Processing and properties of SiC/SiC composites for nuclear power plant applications.

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

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OUTLINE

- 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 irradation creep

- **Gas tightness for cladding applications**

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

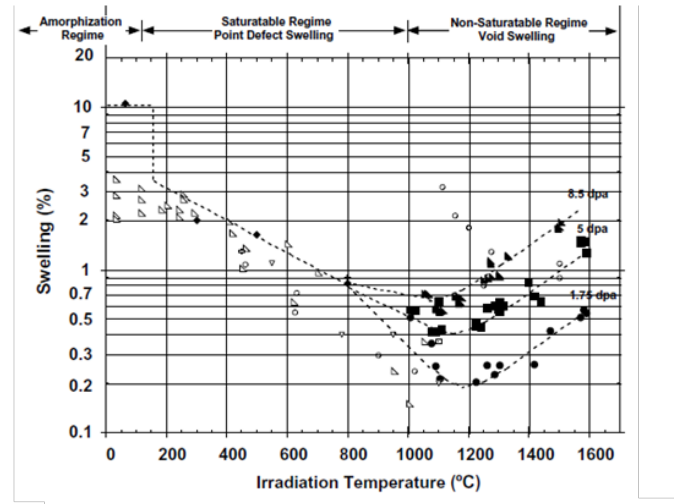
- **Resistance in accidental situations (very high temperatures)**

- **Compatibility with waster reprocessing**

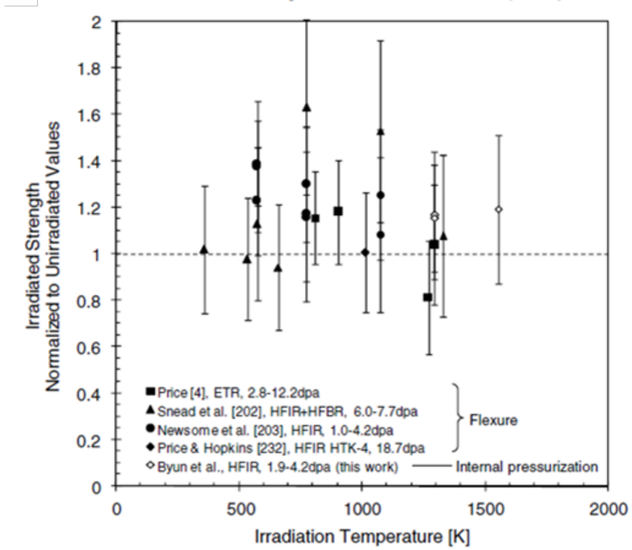
- **Low activation materials (ideally)**

SiC (high purity CVD) for nuclear reactors

- **High decomposition temperature** of SiC (over 2000°C)
- **Swelling** under irradiation:
  - **Low** (< 3%) for T > 200°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

