

DE LA RECHERCHE À L'INDUSTRIE



EVALUATION OF POTENTIAL ALTERNATIVE NUCLEAR FUEL CLADDING MATERIALS FOR LWRS – CEA STUDIES –

M. LE FLEM, A. MICHAUX, C. SAUDER
and J.C. BRACHET

CEA SACLAY, NUCLEAR MATERIAL DEPARTMENT

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www.cea.fr

INTRODUCTION – STUDIES ON LOCA AT CEA (1/2)

Extensive LOCA tests on Zr base cladding these last 15 years

→ more than 1000 thermal-mechanical tests (including irradiated materials)
+ deep metallurgical analysis



(b) High temperature steam oxidation

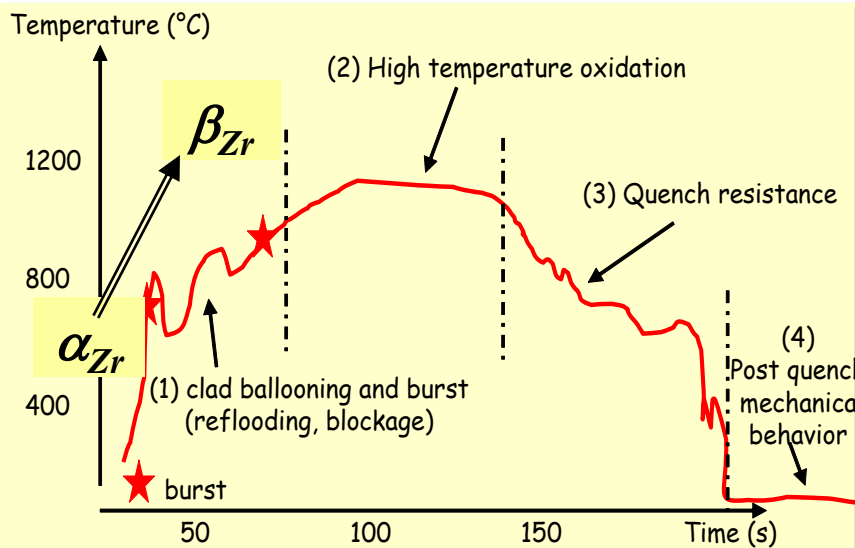
- underlying metallurgical analysis
- oxygen diffusion modeling



(a) Internal pressure creep-burst tests

Link with

- $\alpha \rightarrow \beta$
- Irradiation
- hydrogen effects



(c) Quenching resistance

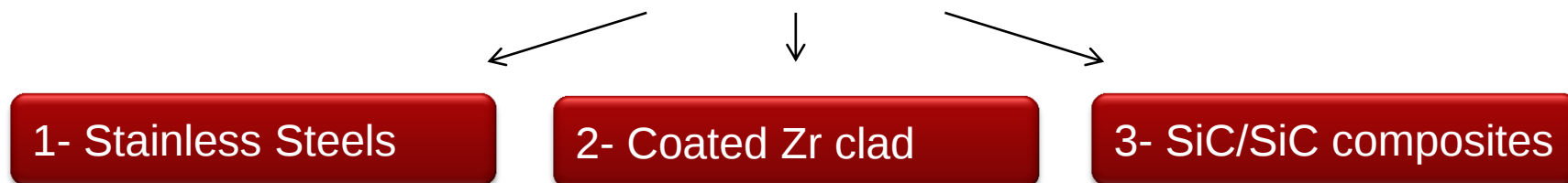
- Post-Quenching mechanical tests (RCT, 3-PBT, Impact)
- extensive metallurgical analysis

- Relationship between
- phases thicknesses
 - oxygen/hydrogen profiles
 - and PQ properties
- Effects of cooling scenario, of pre-hydriding, of pre-transient oxides...

Motivation for a new cladding to sustain LOCA transient

- Decrease the reaction with steam water to reduce hydrogen risk
 - Lowering oxidation rate
 - Creating more stable oxides
- Improve the mechanical properties
 - Lowering deformation level to keep coolability of the core
 - Maintain ductility to avoid fracture/fragmentation
- Increase the margin to melting

Accident tolerant fuel/cladding at CEA



Assess the advantages in terms of performance towards LOCA and check the good in-service behaviour

1. 304 STAINLESS STEELS FUEL CLADDING

L. Portier, et al. (CEA Saclay),

Creep-rupture, steam oxidation and recovery behaviors upon dynamic transients up to 1300°C of cold-worked 304 stainless steel tubes dedicated to nuclear core fuel cladding

