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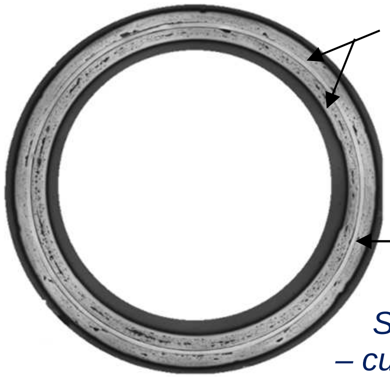
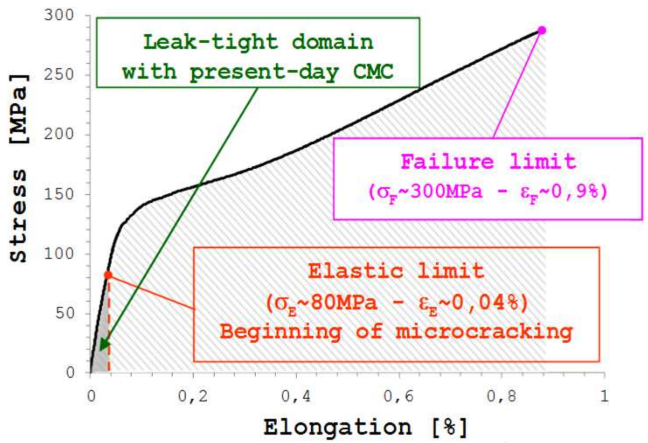
INTRODUCTION

A Decade of R&D activity at CEA has been dedicated to the development of SiC/SiC composites for GFR fuel cladding application: 2005-2015

- ***Focus on metal/ceramic hybrid cladding: a solution to leak-tighness***

CEA « Sandwich » cladding design





Patent WO 2013/017621 A1

The potential benefits in terms of application temperature and dimensional stability make this concept have a very high potential for EATF

Transposition to LWR is under investigation with the current manufacturing process

Objectives for current research (French Nuclear Institute)

- Assess the SiC resistance to corrosion/interaction with coolant in normal operating conditions
- Define the overall performance under high temperature steam

EXPERIMENTAL

- **Materials examinated**

TUBULAR SIC/SIC COMPOSITES (WITHOUT LINER)

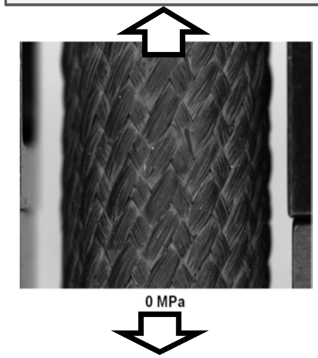
Thickness 1 mm, ∅ 10 mm, L 75 mm

Nuclear grade materials (from CEA)
- Hi-Nicalon S fibers + CVI-SiC matrix
- Multilayered 2D architectures (filament winding, braiding with 45° angle)
- Pyrocarbon interphase between fibers and matrix

HIGH PURITY CVD-SIC

∅ 10 mm, L60 mm

Monolithic rod samples
- For understanding and comparison to CVI-SiC matrix



As-received and intentionally pre-damaged SiC/SiC at different level (0.05 to 0.5 % σ_R)
- Acess to PyC interphase allowed to oxidizing species

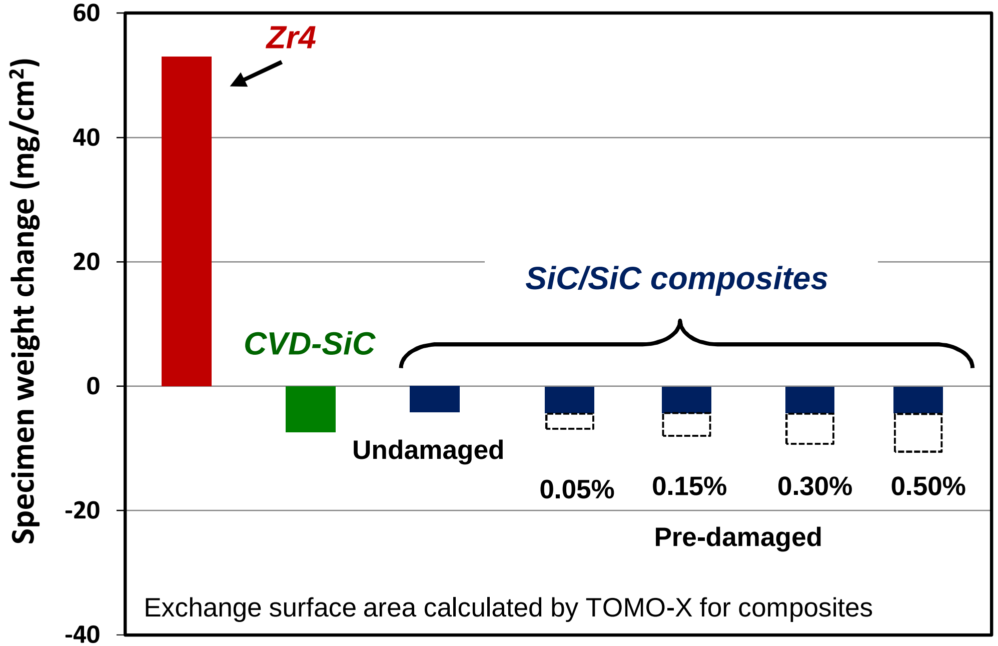
- **First oxidation tests in CEA autoclaves – Static and closed system**
  - **Representative LWR nominal conditions (360°C / 180 bar) up to 3500 h – 5 months**
  - **2 compositions of water**