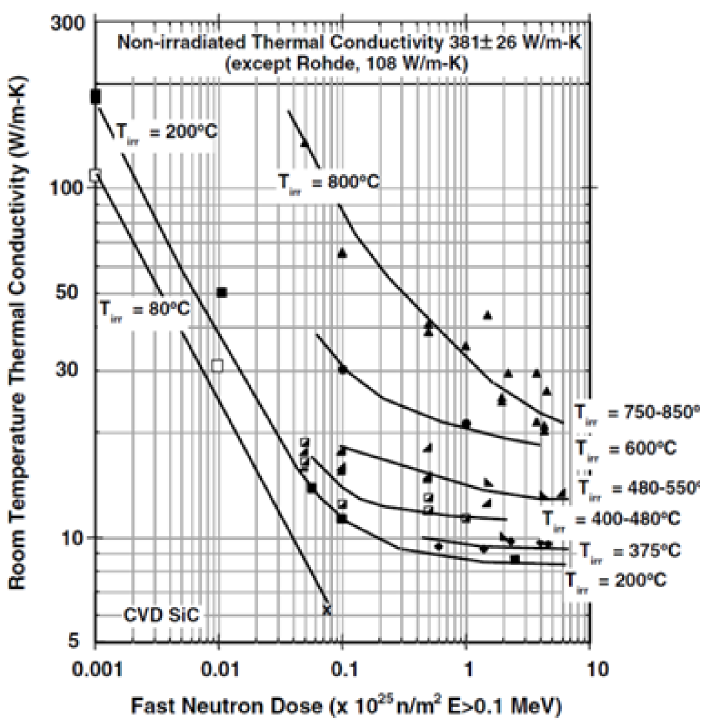


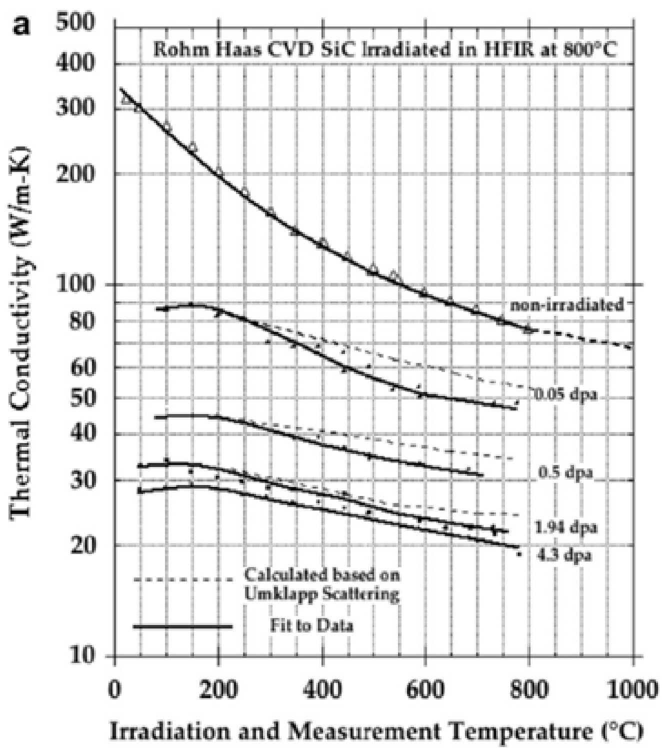
SIC AND SIC/SIC FOR NUCLEAR APPLICATIONS

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 ?**

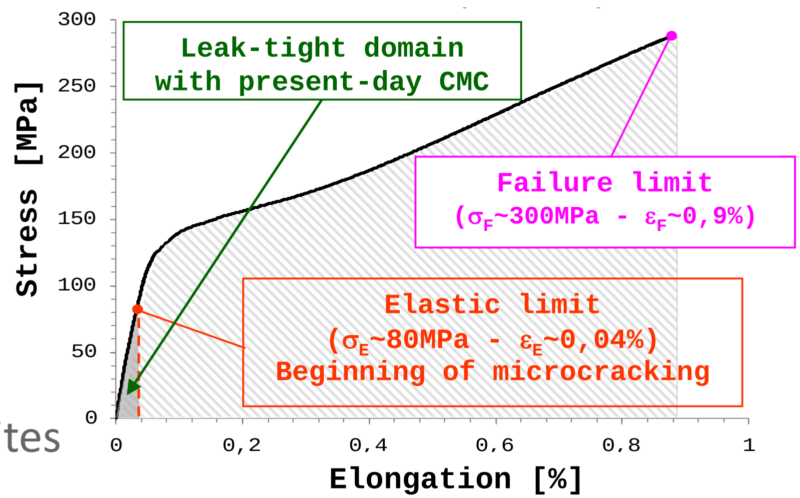


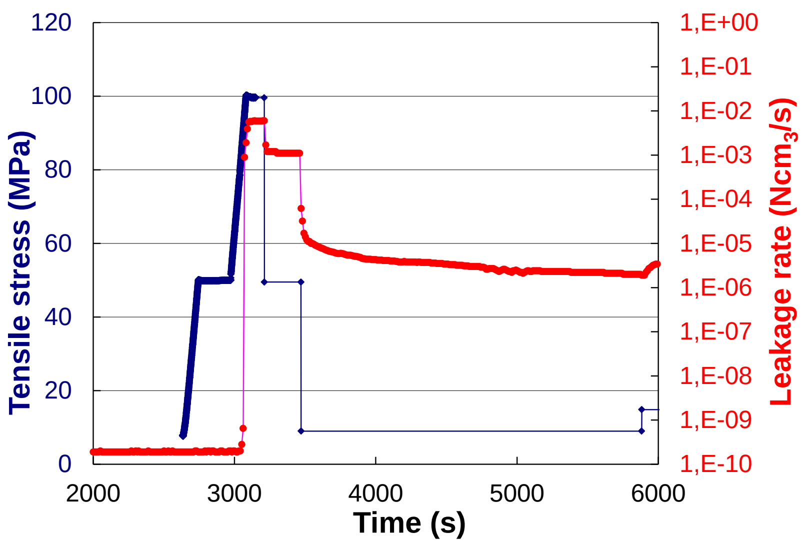


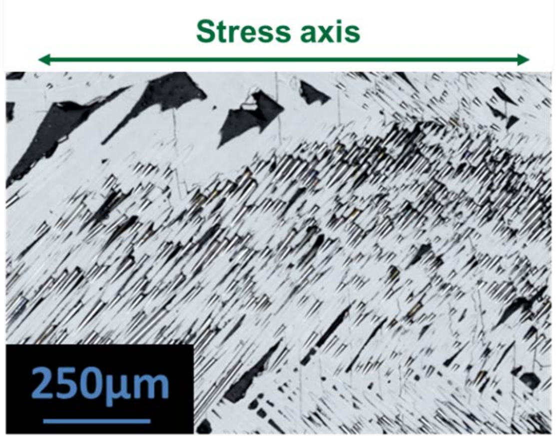
L.L. Snead et al. JMN 371 (2007) 329-377

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**







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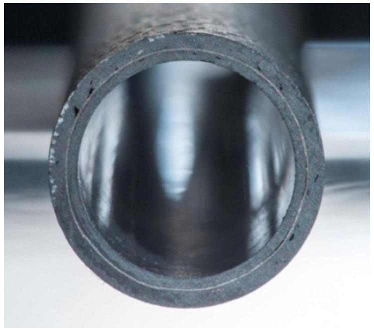
SIC AND SIC/SIC FOR NUCLEAR APPLICATIONS

