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J. Braun, C. Sauder, C. Lorrette, L. Gélébart, G. Loupiau, et al.. Processing and properties of SiC/SiC composites for nuclear power plant applications.. PACRIM 11 - The 11th Pacific Rim Conference of Ceramic Societies, Aug 2015, Jeju, South Korea. cea-02509723

HAL Id: cea-02509723

<https://cea.hal.science/cea-02509723v1>

Submitted on 17 Mar 2020

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

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DEN/DANS/DMN/SRMA

SEPTEMBER, 4 2015

- **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)

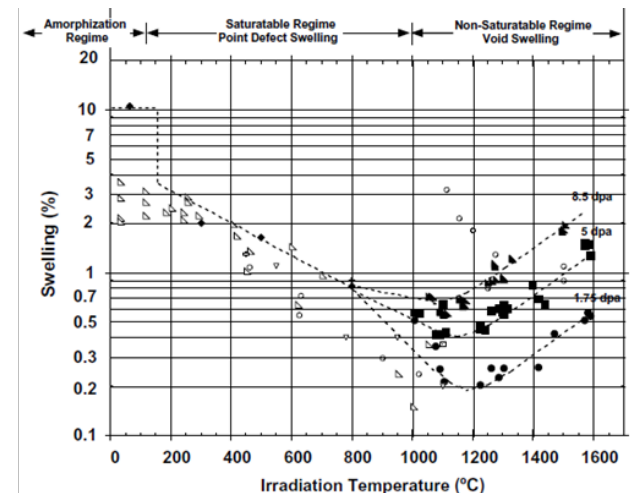
Resistance in accidental situations (very high temperatures)

Compatibility with waster reprocessing

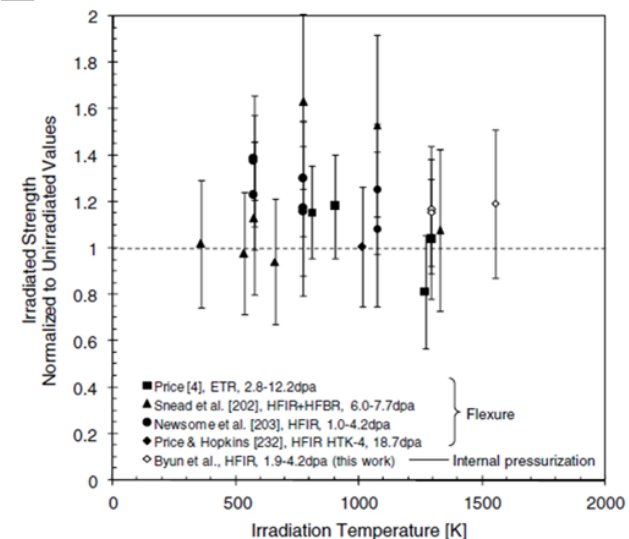
Low activation materials (ideally)

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

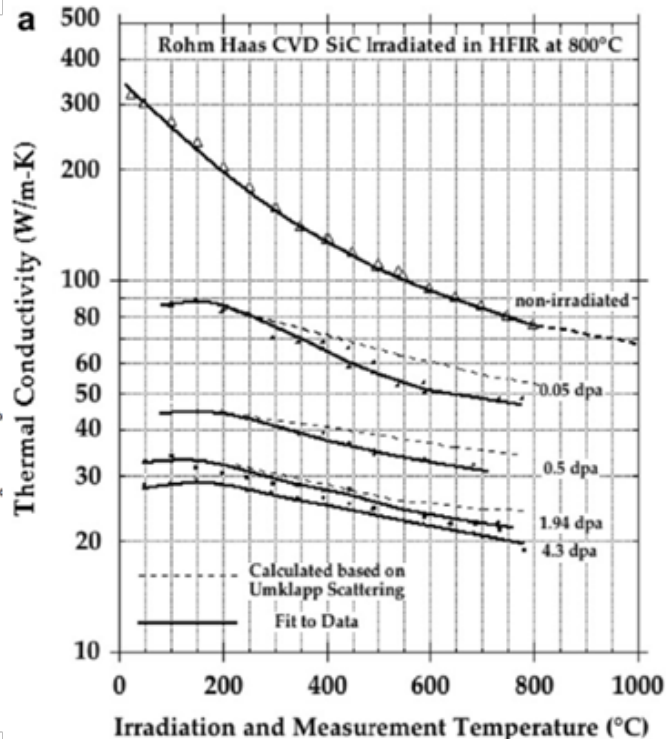
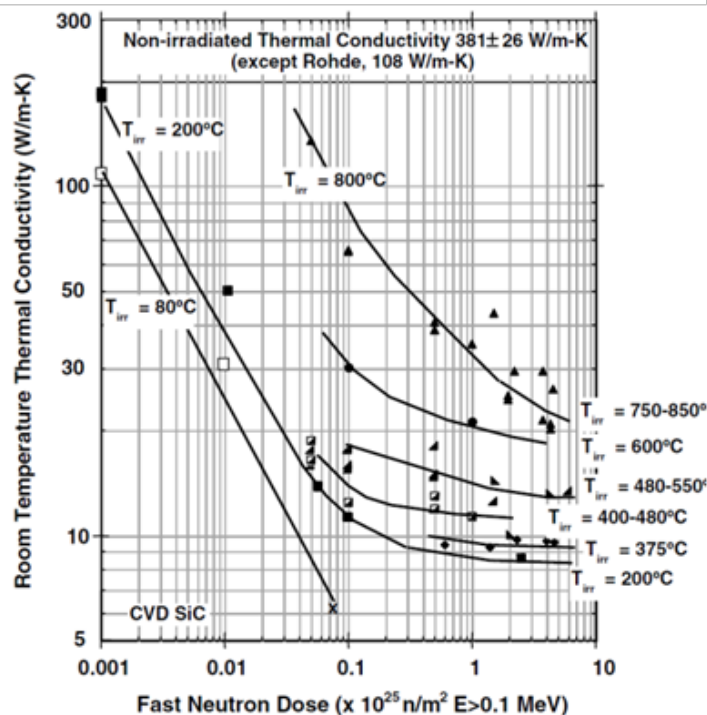