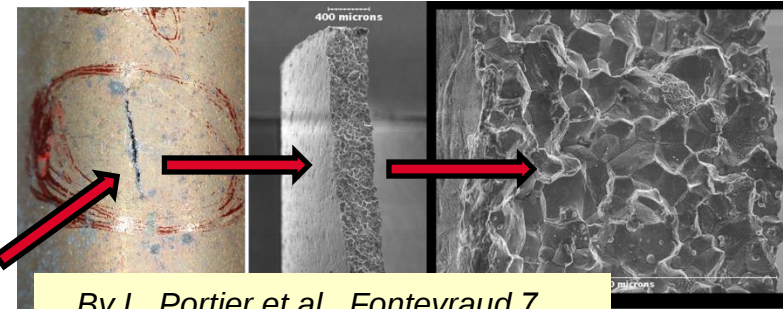
Proceeding of Fontevraud 7 - "Contribution of Materials Investigations to Improve the Safety and Performance of LWRs", 26-30 September, 2010, Avignon, FRANCE

Potential margins of stainless steel clad behavior upon LOCA conditions (vs. Zr claddings)

- Higher creep resistance at high temperature
- Lower oxidation kinetics up to 1300°C at least
- Better Post-Quenching ductility (and likely during the water quench itself) as far a significant internal metallic layer remains (no oxygen, nor hydrogen embrittlement of the remaining metallic layer)

BUT

- Important neutron penalty
- **Lower melting temperature**
- Potential intergranular brittle failure mode in LOCA
- Potential in-service PCI/IASCC cracking;
- In-service activation and post-service remaining radioactivity, etc...



By L. Portier et al., Fontevraud 7...

→ **CEA prospective studies on innovative nuclear fuel cladding materials/designs**

2. COATED ZR BASE CLADDING (1/5)

Purpose

- Delay or avoid oxidation of the Zr alloy in nominal conditions (higher burn-up)
- **Delay or avoid oxidation of the Zr alloy in accidental conditions**
 - In order to keep post-quenched ductility
 - and to decrease hydrogen release
- Having an iterative solution involving thin coatings on well-known Zr cladding
 - No significant change in geometry
 - No significant change in mechanical / thermal properties
 - Potential use of penalizing elements (in terms of neutron compatibility)

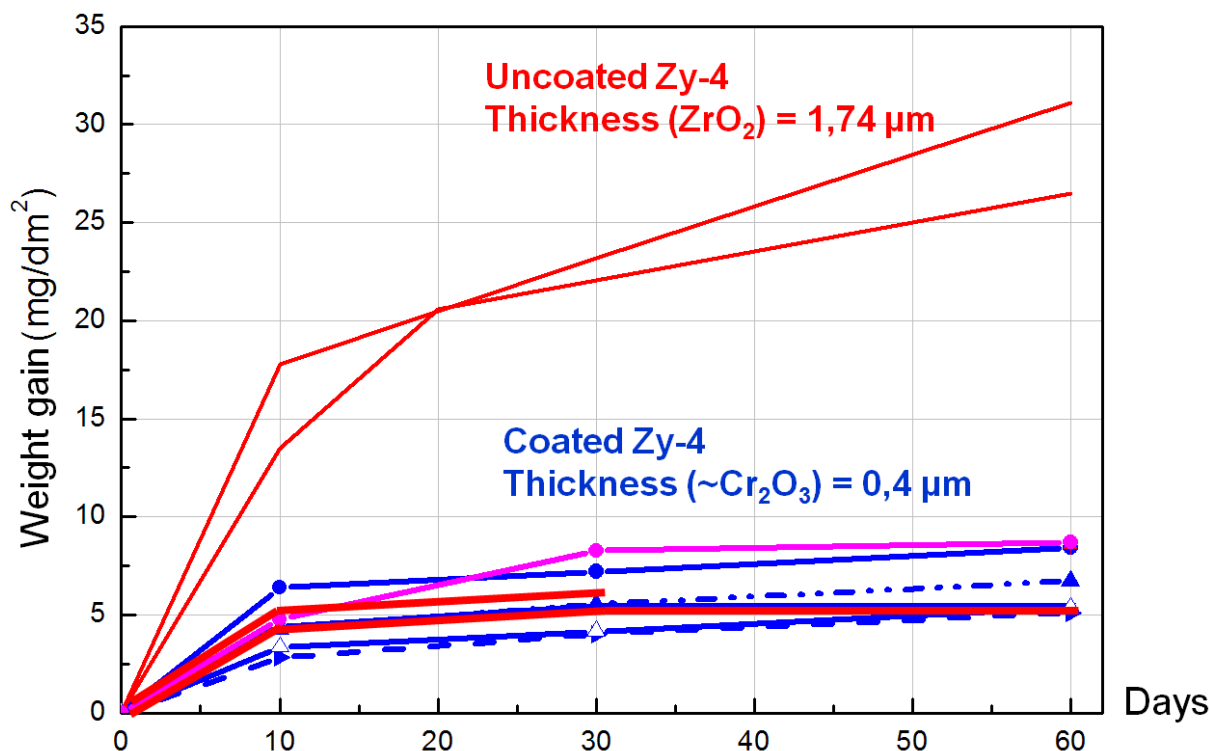
Main challenges

- Find the appropriate composition of the coating
- Fabricate an homogeneous coating with suitable process
- Keep the coating adherent in nominal conditions
- Avoid spalling of the (oxidized) coating at high temperature