GFR and LWR: Cladding

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



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

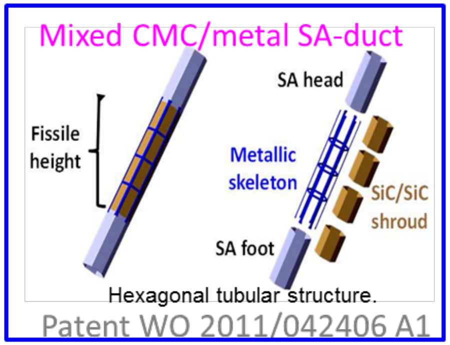
- **Nominal** temperature: ≈ 600 – 1000°C for the cladding
- **Accident** temperature: maintenance of the gas-tightness (up to 1600°C) and preservation of the geometry (up to 2000°C)

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**



PROCESSING OF SIC/SIC PIN CLADDING

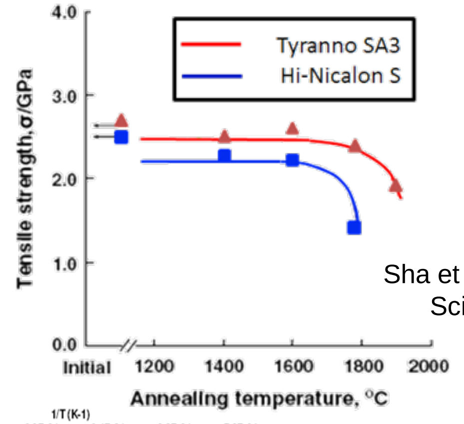
Which fiber ?

- **Stability under irradiation**:
  - Ideally boron-less (activation under irradiation)

$$ {}^{1}_{0}n + {}^{10}_{5}B = {}^{7}_{3}Li + {}^{4}_{2}He $$

  - Non-stoechiometric fibers (Nicalon and Hi-Nicalon)
    → Shrinkage → Poor mechanical behavior
  - Stoechiometric 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**

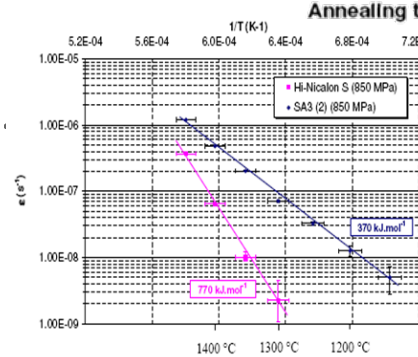
Chem. elem.	HNS	TSA3	Chem. elem.	HNS	TSA3
C (% at.)	50.0	53.0	K (ppm)	0.12	0.77
Si (% at.)	49.1	46.4	Ca (ppm)	1.9	16
C/Si	1.02	1.14	Ti (ppm)	0.05	46
N (ppm)	170	630	Cr (ppm)	7.7	0,54
O (ppm)	8500	770	Fe (ppm)	50	1,1
H (ppm)	300	460	Co (ppm)	0.04	< 0.02
B (ppm)	2.0	3000	Ni (ppm)	0.41	0.19
Na (ppm)	0.31	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

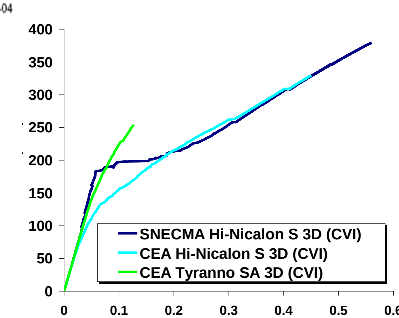


Sha et al, J. Mater. Sci (2007).

Conclusion: Both fibers seem interesting but..

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





HNS fibers have been chosen

PROCESSING OF SIC/SIC PIN CLADDING

Densification ?

- Reference process: **CVI**
  - **High purity**
  - Crystalline SiC (β) matrix phase
  - Relatively **low temperature process** (≈ 1000°C)
  - Along with the deposition of an **interphase**

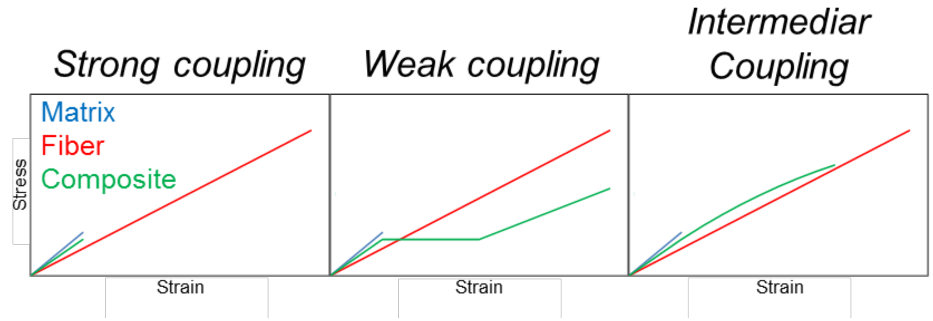
- Drawbacks:
  - Time consuming → **High costs**
  - **Porosities** in the final material (< 10%)

- Other processes (SITE, NITE, PIP)
  - Less data on the viability/advantages of those processes for nuclear applications
  - Cladding application → Thin tubes → Processes might not be suited

