DE LA RECHERCHE À L'INDUSTRIE

Innovative SiC/SiC composites for nuclear applications

C. Sauder, C. Lorrette, A. Michaux, L. Gélébart, E. Buet, S Poissonnet, A Coupé, J. Braun, L Briottet, M. Zabiego, J.L. Séran, M. Le Flem, L. Chaffron

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CONTEXT

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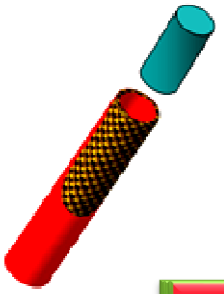


Developpment of refractory materials for pin cladding of 4th generation reactors

- **R&D mostly driven by GFR fuel objectives (2004-2010)**
- **Recently extended to other applications : SFR & PWR**

<u>Focus on SiC/SiC composites</u> :

✓ Refractory material (>> 1000°C)

✓ Irradiation resistance

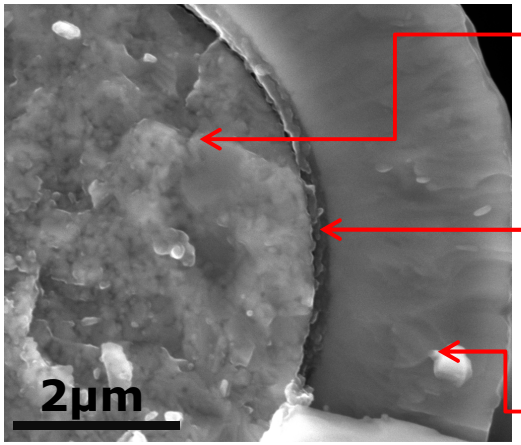
✓ Low activation

✓ Neutron transparency

✓ Corrosion resistance

Issues: gastightness + mechanical properties + thermal properties

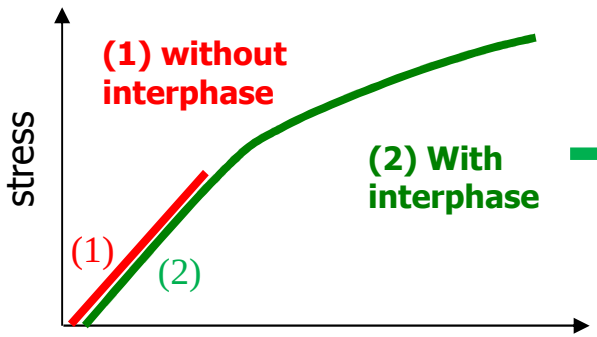
WHAT IS A SIC/SIC COMPOSITE ?



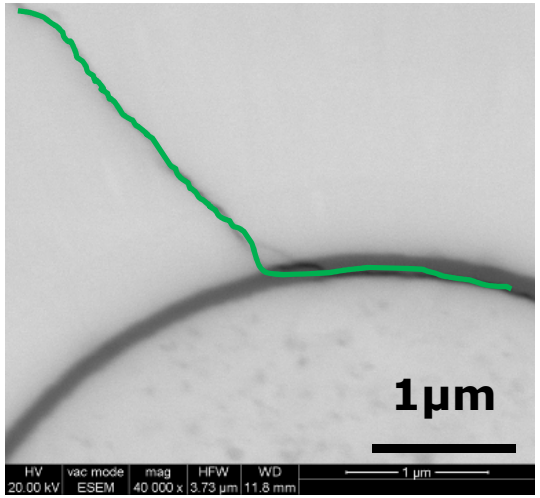
Fibre: ensures the mechanical strenght

Interphase: bonding between fiber and matrix

Matrix: protects the fiber and displys load transfer



Deflection of the cracks



→ SiC/SiC is a non brittle ceramic

WHICH SIC/SIC FOR NUCLEAR APPLICATION?

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Choice of the fiber:

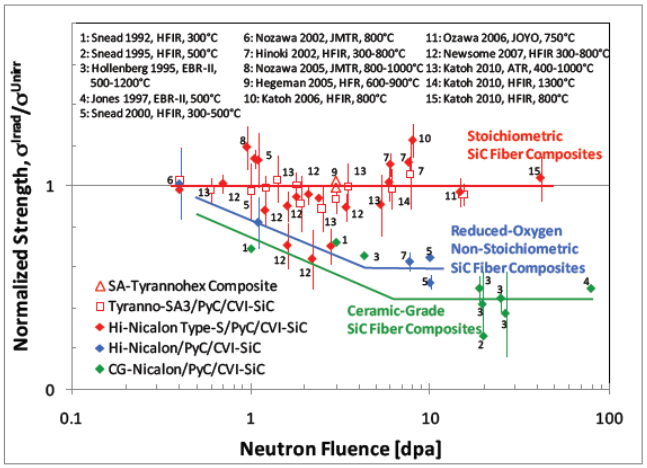
Stability under irradiation ⇒
Hi-Nicalon S ou Tyranno SA3 fibers only

