

IRSN

INSTITUT
DE RADIOPROTECTION
ET DE SÛRETÉ NUCLÉAIRE

Enhancing nuclear safety

HT cladding oxidation in SFP-LOCA conditions examined with micro Raman imaging and ^{18}O tracer techniques

M. Mermoux², I. Idarraga^{1,2}, M. Guerain^{1,2}, A. Kasperski^{1,2}, M. Gestin³, C. Duriez¹

1- IRSN/PSN-RES/SEREX/LE2M, Cadarache, 13115 Saint-Paul-lez-Durance, France

2- Univ. Grenoble Alpes, CNRS/LEPMI, 38402 Saint-Martin d'Hères cedex, France

3 Ecole Nationale Supérieure des Mines, 158 Cours Fauriel, 42023 Saint-Etienne, France

25th QUENCH Workshop, Karlsruhe, 22-24 Oct. 2019

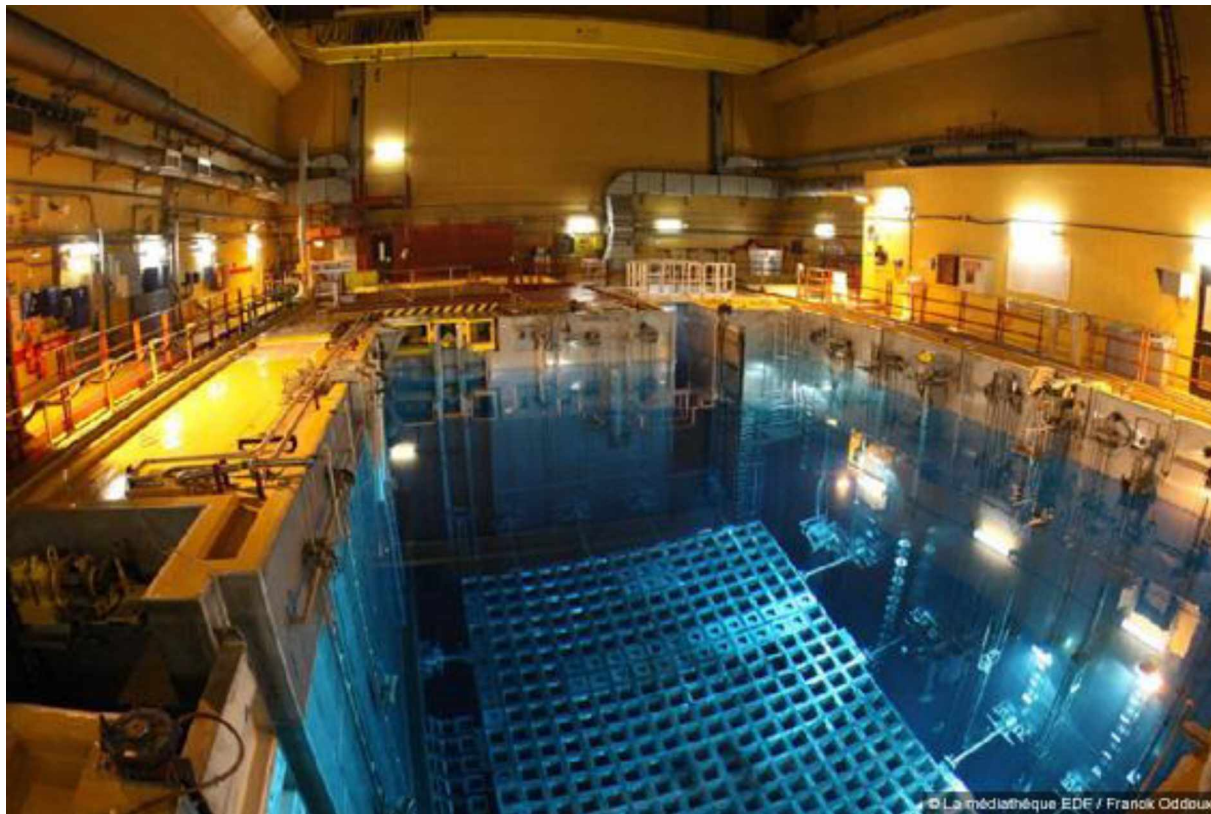
MEMBER OF

ETSON

EUROPEAN
TECHNICAL SAFETY
ORGANISATIONS
NETWORK

For Spent Fuel Pool Loss of Cooling or Loss of coolant Accidents:

- ⇒ The temperature range of interest is ~ **700-1000°C**
- ⇒ The atmospheres considered are **air + steam** mixtures



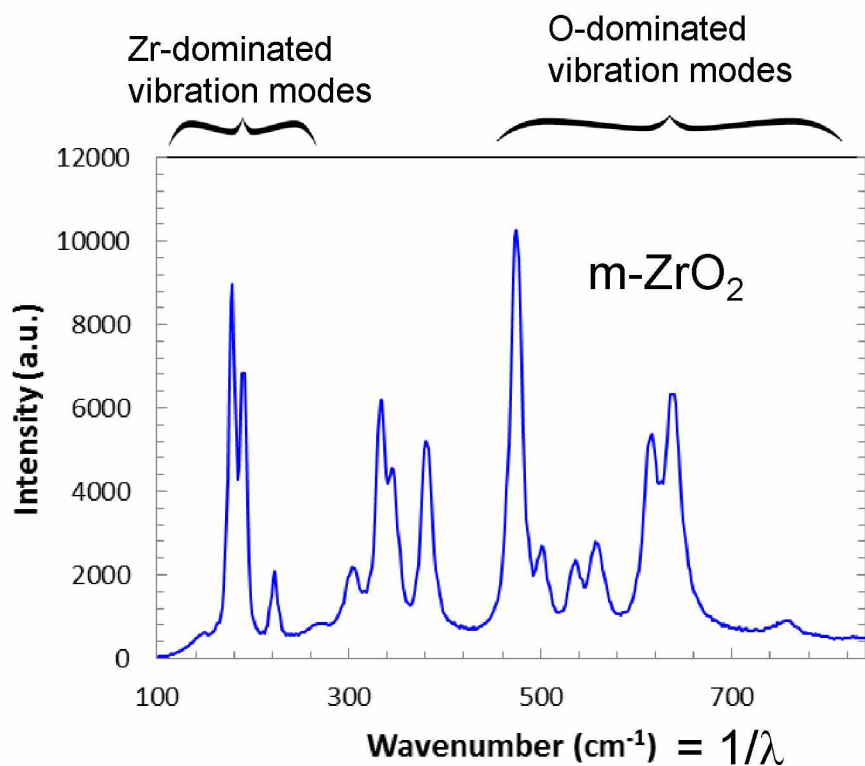
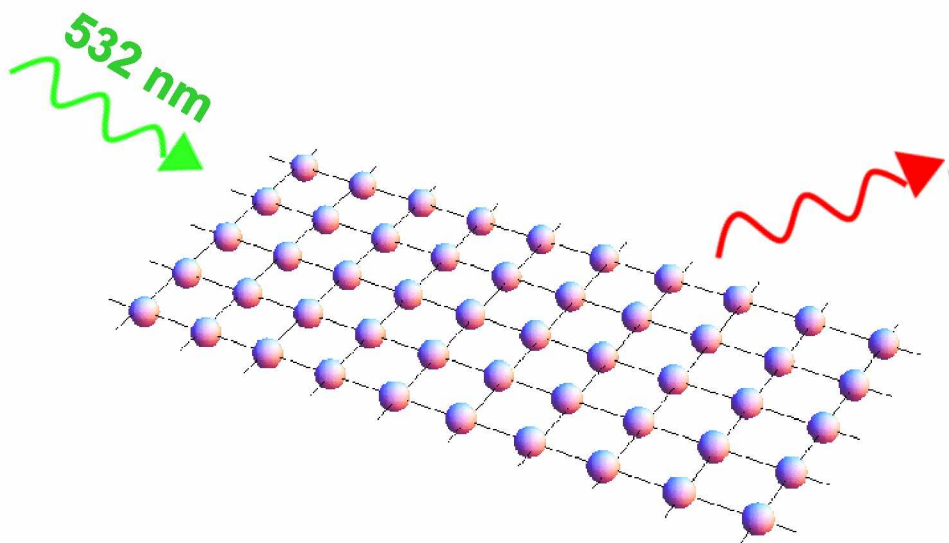
Content

