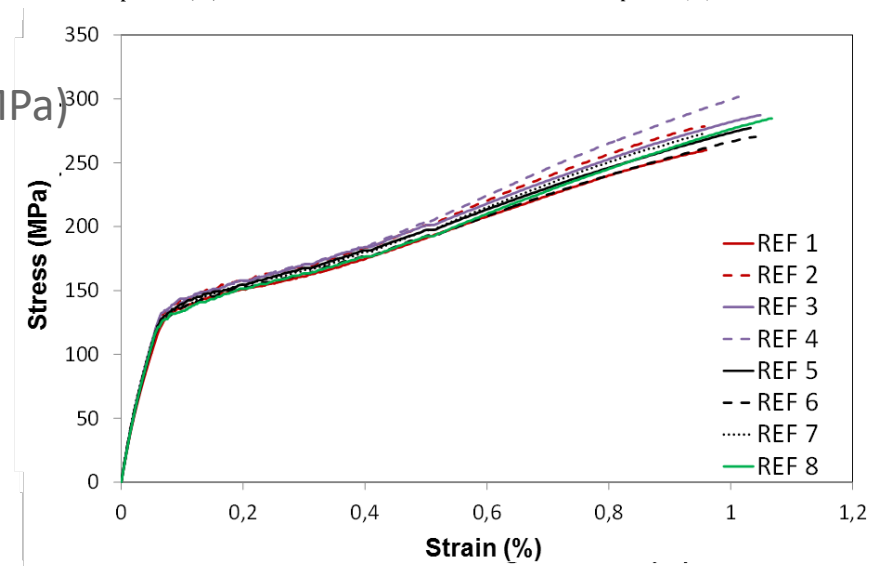
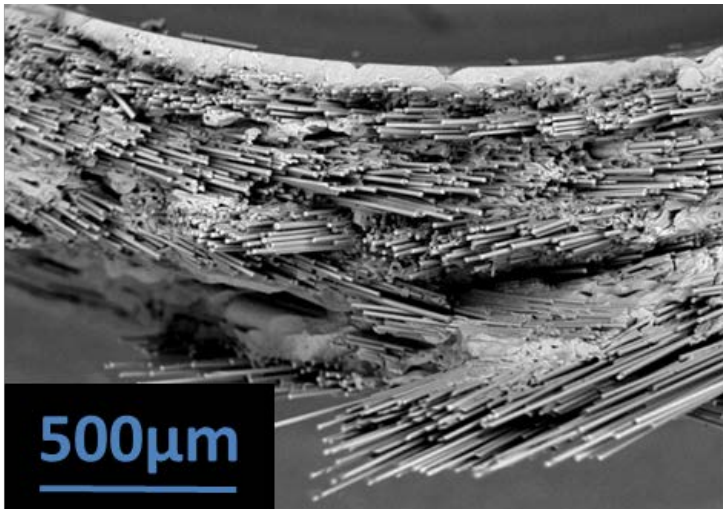
- Thermal stability of SiC/SiC composites: residual RT mechanical tensile behavior after HTT for 2h in Ar atm

→ **No degradation of the mechanical characteristics up to 1300°C**



- Tensile strength properties:

- Beginning of matrix cracking: (0,05 % ; 112 MPa)
- Failure strength: (1,01 % ; 279 MPa)
- **High reproducibility**



## Mechanical behavior (2/2)

- Acoustic emission = characteristic of matrix cracking
- Deviation from linearity** before matrix multi-cracking

→ Never observed on SiC/SiC composites (plates)