Conclusion: **CVI has been chosen**

PROCESSING OF SIC/SIC PIN CLADDING

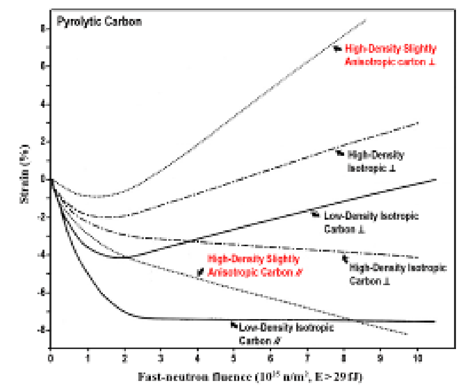
Interphase



- 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:
    - Degration of SiC/PyC/SiC if e(PyC) ≥ 300 nm
    - Stability if e(PyC) ≤ 150 nm
  - CEA PyC properties (**confidential**)



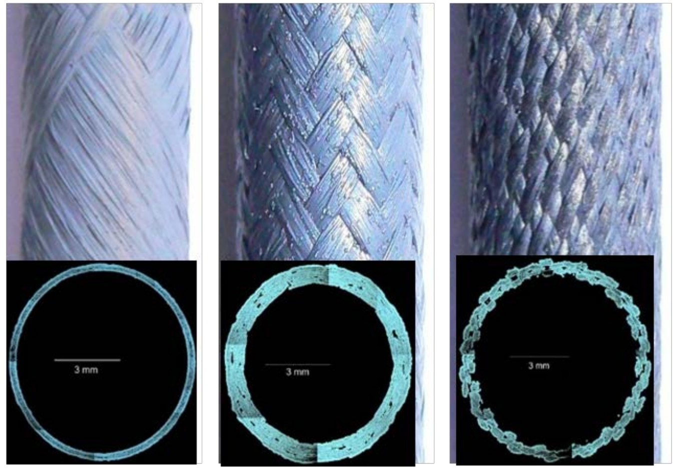
Référence

PROCESSING OF SIC/SIC PIN CLADDING

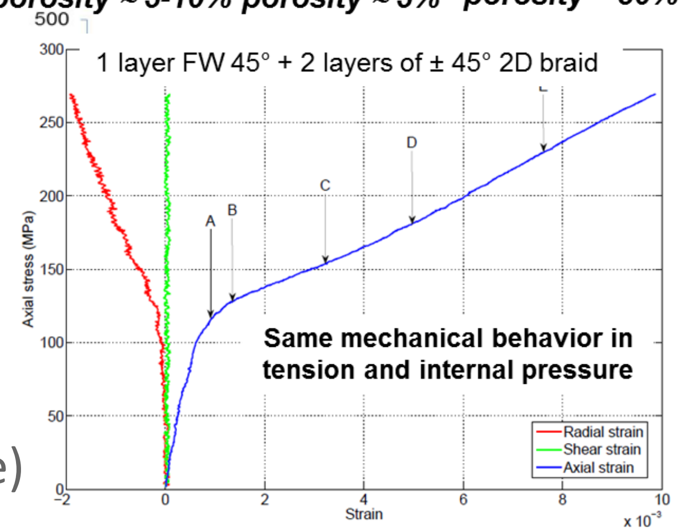
Texture ?

- 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 betters mechanical properties for a given angle
  - Despite its high porosity, 3D braiding offers great mechanical properties

Filament winding | *2D braiding* | *3D braiding*



porosity ~ 5-10% | **porosity ~ 5%** | **porosity ~ 30%**



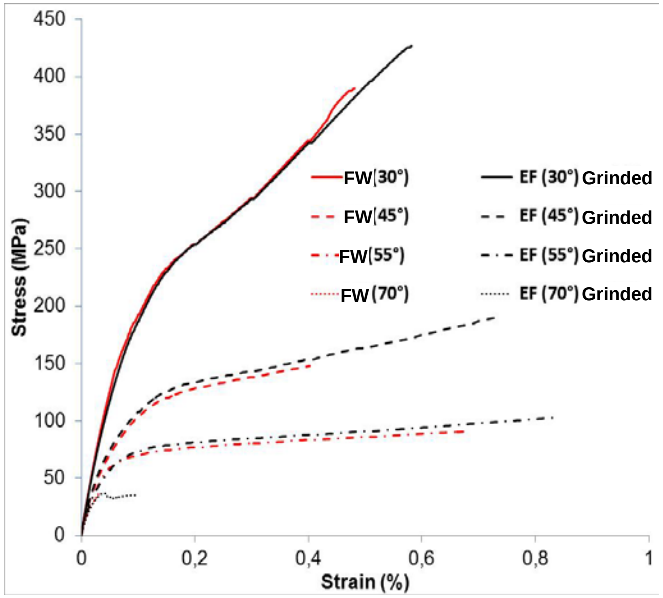
Choice:

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

Influence of the surface roughness

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

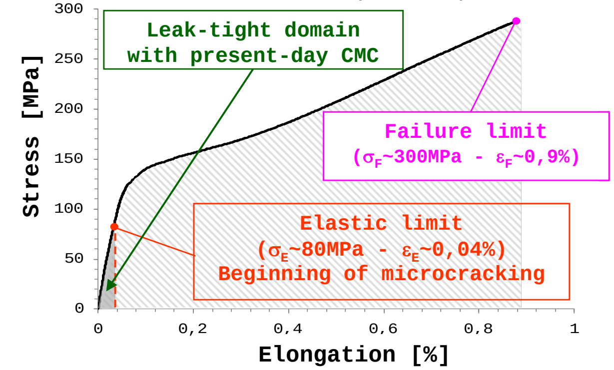
- Properties of the grinding:
  - External and internal cylindricities < 0.05 mm
  - Concentricity < 0.05 mm
  - Straightness on the interior and exterior < 0.04 mm
  - Ra < 5 µm ; Rz < 30 µm



