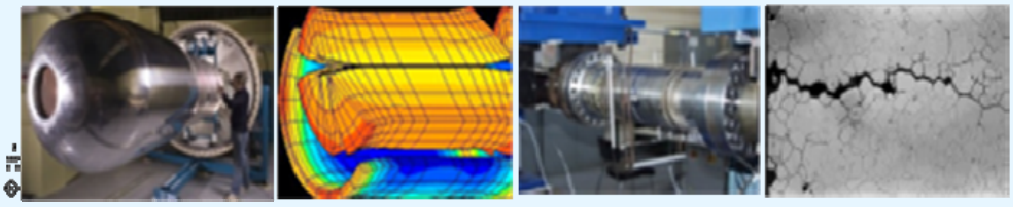
MINOS

Centre of Excellence for Nuclear Materials

Workshop

Materials Innovation for Nuclear Optimized Systems



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

Laurent CHAFFRON et al.

CEA (France)

Innovative SiC/SiC Composite for Nuclear Applications

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Workshop Materials Innovation for Nuclear Optimized Systems
December 5-7, 2012, CEA – INSTN Saclay, France

Innovative SiC/SiC Composite for Nuclear Applications

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[3] CEA-DEN-DEC, Service d'Etudes et de Simulation du Comportement des Combustibles, SESC (Cadarache, France)

Among various refractory materials, SiC/SiC ceramic matrix composites (CMC) are of prime interest for fusion and advanced fission energy applications, due to their excellent irradiation tolerance and safety features (low activation, low tritium permeability,…). Initially developed as fuel cladding materials for the Fourth generation Gas cooled Fast Reactor (GFR), this material has been recently envisaged by CEA for different core structures of Sodium Fast Reactor (SFR) which combines fast neutrons and high temperature (500°C). Regarding fuel cladding generic application, in the case of GFR, the first challenge facing this project is to demonstrate the feasibility of a fuel operating under very harsh conditions that are (i) temperatures of structures up to 700°C in nominal and over 1600°C in accidental conditions, (ii) irradiation damage higher than 60 dpa_{SiC}, (iii) neutronic transparency, which disqualifies conventional refractory metals as structural core materials, (iv) mechanical behavior that guarantees in most circumstances the integrity of the first barrier (e.g.: $\varepsilon > 0.5\%$), which excludes monolithic ceramics and therefore encourages the development of new types of fibrous composites SiC/SiC adapted to the fast reactor conditions. No existing material being capable to match all these requirements, CEA has launched an ambitious program of development of an advanced material satisfying the specifications [1]. This project, that implies many laboratories, inside and outside CEA, has permitted to obtain a very high quality compound that meets most of the challenging requirements. We present hereinafter few recent results obtained regarding the development of the composite. One of the most relevant challenges was to make a gastight composite up to the ultimate rupture. Indeed, multicraking of the matrix is the counterpart of the damageable behavior observed in these amazing compounds. Among different solutions envisaged, an innovative one has been successful. It consists of inserting a metallic layer between two tubes of CMC [2]. The concept, illustrated in figure 1, guaranties a perfect helium tightness up to fracture of the CMC.

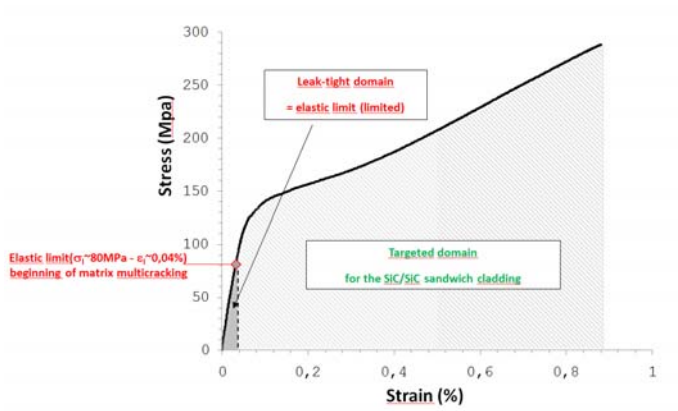

Fig. 1: Sandwich cladding concept: tightness is ensured up to CMC failure thanks to the elastic metallic layer.

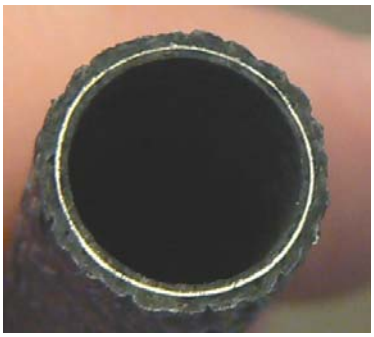

Fig. 2: Sandwich cladding Cross section (metal is in white).

Another challenge was to prepare a representative cladding with very strict geometrical tolerances. Revisiting the fabrication of the entire breading process has allowed to ensure a perfect geometry of the final tube. Thanks to the high quality of manufacture and the high level of purity of composite materials manufactured at CEA, few tens of CMC objects (tubes, disks and plates) have been prepared in order to be irradiated in the Russian reactor “BOR 60”. For the first time, composite materials will be submitted to swift neutrons at very high damaging doses (up to 80 dpa_{SiC}) between 400 and 520°C. Post irradiation examinations expected for 2015 should give reliable results on the behavior of this multi-materials component. In parallel, other basic researches are conducted to improve the properties of the CMC and round off the understanding [3, 4, 5]. Some new results allowed to extend the field of use of the CMC through an optimization of the interphase of the composite. The figure 4 shows the relative elongation of a CMC after a two hours dwell time annealing in argon at different temperatures: optimized composite can sustain very high temperature without drastic drop of its mechanical properties.