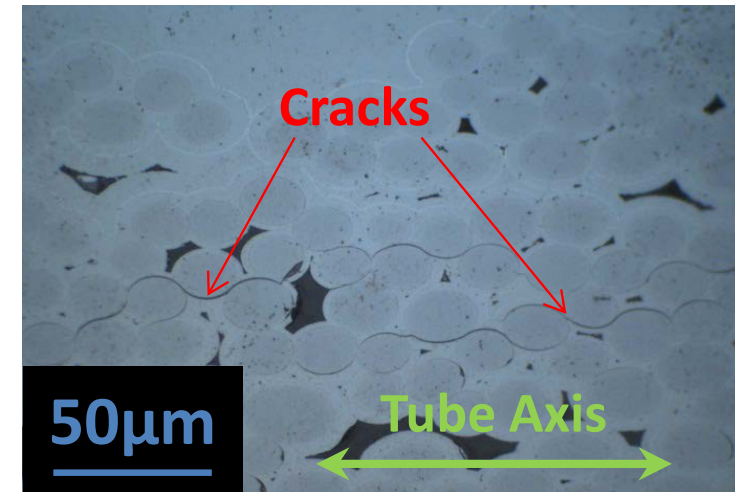
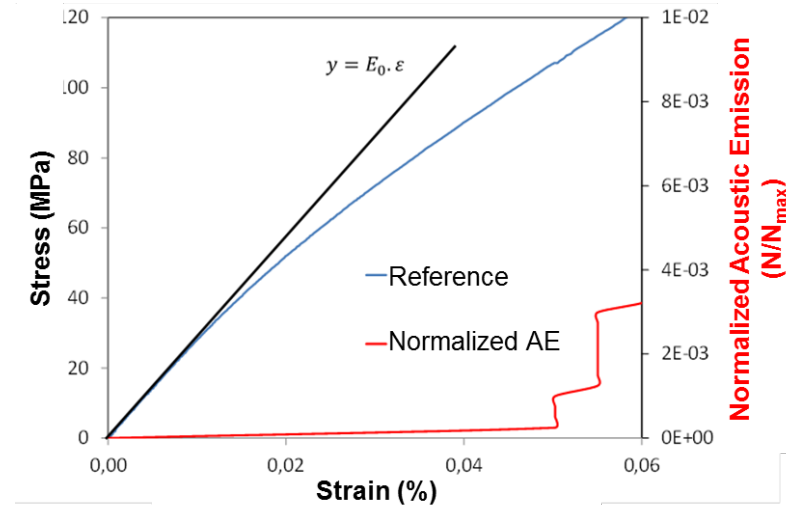
Linear elastic range		First Acoustic emission signal	
$\epsilon_l$ (%)	$\sigma_l$ (Mpa)	$\epsilon_{EA}$ (%)	$\sigma_{EA}$ (Mpa)
0,012	35	0,053	110

### Due to processing route ?

- Filament winding + braiding on mandrel
- Deposition of interphase and consolidation
- Mandrel withdrawal

### **Hypothesis:** $\neq$ coefficient of expansion mandrel/composite

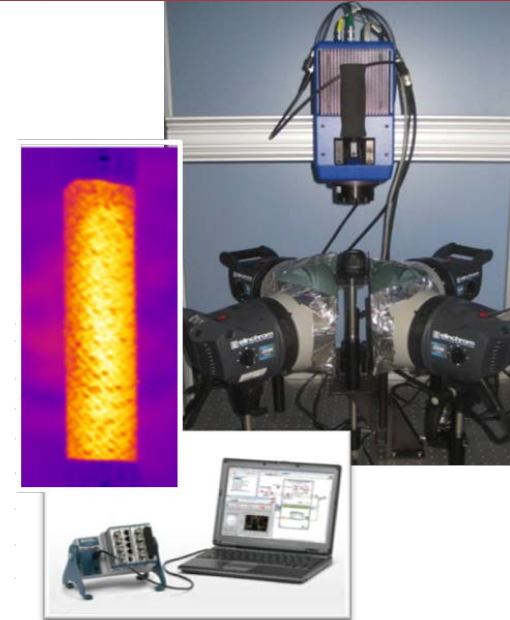
→ Thermal stresses → Microcracks of the fabricated composite





## Thermal properties

- Heat conductivity measured by pulsed “flash method” with the combination of IR thermography
- Impossible for the “sandwich cladding”  
→ Calculations needed



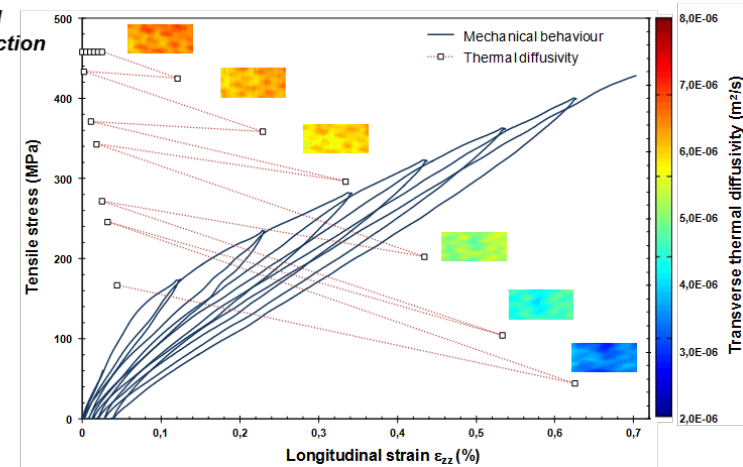
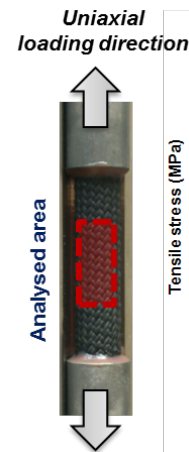
Texture type	Génération	$\alpha_f$ (%)	Surface Traitement External	Thickness mm	Density $g.cm^{-3}$	Transverse diffusivity $m^{-2}.s^{-1}$	Conductivity <sup>(#)</sup> $W.m^{-1}.K^{-1}$
Filament Winding 30°	2009-2013	44	machined	0,759	2,71	$5,75.10^{-6}$	10,6
2D Braiding 45°		42	without	0,830	2,67	$7,43.10^{-6}$	13,5
Interlock 3D Braiding 30°		34	without	0,925	2,05	$7,40.10^{-6}$	10,3
2D Braiding 45°	from 2014	45	machined	0,865	2,83	$1,51.10^{-5}$	28,9