Conclusion:

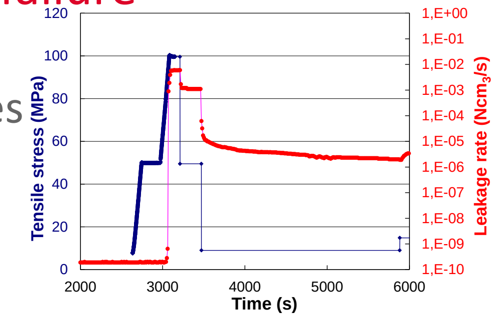
- **No effect** of grinding on the mechanical properties
- **Very good** surface roughness (tolerance)
- **Necessity for the "sandwich" cladding**

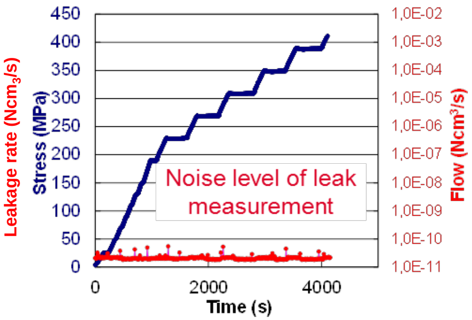
PROCESSING OF SIC/SIC PIN CLADDING

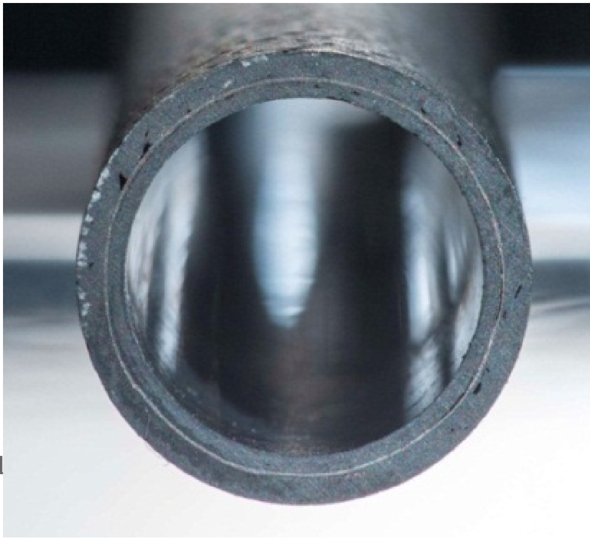


The "sandwich" pin cladding: GFR and LWR

- 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 ≈ 0.3 mm
  - Liner ≈ 0.1 mm (limited because of neutronic calculations)
  - Outer SiC/SiC ≈ 0.6 mm
- Tantalum has been chosen for GFR
- **On-going investigation** to determine the most suited metal for **LWR**





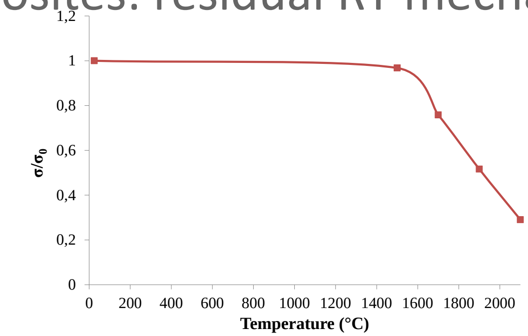


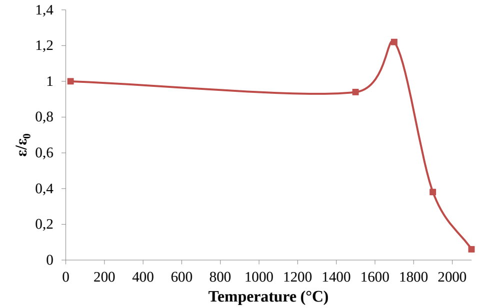
PROPERTIES OF SIC/SIC COMPOSITES

Mechanical behavior (1/2)

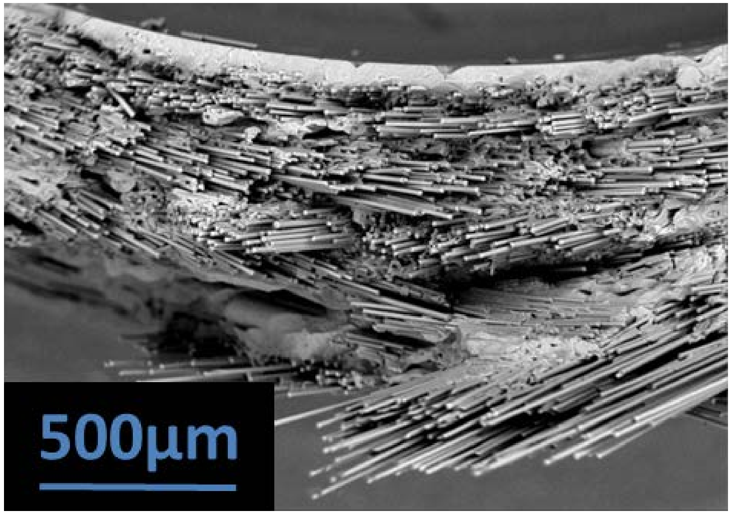
- Thermal stability of SiC/SiC composites: residual RT mechanical tensile behavior after HTT for 2h in Ar atm