2. COATED ZR BASE CLADDING (2/5)

Behavior in nominal conditions

- More than 20 coatings investigated these last 7 years
- Ceramics (carbides/nitrides), metals, optimised microstructure
- With Cr base-coatings → **Significant decrease in the oxidation kinetics**



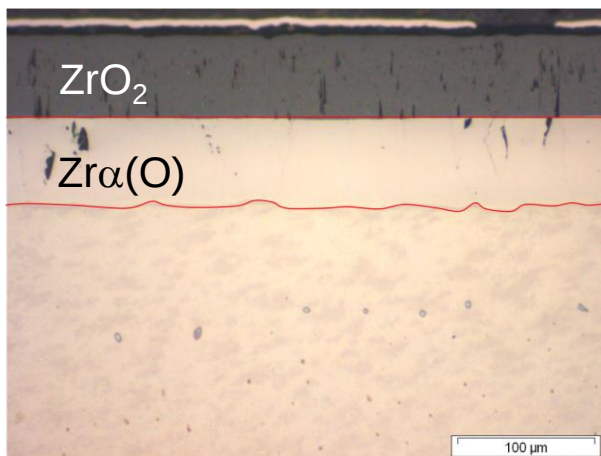
Oxidation at 360°C, 60 days, liquid water at 190 bar, relevant chemistry

2. COATED ZR BASE CLADDING (3/5)

Behavior in LOCA conditions

- Made on the most promising coatings (flat specimens)
- 1100°C 850 seconds, **1200°C 300 seconds** in steam water + quench
- Weight gain, microstructure observations, Post-quench flexural/tensile tests

Zy-4

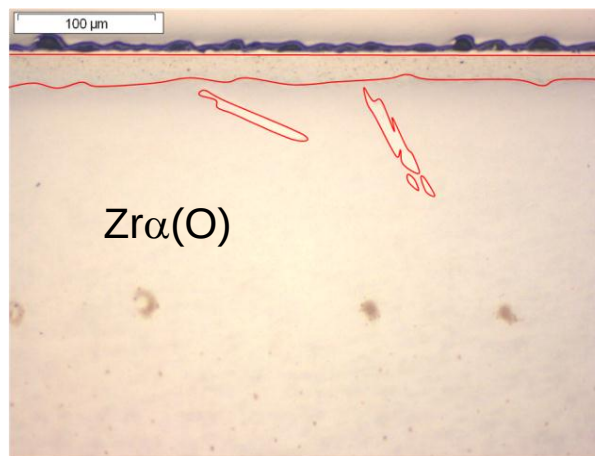


ZrO₂ 60 μm

Zrα(O) 60 μm

Equivalent Zr = 100 μm

Zy-4 + Cr-base coating

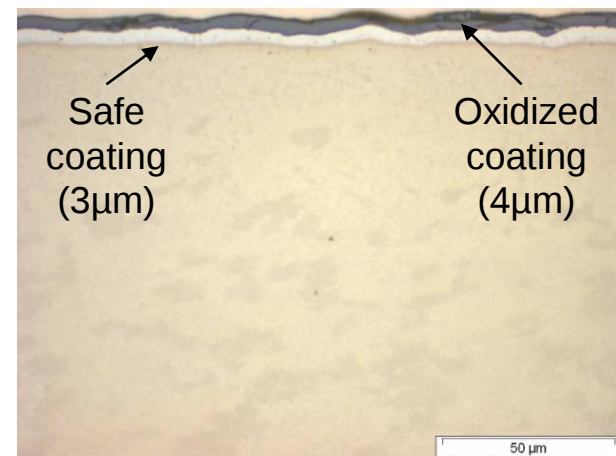


no ZrO₂

Zrα(O) 14 μm

Equivalent Zr = 14 μm

Zy4 + optimized Cr-base coating



no ZrO₂

no Zrα(O)