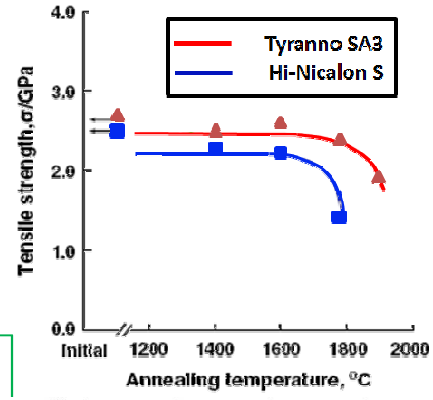
Stability at high temperature ⇒
Tyranno SA3 fibers looks better

Thermal conductivity ⇒
Tyranno SA3 fibers looks better

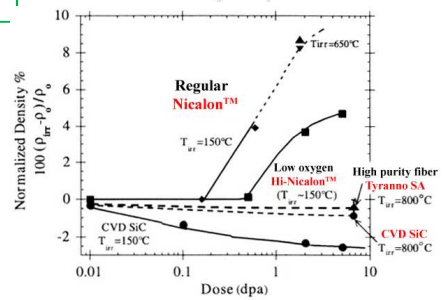
Cost ⇒
Tyranno SA3 fiber is cheaper (30%)

	HNS	TSA3
Thermal stability	☹	☺
Thermal conductivity	☹	☺
Cost	☹	☺
Mechanical properties	☺	☹





TSA is the target!



Choice of the interphase: **PyC**

Choice of the matrix: **SiC CVI**

THE MAIN CONCERNS FOR PIN CLADDING

FP retention = gas-thightness	Thermal exchange = High λ	Irradiation mechanical behavior
SiC/SiC is not gastight upon its linear elastic domain.	λ_{SiC} is lowered under irradiation (highly lowered at low temperatures)	Strain to failure $\varepsilon_R > 0,5\%$
Introduction of a liner for gas-tightness = **CEA sandwich concept**	- **Deal with it !** - Use of SA3 reinforcement - Process a specific matrix for composites $\Rightarrow$ very long term work	- **Ok with HNS** - No solutions with SA3 - Look for high dose irradiated mechanical behavior.

Goal:→ Development of a gastight component prepared from HNS SiC/SiC composite

PROCESSING : INFLUENCE OF BRAIDING AND GRINDING

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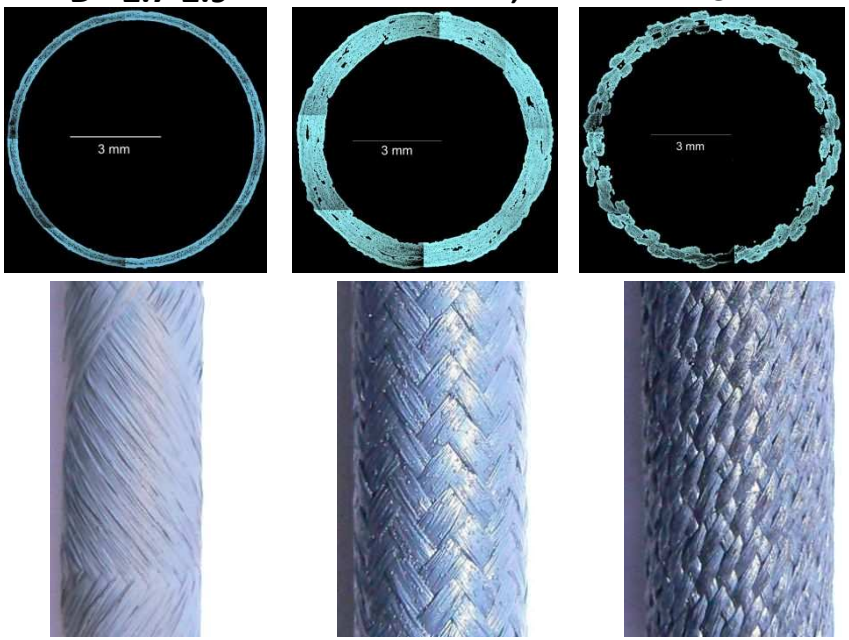
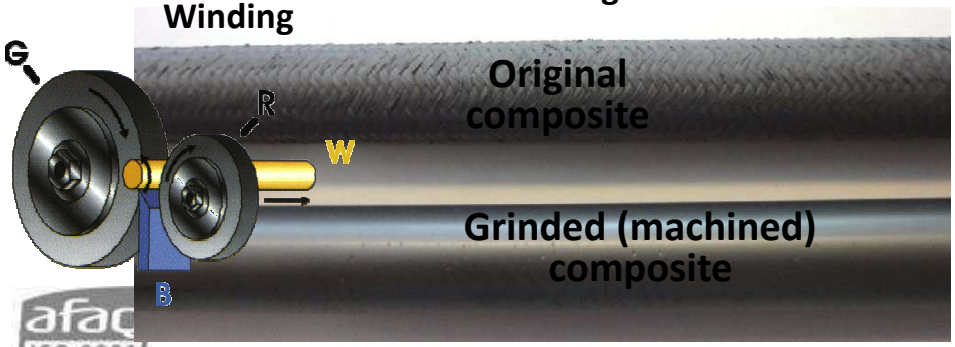
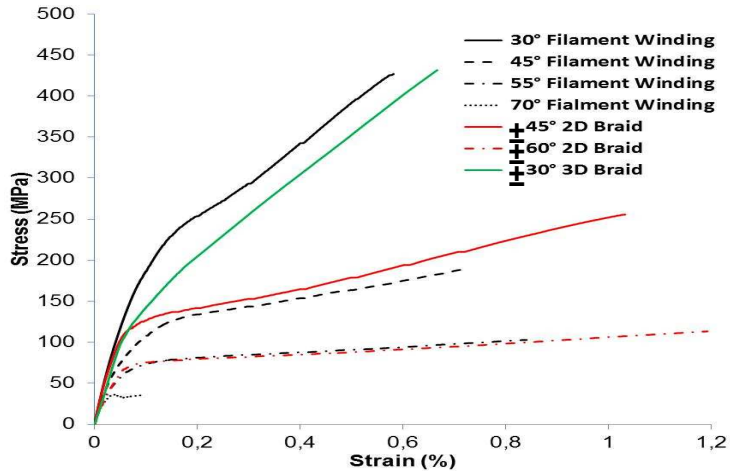
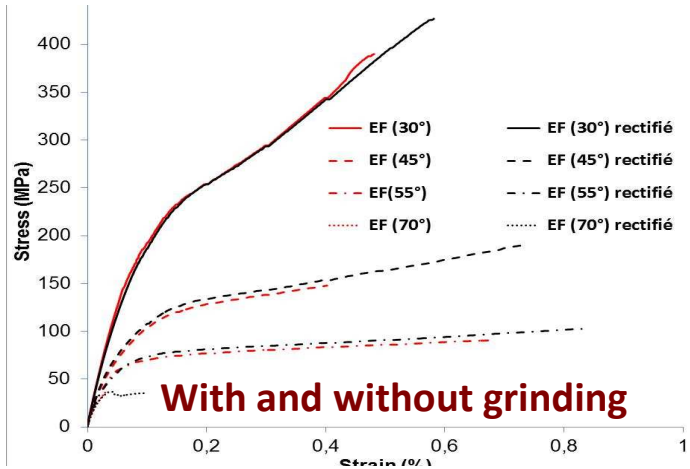
D~ 2.7-2.9 | D~ 2.8 – 2,9 | D~ 2.3-2.4