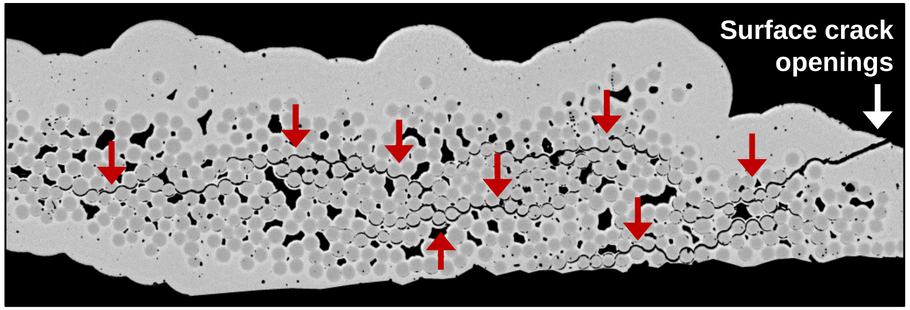
Distilled water	**vs**	**LWR water composition**
pure		**1000 ppm H_3BO_3 + 2 ppm LiOH**

OXIDATION IN NORMAL LWR CONDITIONS

WEIGHT CHANGE (LWR RESULTS PRESENTED)

- After 5 months of testing





- **No visible effect of water chemistry**
  Similar results between DW and LWR water
- **Confirmation of weight loss for SiC-based samples in comparaison to weight gain for Zr**

Zr4	SiC samples
~ 3-4 µm ZrO_2 growth	Recession Thickness < 0.5 µm

- **Greater weight loss for pre-damaged materials in comparison to undamaged**
  But not be quantifiable exactly due to uncertinity on exchange surface

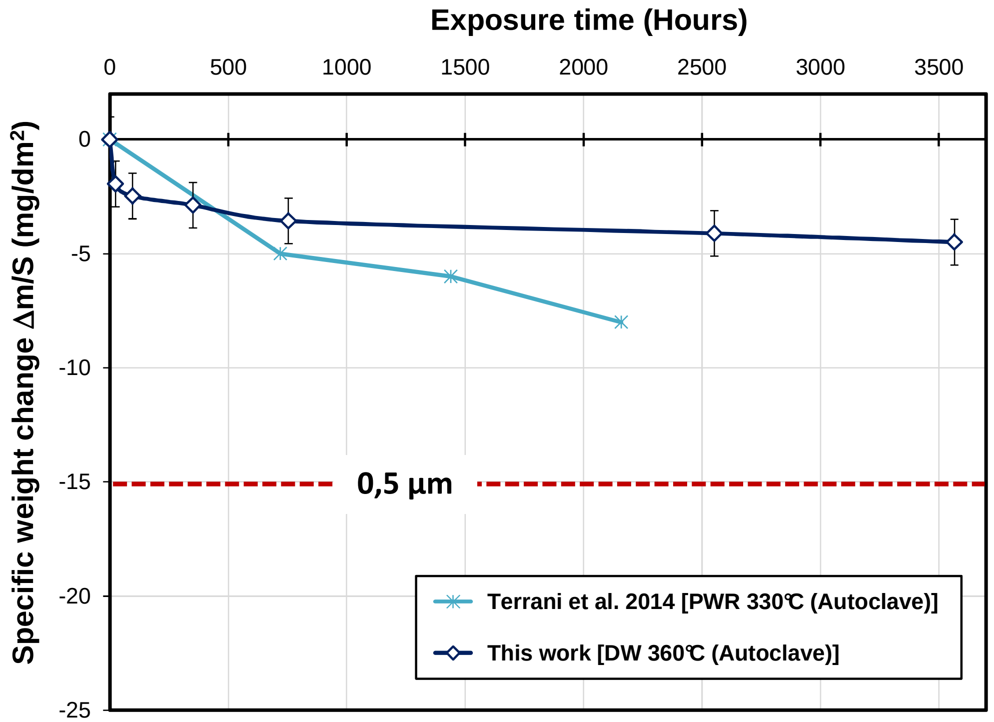
Water infiltrates through the larger crack openings and oxidizes the SiC materials from inside and not just on the surface