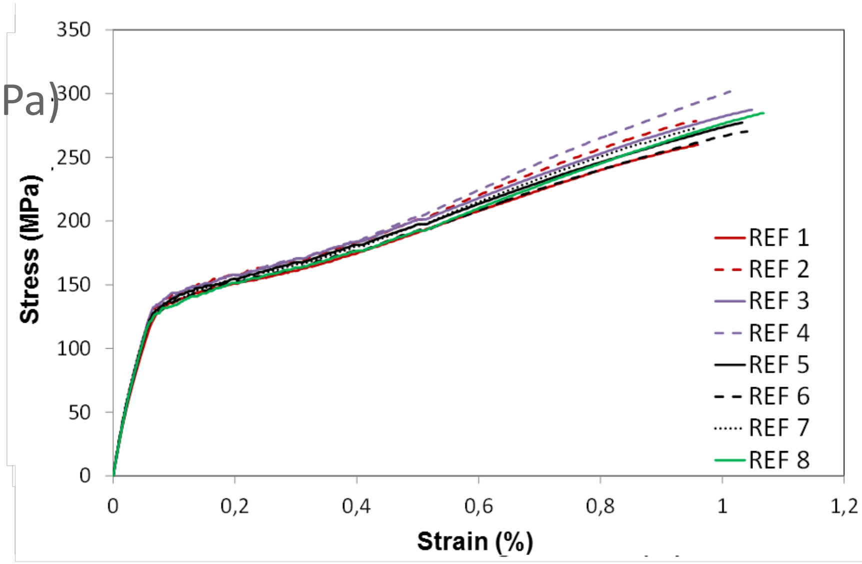
  → **No degradation** of the mechanical characteristics **up to 1300°C**





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

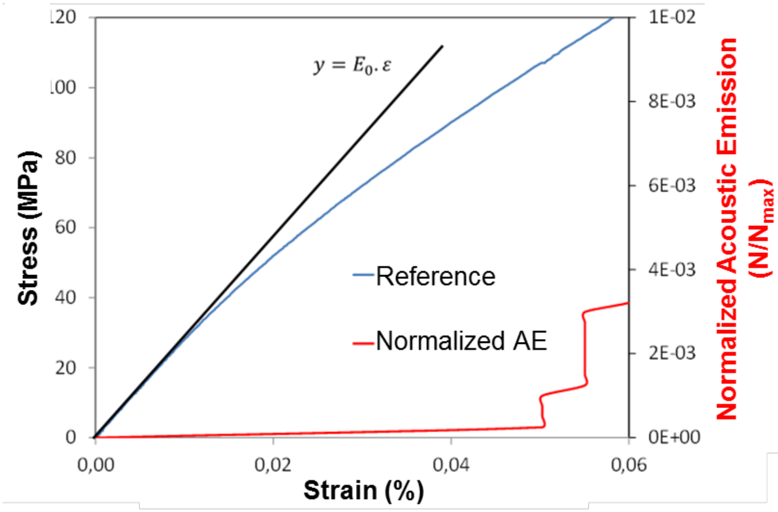




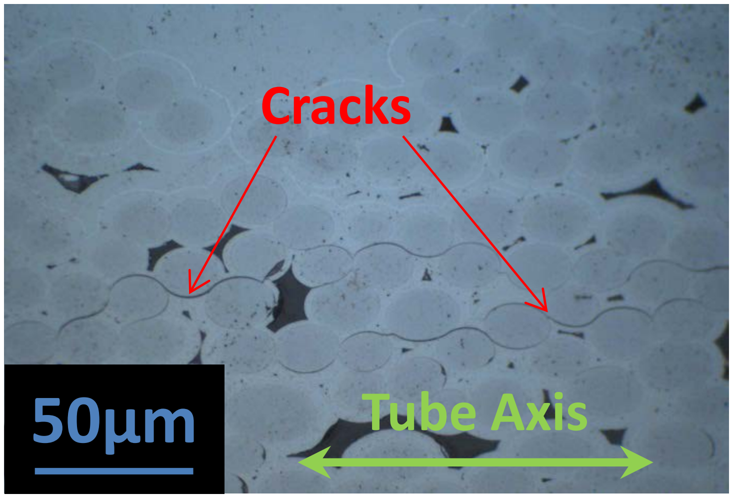
Mechanical behavior (2/2)

- 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:** ≠ coefficient of expansion mandrel/composite
  → **Thermal stresses** → **Microcracks** of the fabricated composite