Filament Winding | 2D braiding | 3D braiding



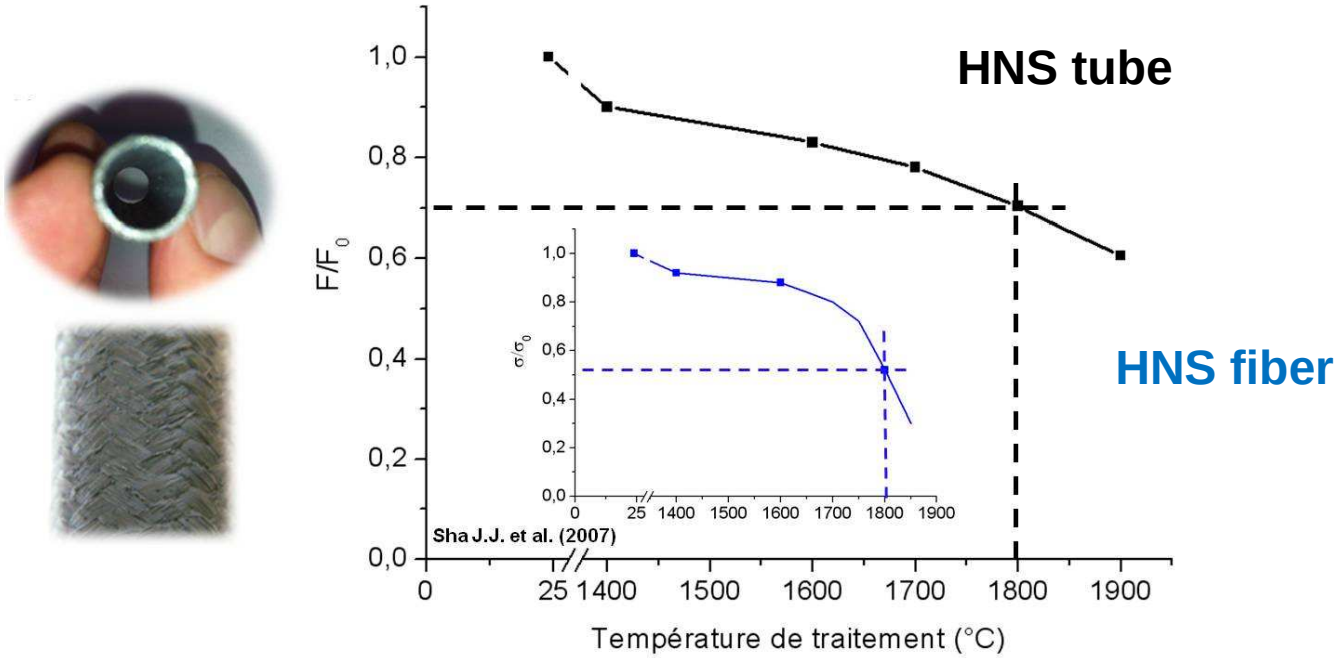




- **Properties can be tailored thanks to appropriate braiding**
- **Grinding has no significant effect on CMC**

CHARACTERIZATION: WHICH TEMPERATURE LIMITATION?

