

Structural evolutions and internal stresses in Zr alloys during oxidation at high temperature and subsequent cooling

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STRUCTURAL EVOLUTIONS AND INTERNAL STRESSES IN ZR ALLOYS DURING OXIDATION AT HIGH TEMPERATURE AND SUBSEQUENT COOLING

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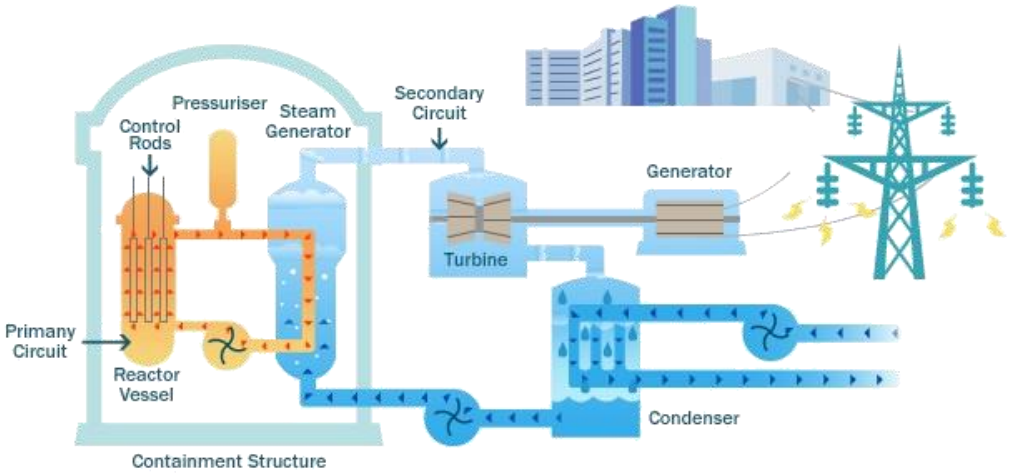
[3] *Synchrotron SOLEIL, Gif-sur-Yvette, France*

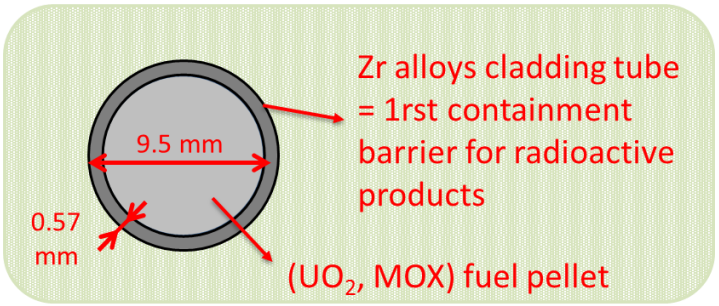
OUTLINE

- ✓ Background and objectives of the study
- ✓ Experimental method
- ✓ Results obtained
  - ✓ Structural evolution
  - ✓ Residual stress evolution
- ✓ Conclusions