PROPERTIES OF SIC/SIC COMPOSITES

Thermal properties

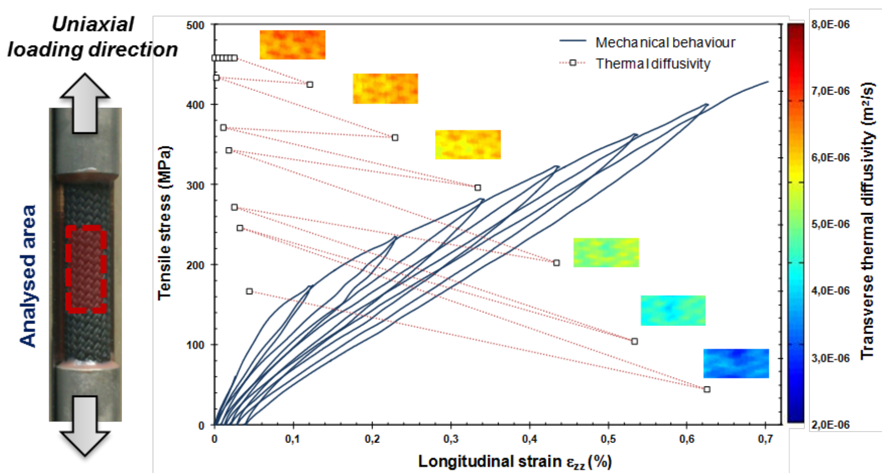
- Heat conductivity measured by pulsed **"flash method"** with the combination of **IR thermography**
- Impossible for the "sandwich cladding"
  → Calculations needed

Texture type	Génération	α_f (%)	Surface Traitment *External*	Thickness *mm*	Density *$g.cm^{-3}$*	Transverse diffusivity *$m^{-2}.s^{-1}$*	Conductivity [#] *$W.m^{-1}.K^{-1}$*
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**

[#] 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



PROPERTIES OF SIC/SIC COMPOSITES

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 (UO_2)** 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

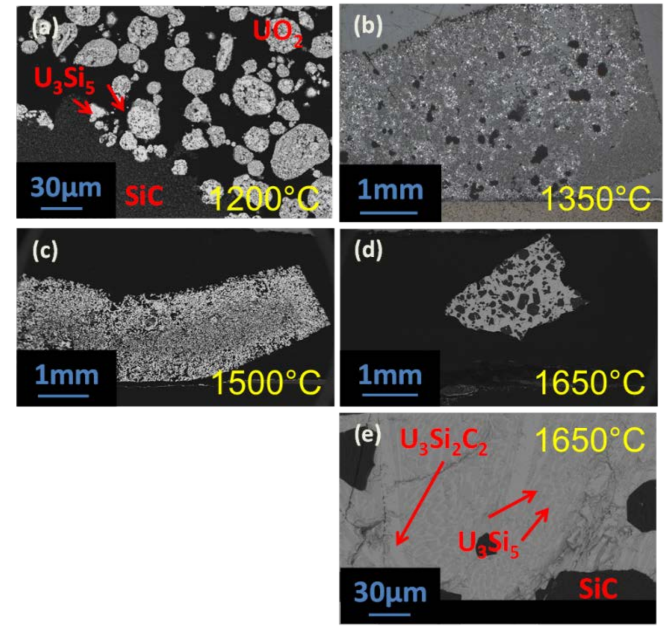
- **Few thermodynamical compatibility studies**
- SiC or SiC/SiC **reaction** with:
  - UO_2
  - GFR liner (tantalum/niobium)
  - Sodium

PROPERTIES OF SIC/SIC COMPOSITES

UO_2/SiC interaction:

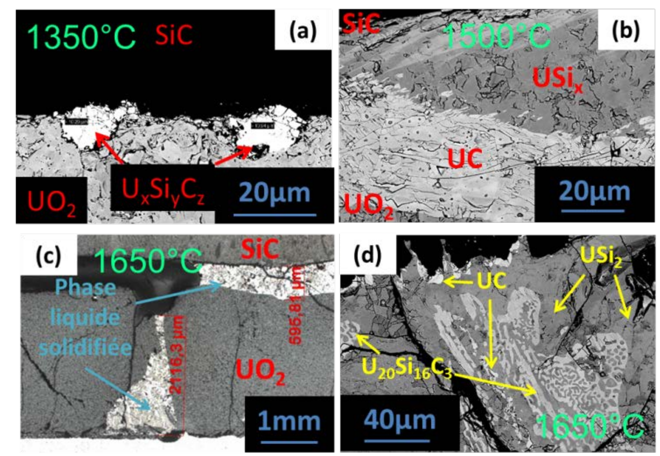
In open system (HT Mass Spectrometry):

- Low reaction **up to 1350°C**
- Formation of **mainly U_3Si_5** 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



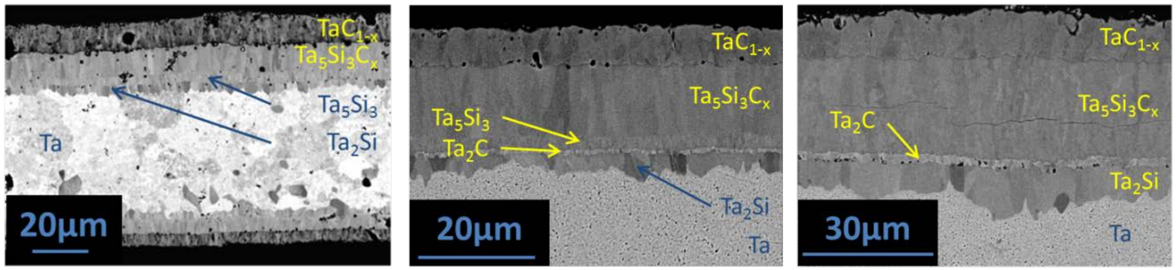
Applications:

- **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 ?