Influence of a thermal treatment (2h in Ar) on mechanical properties



CVI SiC/SiC tube is not sensitive to very high temperature in <u>inert atmosphere</u>

CHARACTERIZATION : FATIGUE

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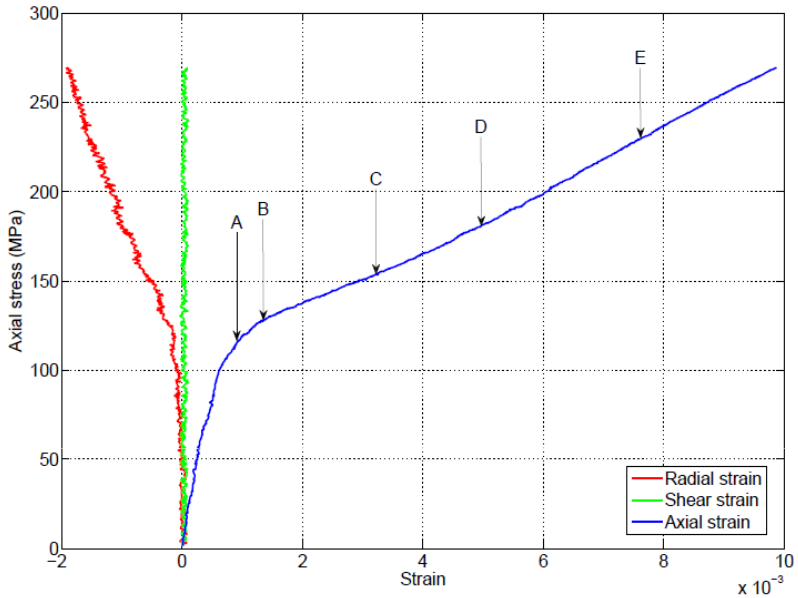
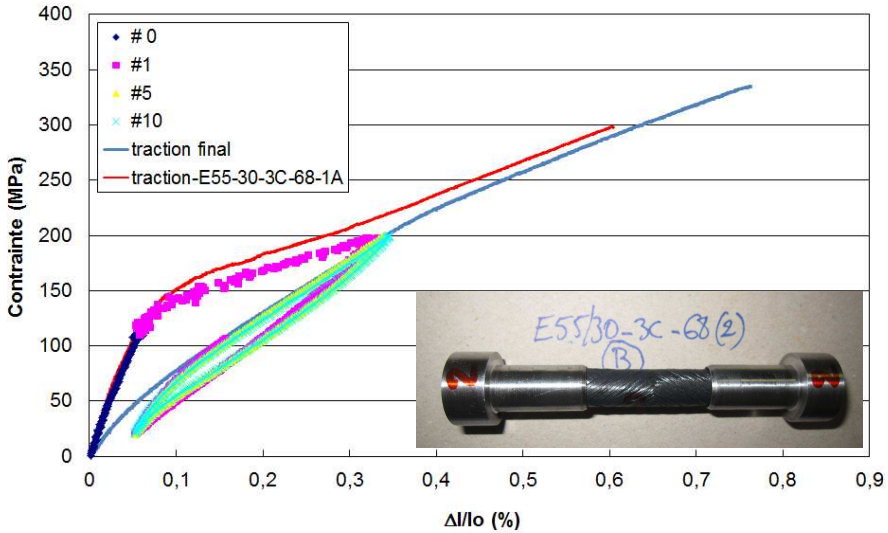
Reference SiC/SiC material for Pin cladding:

FW (45°) 1 layer + 2D braiding (45°) 2 layers



mechanical behavior is the same for traction or internal swelling



Fatigue tests:
20 -200MPa at 5 Hz
No failure after 500 000 cycles!

CHARACTERIZATION : DIMENSIONNING

3 Patents:

⇒ ***Control of dimensions and tolerances of CMC composites***

CEA/LTMEx Products

External and internal dimensions within 0,01mm tolerance

- external and internal dimensions: ±0.01 mm
- external cylindricity < 0.03mm with mean value of 0.02 mm.
- internal cylindricity < 0.05mm with mean value of 0.04 mm.
- concentricity < 0.05mm with mean value of 0.04 mm
- external Straightness < 0.02mm with mean value of 0.005 mm
- internal Straightness < 0.04mm with mean value of 0.02 mm
- R_a (mean roughness) < 5µm and R_z (max roughness) < 30µm

Very good dimensional accuracies (could be improved for internal part)

CHARACTERIZATION: IMPURITIES CONCENTRATION

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Purity of CEA SiC/SiC composites