BACKGROUND OF THE STUDY: FUEL CLADDING TUBE

Pressurized Water Reactor



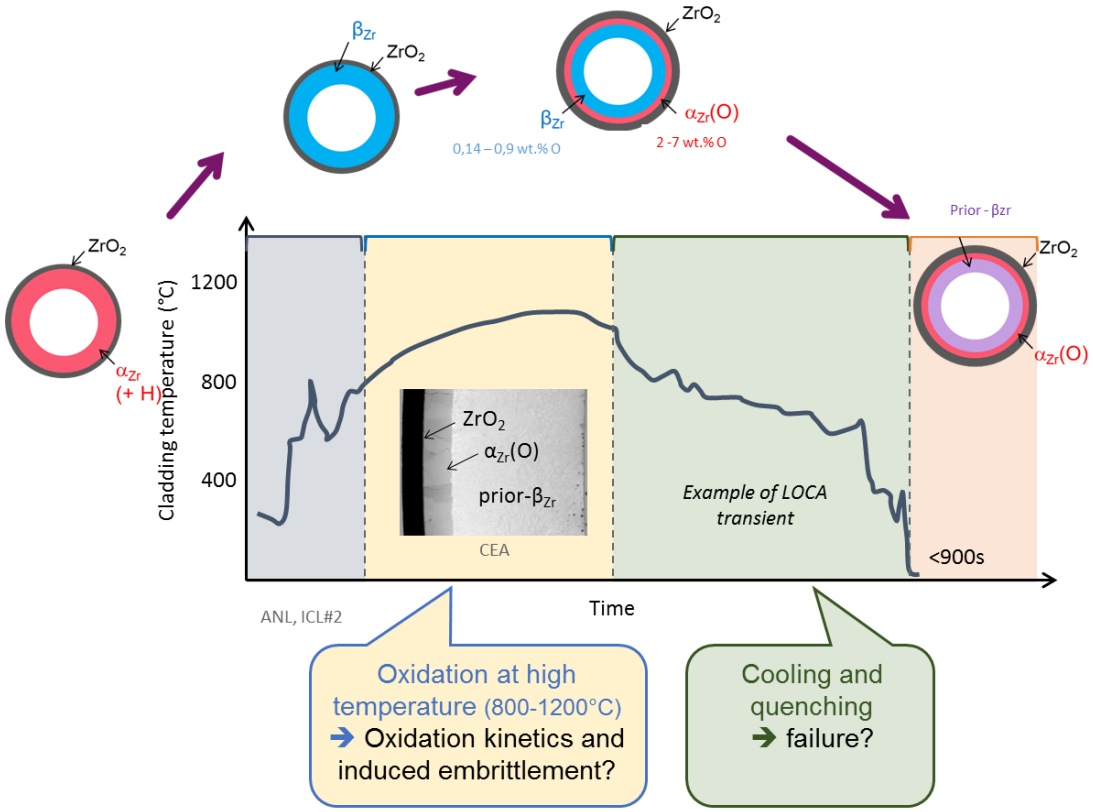


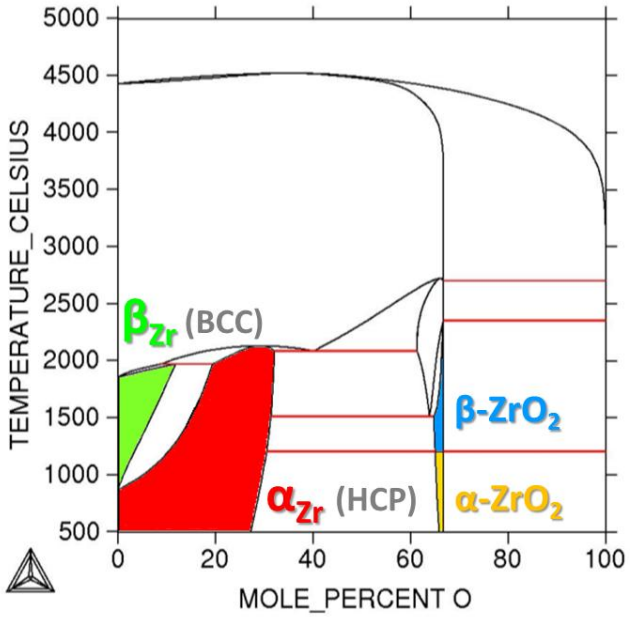
	Zr	Sn	Fe	Cr	O
Zircaloy-4 (Zy-4) (wt.%)	Base	1.30	0.21	0.1	0.12

BACKGROUND OF THE STUDY: LOSS OF COOLANT ACCIDENT (LOCA)

→ Formation of a breach in the primary circuit, pressure drop

→ Loss of water in the primary circuit, vaporization of water…





OBJECTIVES OF THE STUDY

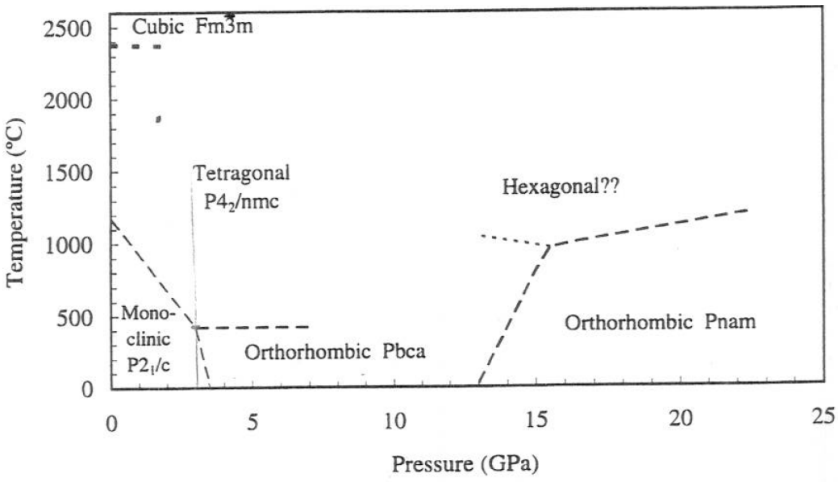
Why?

During oxidation: internal stresses may result from the formation of the oxide layer, the diffusion of oxygen into the underlying metal, the β_{Zr} to $\alpha_{Zr}(O)$ phase transformation → potential effect on the oxide structure and the oxidation kinetics of the material

During cooling: internal stresses are due to differences between the thermal expansion coefficients of the various phases / layers, phase transformations of the metal and the oxide... These stresses may result in the failure of the oxidized cladding during quenching.

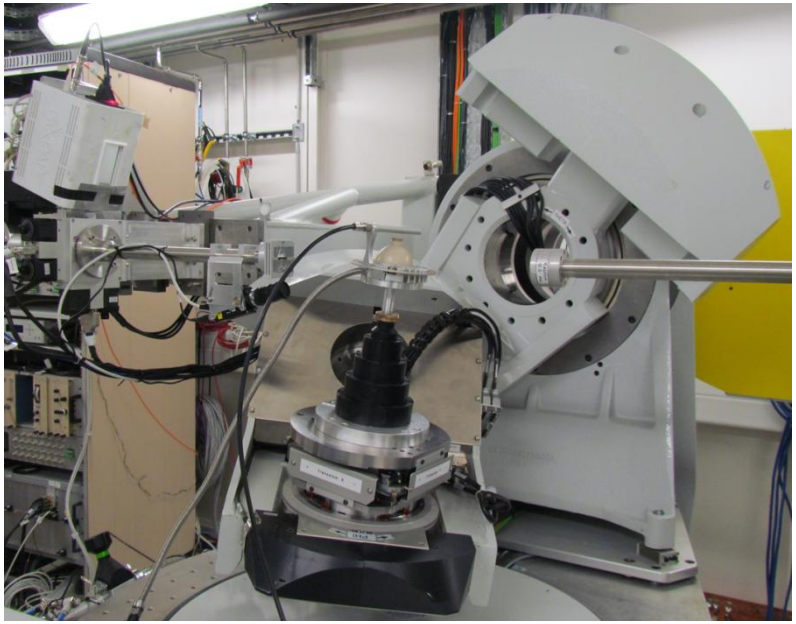
The objective of this study is to improve our knowledge on internal stresses measurements, generated for:

- The oxidation at high temperature and the subsequent cooling;
- In the oxide and the underlying metallic layers of zirconium alloys ;



EXPERIMENTAL METHOD

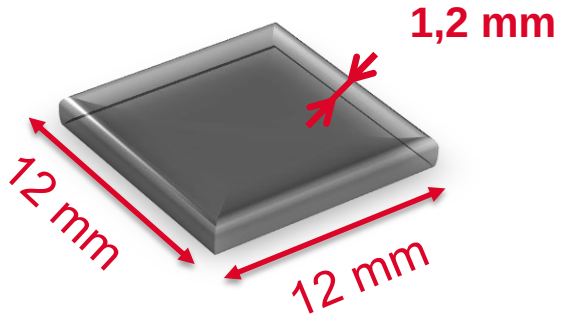
Experiments performed on the DiffAbs beamline (SOLEIL synchrotron) → 6-circles kappa diffractometer



Oxidation (700 / 800 / 900°C)
→ Anton Paar DHS 900 domed hot stage
Oxidant mixture : He 90% / O_2 10%



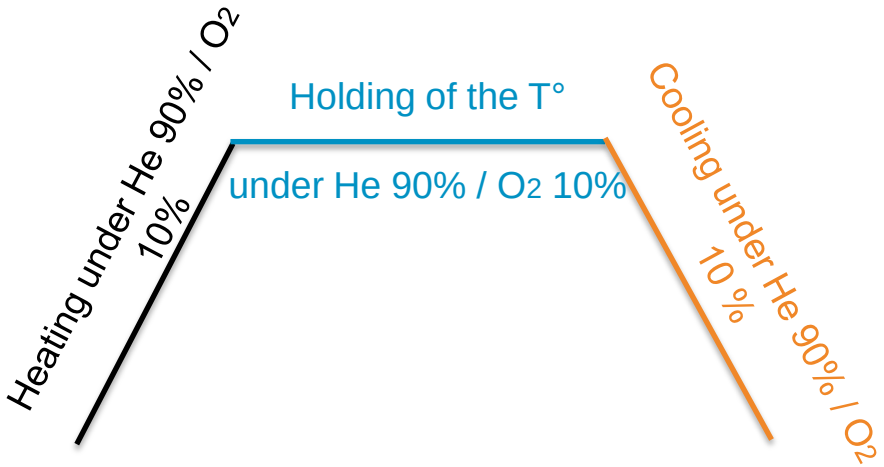
Geometry: sheets → imposed by the furnace



EXPERIMENTAL METHOD

Given the temperatures tested (700/800/900°C) and expected oxidation kinetics

Target oxide layer thickness at the end of the oxidation
→ ≈ 10 µm

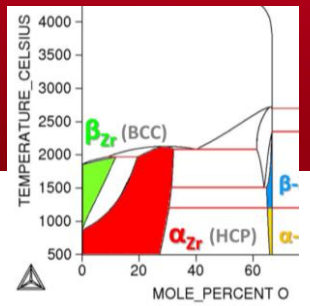


Oxidation T° (°C)	Oxidation time (sec)
700	10 800
800	4500
900	900

Heating rate : 20°C /min
Cooling rate: 50°C / min

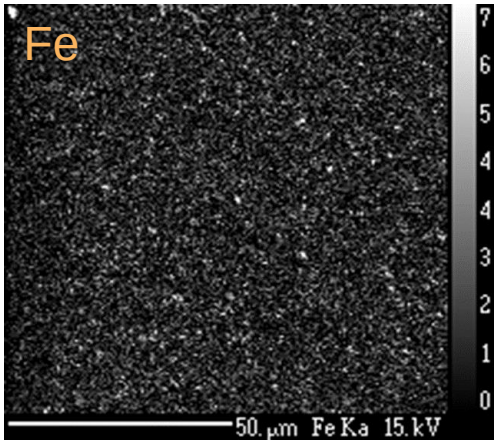
T° mesured by the furnace thermocouple → post-Mortem characterisations
→ verify the sample T°

EXPERIMENTAL METHOD



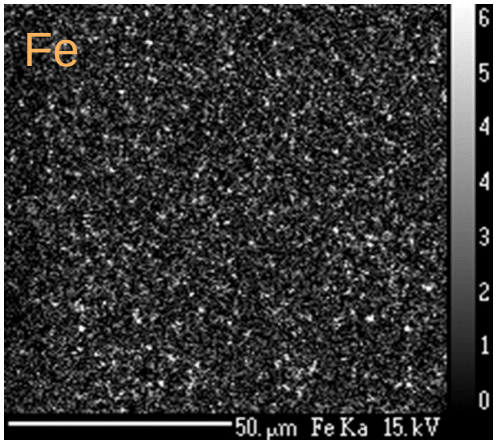
Post-test characterization by Electron-Probe Micro Analysis

700°C



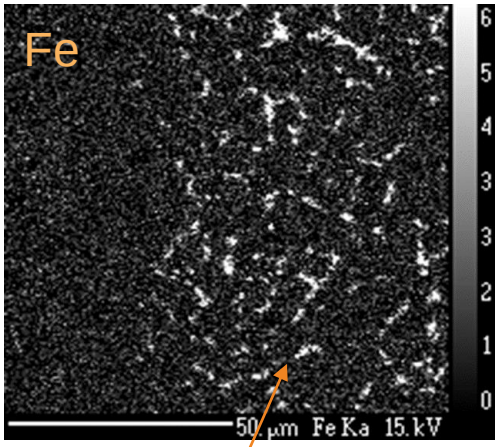
Distribution of Fe and Cr (βZr stabilizers) show that Zr remained αZr
→ T° actually close to 700°C