- Principle of Raman imaging → 2 slides
- Phases mapping → 2 slides
- Stress mapping → 2 slides
- ^{18}O isotopic distribution mapping
 - Principle → 1 slides
 - Two-stage diffusion experiments → 4 slides
 - HT oxidations in $^{18}\text{O}_2 + \text{H}_2^{16}\text{O}$ → 5 slides
- Summary

Micro-Raman spectroscopy



Raman imaging system
=
laser source
+ optical microscope
+ Raman spectrometer

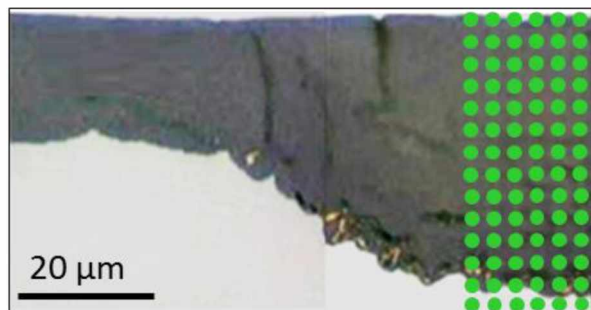


Phase identification and mapping (1/2)

1- **Sample scanning:** $\lambda = 532 \text{ nm}$, $\sim 1 \mu\text{m}$ resolution \rightarrow Dataset of experimental spectra

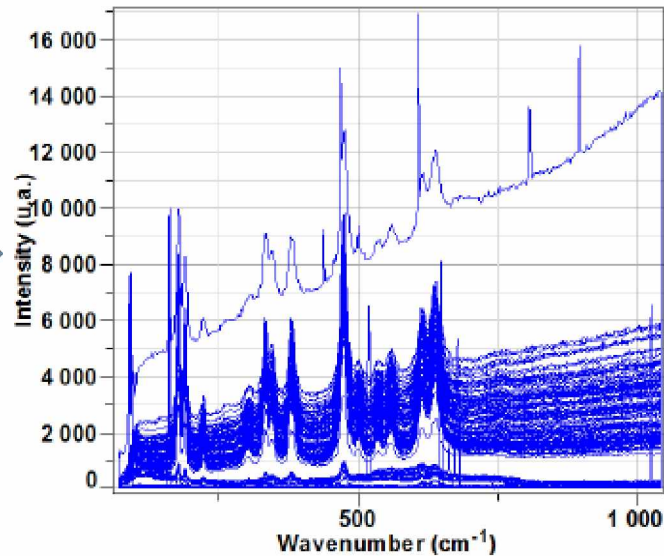
2- **Visual examination** of the dataset and **subtraction** between spectra \rightarrow 5 pure phase spectra were identified (m-ZrO₂, t-ZrO₂, distorted t-ZrO₂, c-ZrO₂, ZrN) + 1 broad band signal likely due to substoichiometry.

Metallographic cross section of Zy-4 oxidized in air at 800°C

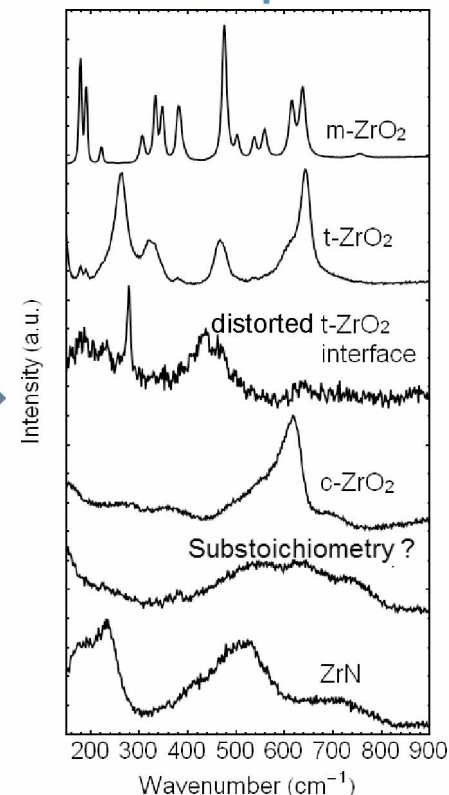


Scanned area 85 x 45 μm, step 0.7 μm

~ 9000 experimental spectra
 $\sim 7 \text{ h}$ acquisition



Model spectra



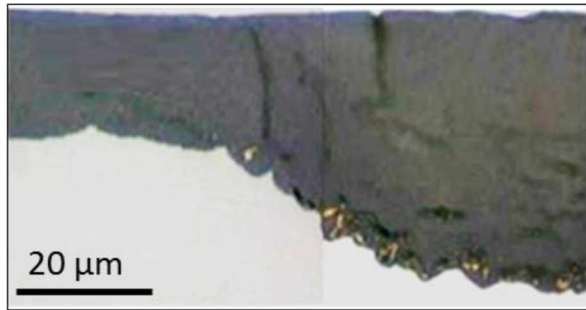
3- **Phase maps construction:** Method 1: Integrated intensity of a given line

Method 2: Linear combinations of the model spectra

\rightarrow **not quantitative !**

Phase identification and mapping (2/2)

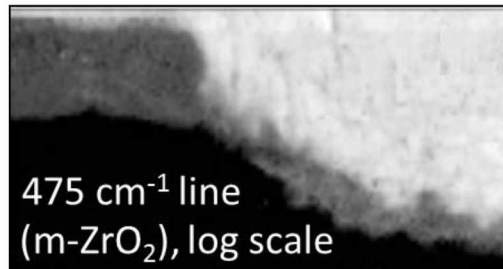
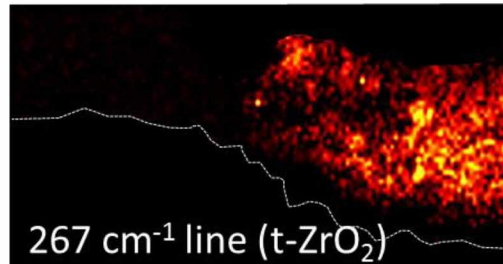
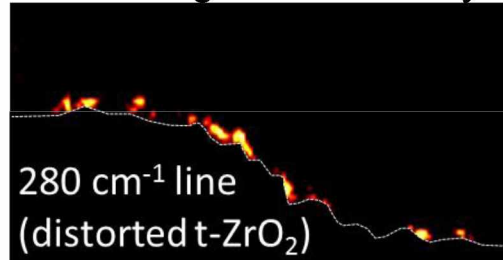
Zy-4 oxidized in air at 800°C



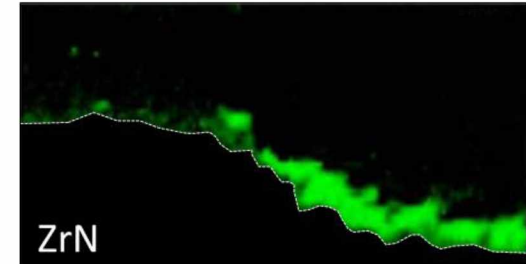
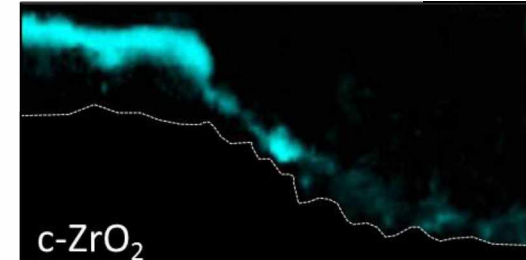
Pre-BA,
dense scale

Post-BA,
nitrided scale

Line integrated intensity



Linear combination



I. Idarraga et al, Oxid. Met. 79 (2013) pp. 289-302.

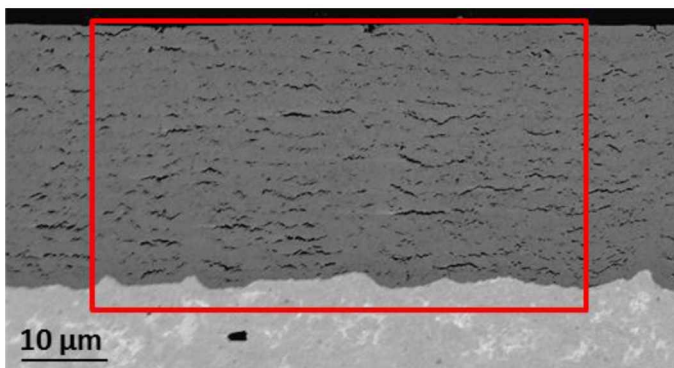


- Significant amount of t-ZrO₂ in the post-BA region (effect of nitriding ?).
- Distorted t-ZrO₂ found at the M/O interface, for both pre and post-BA regions.
- Cubic ZrO₂ detected (low amount).
- Good sensitivity for ZrN detection.
- m-ZrO₂ intensity linked to stoichiometry.