	SiC/SiC CEA	SiC CVD (R&H)
C	51,7	50,7
N	**0,0089**	< 0,0007
O	0,35	**0,0043**
S		
H	0,032	**0,026**

Element	Concentration (ppm at)	Concentration (ppm at)
B	0,2200	**2,54**
C	matrix	matrix
Na	< 0,04	< 0,04
Mg	< 0,04	< 0,04
Al	0,52	< 0,007
Si	matrix	matrix
P	0,22	0,058
S	**15,60**	**4,4**
Cl	2,86	0,12
K	0,0560	<0,03
Ca	1,50	0,15
Ti	< 0,04	< 0,04
Cr	< 0,1	< 0,1
Fe	5,36	< 0,02
Co	< 0,01	< 0,01
Ni	0,34	0,03
Cu	< 0,01	< 0,01
As	< 0,01	< 0,01
Zr	0,02	<0,002
Nb	< 0,01	< 0,01
Mo	< 0,01	< 0,01
Sn	< 0,008	< 0,008
Hf	< 0,005	< 0,005
Ta	< 1	< 1
W	< 0,001	< 0,001
Pt	< 0,005	< 0,005

Very few impurities

Residual Impurities (Fe, S, N, O, H) belong to Hi-Nicalon S fibers

ALTERNATIVE PROCESSING

Liquid Phase Process:

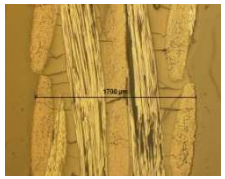
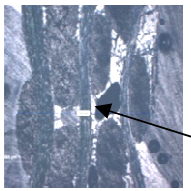
→ ***Hybrid Process_ CVI + EPI + PIP***

Objective : Increase thermal conductivity of SiC_f/SiC

by lowering porosity

weaved C_f or SiC_f → ***CVI*** → ***Interphase PyC + SiC Pre-densification*** → EPI + PIP → ***SiC green Matrix*** → T°, P

Raw material

SiC nanopowder LTMEx pyrolysis	***C_f/ PyC/ SiC nano***	***C_f/ PyC/ SiC nano + SiC Polymer***	***C_f/ PyC/ SiC/ SiC nano + SiC Polymer***
t = 4 min			 ***Bubbles: Polymer/resin reactions***

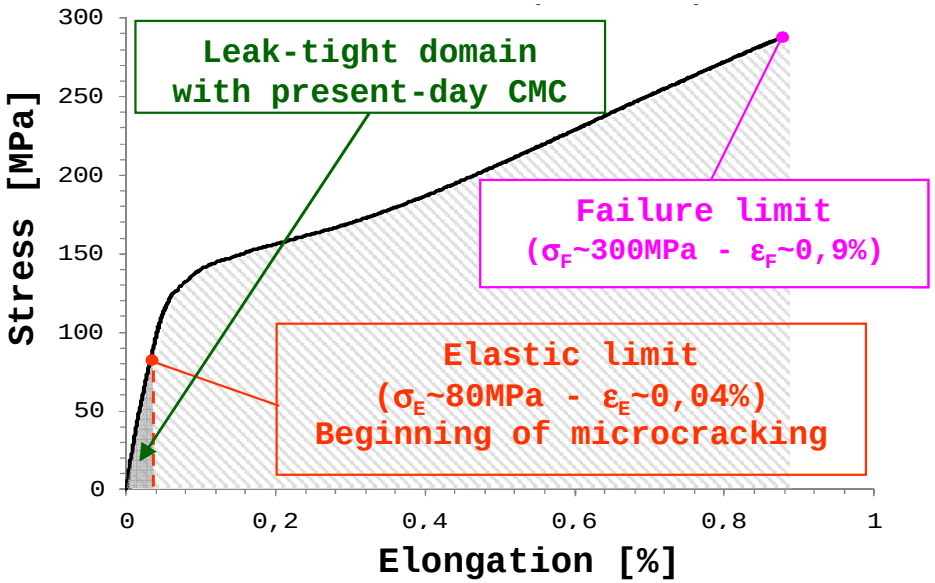
→ ***Processing of a SiC layer on composites***

Objectives : Densification and smoothing of SiC_f/SiC composites

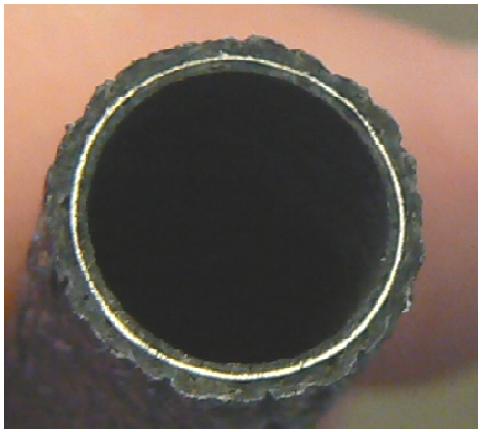
This alternative process could be used for densification of hexagonal tubes (cf P David oral) for which requirements are less harsh

PROCESSING : « SANDWICH » CONCEPT

Sandwich concept (CEA Patent)