<sup>(#)</sup> Heat capacity Cp : 680 J.Kg<sup>-1</sup>.K<sup>-1</sup>

Optimization of the thermal properties → Process

Drawback of SiC/SiC composites:

- **Decrease** of the thermal conductivity as a function of the longitudinal strain
- **Memory** of the stress encountered by the composite



## Chemical compatibility

GFR – Cladding	SFR – Hexagonal tubes	REP - Cladding
(U,Pu)C <b>SiC/SiC - Liner</b> Helium	MOX fuel Structural steels <b>Liquid sodium (Na<sub>(l)</sub>)</b>	<b>Uranium oxide (UO<sub>2</sub>)</b> SiC/SiC - Liner Water/Air
<b>Temperature of SiC/SiC composites</b>		
Nominal : 600 – 1000°C Accidental : ≥ 1600°C	500 - 550°C ~ 900°C	300 – 500°C ≥ 1000°C

## Few thermodynamical compatibility studies

### SiC or SiC/SiC reaction with:

- UO<sub>2</sub>
- GFR liner (tantalum/niobium)
- Sodium

## UO<sub>2</sub>/SiC interaction:

### In open system (HT Mass Spectrometry):

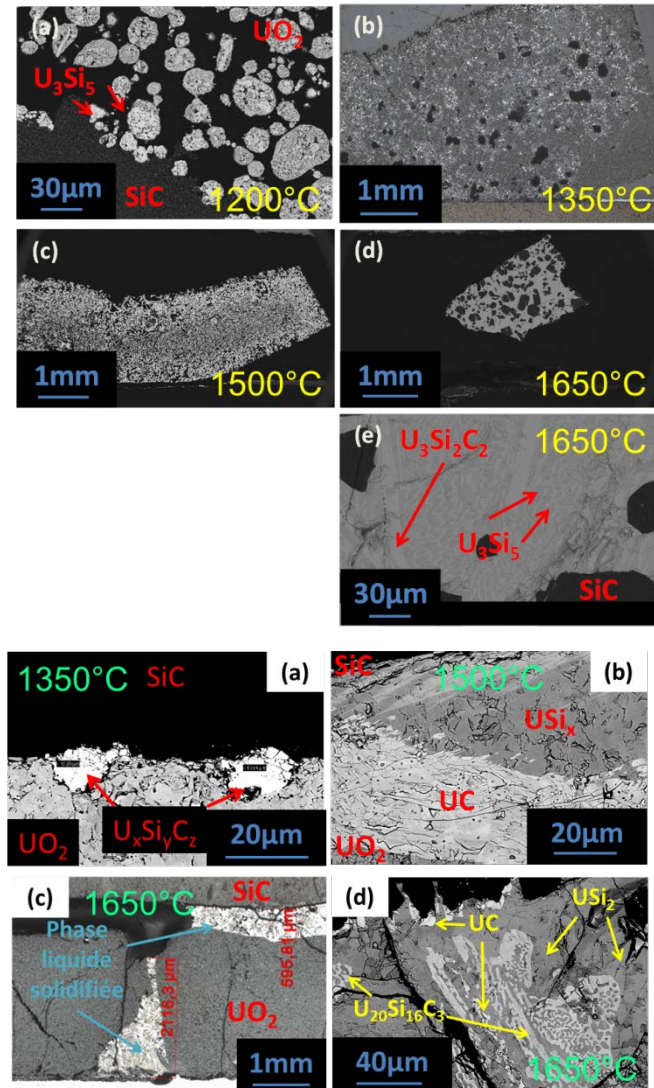
- Low reaction up to 1350°C
- Formation of mainly U<sub>3</sub>Si<sub>5</sub> and, to a lesser extent, UC<sub>x</sub>
- Gas phase: mainly CO (99%)
- **Liquid phase** appears between 1500 and 1650°C