L.L. Snead et al. / Journal of Nuclear Materials 371 (2007) 329–377



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

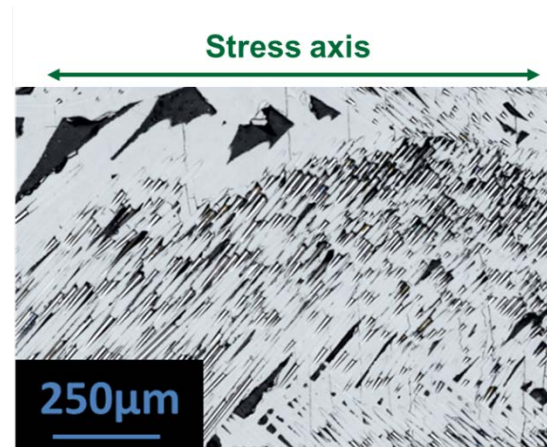
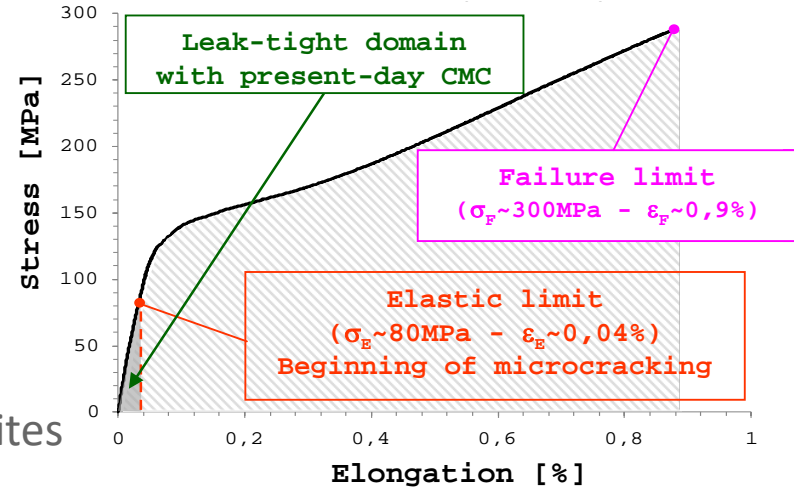
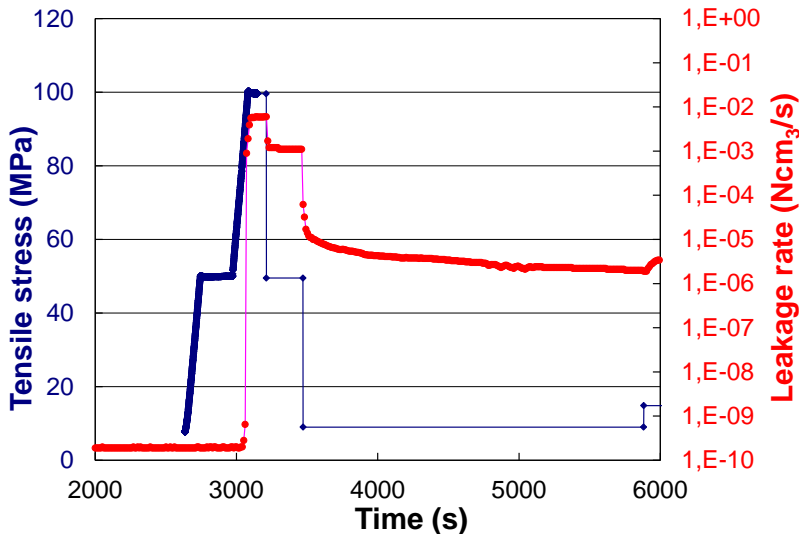
Lower thermal conductivity of CVI processed SiC/SiC composites (porosities)

Anisotropic mechanical behavior

Hermeticity of SiC/SiC composites:

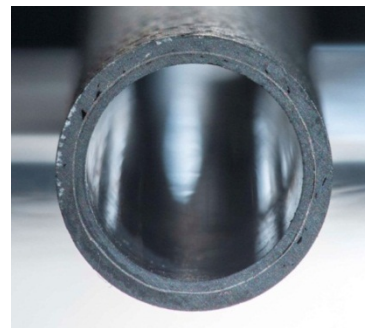
- Porosities
- Pseudo-ductility of the SiC/SiC composites
→ microcracks (matrix multicracking) generated over the elastic limit of the composites

- **Loss of gas-tightness**



GFR and LWR: Cladding

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



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

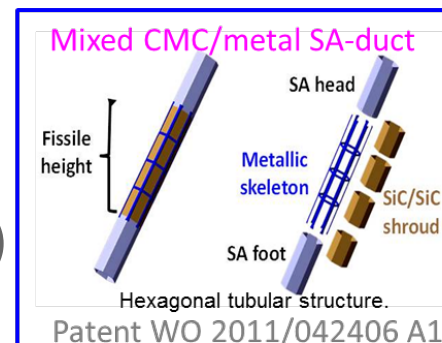
- **Nominal** temperature: $\approx 600 - 1000^{\circ}\text{C}$ for the cladding
- **Accident** temperature: maintenance of the gas-tightness (up to 1600°C) and preservation of the geometry (up to 2000°C)

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

SFR: Structural material

→ Hexagonal tube:

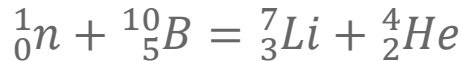
- avoid steel issues (**swelling** under irradiation, **creep** at high temperature)
- resistance to **fusion**



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**

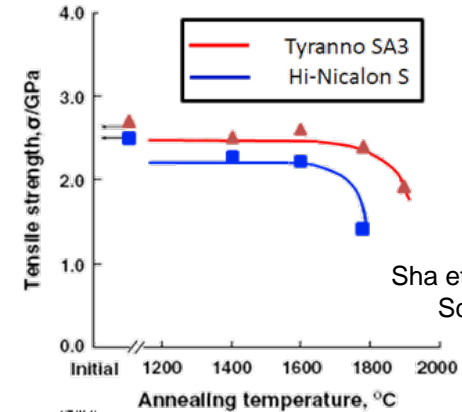
Thermal conductivity (without irradiation):

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

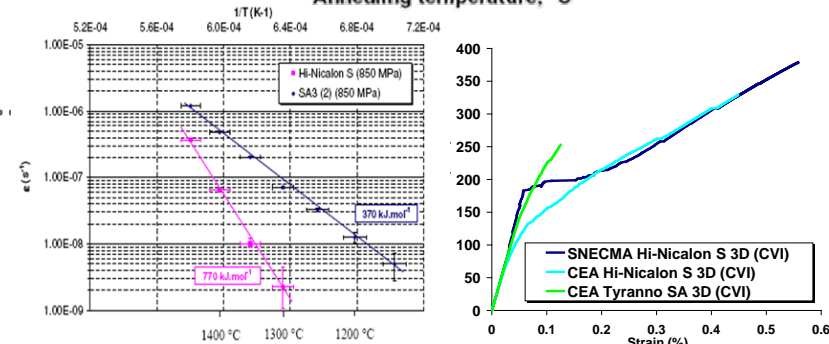
Stability at high temperatures: **TSA3 > HNS**

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 (β) 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

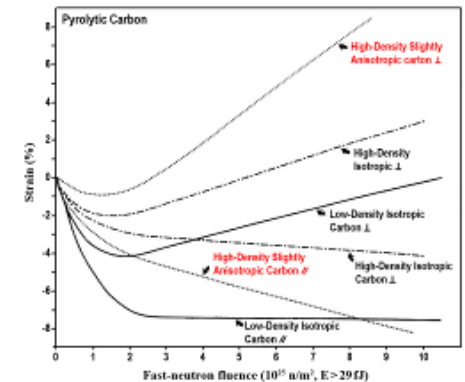
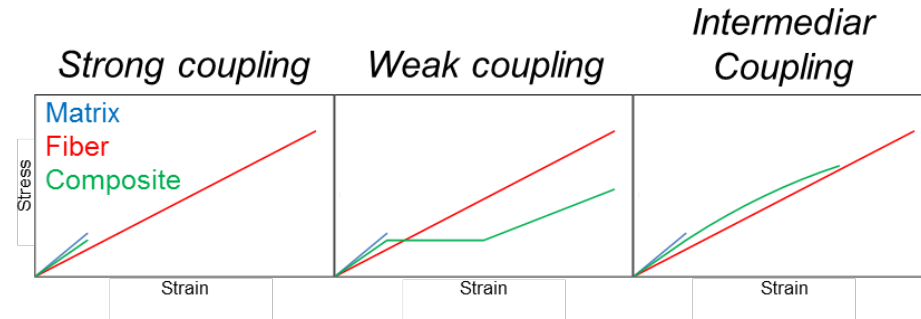
- Necessity of an interphase between at the fiber/matrix interphase otherwise **brittle behavior**
- Which choice ?