All stages of process are done in CEA



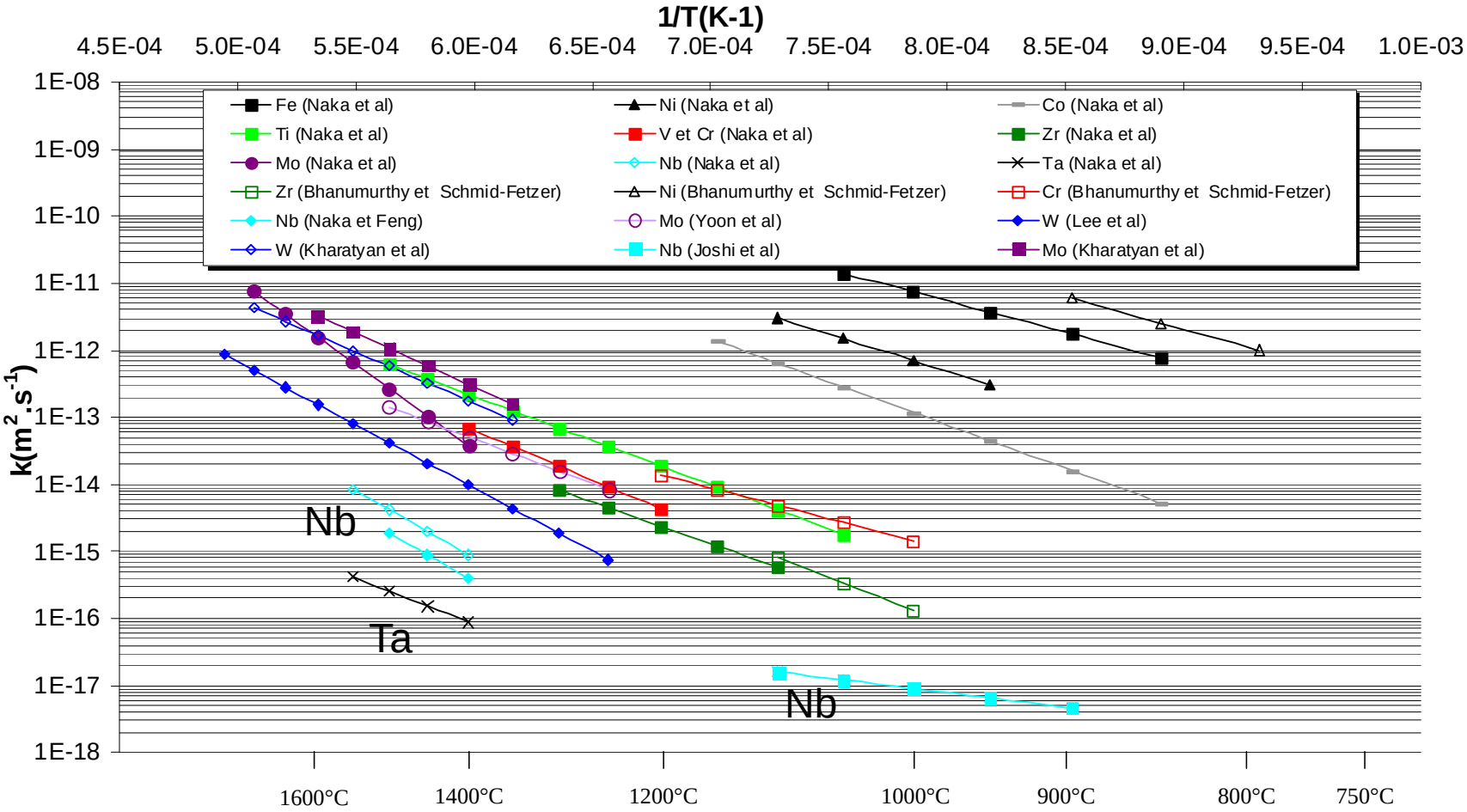
- Metallic liner only ensures tightness (processing in LTMEX)
- Composite ensures mechanical resistance
- Process is simple and reproducible

Internal tube SiC/SiC:	***e~0.3mm***
liner Ta :	***e <0.1mm***
External tube SiC/SiC:	***e~0.6mm***

This type of cladding is supposed to be tight up to failure of the pin

« SANDWICH » CONCEPT: WHICH LINER?