800°C



Some fluctuations in Fe and Cr contents → some zones transformed in βZr phase during treatment
→ T ° actually close to 800°C

900°C



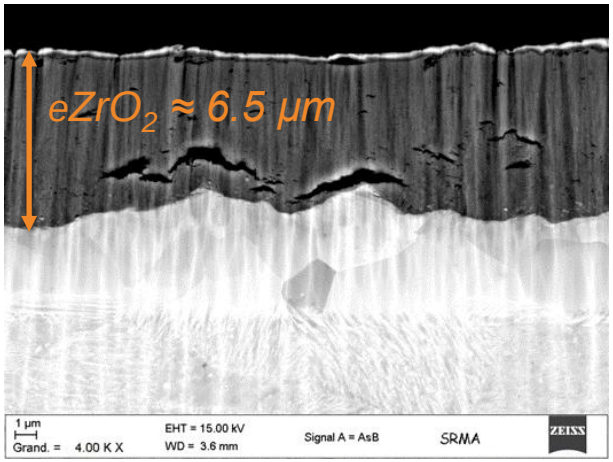
Enrichment on Fe

Local enrichments in Fe (20% wt.%) and Cr (12% wt.%) → zirconium partially transformed in βZr phase
→ T ° actually close to 900°C

Microstructure analyses after cooling by SEM

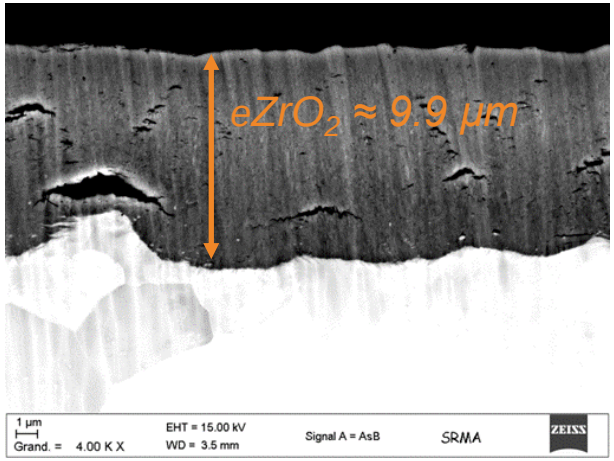
→ microstructure

700°C



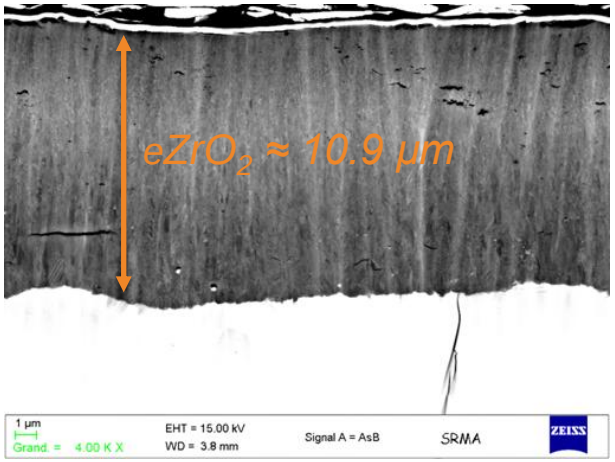
Small equiaxed grains, no columns (size ≈ 100 nm)
→ microstructure very fine

800°C



Small equiaxed grains (size ≈ 100 nm)
Columnar grains at the interface (size ≈ 1 µm) :
→ microstructure very fine

900°C



Columnar oxide (size increases near the interface) :
→ microstructure very fine

EXPERIMENTAL METHOD

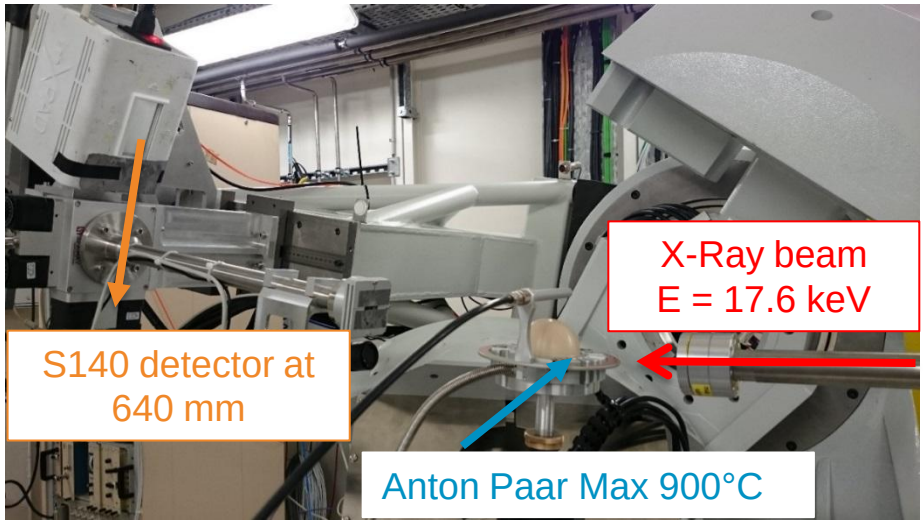
Experimental conditions at SOLEIL:

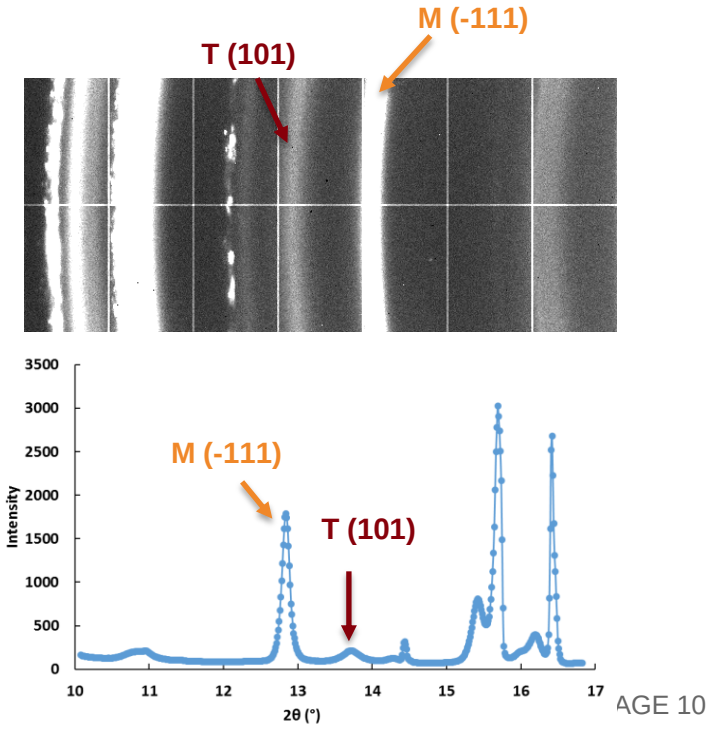
Energy below the K-edge of Zr (18 keV) → avoid the fluorescence

High energy → important X-Ray penetration (≈ 50 µm) : data obtained simultaneously for the oxide and the metallic substrate

XPAD S140 2D detection → Parts of Debye Scherrer rings and very fast detector

Large detector-sample distance: better angular resolution



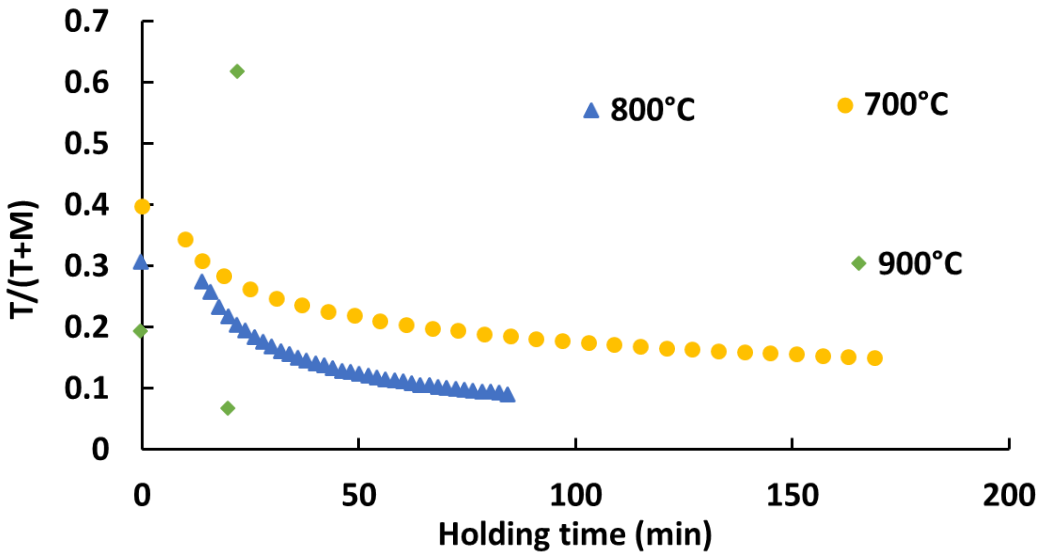


RESULTS OBTAINED: STRUCTURAL EVOLUTIONS

Analysis during oxidation

$$\frac{T}{(T+M)} = \frac{T(101)}{[M(-111)+M(111)+T(101)]}$$

Does not take into account an eventual texture effect



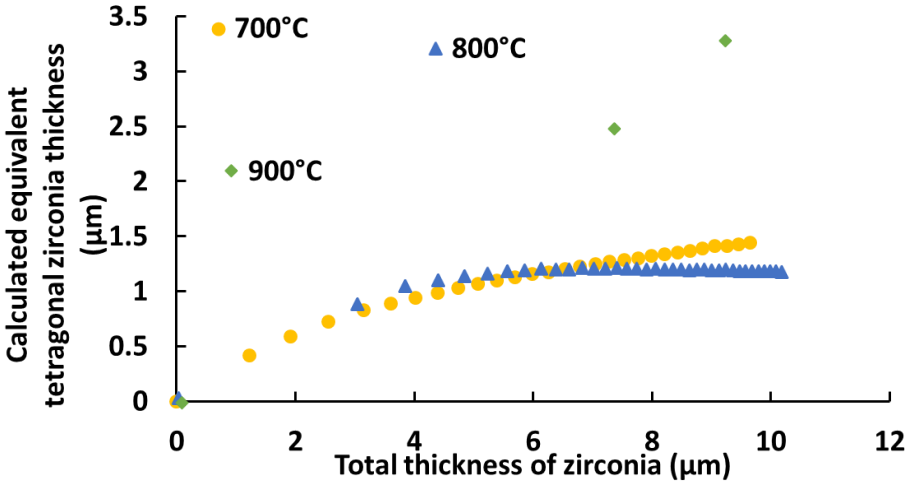
- Average amount of zirconia tetragonal phase higher at 900°C compared to the amounts at 700 and 800°C for a similar oxidation time

