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# MECHANICAL BEHAVIOR AT HIGH TEMPERATURE OF HIGHLY OXYGEN- OR HYDROGEN- ENRICHED $\alpha$ AND (PRIOR-) $\beta$ PHASES OF ZIRCONIUM ALLOYS

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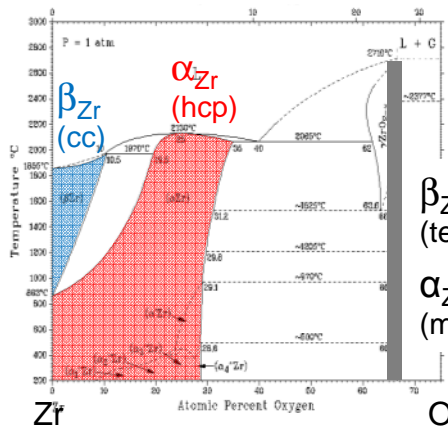
<sup>2</sup> MINES ParisTech, PSL Research University, Centre des matériaux, CNRS UMR 7633, BP 87, 91003 Evry, France

<sup>3</sup> Now at AREVA NP, 69456 Lyon Cedex 06, France

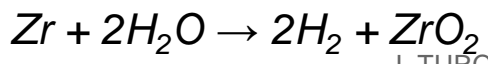
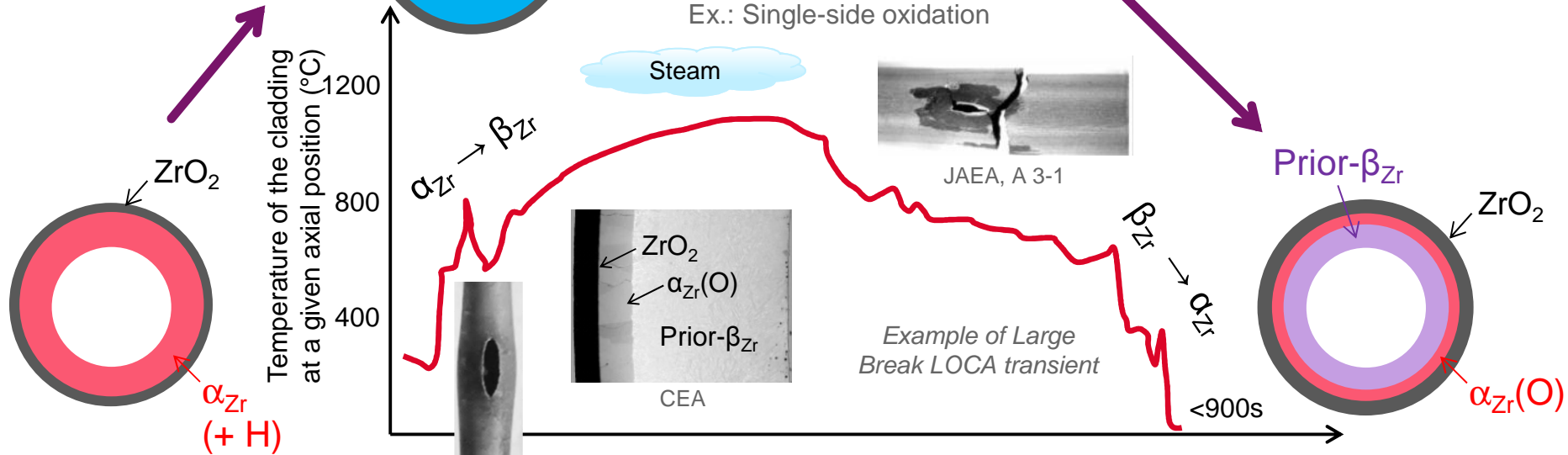
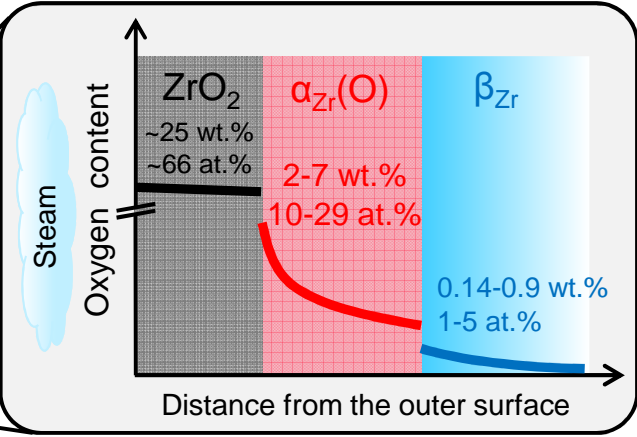
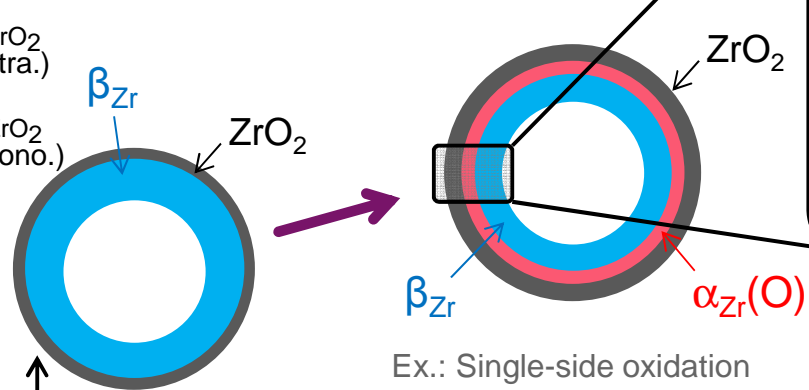
<sup>4</sup> Now at DEN-Service d'Etudes Mécaniques et Thermiques (SEMT), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