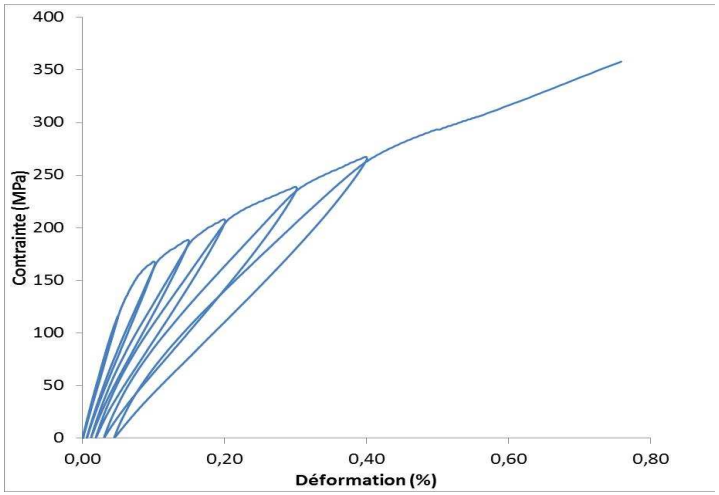
Sandwich Concept – Choice of liner

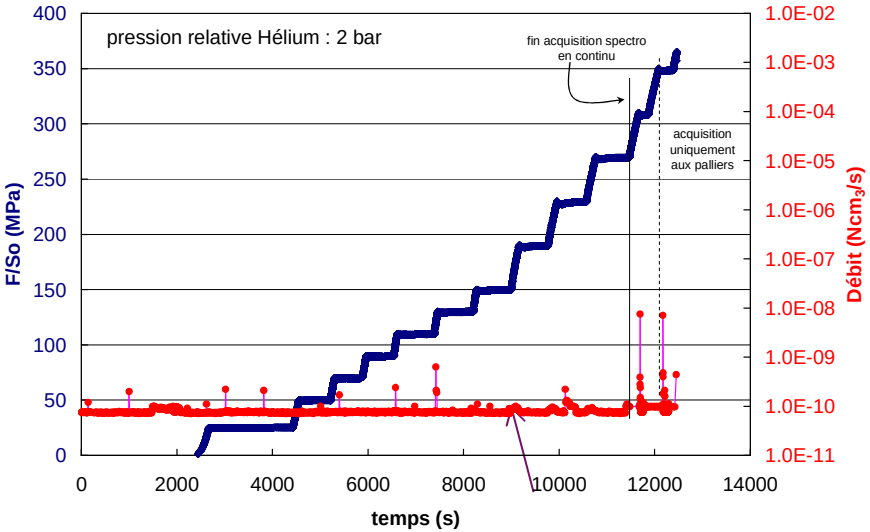


Tantalum and Niobium are the best candidates for GFR
Is it still true for PWR or BWR ?

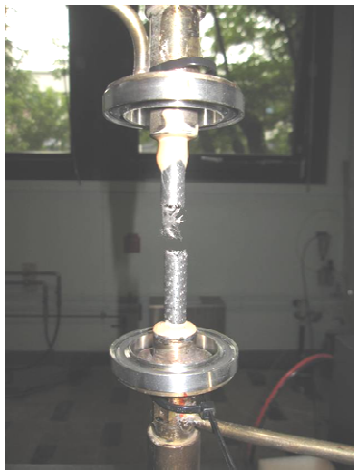
SANDWICH CHARACTERIZATION: PERMEATION

Sandwich Concept – tightness during tensile test





Detection limit



« sandwich » concept allows to keep tightness up to failure of SiC/SiC pin cladding

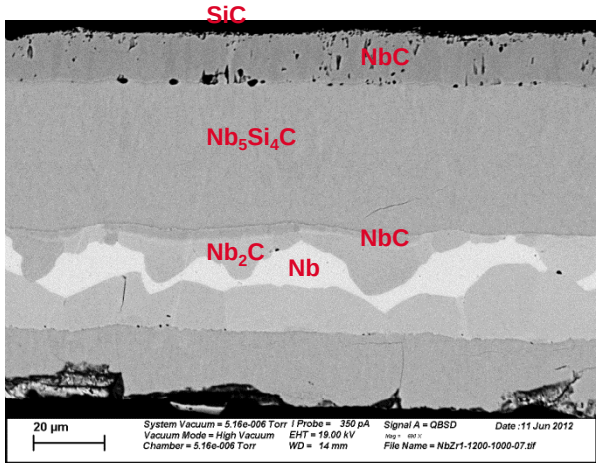
3. SANDWICH CHARACTERIZATION

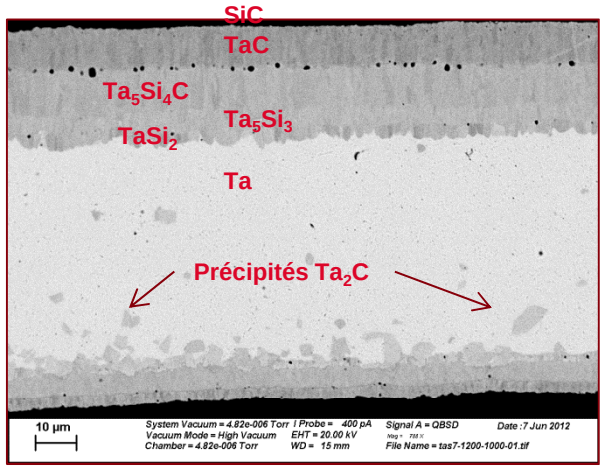
Sandwich Nb – 1000h – 1200℃ – Sandwich Ta