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

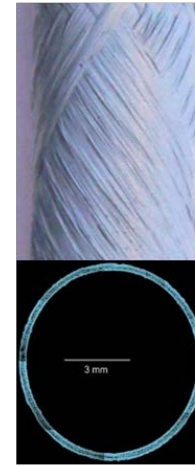
Texture ?

- 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

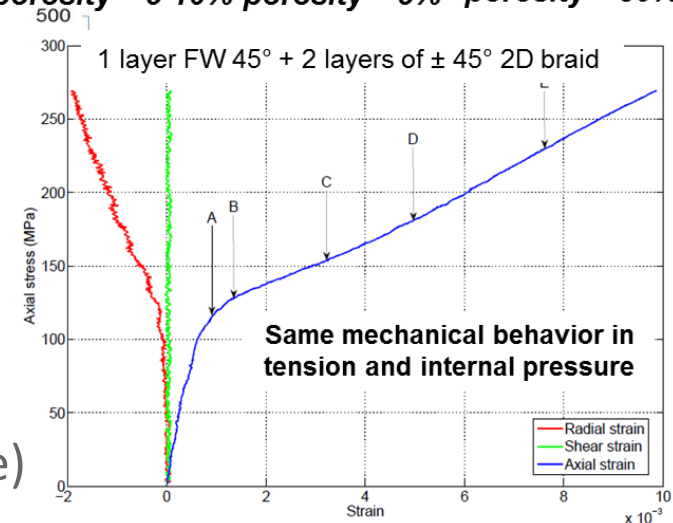


porosity ~ 5%

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 ?

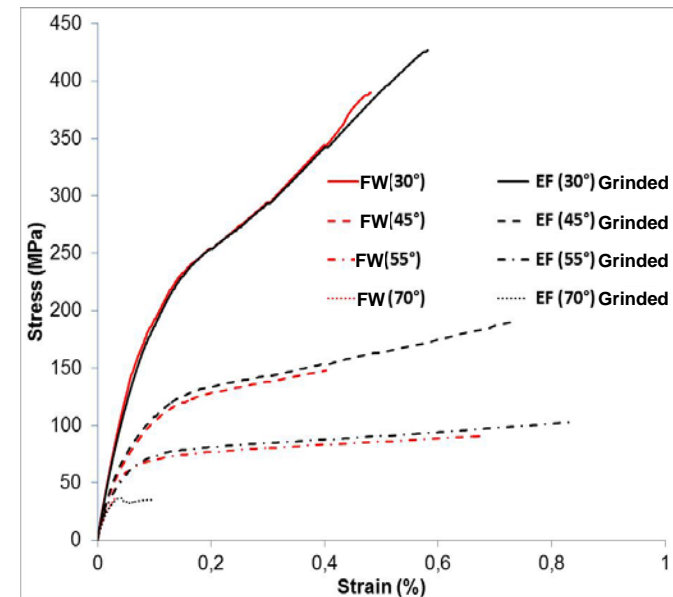


Properties of the grinding:

- External and internal cylindricalities < 0.05 mm
- Concentricity < 0.05 mm
- Straightness on the interior and exterior < 0.04 mm
- Ra < 5 μm ; Rz < 30 μm

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 ?

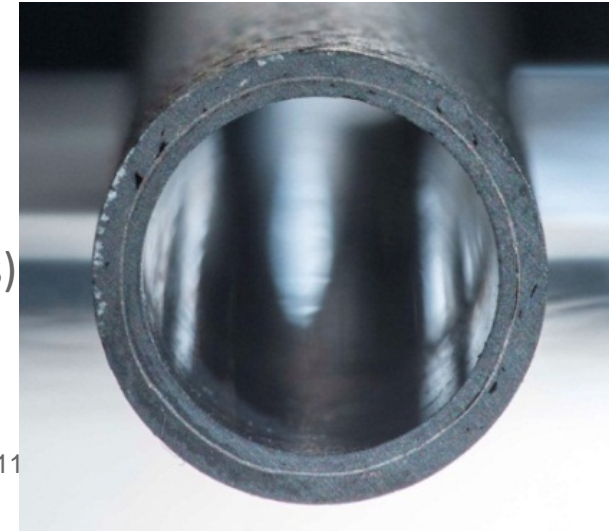
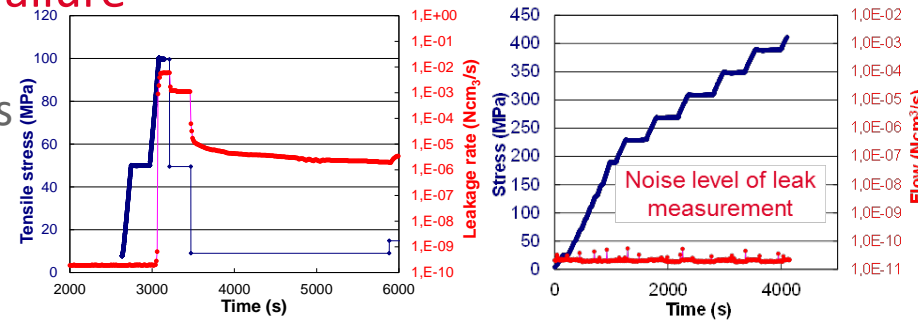
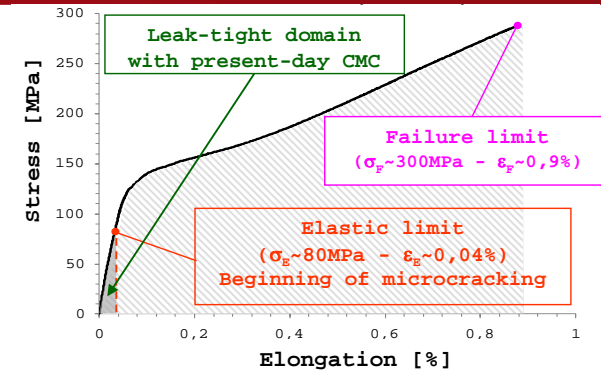
- SiC/SiC = to solve high temperature issues
→ **Refractory materials**
- Has to be ductile to be manufactured
+ end-plugs → **Refractory metals**
- **Welding** practicable (end-plugs)
- **Thermochemical compatibility** with SiC/fuel
- Necessity to **grind** the composite surface