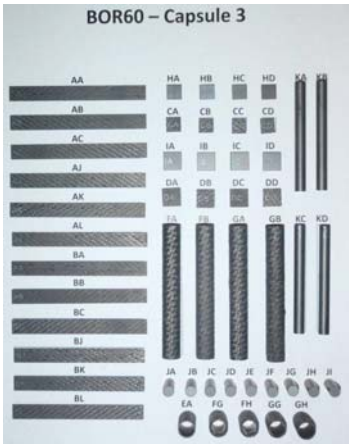

Fig. 3: CMC specimen prepared for BOR60 irradiation

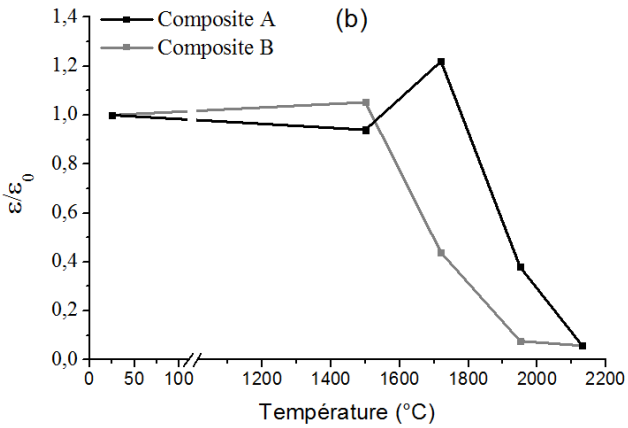

Fig. 4: Evolution of the relative elongation of two composites with the annealing temperature: optimized CVI conditions to improve mechanical properties.

References

[1] L. Chaffron, J. L. Séran, C. Sauder, C. Lorrette, A. Michaux, L. Gélébar1, A. Coupé, SiC/SiC Composite Materials for Fast Reactor Applications. Proceedings of ICAPP 2011, Nice, France, May 2-5, 2011, Paper 11433.

[2] M. Zabiégo, C. Sauder, C. Lorrette, P. Guédeney, Tube multicouche amélioré en matériau composite à matrice céramique, gaine de combustible nucléaire en résultant et procédés de fabrication associés.Patent submitted 1 August 2011, in French.

[3] C. Sauder, J. Lamon, Influence of fiber surface roughness on mechanical behaviour of SiC/SiC minicomposites with Hi-Nicalon S and SA3 reinforcement. 35ème International Congress on Advanced Ceramic and Composites, Daytona beach 25 Janvier 2011.

[4] E. Buet, C. Sauder, S. Poissonnet, P. Brender, R. Gadiou, C. Vix-Guterl, Influence of chemical and physical properties of the last generation of silicon carbide fibres on the mechanical behaviour of SiC/SiC composite. Journal of the European Ceramic Society, 2012. 32(3): p. 547-557.

[5] A. Coupé, H. Maskrot, E. Buet, A. Renault, P.J. Fontaine, L. Chaffron, Dispersion Behavior of Laser-synthesized silicon carbide nanopowders in ethanol for Electrophoretic Infiltration. Journal of the European Ceramic Society, Vol 32, Issue 14, 3837-3850, 2012.

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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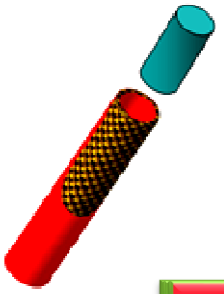


Developpment of refractory materials for pin cladding of 4th generation reactors

- **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

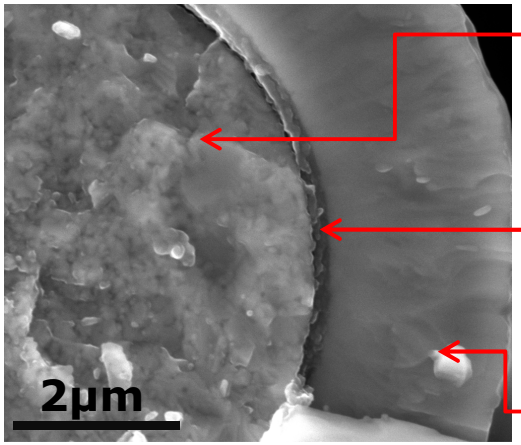
✓ Low activation

✓ Neutron transparency

✓ Corrosion resistance

Issues: gastightness + mechanical properties + thermal properties

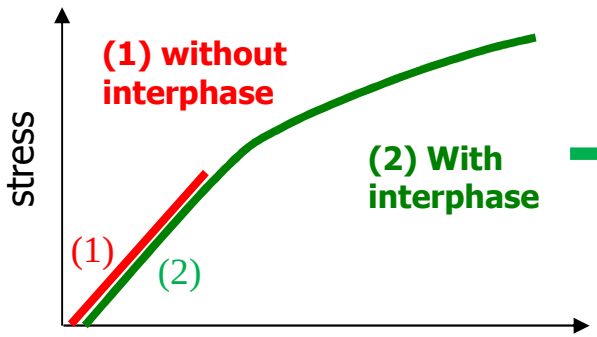
WHAT IS A SIC/SIC COMPOSITE ?