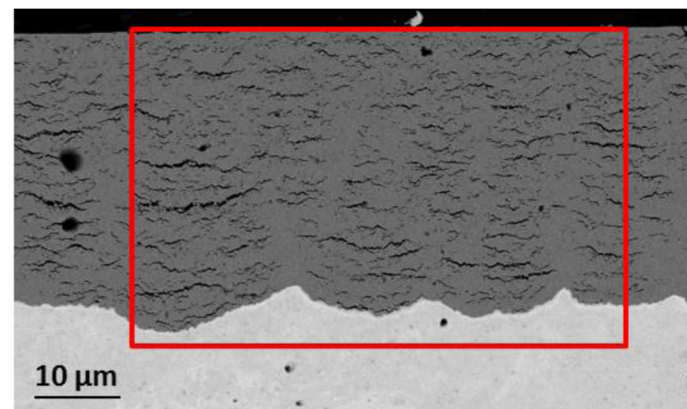
Stoichiometry of pre-oxidation scales

360°C, autoclave, 1265 days

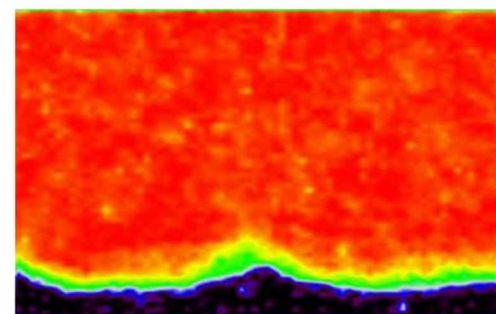
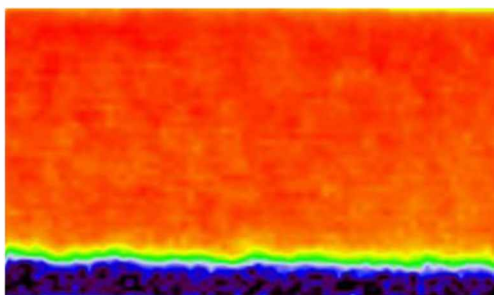
SEM/BSE



425°C, O₂ + H₂O, 250 days



Integrated intensity
of the 475 cm⁻¹ line
(m-ZrO₂), log scale

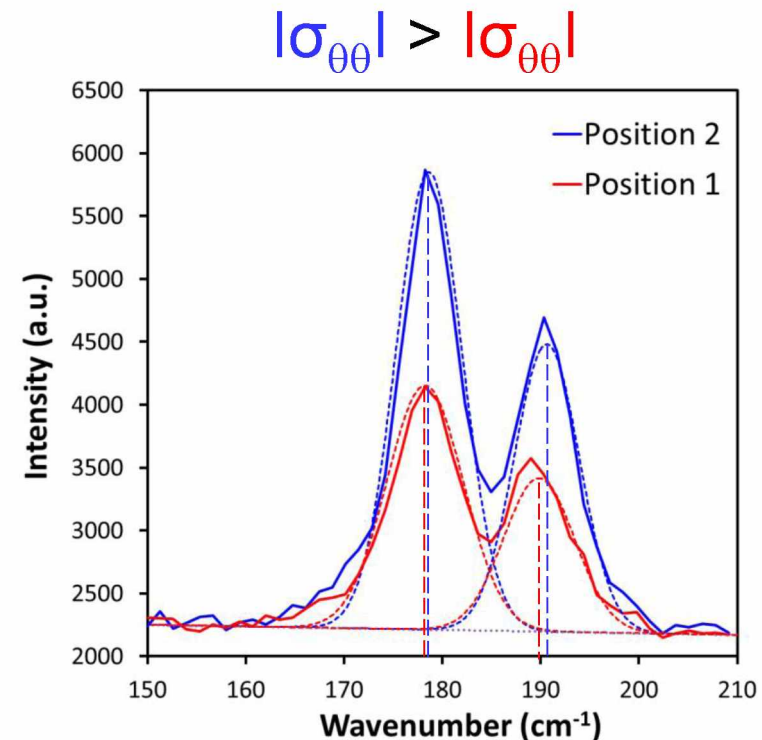
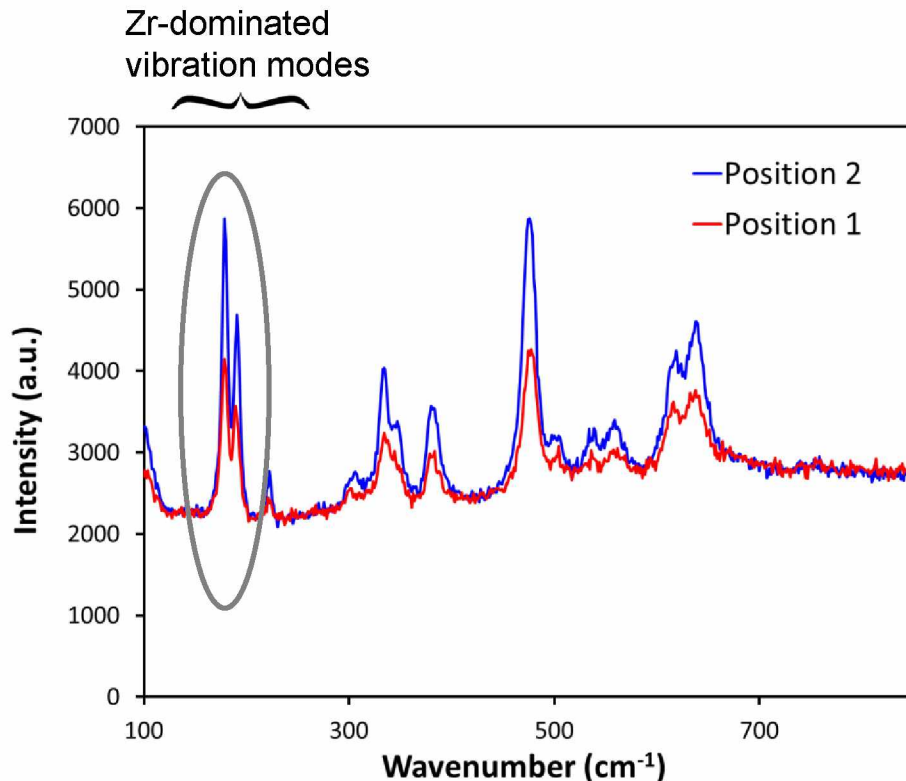


For both pre-oxidation conditions :

- The scales are mostly stoichiometric
- The last formed layer at the M/O interface is sub-stoichiometric.

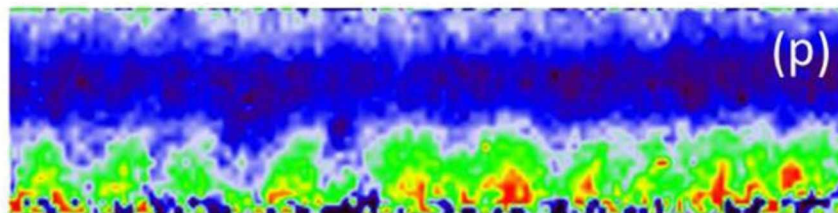
Stress mapping (1/2)

- Stress \rightarrow Lattice strain \rightarrow Slight shifts of Raman lines (few $\text{cm}^{-1}/\text{GPa}$).
- Shifts due to bi-axial stresses **cannot be calibrated** through isostatic compression tests (diamond anvil-cell).
 - \Rightarrow **Stresses can be qualitatively mapped** by measuring the shifts of the low-frequency lines (not influenced by stoichiometry) from a reference signal (relaxed sample).