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

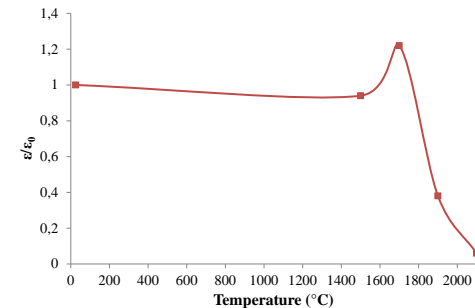
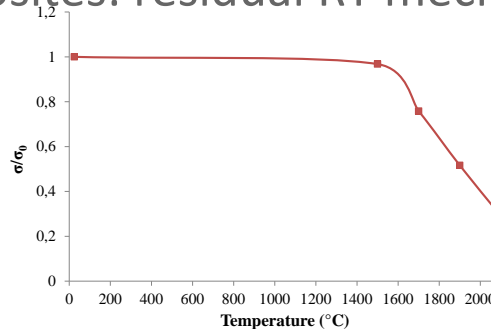
- On-going investigation** to determine the most suited metal for **LWR**



Mechanical behavior (1/2)

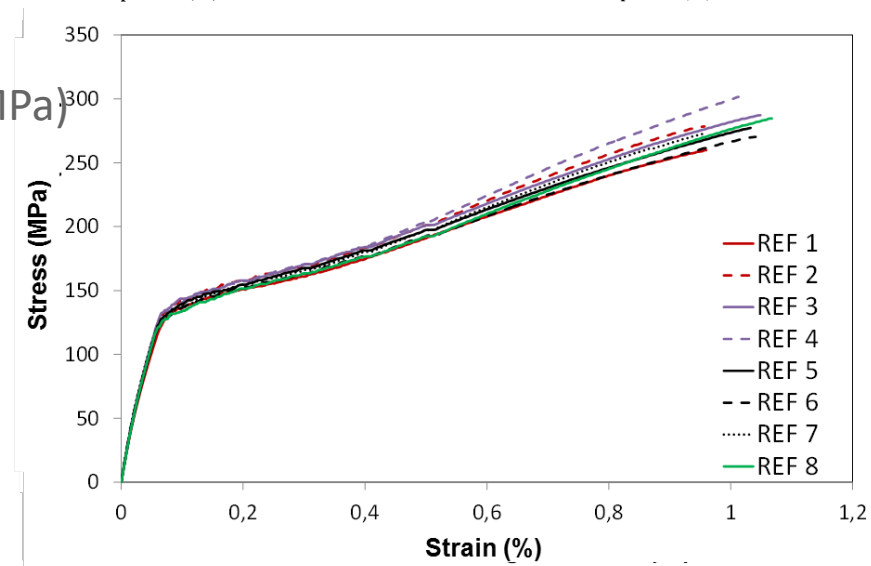
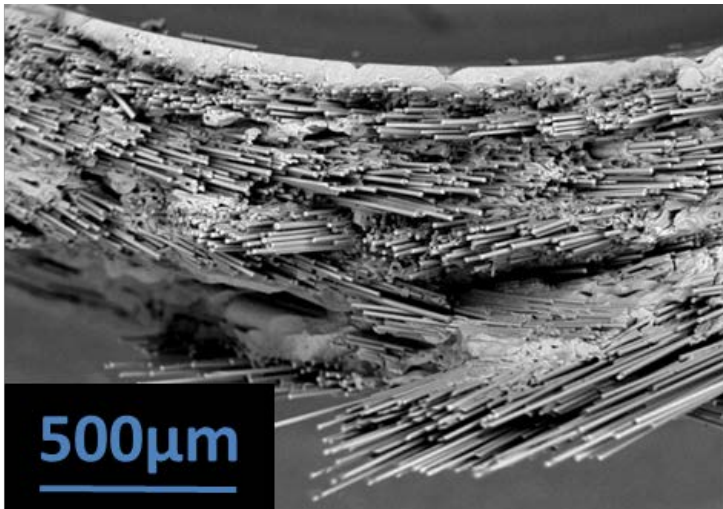
- Thermal stability of SiC/SiC composites: residual RT mechanical tensile behavior after HTT for 2h in Ar atm