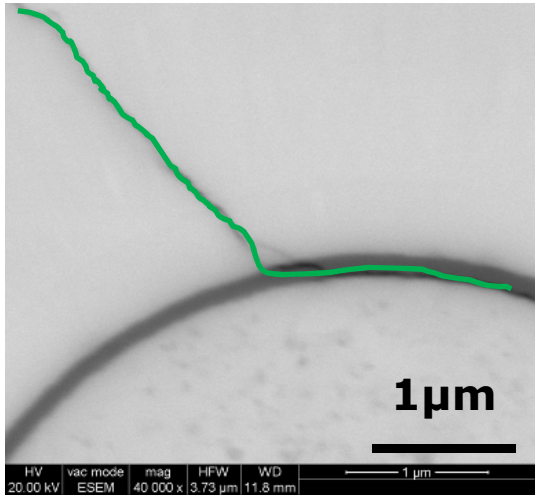
Fibre: ensures the mechanical strenght

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?

Choice of the fiber:

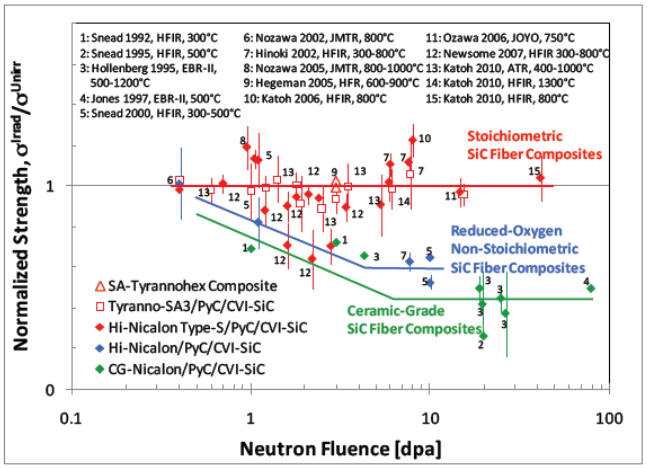
Stability under irradiation ⇒
Hi-Nicalon S ou Tyranno SA3 fibers only

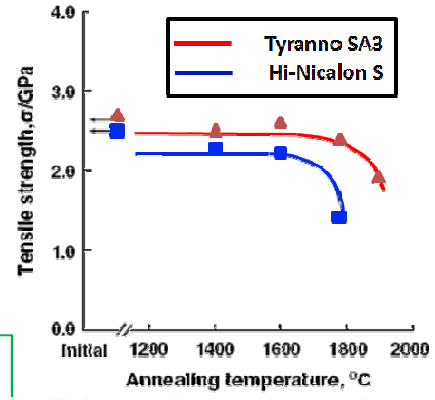
Stability at high temperature ⇒
Tyranno SA3 fibers looks better

Thermal conductivity ⇒
Tyranno SA3 fibers looks better

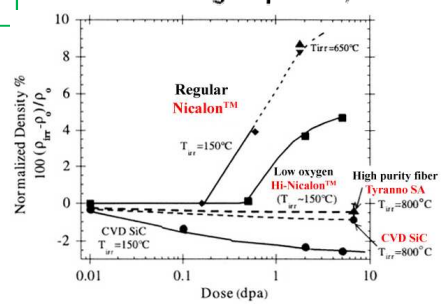
Cost ⇒
Tyranno SA3 fiber is cheaper (30%)