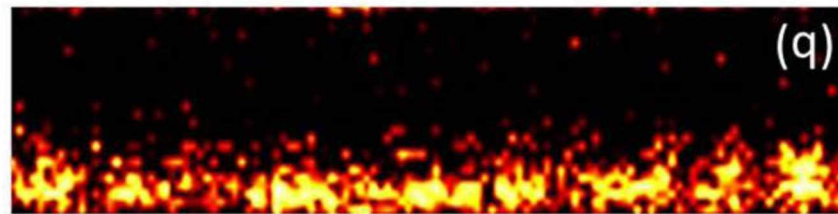


Stress mapping (2/2)

Pre-breakaway scale formed on M5 at 800°C in air



Frequency of the m-ZrO₂ line at 178 cm⁻¹



Integrated intensity of the t-ZrO₂ line at 280 cm⁻¹

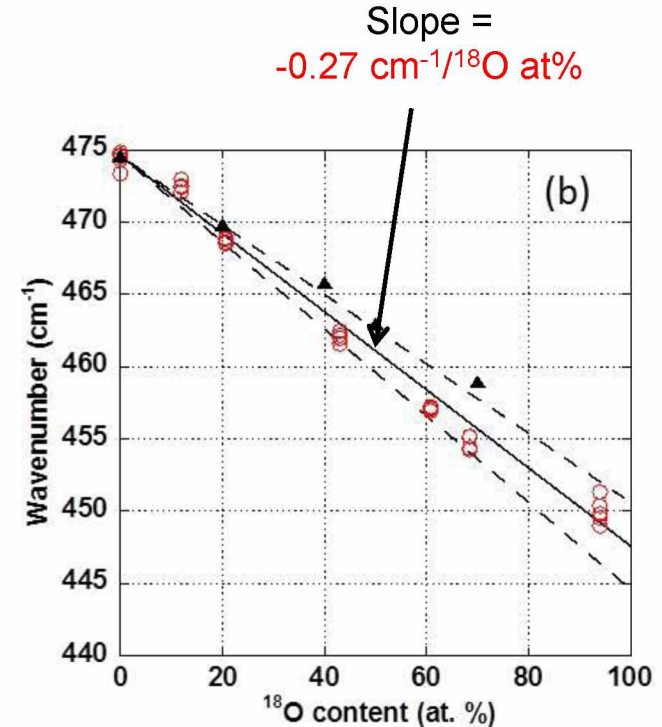
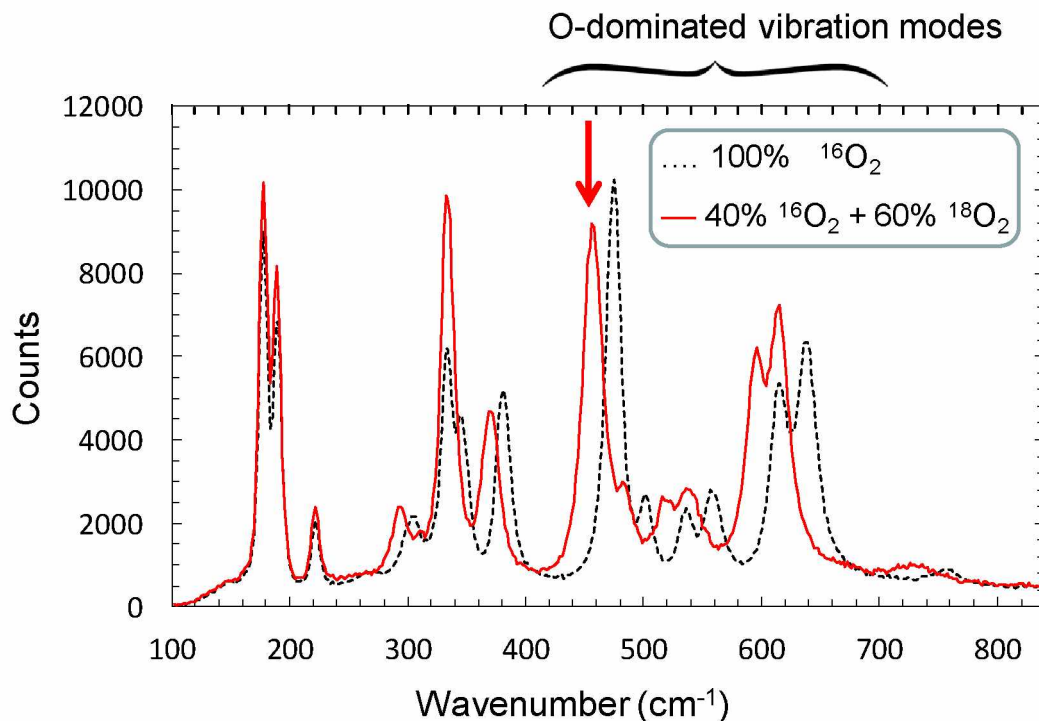
I. Idarraga et al, Oxid. Met. 79 (2013) pp. 289-302.



- Compressive stresses at the M/O interface.
- Distorted t-ZrO₂ distribution linked to the stress distribution.

^{18}O distributions mapping

- $^{16}\text{O} \rightarrow ^{18}\text{O}$ substitution induces strong downward shifts of **O-dominated lines** of the m-ZrO₂ Raman spectrum.
 - Shifts are proportional to the ^{18}O fraction and **can be calibrated** with Zr($^{18}\text{O}, ^{16}\text{O}$)₂ standards (Powders prepared by Zy-4 total oxidation in $^{16}\text{O}_2 + ^{18}\text{O}_2$ atmospheres).
- ⇒ Raman imaging can be used to quantitatively map the ^{18}O distribution in a zirconia scale by measuring the position of the **475 cm⁻¹** line.



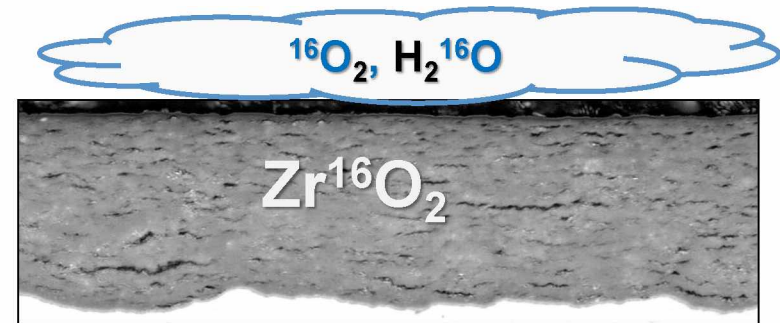
M. Guerin et al, Corrosion Science 98 (2015) 140-149

Two-stage oxidation experiments

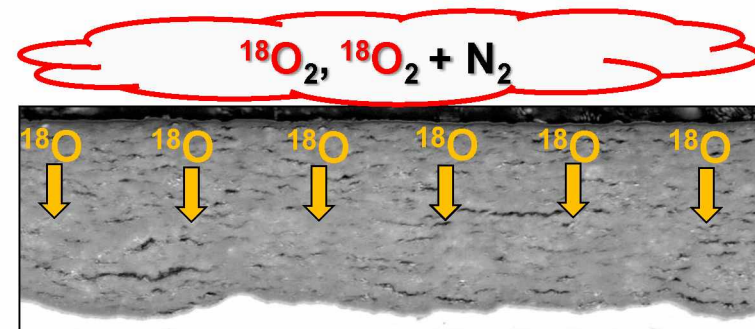
- **Objective:**
Investigate oxygen ingress at high T through a low T pre-oxidation scale

- **Principle:**

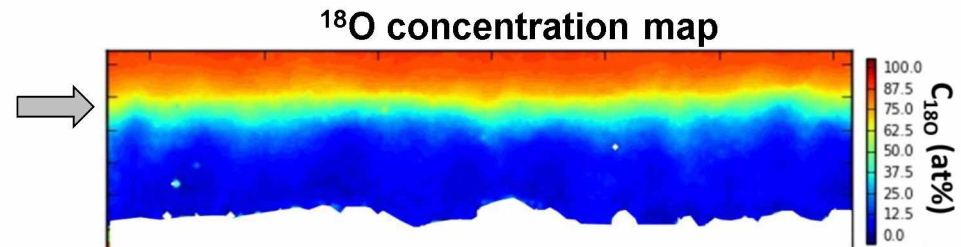
1) Low T pre-oxidation in $^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$ →



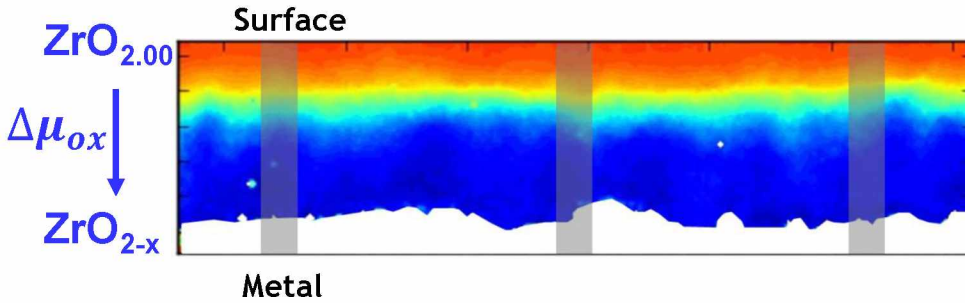
2) HT exposure in $^{18}\text{O}_2$ or $^{18}\text{O}_2 + \text{N}_2$ →