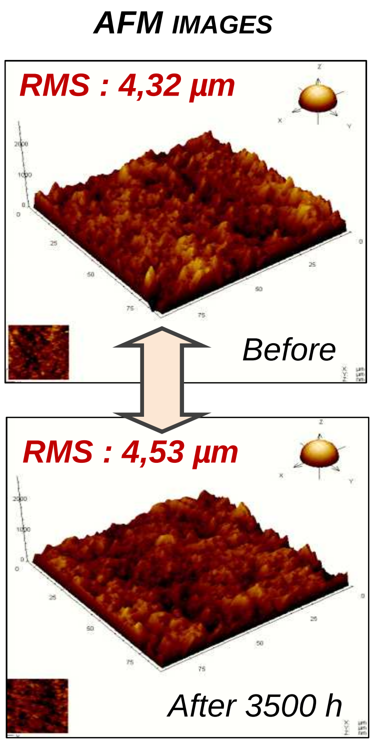
➡ ***CORROSION RATE IS INCREASING***

OXIDATION IN NORMAL LWR CONDITIONS

KINETICS AND SURFACE ROUGHNESS

- **Results on CVD-SiC samples (representative of the CVI-SiC matrix)**





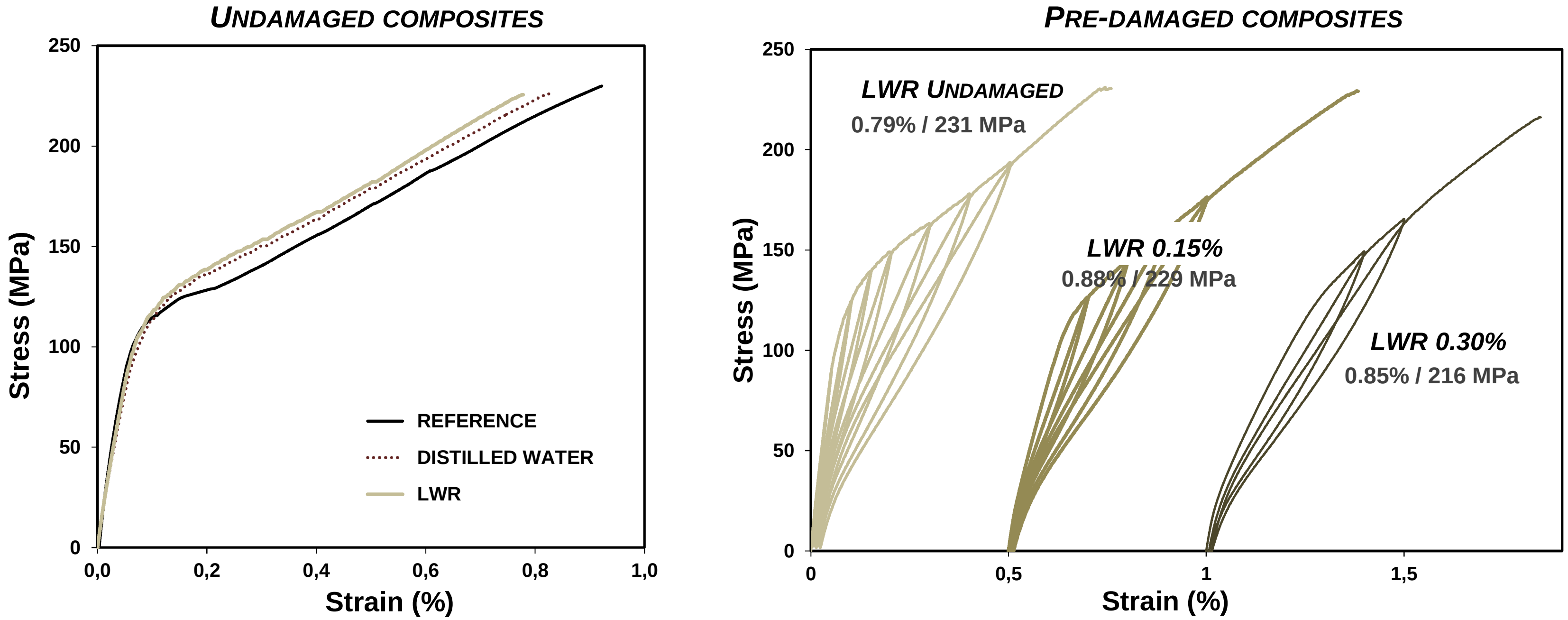
- **Slow kinetics of SiC recession which tends to stabilize at long time in static conditions (closed system)**
- **Limited effect on surface specimen (Roughness) – No passivation layer (to be confirm)**

Presence of « Si » content in water after exposure suggests a release from samples

OXIDATION IN NORMAL LWR CONDITIONS

POST-EXPOSURE MECHANICAL TENSILE BEHAVIOR

- **No significant degradation of the mechanical behavior after long-term exposure**



- **Characteristic damageable behavior with a low fiber-matrix bonding after oxidation (DW and LWR)**
- **Slight reduction of strength (5%) for pre-dammaged samples in comparaison to the reference**

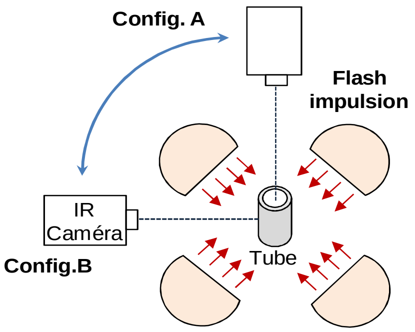
  ➡ ***Pyrocarbon interphase is not significantly degraded for these oxidation conditions***