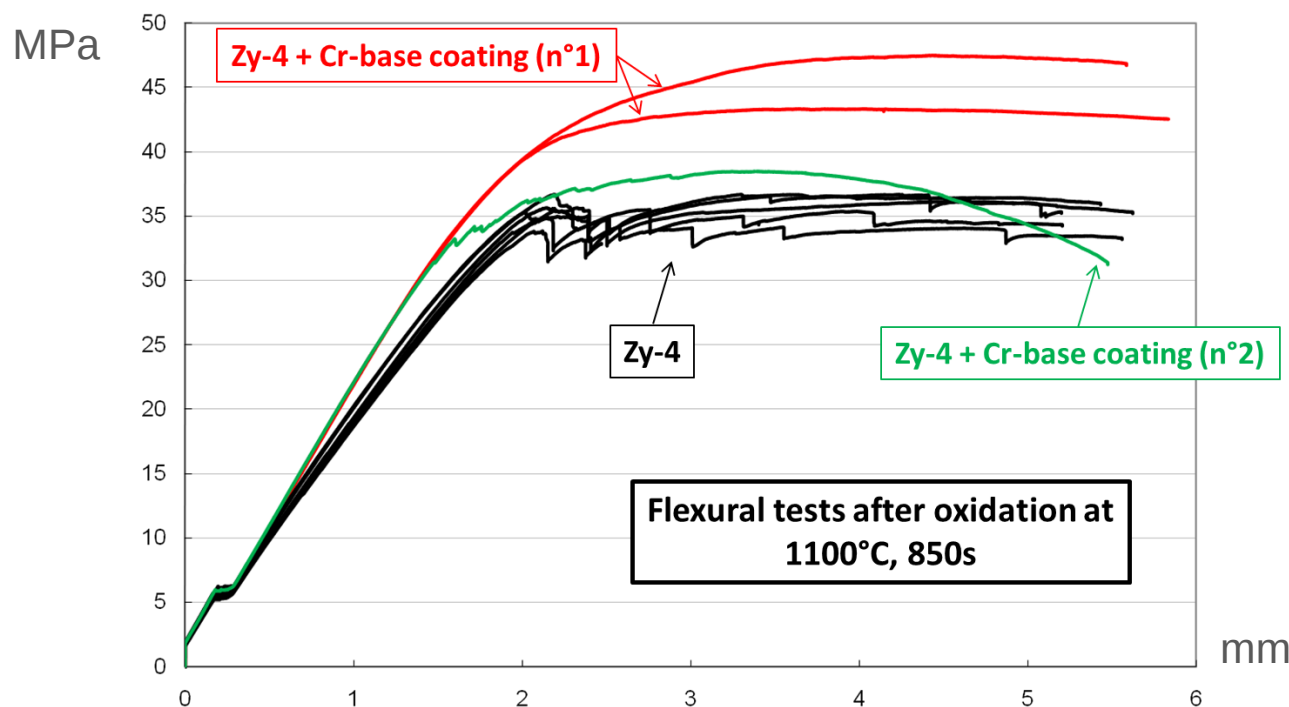
Equivalent Zr = 0 μm

- Significant decrease in the amount of oxidized Zr
- Mitigation of hydrogen risk
- Decrease in the fraction of brittle layers formed upon HT oxidation

2. COATED ZR BASE CLADDING (4/5)

Behavior in LOCA conditions

- Made on the most promising coatings (flat specimens)
- 1100°C 850 seconds, **1200°C 300 seconds** in steam water + quench
- Weight gain, microstructure observations, Post-quench flexural/tensile tests



- Significant increase in remaining ductility
- Margins on the PQ ductility vs. ECR

2. COATED ZR BASE CLADDING (5/5)

Behavior in LOCA conditions

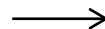
- Experiments performed on made on the most promising coatings (flat specimens)
- 1100°C 850 seconds, **1200°C 300 seconds** in steam water + quench
- Weight gain, microstructure observations, Post-quench flexural/tensile tests



First coatings



Improved coatings



Optimized coatings



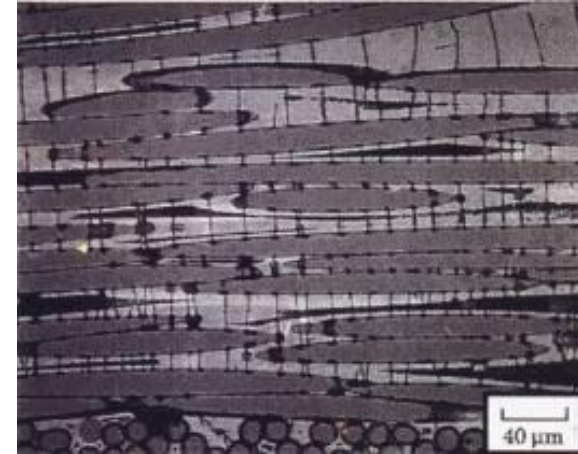
→ Transposition to tubes has been achieved
Weight gain has been decreased
from 10 mg/cm² to 0,4 mg/cm²