^{18}O distribution Raman mapping



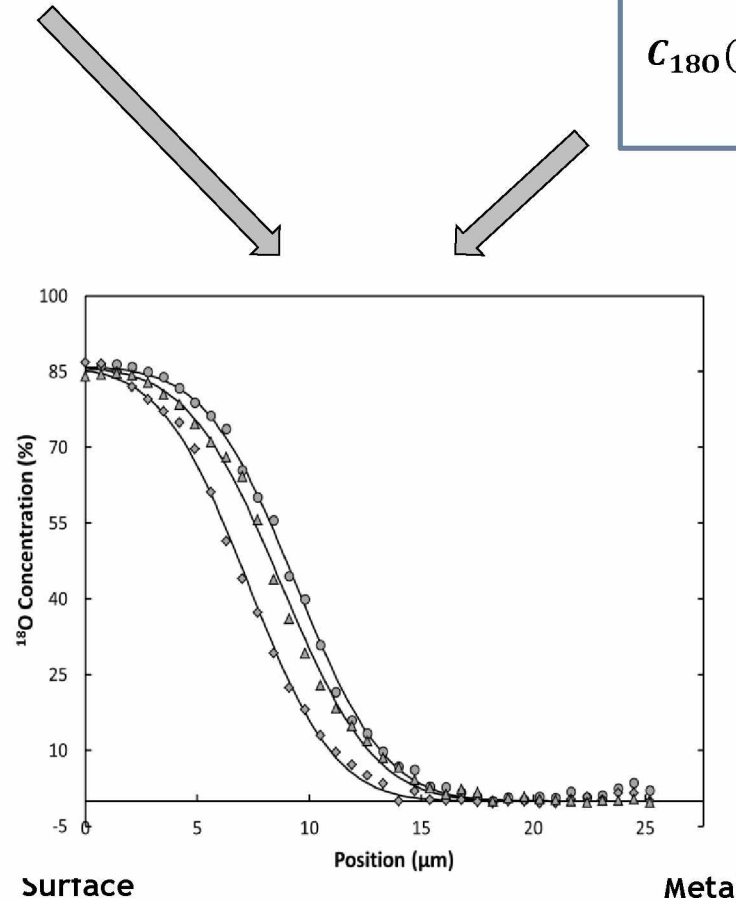
^{18}O two-stage oxidation experiments: oxygen diffusion modelling



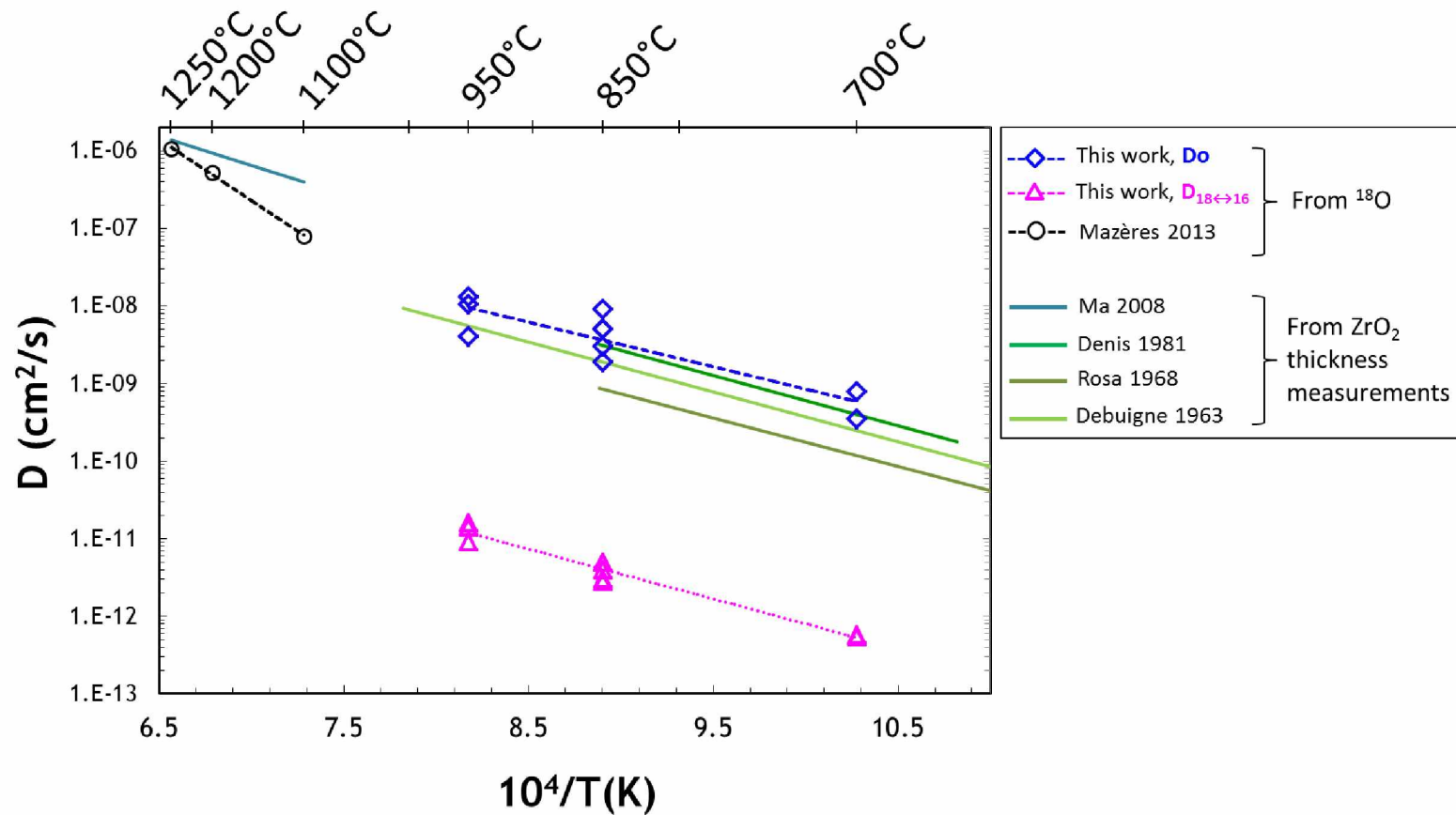
$$\frac{\partial C_{180}}{\partial t} = \frac{D_O \Delta\mu_{ox}}{RT e} \frac{\partial C_{180}}{\partial x} + D_{16\leftrightarrow 18} \frac{\partial^2 C_{180}}{\partial x^2}$$

Gradient of oxygen chemical potential \downarrow isotopic exchange

$$C_{180}(x, t) = C_s \operatorname{erfc} \left(\frac{x + \frac{D_O \Delta\mu_{ox} t}{RT e}}{2\sqrt{D_{16\leftrightarrow 18} t}} \right)$$



Oxygen diffusion coefficients



Our D_{O} data are comparable with apparent diffusivity derived from high T Kp
 Our pre-oxide scales behave at high T as dense, protective scales ...
 ... away from radial cracks !

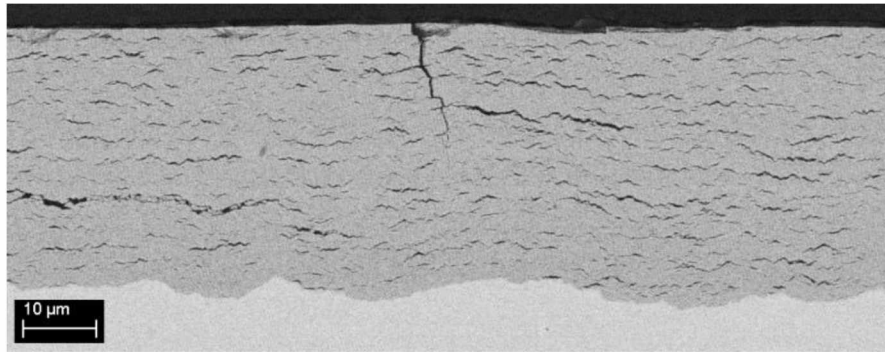
C. Duriez et al., JNM 513 (2019) 152-174.