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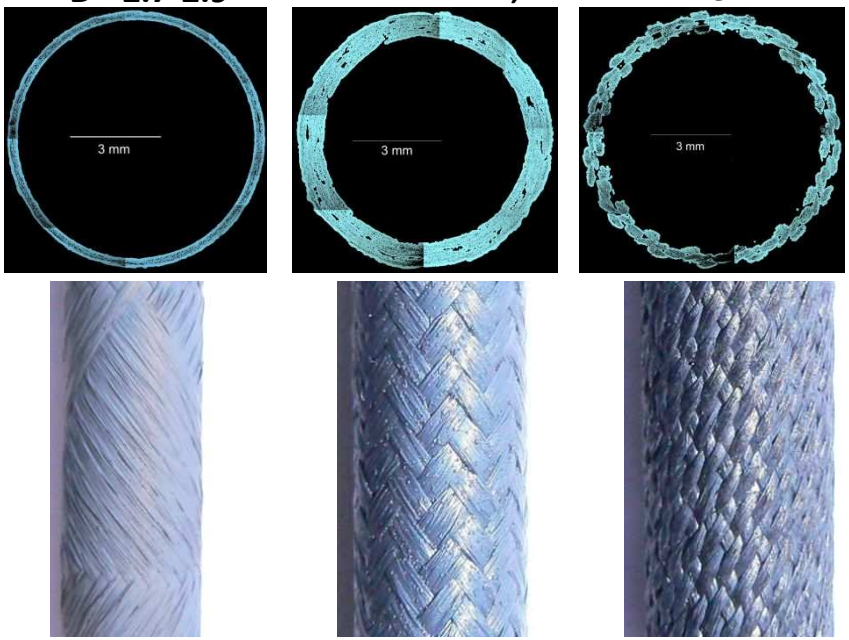
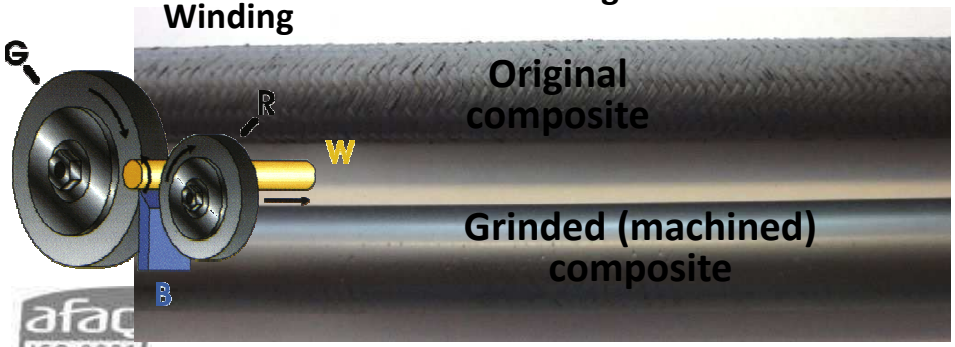
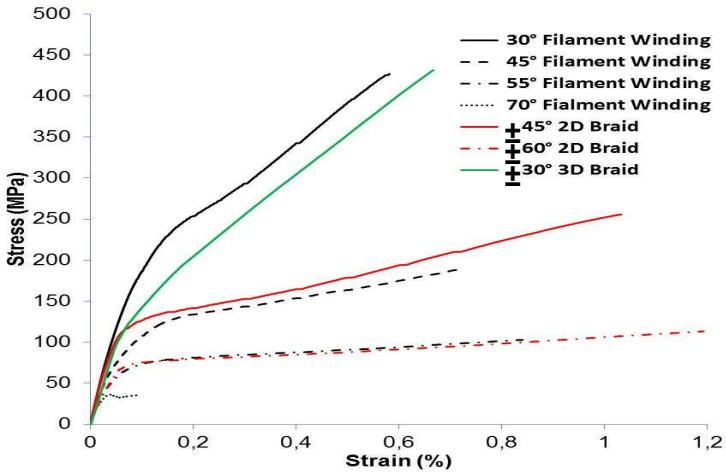
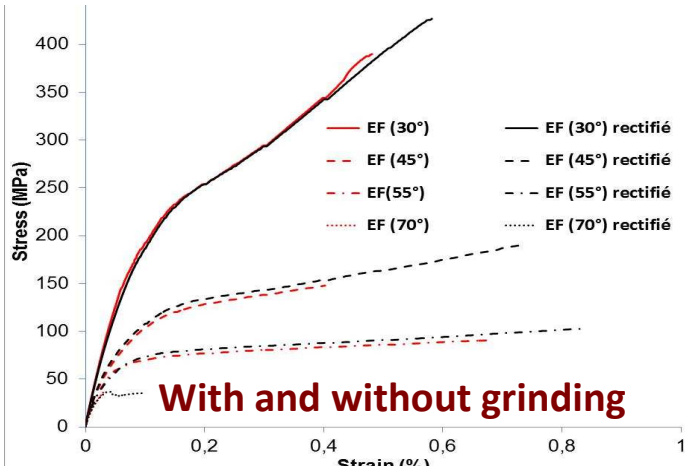
D~ 2.7-2.9 | D~ 2.8 – 2,9 | D~ 2.3-2.4