[Idarraga, Lomello, Billard et al. 2012, unpublished results]

3. SiC/SiC COMPOSITE CLADDING (1/5)

Purpose

- Enhance oxidation resistance (thermodynamics, kinetics)
- Increase margin to fusion (decomposition temperature of 2700°C)
- Providing a stiff and resistant cladding
 - in order to keep a « coolable » core
 - to avoid fuel relocation
 - and to keep the fuel confinement



Guillaumat, LCTS 1994

Main challenges of SiC/SiC for PWR cladding

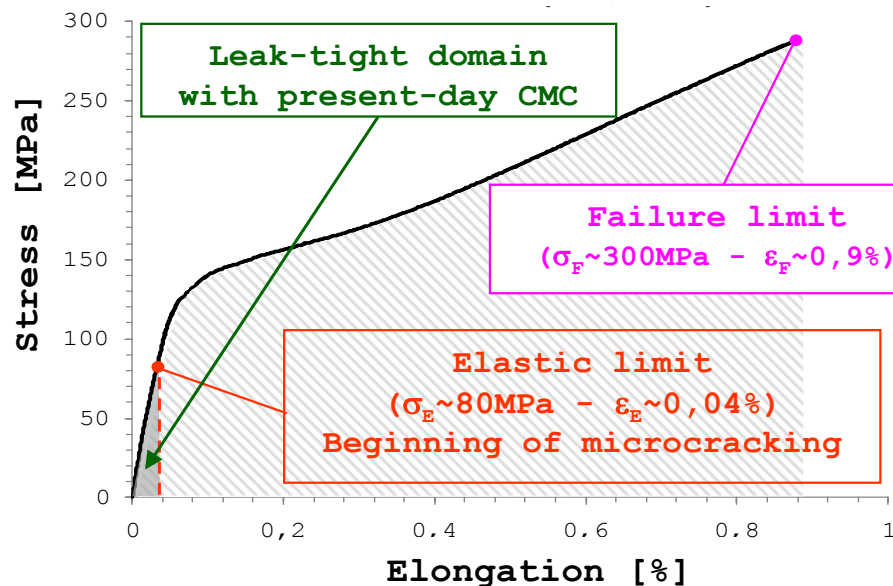
- Consider an elastic/damageable material for the design (with low thermal conductivity)
- Providing gas-tightness (at the level of the cladding, or of the fuel)
- Fabrication of elongated clads
- Describe the oxidation phenomena (passive/active) and consider erosion mechanism
 - Avoid surface spoiling in nominal condition
 - Determine the gaseous species induced by LOCA

3. SiC/SiC COMPOSITE CLADDING (2/5)

SiC/SiC cladding mainly driven by GFRs applications

- Significant R&D at CEA in terms of fabrication of suitable cladding
- “Sandwich” concept with a metallic liner providing gas-tightness (demonstrated)
- Tailorable mechanical properties thanks to optimisations of interphase and braiding
- Very good dimension control and fabrication reproducibility
- End-plugging solutions

winded 2D braid 3D braid



**Transposition
to LWR is
achievable**

CEA sandwich cladding

3. SiC/SiC COMPOSITE CLADDING (3/5)



Preliminar corrosion testing of SiC/SiC for PWR



Corrosion tests on SiC/SiC

Mechanical tests
(*tensile test at RT*)

Characterizations
(*optical / SEM / XRD*)

SiC/SiC tubes

and

SiC wafers (A to C)

Zircaloy clad

{
 Condition A
 Condition B
 Condition C
 Condition D
 → Condition C

1 MPa – 1200°C – Air/H₂O (95/5)

0,1 MPa – 1200°C – O₂/H₂O (50/50)

0,1 MPa – 1200°C – Air/H₂O (50/50)

0,1 MPa – 1400°C – Air/H₂O (50/50)