Two-stage oxidation experiments : effect of cracks

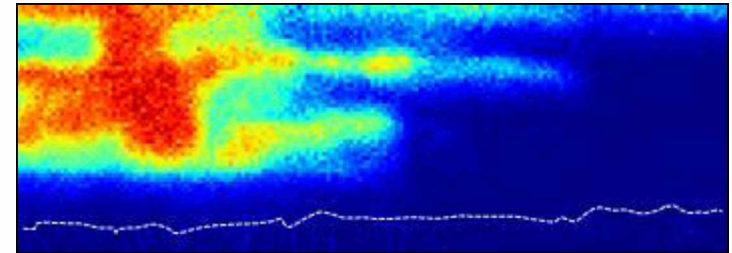
Pre-oxidation at 425°C in $^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$



120 min at 850°C in $^{18}\text{O}_2 + \text{N}_2$

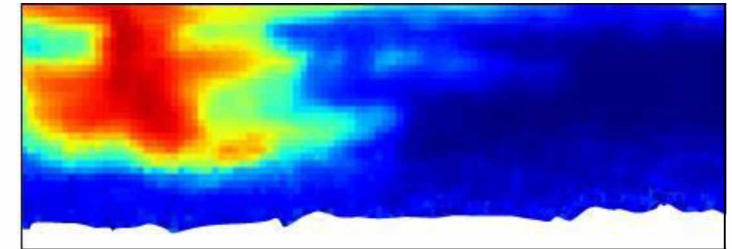


SIMS mapping



C₁₈₀ (at. %)
80
72
64
56
48
40
32
24
16
8
0

Raman mapping



A. Kasperski,, ASTM STP1597, 2018, pp. 1059-1092.



Radial cracks are preferential path for oxygen incorporation and circumferential cracks favor its lateral spreading.

→ The protective influence of the scale is lowered.

- **Objective:**

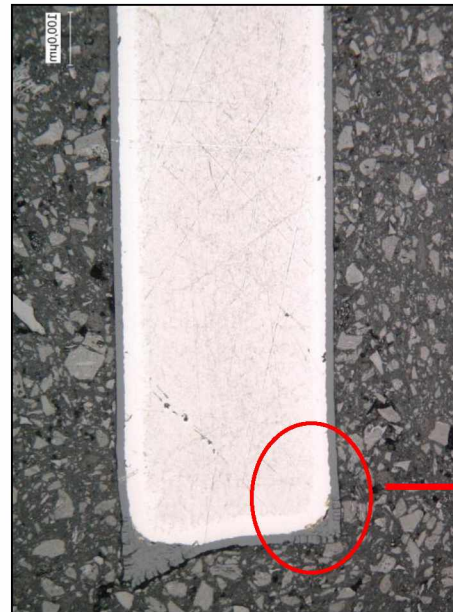
Quantify, in mixed air + steam atmospheres, the **respective contributions** of the O_2 and H_2O species to the oxidation process.

- **Principle:**

1) Bare Zy-4 plates HT oxidation in flowing $^{18}\text{O}_2 + \text{H}_2^{16}\text{O} + \text{N}_2$

Short duration test to limit $^{18}\text{O}_2$ consumption and isotopic exchanges after oxide formation.

2) Raman mapping at the edges \Rightarrow isotopic composition of pre-BA and post-BA oxides.

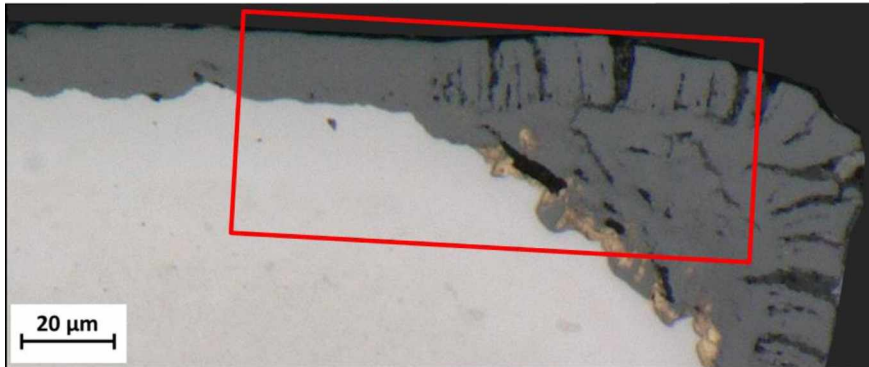
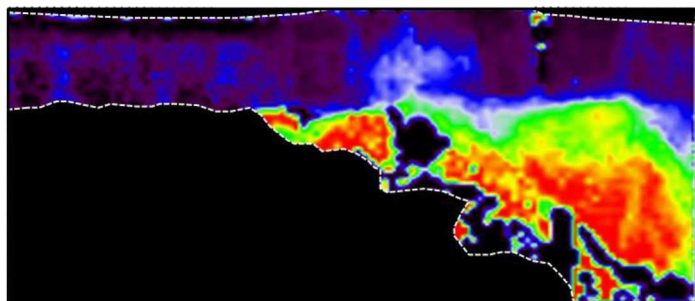
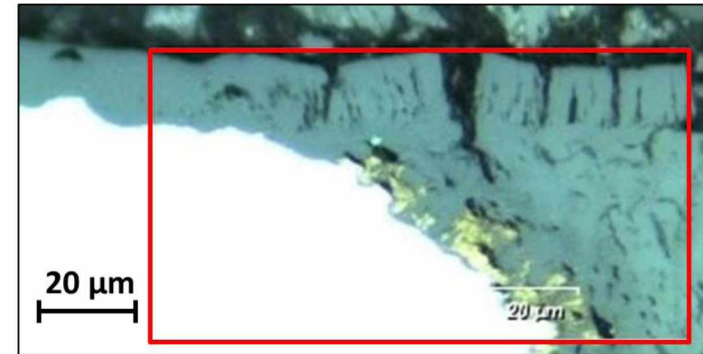
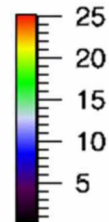
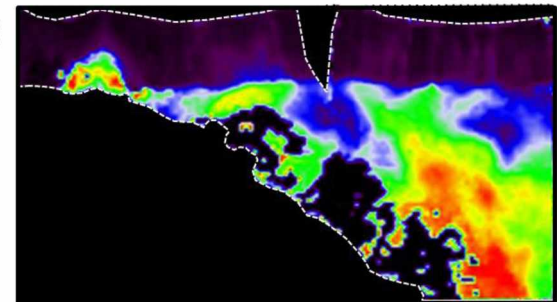
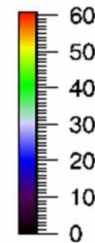


- Two different composition of the gas mixture tested:

	Vol. fraction (%)			$^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$
	$^{18}\text{O}_2$	H_2^{16}O	N_2	
« ^{18}O -poor »	4	16.5	79.5	0.315
« ^{18}O -rich »	14	15	71	0.64

- 3 temperatures investigated:
 - 700°C, $\Delta t = 4$ h
 - 850°C, $\Delta t = 1$ h
 - 950°C, $\Delta t = 15$ min

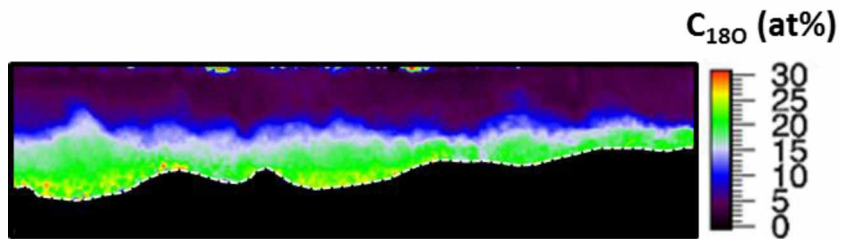
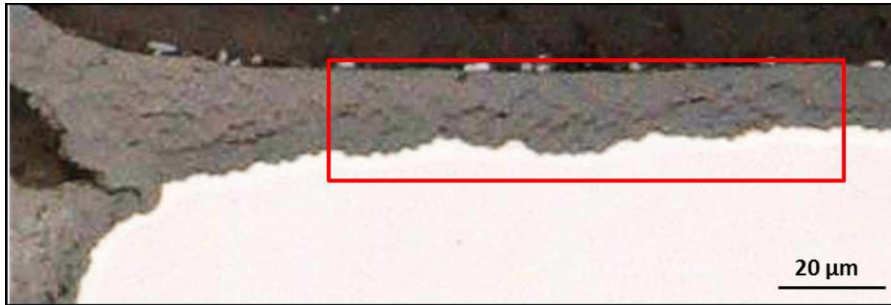
850°C, 60 min

« ^{18}O -poor »« ^{18}O -rich » $C_{18\text{O}}$ (at%) $C_{18\text{O}}$ (at%)

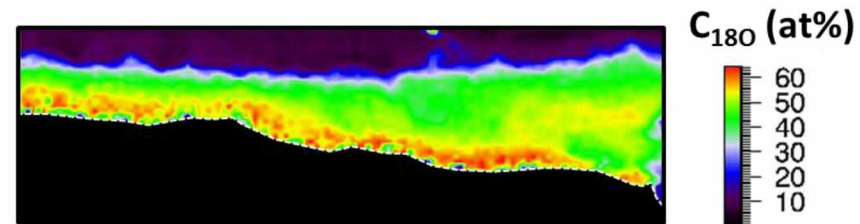
- The dense oxide has low ^{18}O content \Rightarrow it forms mainly from H_2O .
- The porous oxide has \sim same isotopic composition than the gas mixture \Rightarrow H_2O and O_2 contribute \sim proportionally to their partial pressure.