Filament Winding | 2D braiding | 3D braiding



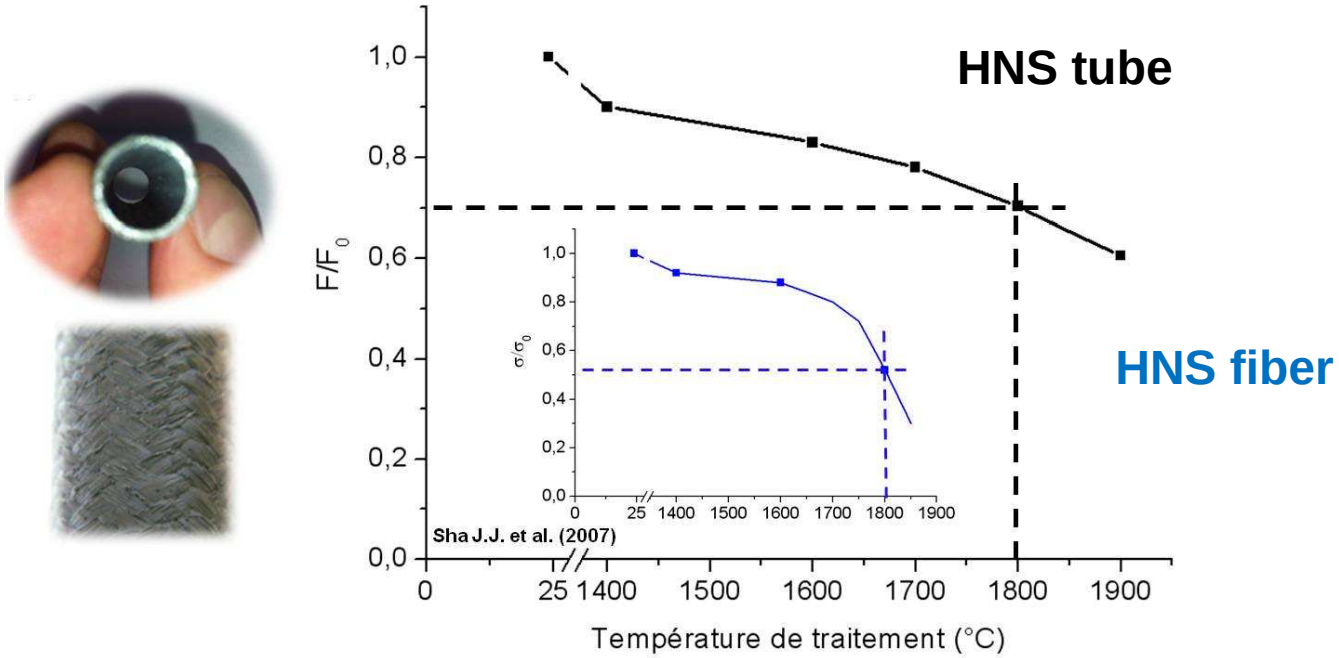




- **Properties can be tailored thanks to appropriate braiding**
- **Grinding has no significant effect on CMC**

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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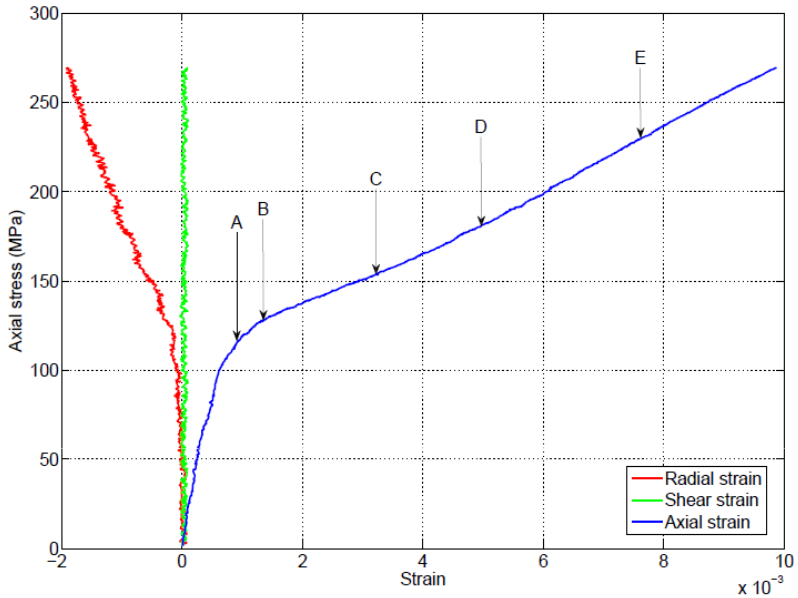
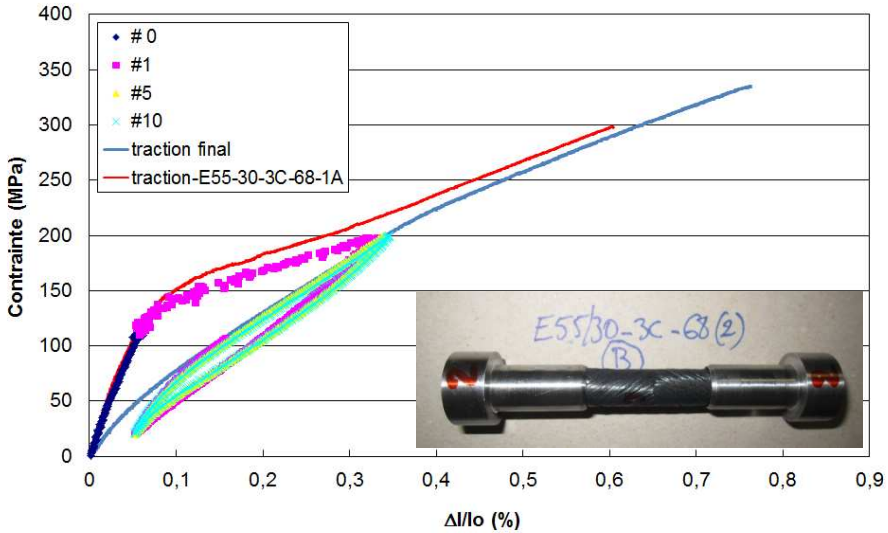
Reference SiC/SiC material for Pin cladding:

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:

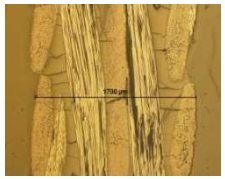
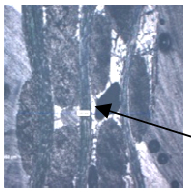
→ ***Hybrid Process_ CVI + EPI + PIP***