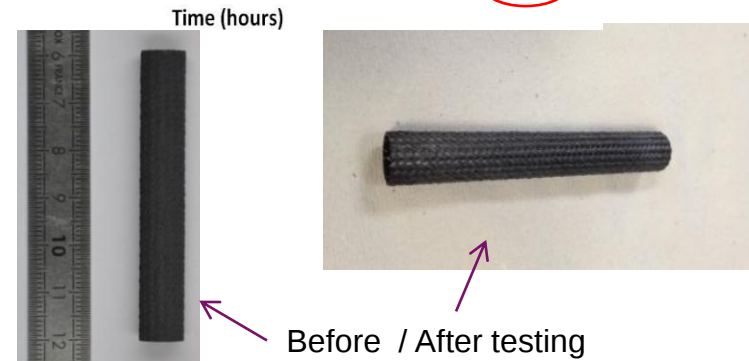
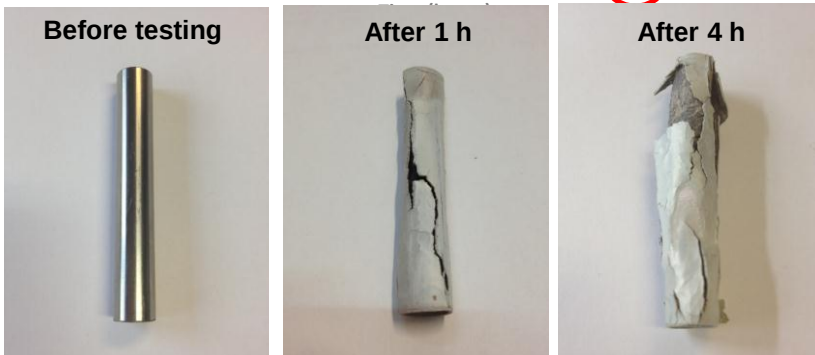
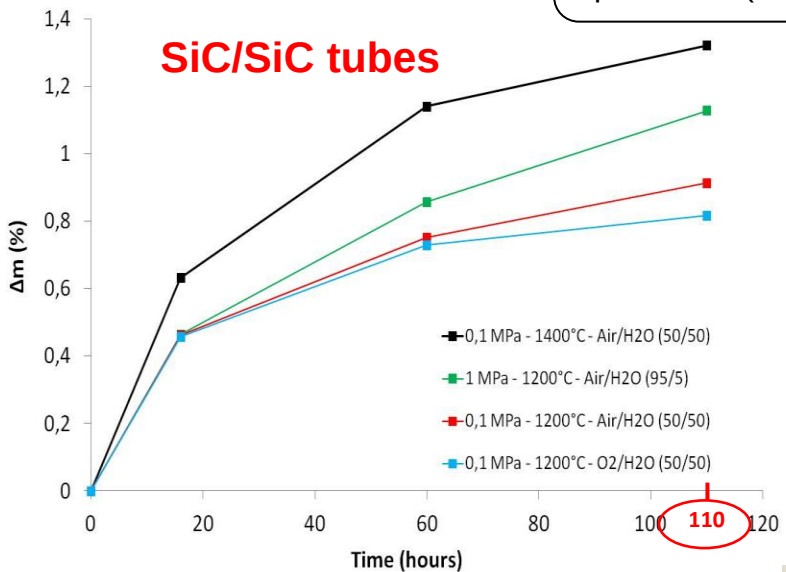
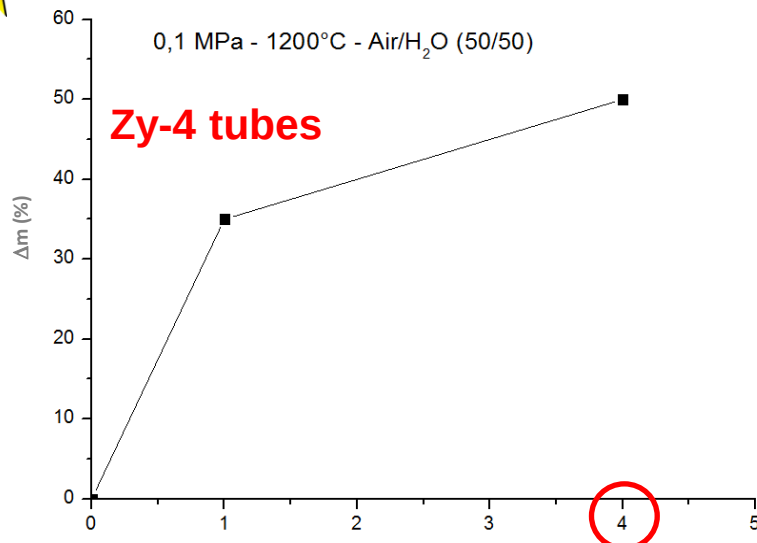
0,1 MPa – 1200°C – Air/H₂O (50/50)

↓ % O₂ ↑



Preliminar corrosion testing of SiC/SiC for PWR

$\Delta m = \text{SiO}_2$
 $T \nearrow \Delta m \nearrow$
 $p \nearrow \Delta m \nearrow (1200^\circ\text{C})$