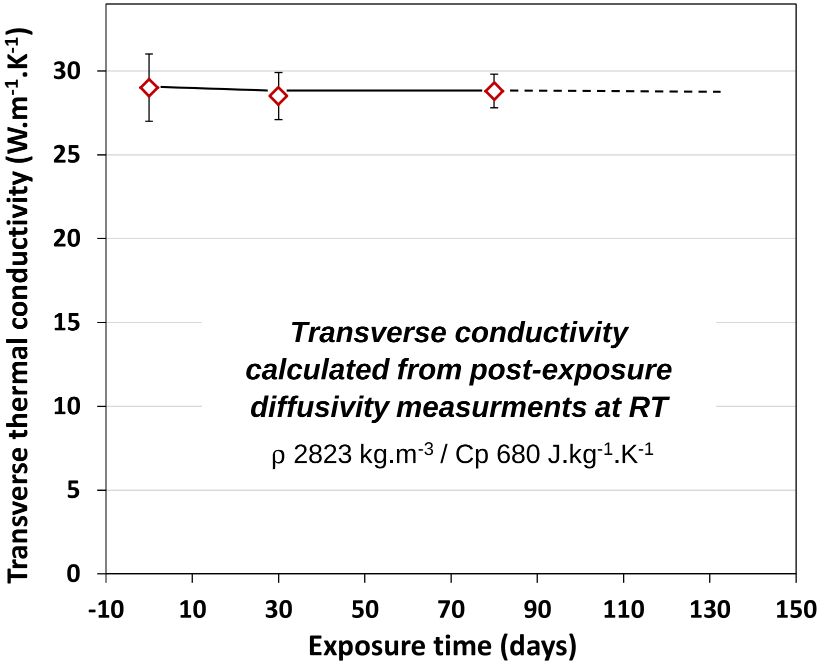
Fiber-matrix load transfer remains efficient to provide ability to deform for SiC/SiC

POST-EXPOSURE THERMAL BEHAVIOR

- **Measured on undamaged SiC/SiC exposed in dynamic conditions (Loop, AREVA Facility)**

$$\begin{cases} T(0,t)+T(e,t)=\dfrac{2Q}{\rho ce}\left[1+2\sum_{k=1}^{\infty}(1)^{k}\exp\left(-\dfrac{4k^{2}\pi^{2}}{e^{2}}at\right)\right] \\ T(0,t)-T(e,t)=\dfrac{4Q}{\rho ce}\sum_{k=0}^{\infty}\exp\left(-\dfrac{(2k+1)^{2}\pi^{2}}{e^{2}}at\right) \end{cases}$$





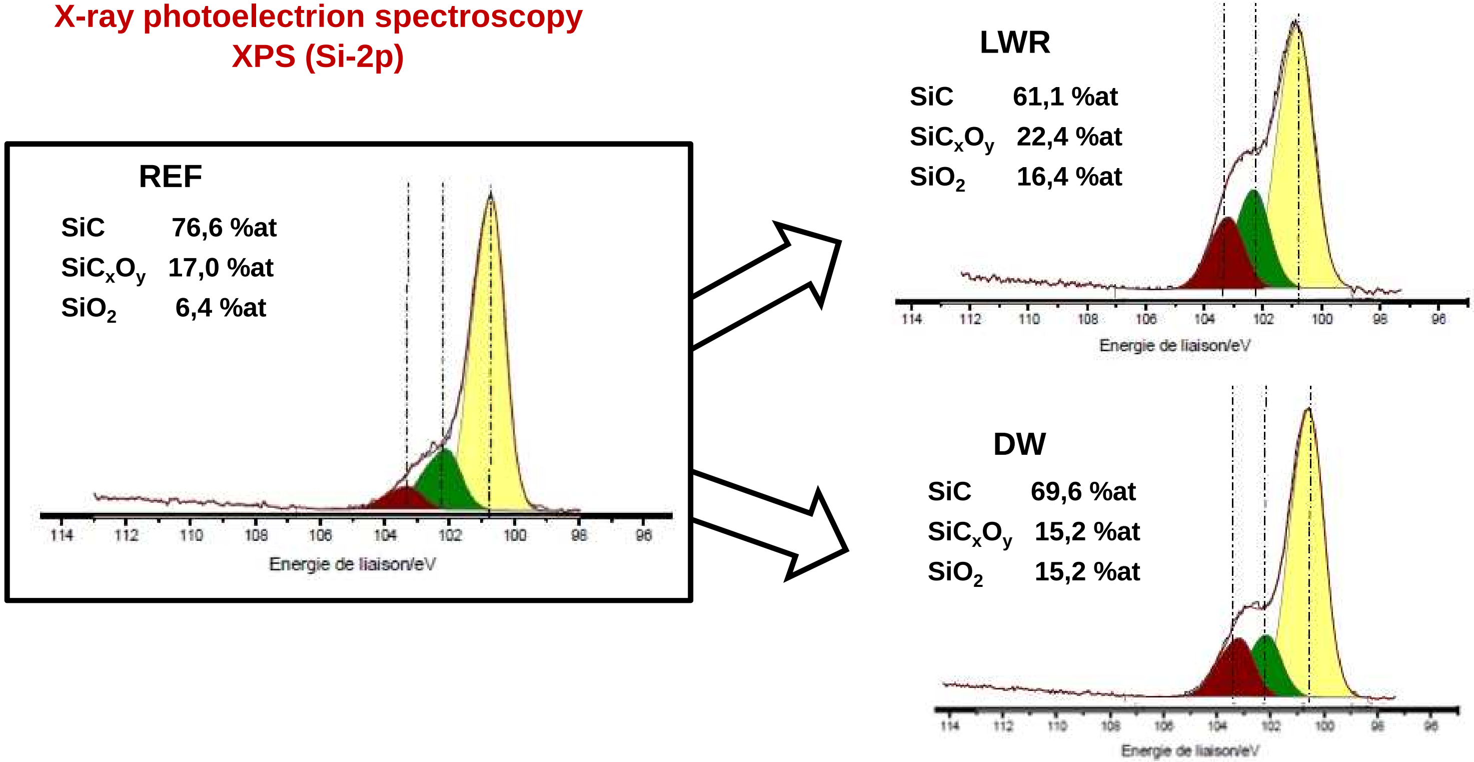
No effect of oxidation on the thermal behavior after 80 days