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

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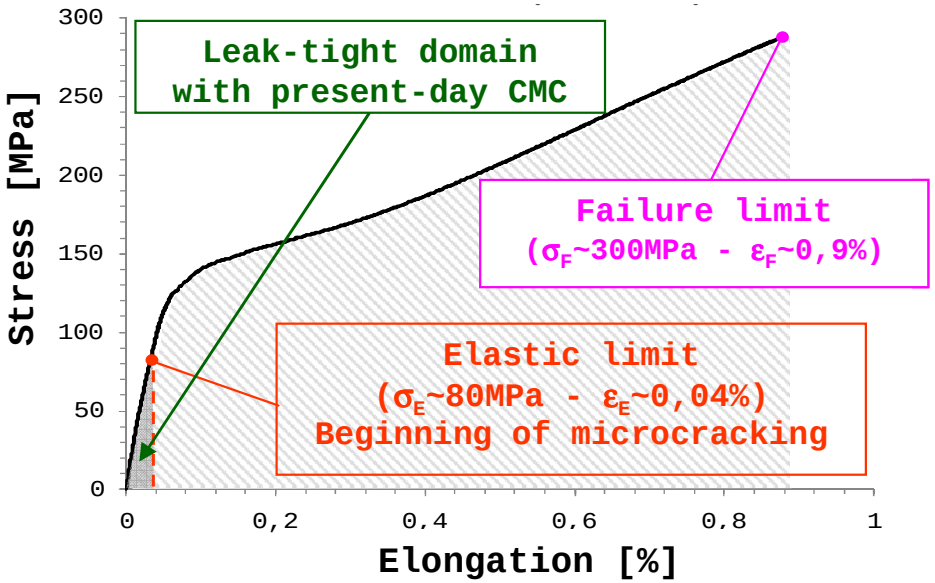
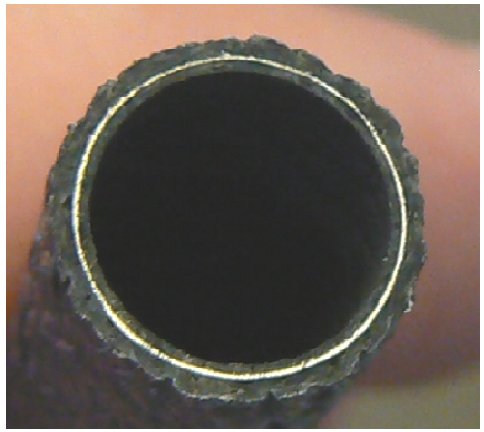
Sandwich concept (CEA Patent)



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

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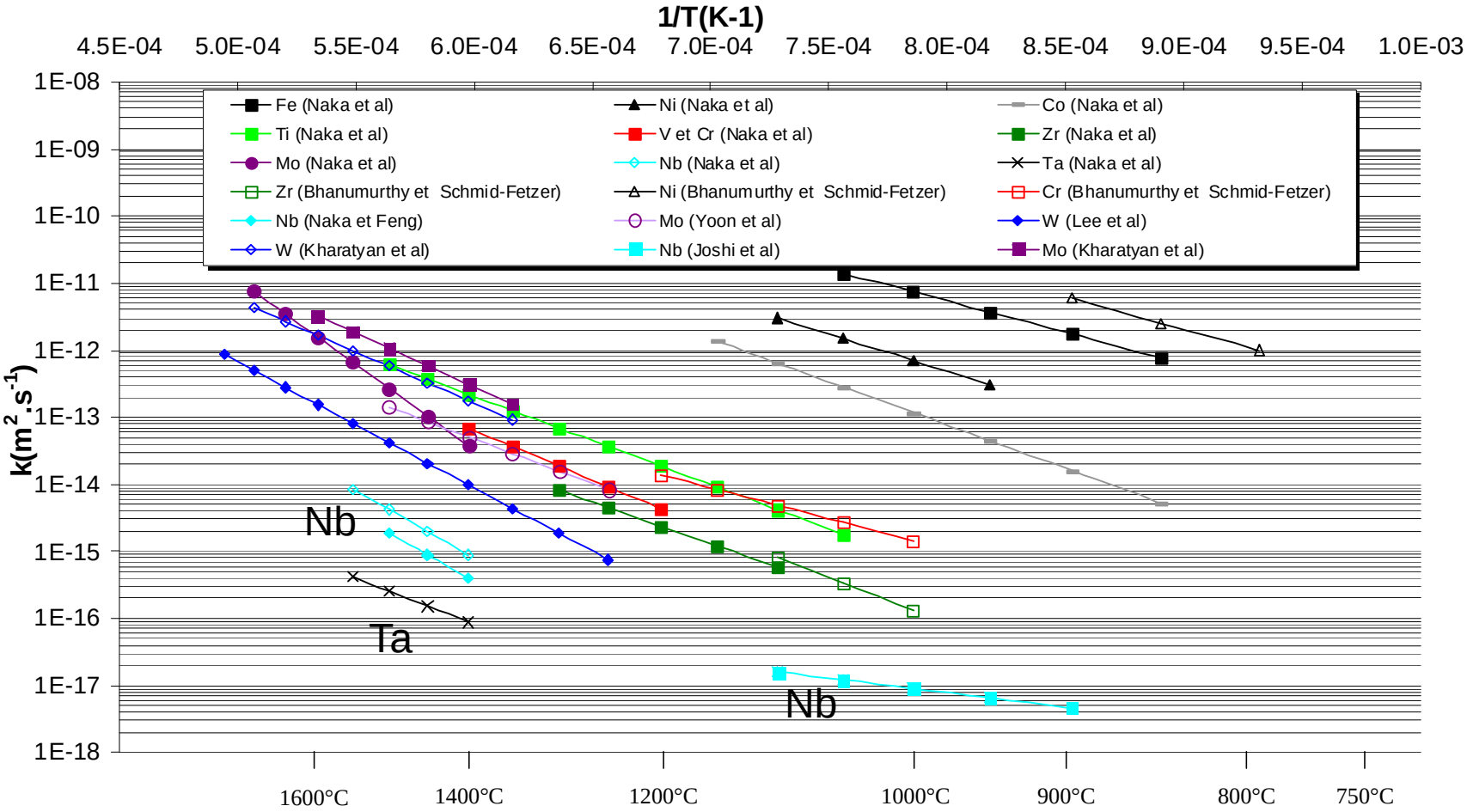
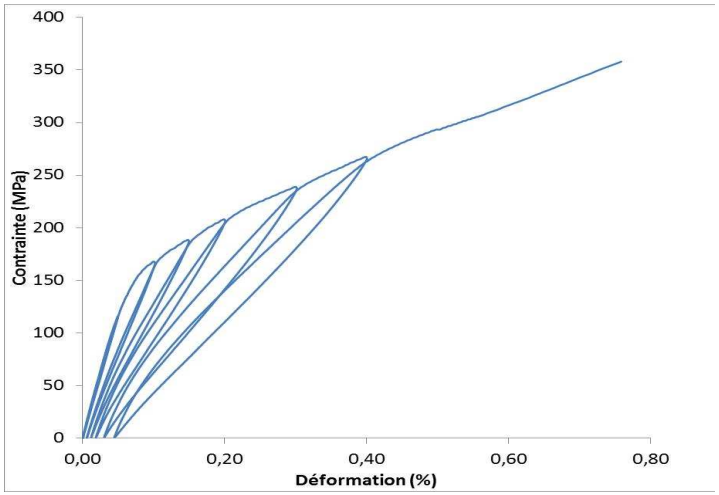
Sandwich Concept – Choice of liner