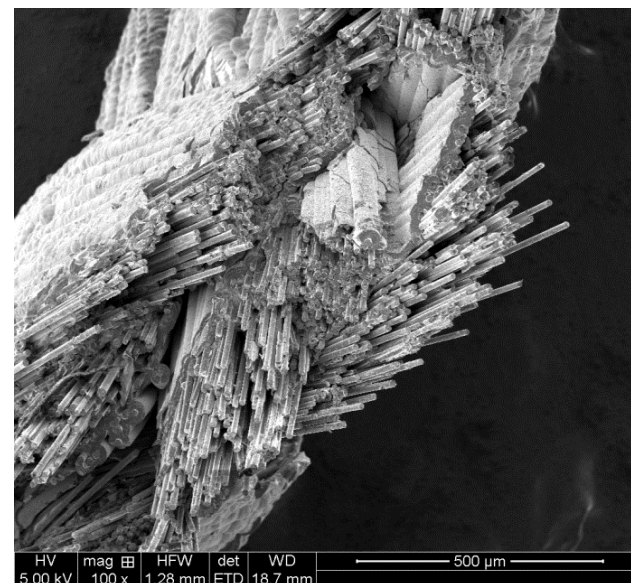
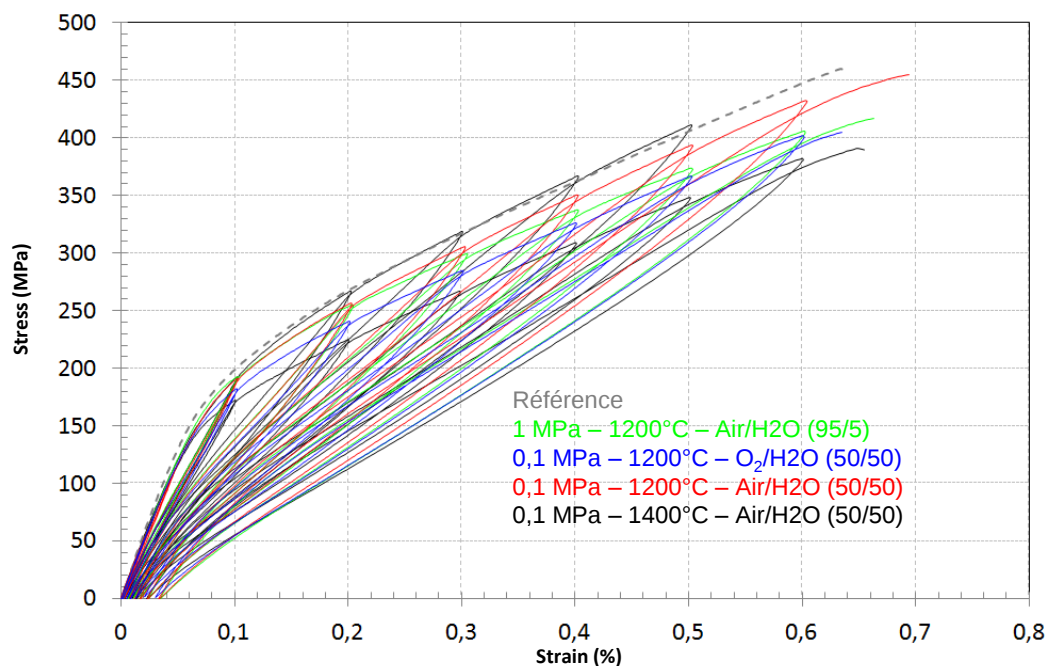


- Loss of geometry
 - Cracking in the zirconia layer
- = well-known result (Steinbruck, 2011)

→ Geometry preservation



Tensile tests after corrosion at high temperature



SEM observation of the fracture surface

- **No change in mechanical behavior**
- **No diminution of stress to rupture**
- Slight decrease in strain to rupture with :
 - total pressure increase
 - temperature increase
 - O₂ increase

CONCLUSIONS AND PROSPECTS (1/2)

Status of the R&D on innovative cladding for PWR at CEA

- Cr base coatings on Zy-4 gave very good results
 - Decrease in weight gain in nominal and LOCA conditions
 - Post-quench ductility is enhanced by avoiding ZrO_2 and $\text{Zr}\alpha(\text{O})$
 - Promising results on hydrogen pick up (no Breakaway phenomena)
- Homogeneous coating of Zy-4 tube is achievable
- Sandwich SiC/SiC cladding must be suitable for PWR
- SiC/SiC resistance to high temperature corrosion (air/ O_2) is demonstrated

Patents

[Le Flem et al.]
 [M. Zabiégo et al.]
 [C. Sauder et al.]
 [Buet et al.]
 etc.