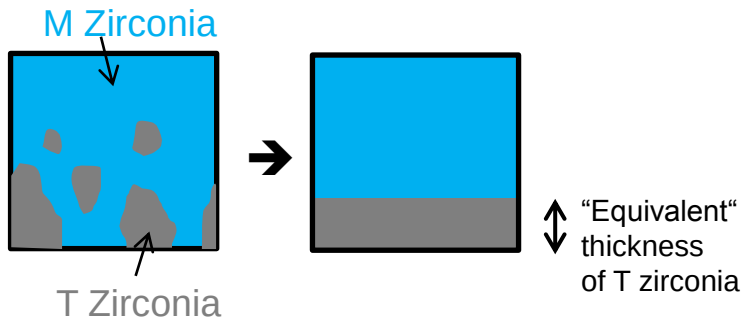
- ~ 20-30% decrease of the average volume fraction of the tetragonal phase during oxidation

RESULTS OBTAINED : STRUCTURAL EVOLUTIONS

Analysis during oxidation

the "equivalent" T zirconia thickness was evaluated from the expected "instantaneous" total oxide thickness and the " instantaneous" tetragonal phase volume fraction deduced from the XRD analyzes





Relatively small increase in "equivalent thickness" of tetragonal zirconia during oxidation. Two hypotheses:

- tetragonal zirconia mainly grows at the beginning of the oxidation and then it is the monoclinic zirconia that mainly forms
- the oxide formed at the oxide/metal interface, during the first oxidation steps is a mixture of both phases, then a phase transformation from tetragonal to monoclinic occurs for longer oxidation times

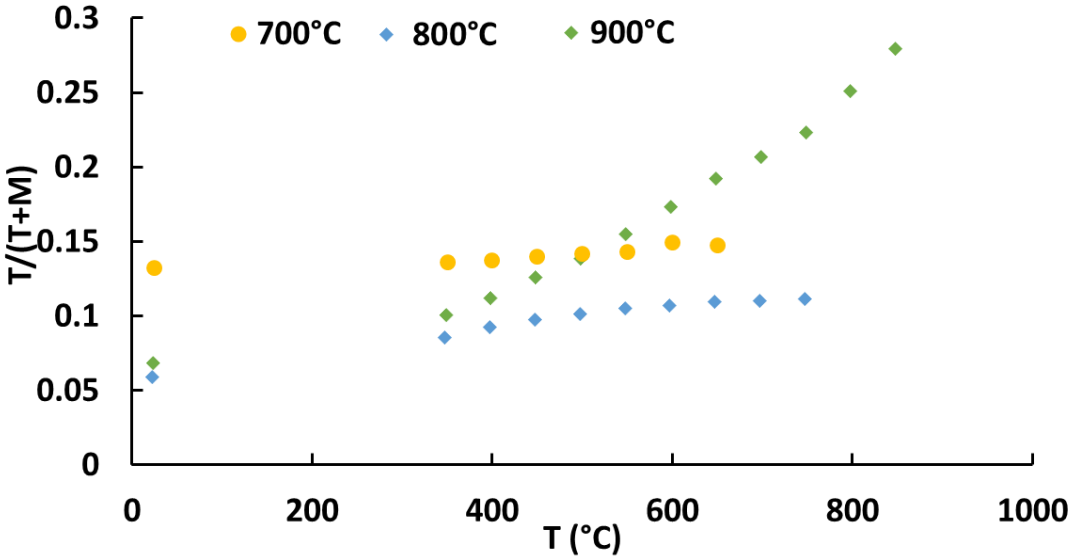
RESULTS OBTAINED: STRUCTURAL EVOLUTIONS

Analysis during cooling

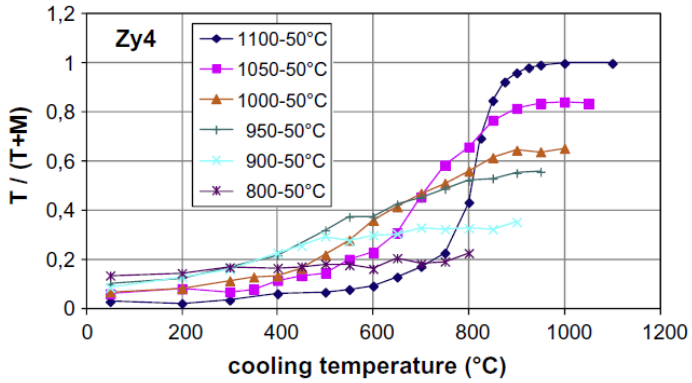
$$\frac{T}{(T+M)} = \frac{T(101)}{[M(-111)+M(111)+T(101)]}$$