Consistent result with the thin sample recession and the surface analysis
Next measurements after 300 et 500 days – no expected change…

DISCUSSION AND MECHANISM

- **Evolution of surface composition on SiC/SiC tubes before and after exposure**

X-ray photoelectrion spectroscopy
XPS (Si-2p)



- **After oxidation, presence of a larger (but low) quantity of SiO_2 oxide**

Surface is mainly composed of SiC after oxidation in both DW/LWR conditions

DISCUSSION AND MECHANISM

- **Probable mechanisms**

1. Direct recession of SiC

$$SiC_{(s)} + 4H_2O_{(l)} \longrightarrow Si(OH)_{4(aq)} + CH_{4(g)}$$

2. Formation and dissolution of silica (not protective)

$$SiC_{(s)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + CH_{4(g)}$$

$$SiC_{(s)} + 3H_2O_{(l)} \longrightarrow SiO_{2(s)} + CO_{(g)} + 2H_{2(g)}$$

$$SiO_{2(s)} + 2H_2O_{(l)} \longrightarrow Si(OH)_{4(aq)}$$

In both cases, material is being consumed

Need further investigation to conclude on mechanism

(see Terrani et al., ICACC 2015 and others)

PARTIAL CONCLUSIONS:

Positive mechanical/thermal behavior of SiC/SiC in LWR conditions (Out of pile)
SiC recession needs to be mitigated by protecting surface from reaction with water

Go to the next step ➡ Assessment of performances in accidental conditions

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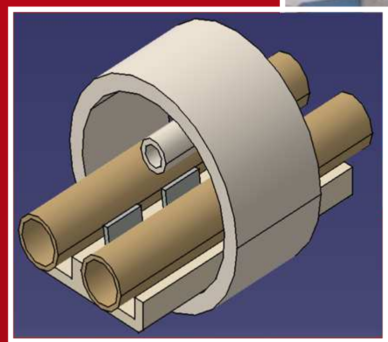
OXIDATION OF SIC/SIC UNDER HIGH TEMPERATURE STEAM CONDITIONS



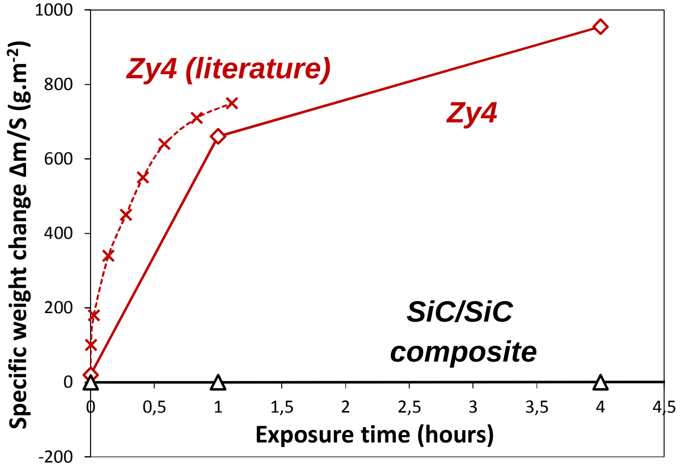
EXPERIMENTAL

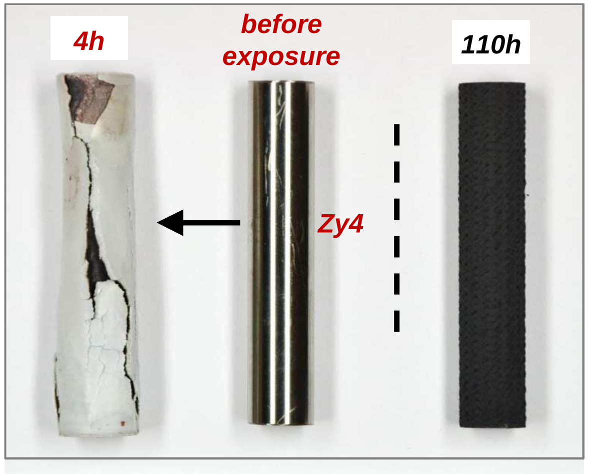
- Double sided oxidation exposure for 4 to 110h
- Steam and air/O2 flow (5cm/s) with various oxygen content – Total pressure between 1 to 10 bar