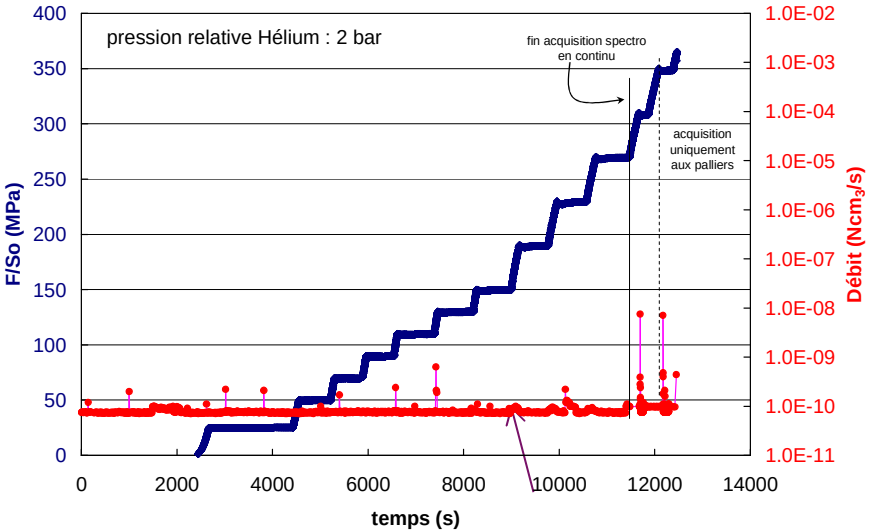


Tantalum and Niobium are the best candidates for GFR
Is it still true for PWR or BWR ?