→ **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)**

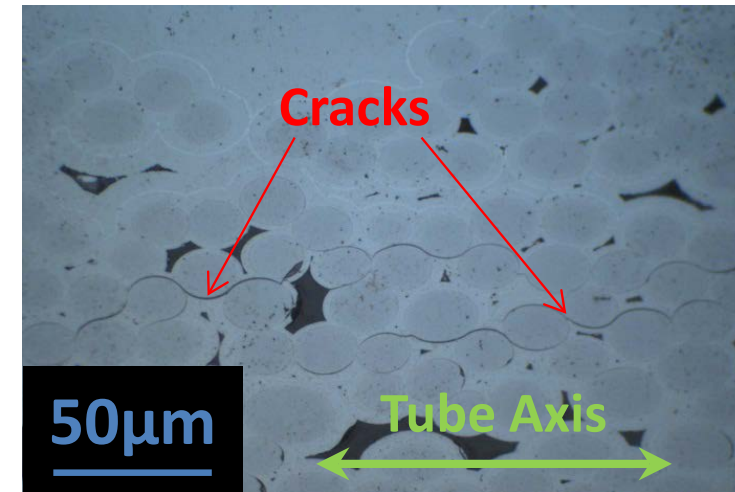
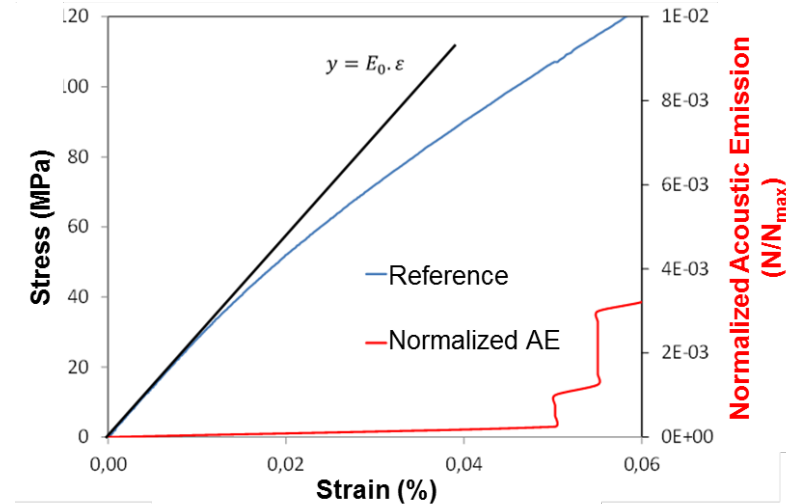
Linear elastic range		First Acoustic emission signal	
ϵ_l (%)	σ_l (Mpa)	ϵ_{EA} (%)	σ_{EA} (Mpa)
0,012	35	0,053	110

Due to processing route ?

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

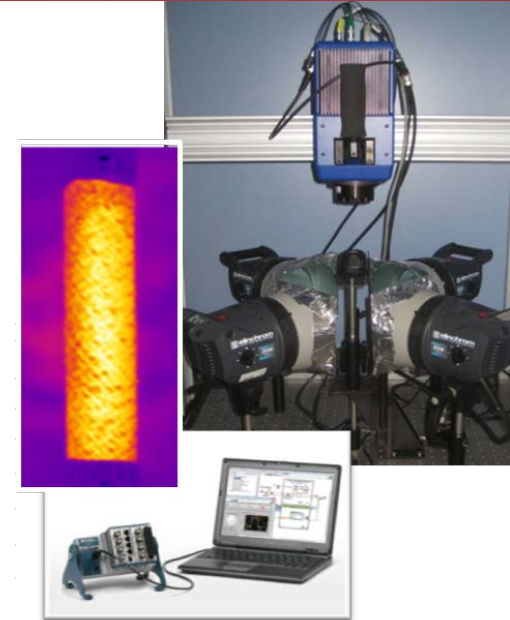
Hypothesis: \neq coefficient of expansion mandrel/composite