Conditions		Temperature (°C)	Pressure (bar) Total	Water	Gas in addition		Pressure ratio (%) P_{H2O}/P_T	P_{O2}/P_T	P_{O2}/P_{H2O}
HP	A	1200	10	0.5	Air	9.5	0,05 (5)	0,19 (19)	3,8
P_{atm}	B	1200	1	0.5	O_2	0.5	0,5 (50)	0,5 (50)	1
	C	1200	1	0.5	Air	0.5	0,5 (50)	0,1 (10)	0,2
	D	1400	1	0.5	Air	0.5	0,5 (50)	0,1 (10)	0,2

Experiments on SiC/SiC tubes and Zircaloy-4 clad segments as baseline material

COND C
1bar, 1200°C
Air/H2O (50/50)





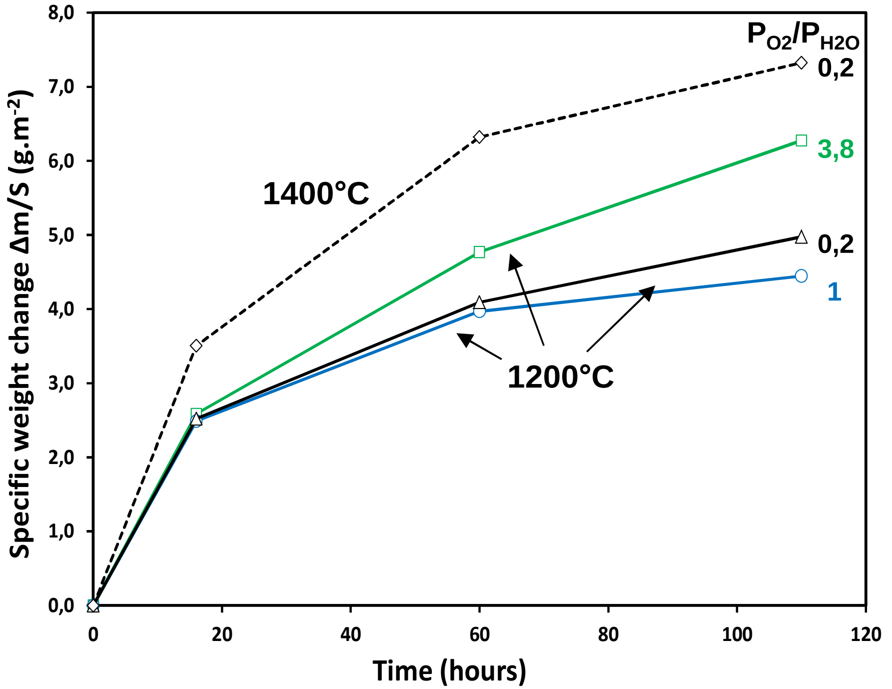
SiC/SiC composite

Extremely slower oxidation kinetics of SiC/SiC than for Zr alloys !

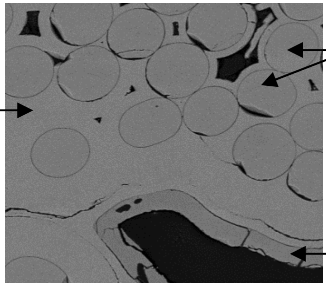
Confirmation of high potential of SiC/SiC for ATF

OXIDATION UNDER HIGH TEMPERATURE STEAM

FOCUS ON SIC/SIC



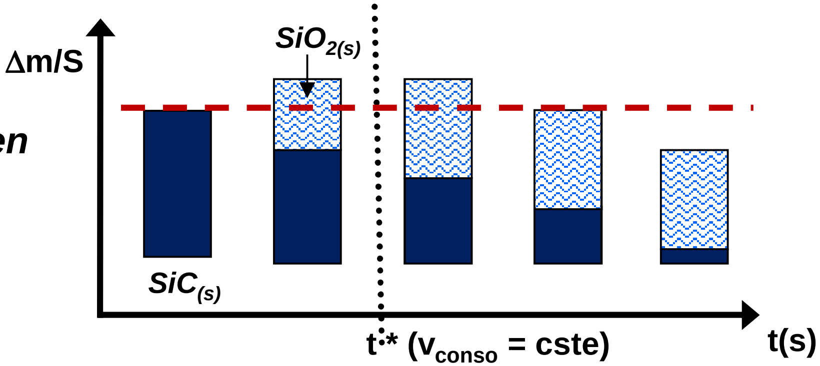
- Oxidation kinetics are strongly dependent on the bondary conditions
  Acceleration effect with temperature
  (1200 vs 1400°c)
- Formation of protective oxide scale (silica)