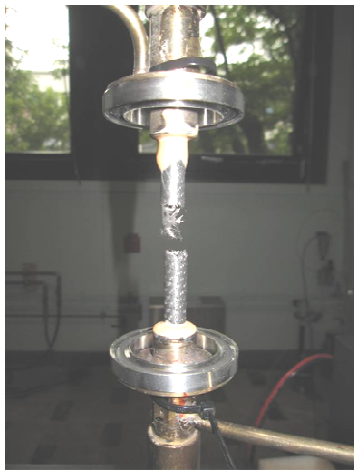
SANDWICH CHARACTERIZATION: PERMEATION

Sandwich Concept – tightness during tensile test





Detection limit



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

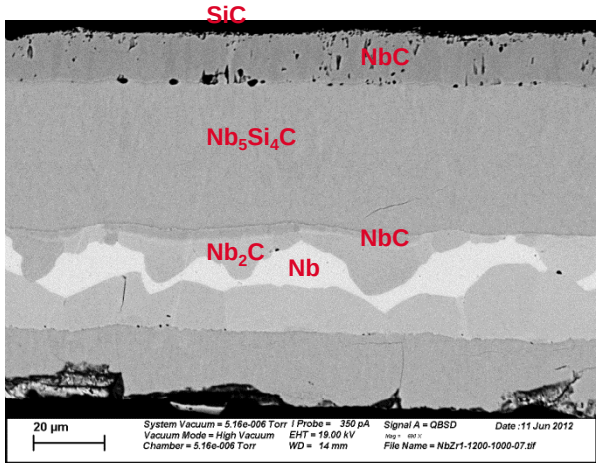
3. SANDWICH CHARACTERIZATION

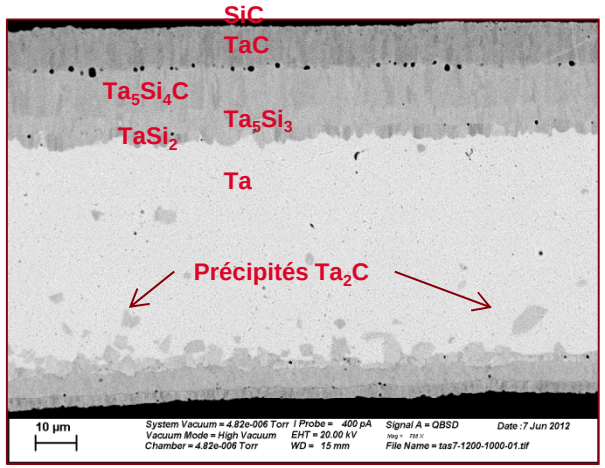
Sandwich Nb – 1000h – 1200℃ – Sandwich Ta

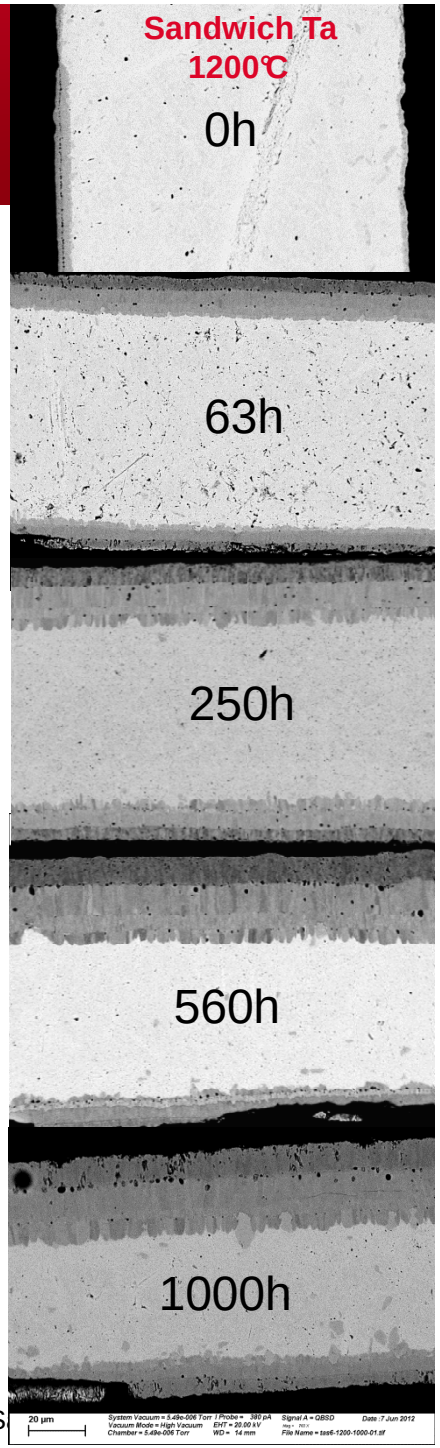
outer

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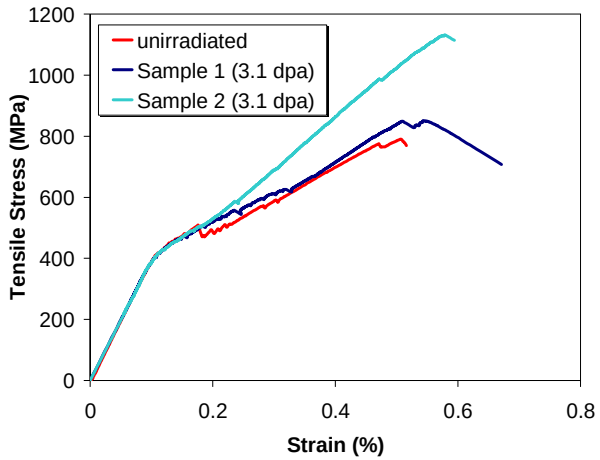
Very encourageing results have being obtained with CVI minicomposite (CROCUS irradiation performed in OSIRIS)



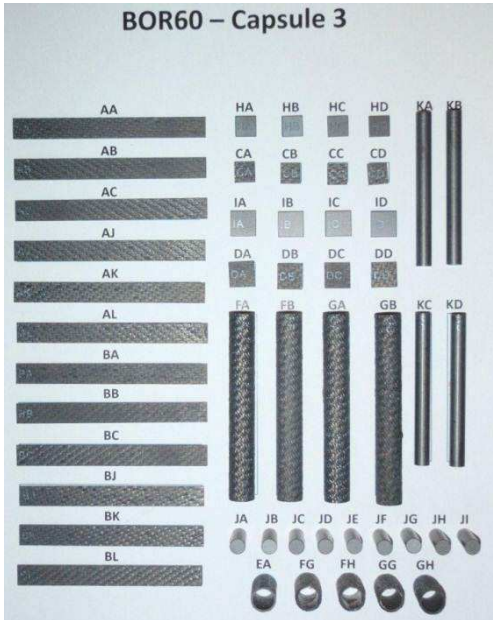
NEXT STEP:

⇒ **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*

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