### In closed system (diffusion couples):

- Only few precipitates at 1350°C
- Formation of USi<sub>x</sub> and UC at 1500°C
- **Liquid phase** forms between 1500 and 1650°C

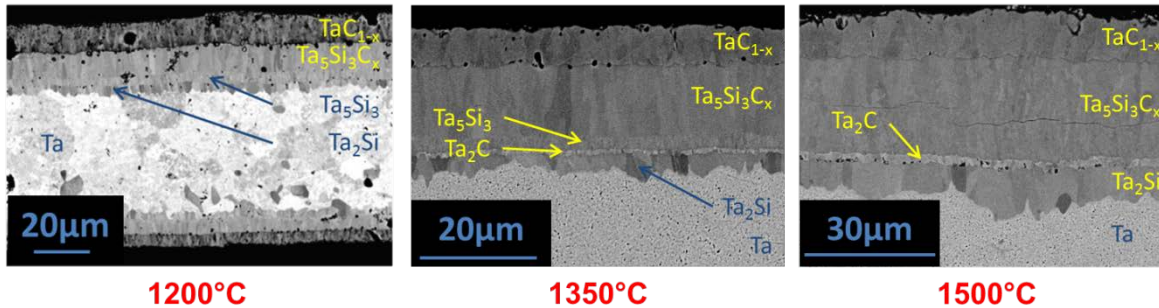
### Applications:

- **SFR**: Accidental condition = open system at T=900°C  
→ OK
- **LWR, (GFR)**: Application limited by the temperature of apparition the **liquid phase**
- **Liner material** to enhance the accident tolerance ?



## Liner (Tantalum – Niobium)/SiC interaction:

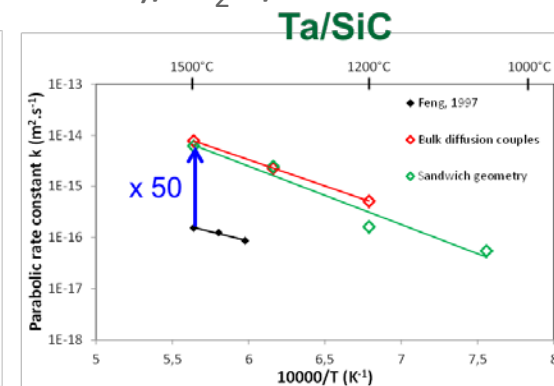
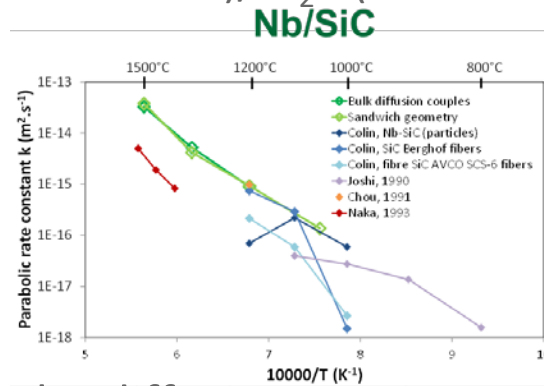
- Determination of the **composition** and the **order** of the different reaction zones:



- SiC/NbC<sub>1-x</sub>/Nb<sub>5</sub>Si<sub>3</sub>C<sub>x</sub>/NbC<sub>1-y</sub>/Nb<sub>2</sub>C/Nb (1050 – 1500°C)
- SiC/TaC<sub>1-x</sub>/Ta<sub>5</sub>Si<sub>3</sub>C<sub>x</sub>/Ta<sub>5</sub>Si<sub>3</sub> (1050 - 1350°C)/Ta<sub>2</sub>C (1350°C – 1500°C)/Ta<sub>2</sub>Si/Ta

### Kinetics:

- Parabolic growth
- Growth ≥ Previous studies
- Tantalum less reactive than niobium towards SiC



- Mechanisms:** Si and C are the diffusing species

### Application:

Niobium **too reactive**  
Tantalum **most suited**

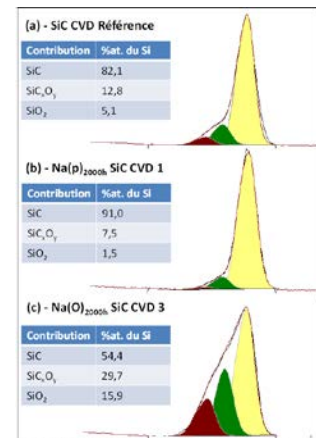
Thickness after 4 years (µm)	600°C	700°C	800°C	900°C	950°C	1000°C
Niobium	0,5	2,5	10	30	50	80
Tantalum	0,4	2	7	20	32	49