- But volatilization of oxide is occuring from its formation (Opila et al. 97)

Global behavior resulting from the competition between simultaneous growth and volatilization of a silica oxide

$$\Delta m/S = \Delta m_{SiO2(s)}/S + \Delta m_{SiO2(vol)}/S$$

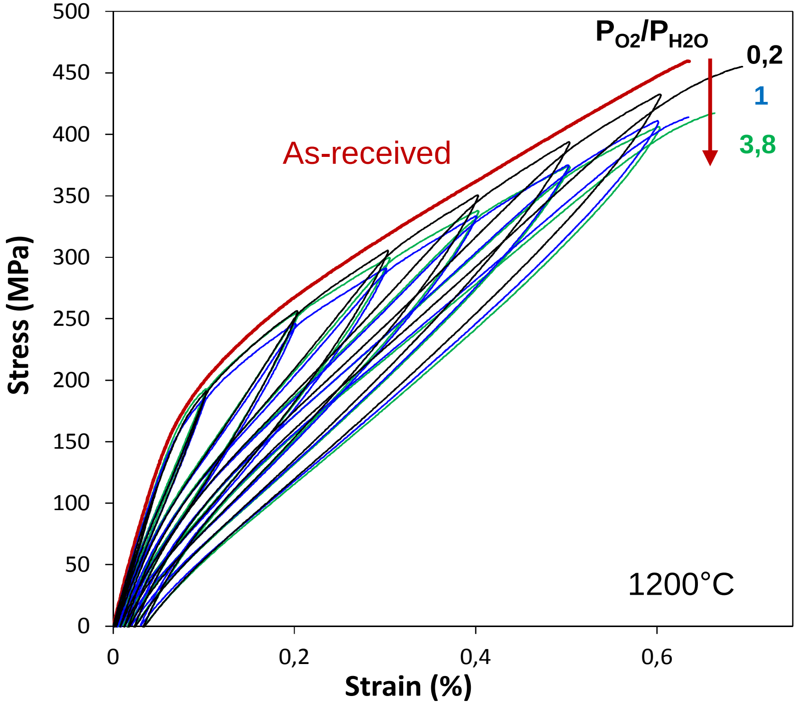


OXIDATION UNDER HIGH TEMPERATURE STEAM

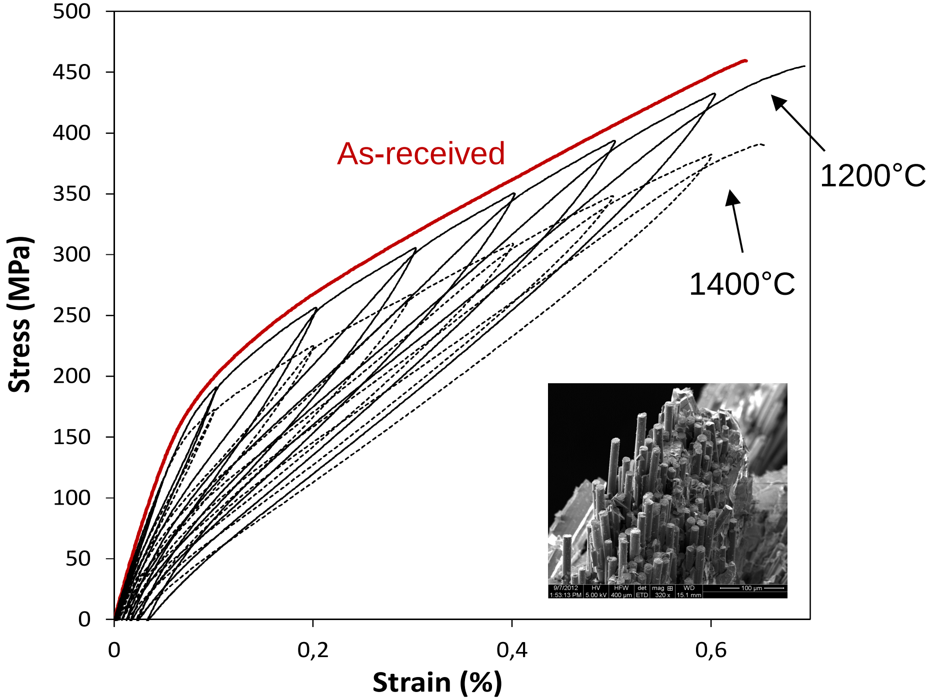
RESIDUAL MECHANICAL TENSILE BEHAVIOR (RT)

Integrity and geometry of specimens fully preserved after 110h exposure

- **Influence of atmosphere**



- **Influence of temperature**



Retention of the characteristic « non-linear elastic damageable » behavior of CMCs

(No reduction of strain to failure / Slight decrease of tensile strength and Young modulus)