Does not take into account an eventual texture effect

Synchrotron XRD : penetration ≈ 50 µm



Laboratory XRD: penetration ≈ 5 µm



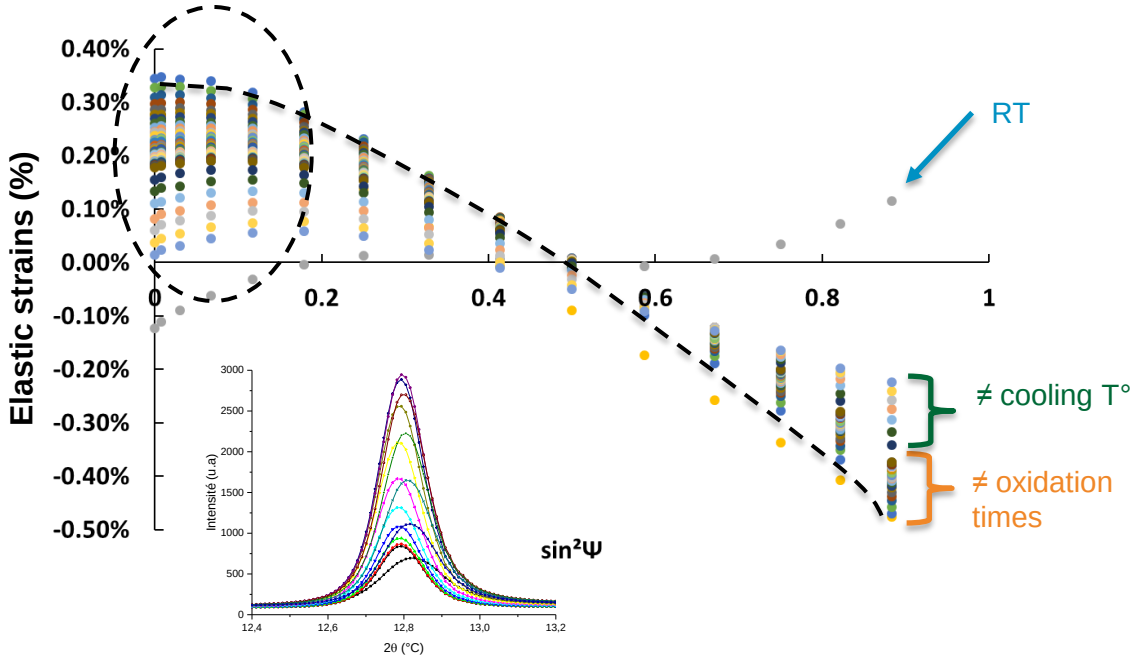
Gosset et al, JNM (2015)

At 900°C : Almost all tetragonal zirconia is transformed into monoclinic zirconia, the residual fraction of T zirconia at 20°C is low

For 700 et 800 °C : Lower but significant decrease of the tetragonal phase fraction, residual fraction of tetragonal zirconia at RT higher after oxidation at 700°C

→ In agreement with D. Gosset et al. results obtained in lab XRD.

RESULTS OBTAINED : INTERNAL STRESSES



- Microstructure gradient
- Texture anisotropy
- …

No simple mechanical model in the literature to extract strains / stresses for textured monoclinic / tetragonal structures

Assumptions :

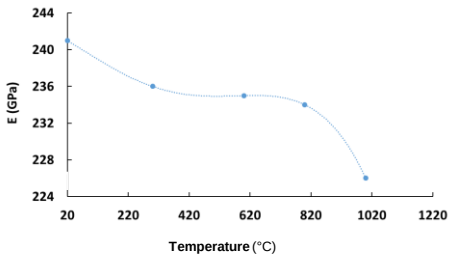
Plane and equibiaxial stresses

$\sigma_{11} = \sigma_{22} = \sigma_r$

$\sigma_{33} = 0$

$\nu = 0.3$

$E = f(T)$



$$\varepsilon_{\phi\psi} = (\sigma_r \frac{1+\nu}{E}) sin^2\psi - 2\sigma_r \frac{\nu}{E}$$

sin²Ψ law

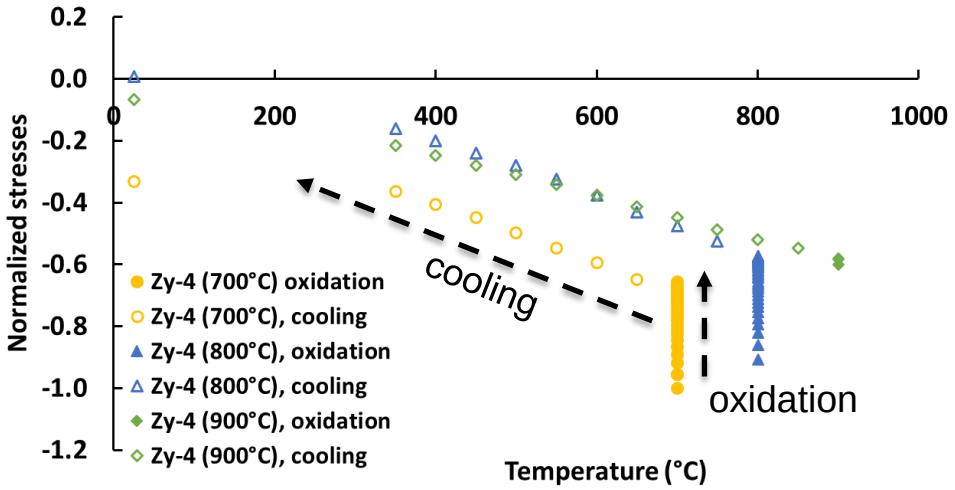
$$\sigma_r = \varepsilon_{\phi\psi} \frac{E}{1+\nu}$$

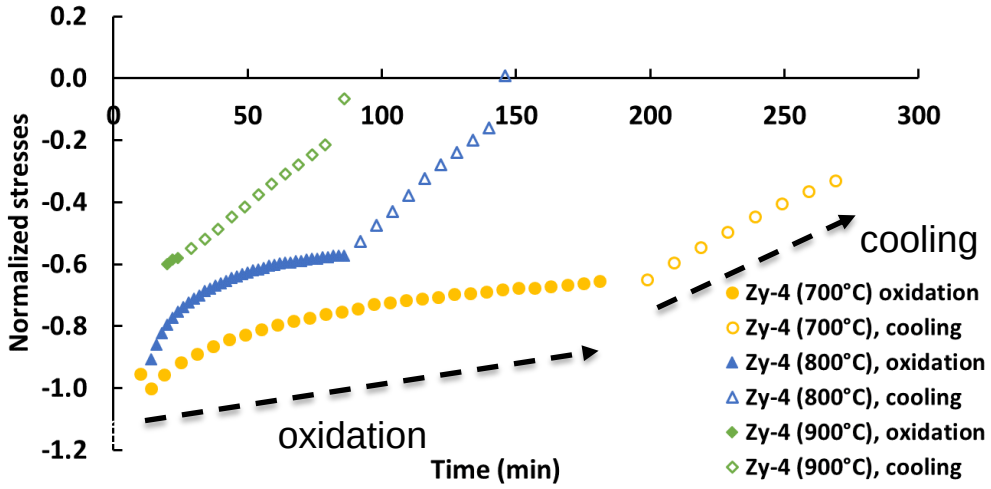
Calculation of the average stress across the thickness