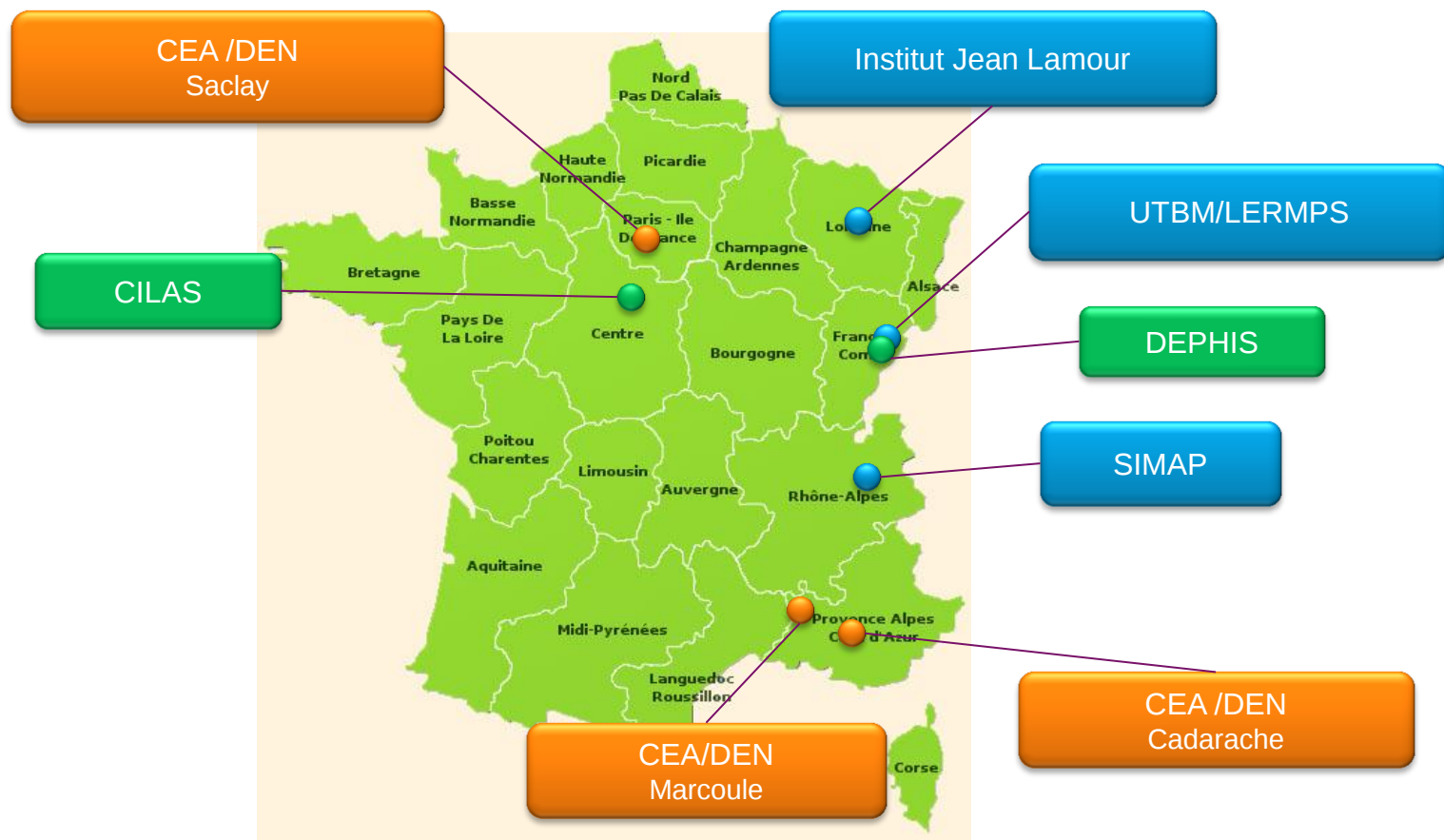
Coming next

- Optimisation of Cr-base coatings (composition, microstructure...)
- Optimisation of the sandwich tube to PWR requirements
- Assessment of corrosion resistance and **description**
 - Thermodynamics, kinetics
 - Gaseous species detection (H_2 risk)
 - Integral tests with fuel up to melting
- Determination/optimisation of the mechanical properties
- Fabrication of **~1m cladding** (coatings, SiC/SiC)
- **Estimation of the costs...**

CONCLUSIONS AND PROSPECTS (2/2)

MHYRACLE Melting and Hydrogen Risk reduction by Advanced Cladding Effect

- 2013 → 2017
- lead by CEA : main investigator: A. Michaux, substitute: M. Le Flem



Special thanks to my colleagues



etc...

Marion LE FLEM
CEA Saclay
Nuclear Energy Division
Nuclear Energy Department
91191 Gif sur Yvette
marion.leflem@cea.fr

And thank you for your attention