→ **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



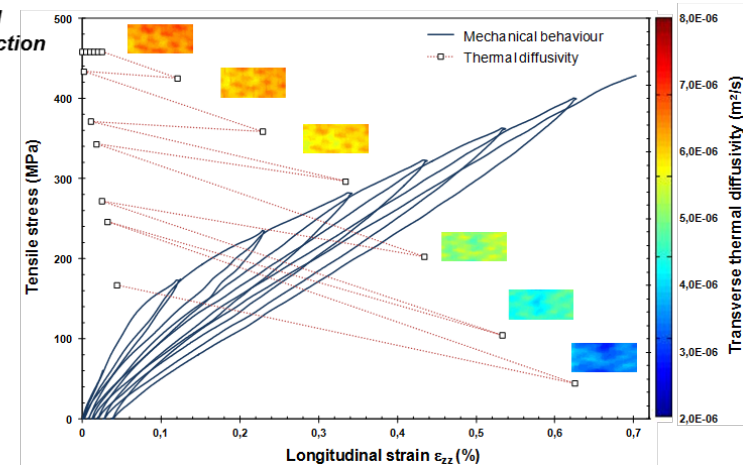
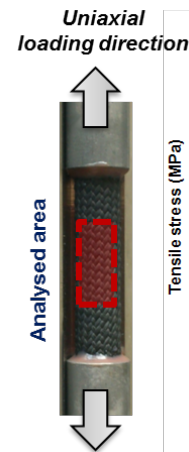
Texture type	Génération	α_f (%)	Surface Traitement <i>External</i>	Thickness <i>mm</i>	Density <i>g.cm⁻³</i>	Transverse diffusivity <i>m⁻².s⁻¹</i>	Conductivity ^(#) <i>W.m⁻¹.K⁻¹</i>
Filament Winding 30°	2009-2013	44	machined	0,759	2,71	5,75.10⁻⁶	10,6
2D Braiding 45°		42	without	0,830	2,67	7,43.10⁻⁶	13,5
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

^(#) Heat capacity Cp : 680 J.Kg⁻¹.K⁻¹

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 SiC/SiC - Liner Helium	MOX fuel Structural steels Liquid sodium (Na_(l))	Uranium oxide (UO₂) SiC/SiC - Liner Water/Air
Temperature of SiC/SiC composites		
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:

- UO₂
- GFR liner (tantalum/niobium)
- Sodium

UO₂/SiC interaction:

In open system (HT Mass Spectrometry):

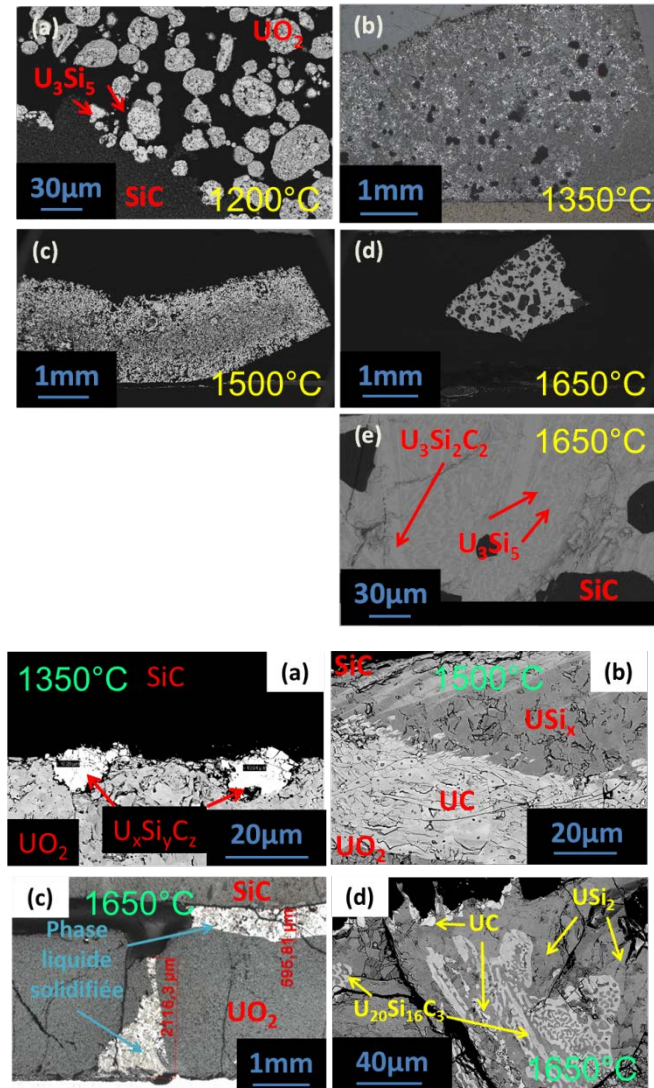
- Low reaction up to 1350°C
- Formation of mainly U₃Si₅ and, to a lesser extent, UC_x
- Gas phase: mainly CO (99%)
- **Liquid phase** appears between 1500 and 1650°C

In closed system (diffusion couples):

- Only few precipitates at 1350°C
- Formation of USi_x and UC at 1500°C
- **Liquid phase** forms between 1500 and 1650°C

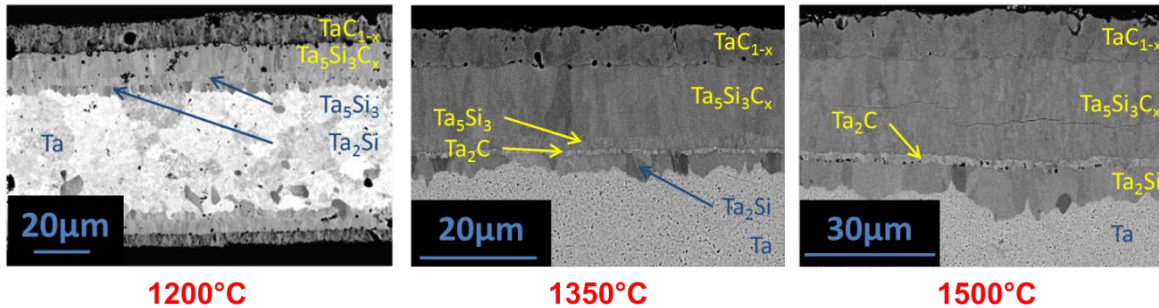
Applications:

- **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:

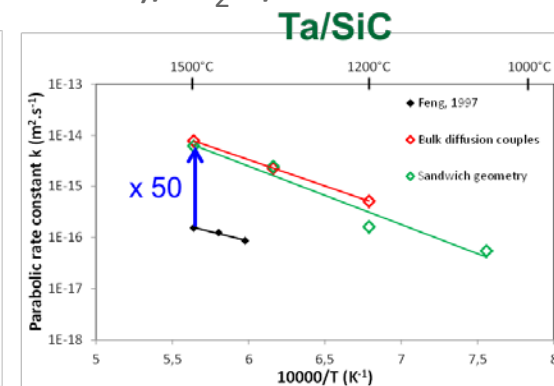
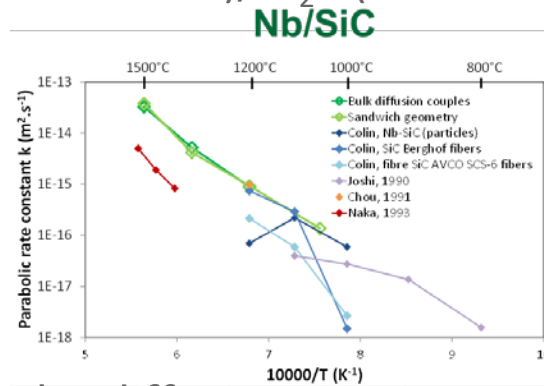
- Determination of the **composition** and the **order** of the different reaction zones:



- SiC/NbC_{1-x}/Nb₅Si₃C_x/NbC_{1-y}/Nb₂C/Nb (1050 – 1500°C)
- SiC/TaC_{1-x}/Ta₅Si₃C_x/Ta₅Si₃ (1050 - 1350°C)/Ta₂C (1350°C – 1500°C)/Ta₂Si/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**

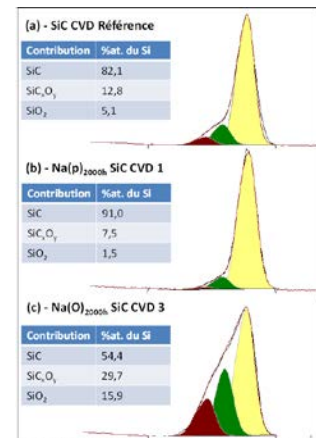
Thickness after 4 years (µm)	600°C	700°C	800°C	900°C	950°C	1000°C
Niobium	0,5	2,5	10	30	50	80
Tantalum	0,4	2	7	20	32	49

Liquid sodium/SiC interaction:

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

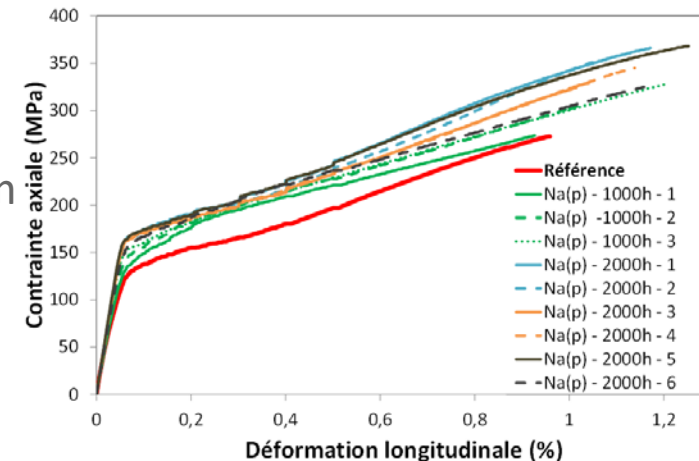
CVD SiC:

- 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



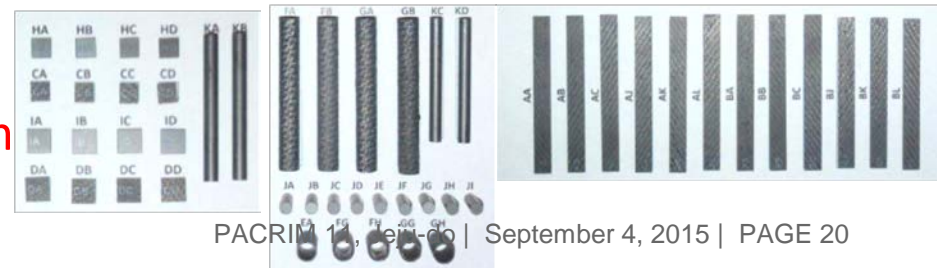
SiC/SiC composites:

- 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 μm) 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:

- **UO₂: 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 ?

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

Direction de l'énergie nucléaire

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