Chan et al, J. Am. Ceram. Soc (1991)

RESULTS OBTAINED INTERNAL STRESSES

The stress is normalized to the highest absolute value of the stresses obtained at the beginning of oxidation.





Monoclinic Zirconia:

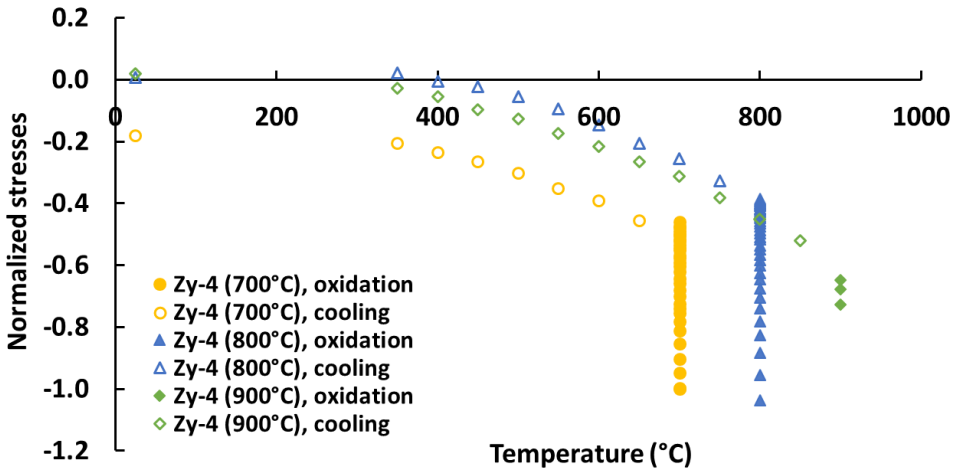
Compressive stresses perpendicular to the main direction of oxide growth

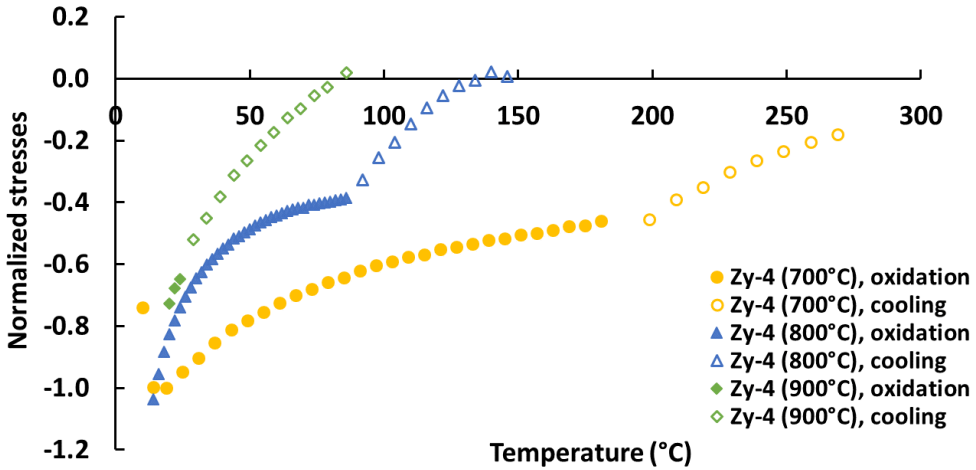
Decrease of the average compressive stresses during oxidation (solid symbols) and cooling (empty symbols)

The oxide formed at 700°C remains more stressed at the end of the thermal cycle compared to those formed at 800 and 900°C.

RESULTS OBTAINED: INTERNAL STRESSES

The stress is normalized by the highest absolute value of the stresses obtained at the beginning of oxidation.





Tetragonal Zirconia:

Compressive stresses perpendicular to the main direction of oxide growth

The mean compressive stresses in the quadratic phase decrease more rapidly in comparison with the monoclinic phase

The average stresses obtained in the tetragonal phase have a similar tendency as those obtained in the monoclinic phase

The oxide formed at 700°C remains more stressed at the end of the thermal cycle than those formed at 800 and 900°C.

CONCLUSIONS

- ✓ First in-situ oxidation experiments performed using synchrotron radiation with XRD analysis of both structural variations as well as internal stresses generated by the oxide growth.

- ✓ Major effect of the oxidation temperature on the oxide structure (tetragonal and monoclinic phases of zirconia) and the internal stresses within the oxide during oxidation and subsequent cooling

- ✓ First results obtained on the evolution of the deformations generated in Zy-4 during *in-situ* experiments in the tetragonal and monoclinic oxide phases.
    - ✓ The monoclinic phase is overall more constrained (compression) than the tetragonal phase
    - ✓ Decrease of average compressive stresses for the monoclinic and tetragonal phases of zirconia during oxidation and cooling

Thank you for your attention