700°C, 4h

« ^{18}O -poor »



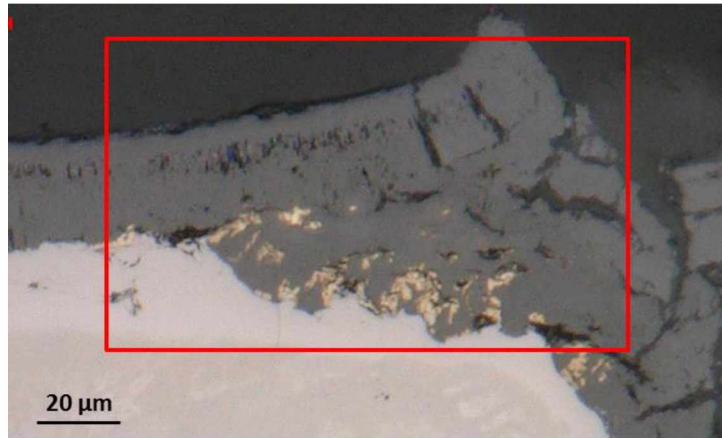
« ^{18}O -rich »



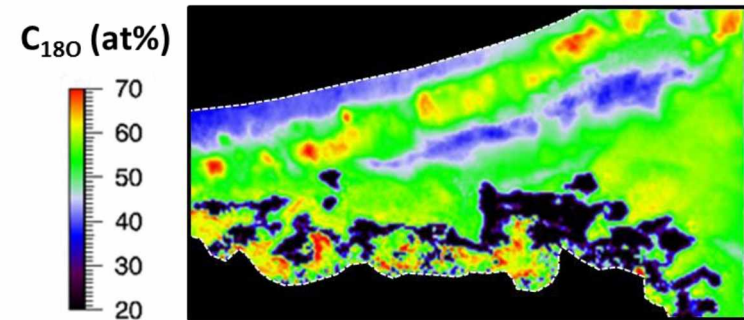
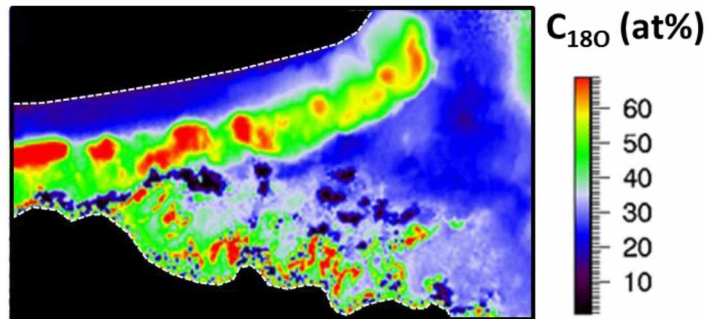
■ Same conclusions than at 850°C

950°C, 15 min

« ^{18}O -poor »



« ^{18}O -rich »



- Not as clear as at 700 and 850°C.
- Effect of isotopic exchanges after oxide formation ? → Shorter tests needed.

Raman imaging is a powerful tool for mapping thermally grown zirconia layers at a μm scale

- ⇒ Phase distribution maps (not quantitative)
- ⇒ Stress distribution maps (not quantitative)
- ⇒ ^{18}O isotopic distribution maps (quantitative)

t-ZrO₂ distributions

- **Significant t-ZrO₂ amounts** after high temperature oxidation **in air**.
- Much lower amounts after low temperature pre-oxidation.

Stress distribution

- In dense high temperature layers, **compressive stresses close to the M/O interface**.
- Low temperature, thick pre-oxidation scales are **mostly relaxed and stoichiometric**.

^{18}O distributions

- Our **pre-oxidation scales are protective** in SFP-LOCA conditions (but detrimental effect of cracks).
- In mixed air + steam atmospheres, the respective contributions of O_2 and H_2O depend on the oxidation regime. At 700-850°C, the **pre-breakaway dense oxide forms mostly from H₂O**.

Aknowledgments

Part of this work has been performed in the frame of the DENOPI project, funded by the French government as part of the “Investment for the Future” Program reference ANR-11-RSNR-0006

Thank you for your attention !