## Liquid sodium/SiC interaction:

- Up to 2000h in the liquid Na with  $[O] < 5$  or  $[O] = 1000\text{ppm}$

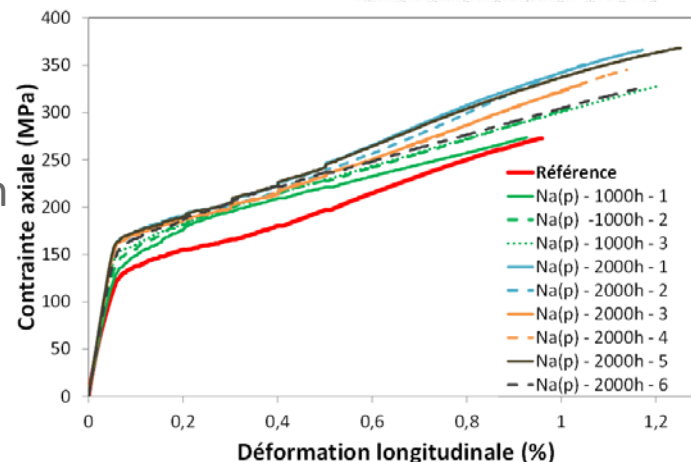
### CVD SiC:

- Slight decrease of oxide and oxycarbide phases on surface (no weight loss) for “pure” Na
- Slight surface oxidation and weight loss for Na(O)
  - SiC is not significantly affected by sodium immersion



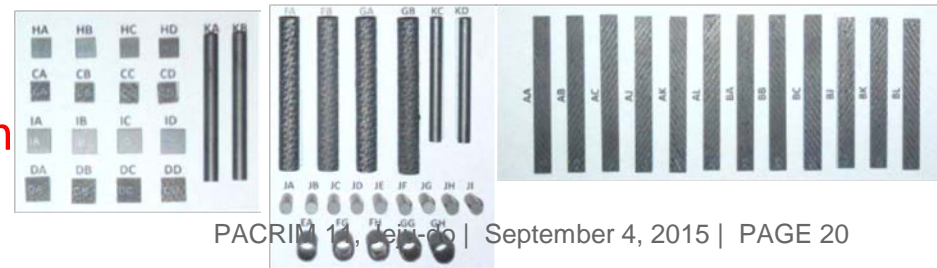
### SiC/SiC composites:

- Increase of rupture stress (+25%) and strain (+13%) on non pre-damaged samples
- No effect of high oxygen concentration in sodium
- No effect of pre-damaging on samples
  - Interphase is not affected
- Hypothesis:** healing of pre-existing cracks by sodium for undamaged samples
  - Tests on SiC/SiC plates



### On-going irradiation in BOR60

- SiC/SiC samples in liquid sodium at 550°C, up to 120 dpa neutron irradiation dose



## ■ Processing:

- Hi-Nicalon S/Pyrocarbon/CVI SiC material
- 1 layer of filament winding – 2 layers of 2D braiding
- Regular shaped surface by grinding without modifying the mechanical properties
- Concept of the “sandwich” cladding: Thin (100  $\mu\text{m}$ ) metal layer placed between two SiC/SiC composites

## ■ Application: Structural materials (SFR) and Cladding (GFR, LWR)

## ■ Properties:

### ■ Thermal:

- Optimization of the process → **Higher conductivity**
- **Degradation of the thermal conductivity** function of the highest strength applied and the strain of the composites

### ■ Mechanical:

- **Process lead** to initial cracking of the matrix (but has no influence on the gas-tightness)
- **Very reproducible** mechanical behavior

### ■ Thermochemical compatibility:

- **UO<sub>2</sub>: Liquid phase** appear between 1500°C and 1650°C. Enhance this temperature with a liner ?
- **Ta/Nb: Only Ta** suitable for GFR application
- **Na: Great for nominal temperature** (independent of O content). Behavior at 900°C ?

# Questions ?

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Commissariat à l'énergie atomique et aux énergies alternatives  
Centre de Saclay | 91191 Gif-sur-Yvette Cedex

Direction de l'énergie nucléaire

Etablissement public à caractère industriel et commercial | R.C.S Paris B 775 685 019