Confirmation of the protective function of silica in these conditions

Pyrocarbon interphase stays efficient to deviate cracks

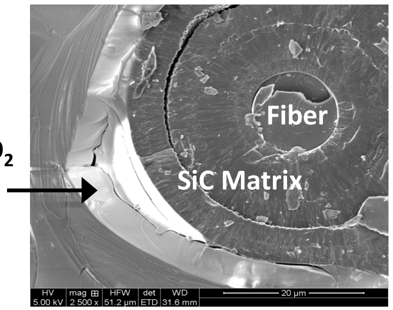
Discussion and mechanism

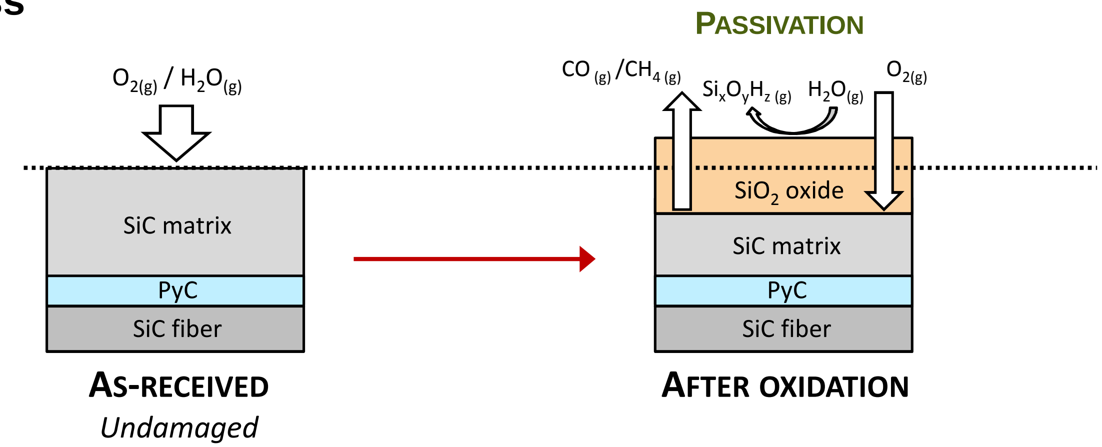
- **Suggested oxidation process**

1200°C – 110h

"Moderate" oxidation kinetics

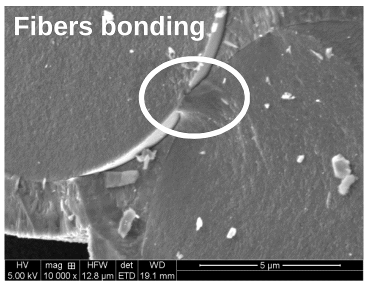
Protective SiO_2 oxide layer

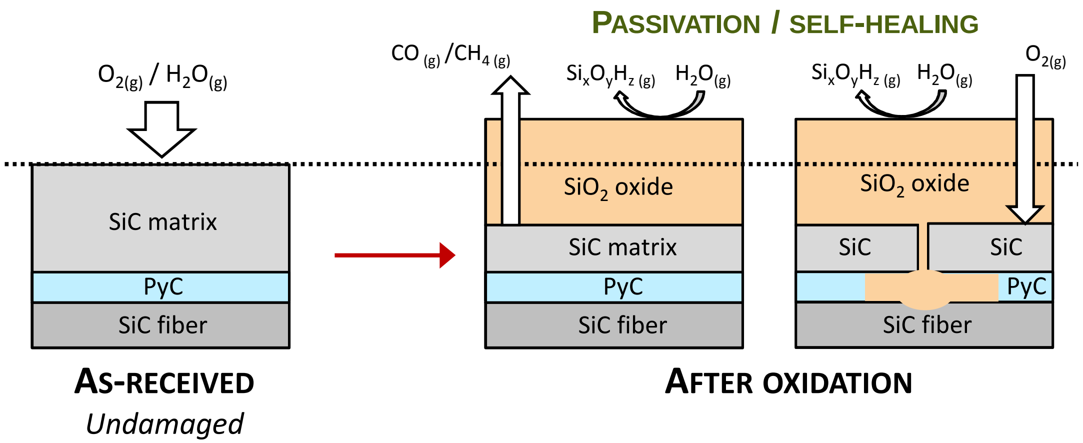




1400°C – 110h

"Accelerated" oxidation kinetics able to locally cause fibers bonding at pre-existing surface cracks





CONCLUSION AND PERSPECTIVES

- **Using SiC_f/SiC composites as fuel cladding element for LWRs represents a considerable challenge related to ambitious objectives (ATF)**

> ***SiC/SiC composites is a break-through solution which requires a long term R&D***

- **Technical update (present work)**
  - **Autoclave tests results in LWR nominal operating conditions are positive in term of mechanical and thermal behavior**

    … but highlight a different behaviour for SiC (recession) than conventional Zr
  - **High temperature strength in steam was demonstrated (up to 1400°C, > 100h)**

Although many progresses have been made, many prospects have been raised to confirm the feasibility of using SiC/SiC for LWR

- **On going work and some pending issues**
  - **Transposition of sandwich clad to LWR requirements (design, most suitable liner)**
  - **Manufacturing of elongated and closed clad – by welding for the « sandwich » design**
  - **Evaluation of neutron irradiation**
  - **Many others…**

THANK YOU FOR YOUR ATTENTION

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