Additional slides

Oxidation furnaces

Pre-oxidation at 425°C in O₂ + steam

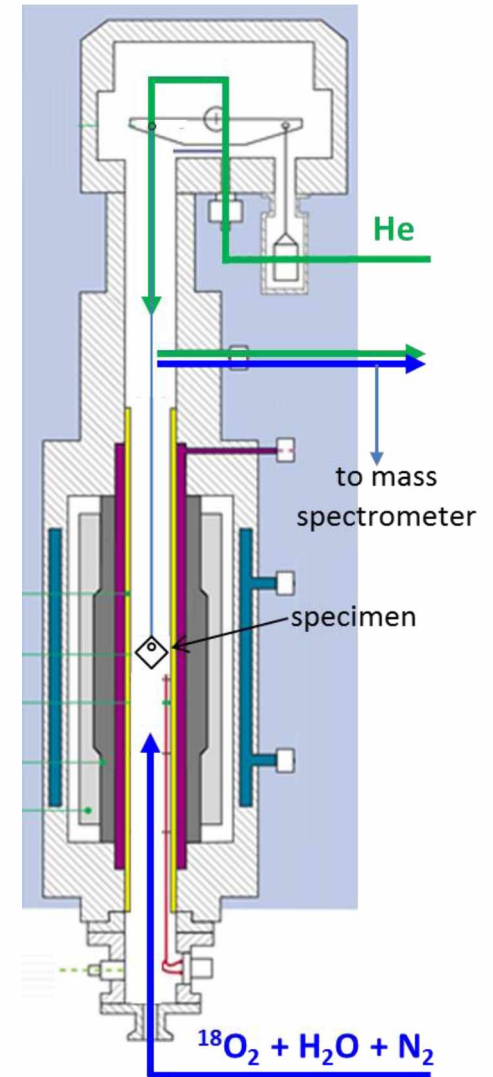


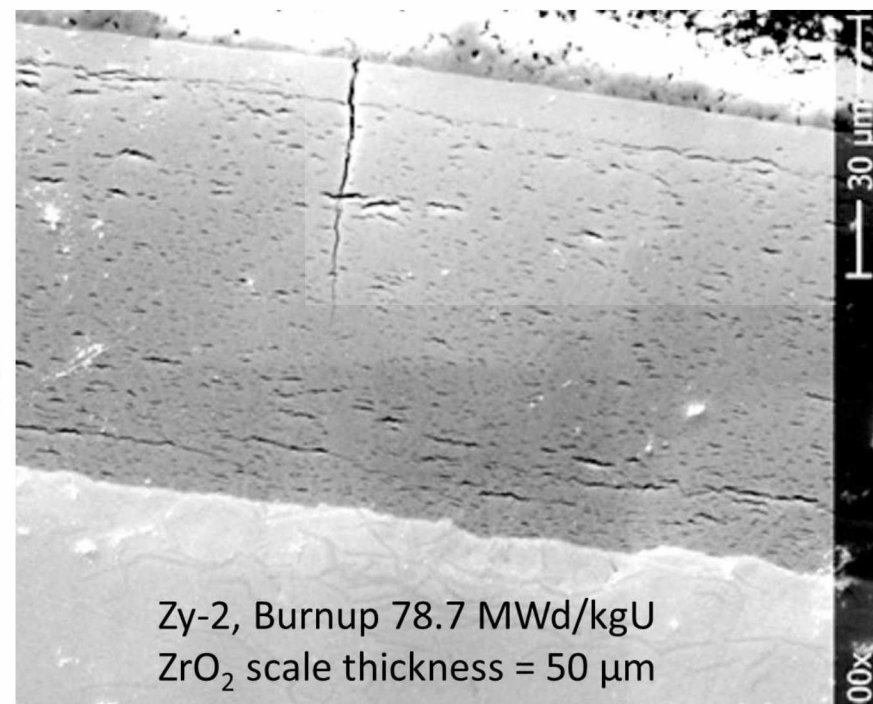
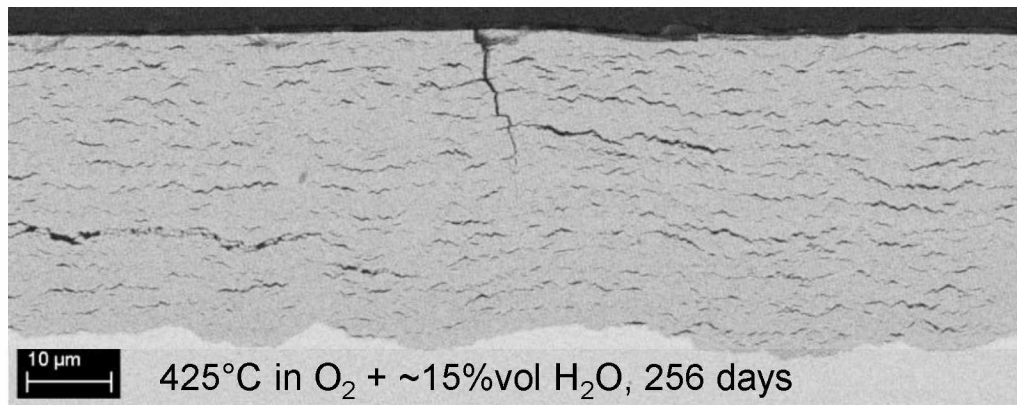
10 mm



Ø 9.5 mm

HT oxidation tests in a SETARAM thermobalance

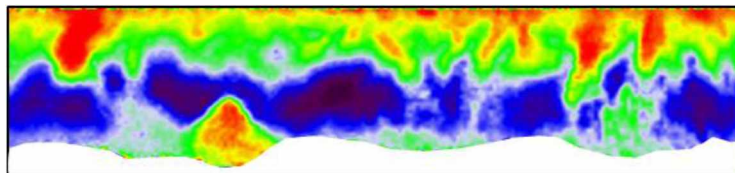




S. Abolhassani et al., Zirconium in the Nuclear Industry, 19th International Symposium, Manchester, May 20-23, 2015.

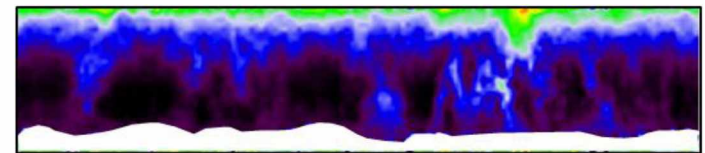
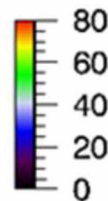
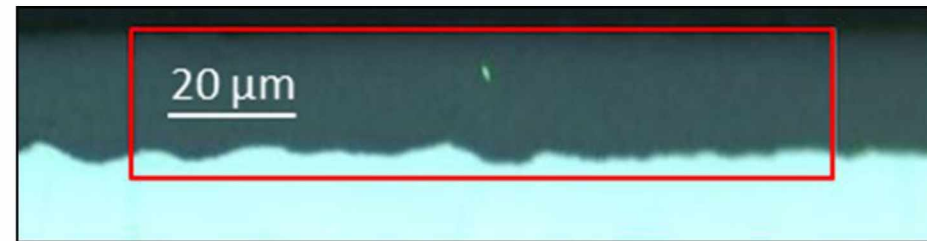
Sequential oxidations, 850 °C

30 min $^{18}\text{O}_2$, then 60 min $\text{H}_2^{16}\text{O} + \text{N}_2$



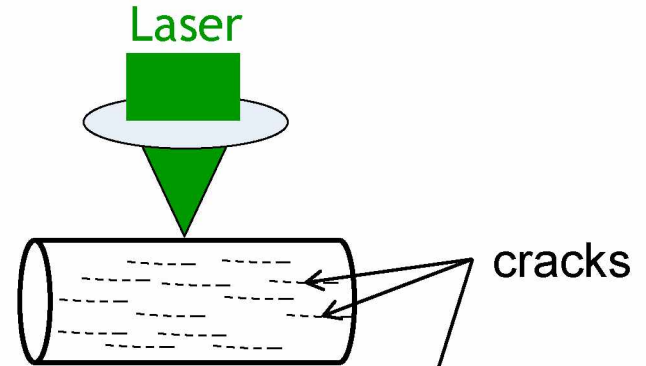
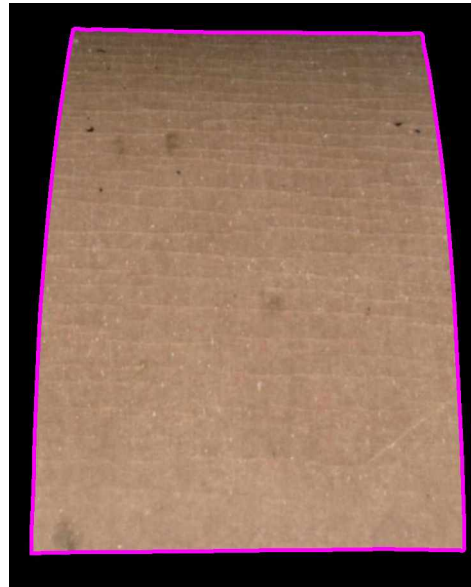
^{16}O Concentration map

30 min $\text{H}_2^{16}\text{O} + \text{N}_2$, then 60 min $^{18}\text{O}_2$



^{18}O Concentration map

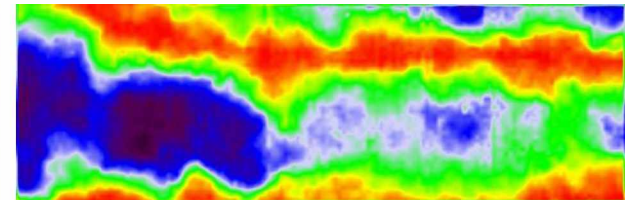
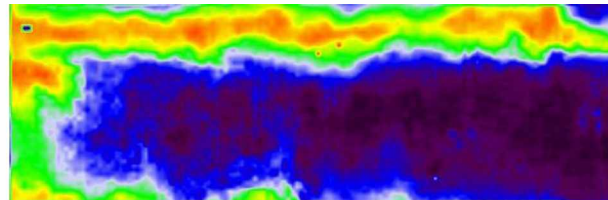
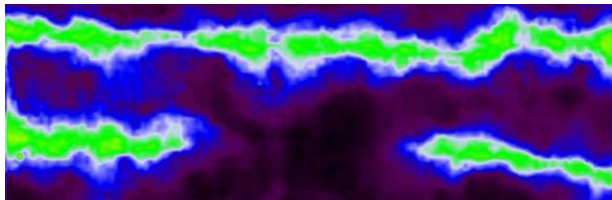
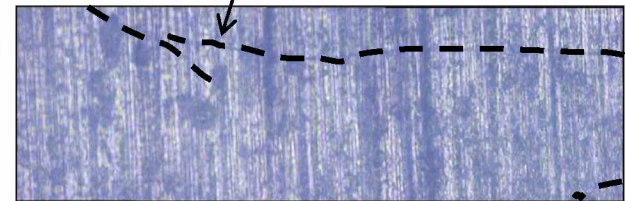
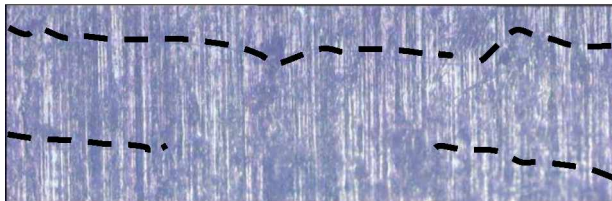
Outer oxide after exposure in $^{18}\text{O}_2$ at 850°C



30 min

60 min

120 min



100 μm

$\text{C}_{18\text{O}}$ (at. %)