PROPERTIES OF SIC/SIC COMPOSITES

Liner (Tantalum – Niobium)/SiC interaction:

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

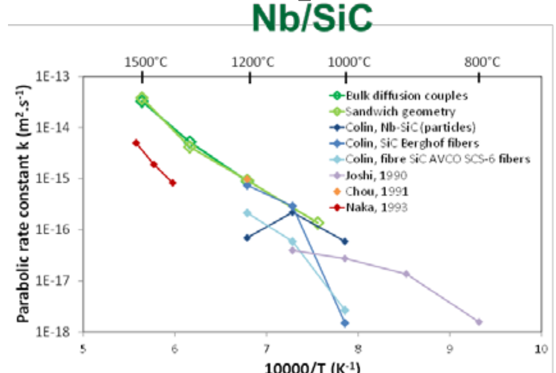


1200°C 1350°C 1500°C

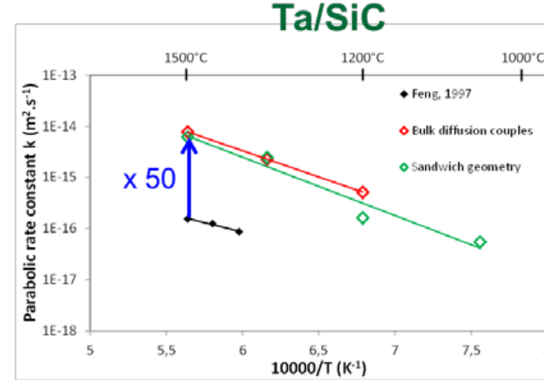
- $SiC/NbC_{1-x}/Nb_5Si_3C_x/NbC_{1-y}/Nb_2C/Nb$ (1050 – 1500°C)
- $SiC/TaC_{1-x}/Ta_5Si_3C_x/Ta_5Si_3$ (1050 - 1350°C)/Ta_2C (1350°C – 1500°C)/Ta_2Si/Ta

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

Nb/SiC



Ta/SiC



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

- **Application:**
  Niobium **too reactive**
  Tantalum **most suited**

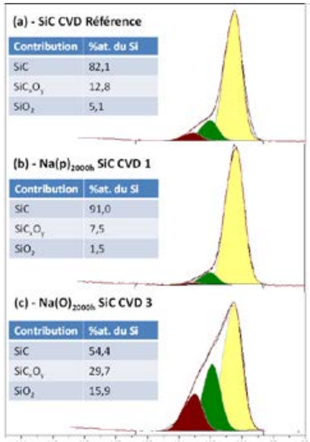
Thickness after 4 years (µm)	600°C	700°C	800°C	900°C	950°C	1000°C
Niobium	0,5	2,5	10	30	50	80
Tantalum	0,4	2	7	20	32	49

PROPERTIES OF SIC/SIC COMPOSITES

Liquid sodium/SiC interaction:

- Up to **2000h** in the liquid Na with **[O]< 5** or **[O]=1000ppm**
- CVD SiC:
  - **Slight decrease** of oxide and oxicarbide phases on surface (no weight loss) for "pure" Na
  - **Slight surface oxidation** and weight loss for Na(O)

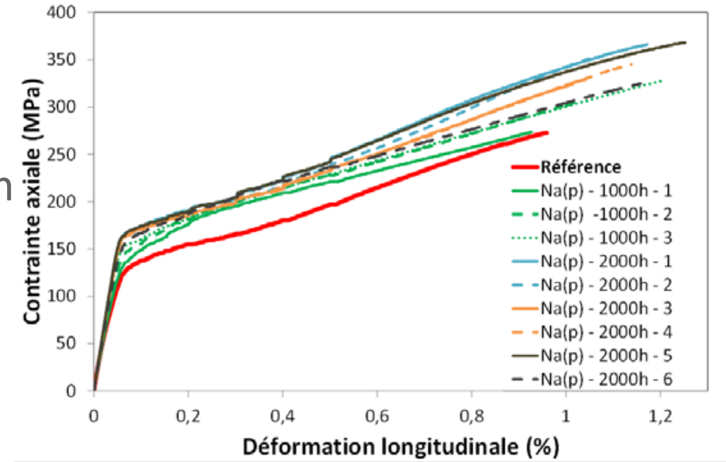
  → SiC is not significantly affected by sodium immersion



- 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

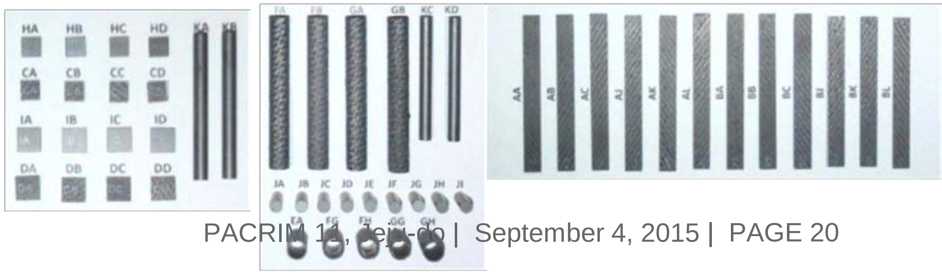
  → **Interphase is not affected**
  - Hypothesis: **healing** of pre-existing cracks by sodium for undamaged samples

  → 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



DE LA RECHERCHE À L'INDUSTRIE

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CONCLUSIONS

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:
  - UO_2: **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
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