outer

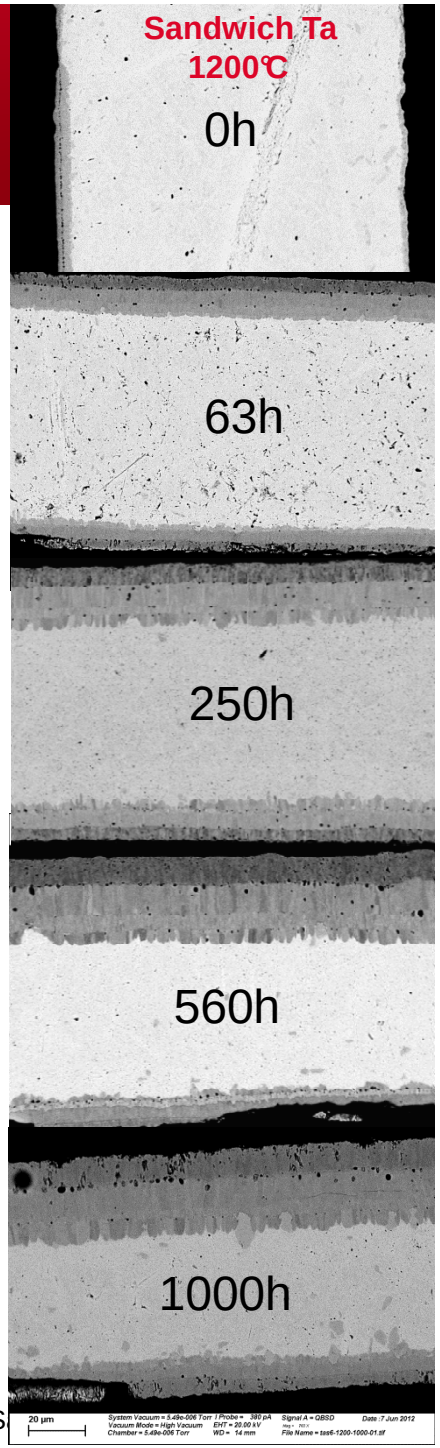
Liner

inner





- **Very encouraging results with Ta**
- **Reaction zones are not symmetric (not observed with plates)**
- **Further characterization needed**



2. CHARACTERIZATION: IRRADIATION

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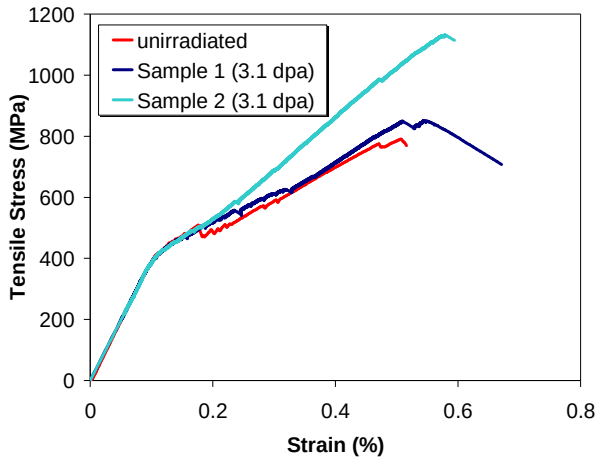
Very encourageing results have being obtained with CVI minicomposite (CROCUS irradiation performed in OSIRIS)



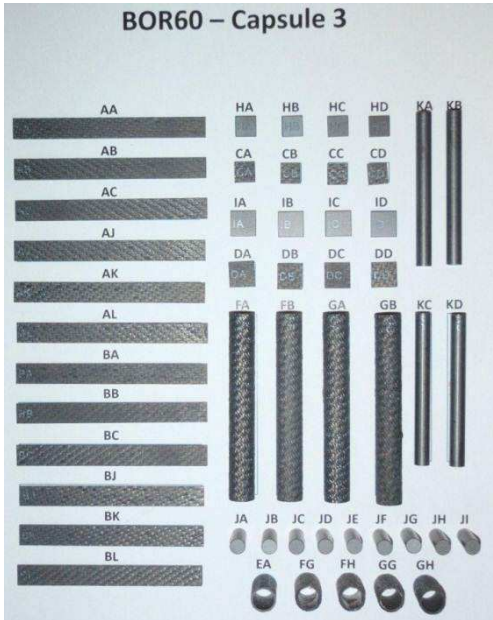
NEXT STEP:

⇒ **Irradiation in BOR60 (sodium, 550℃ up to 105-120 dpa SiC)**

First irradiation of SiC/SiC composites at such doses (Including sandwich specimens)

Irradiation should start on december 19, 2012

→ **PIE are expected for 2015**



CONCLUSION AND PROSPECTS

- *CMC: Tailoring materials*
- *Current work focused on fabrication of gastight closed for fast reactor applications (and hexagonal tube)*
- *Developpment of high skills in CMC manufacturing process at CEA*
- *Robust program of characterization: assessment of the high quality of the composites made at CEA*
- *Pursuit of Investment for CMC development: deliveryof a winding machine in the next days and investment of a braiding machine in 2013*

- *Collaborative work with french universities through Matinex and NEEDs networks (Bordeaux, Mulhouse, Caen, Grenoble) and industrial partners*

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 51 66| F. +33 (0)1 69 08 82 52
laurent.chaffron@cea.fr

Direction de l'Energie Nucléaire
Département des Matériaux pour le Nucléaire
Service de Recherches Métallurgiques Appliquées
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