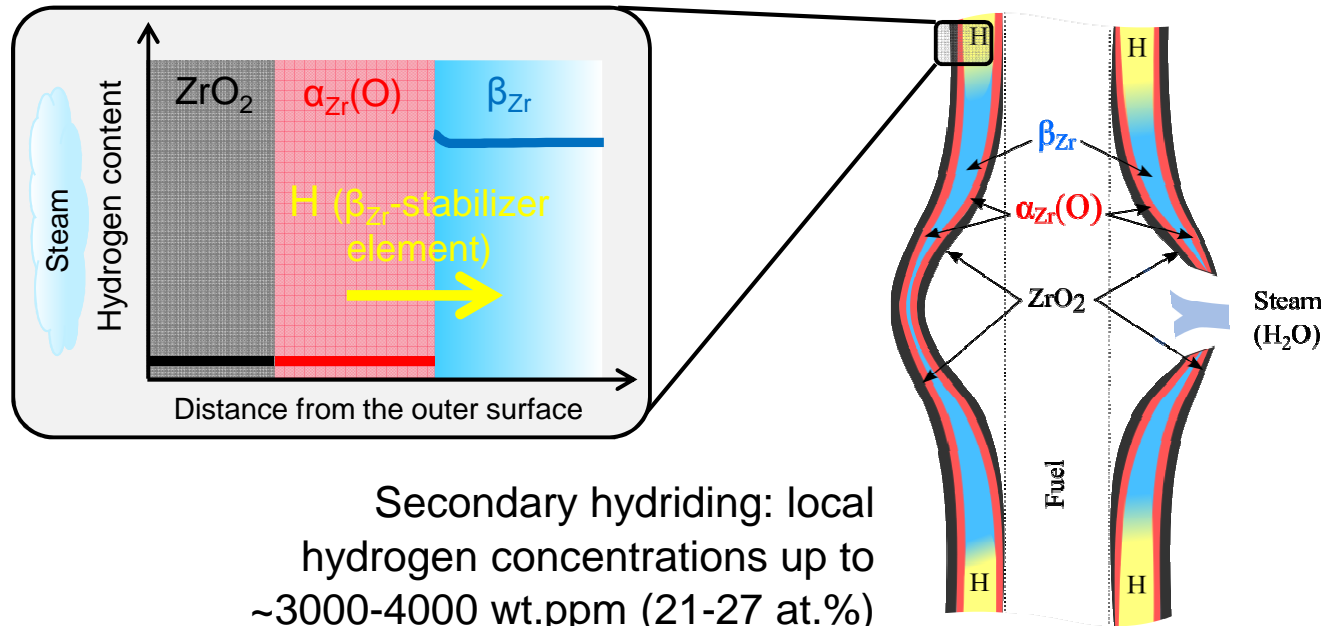
\*Corresponding author, e-mail: [matthieu.lesaux@cea.fr](mailto:matthieu.lesaux@cea.fr)

18<sup>TH</sup> INTERNATIONAL SYMPOSIUM ON ZIRCONIUM IN THE NUCLEAR INDUSTRY, MAY 15-19, 2016, HILTON HEAD, SC, USA



## Loss Of Coolant Accident (LOCA)





Secondary hydriding: local hydrogen concentrations up to ~3000-4000 wt.ppm (21-27 at.%)

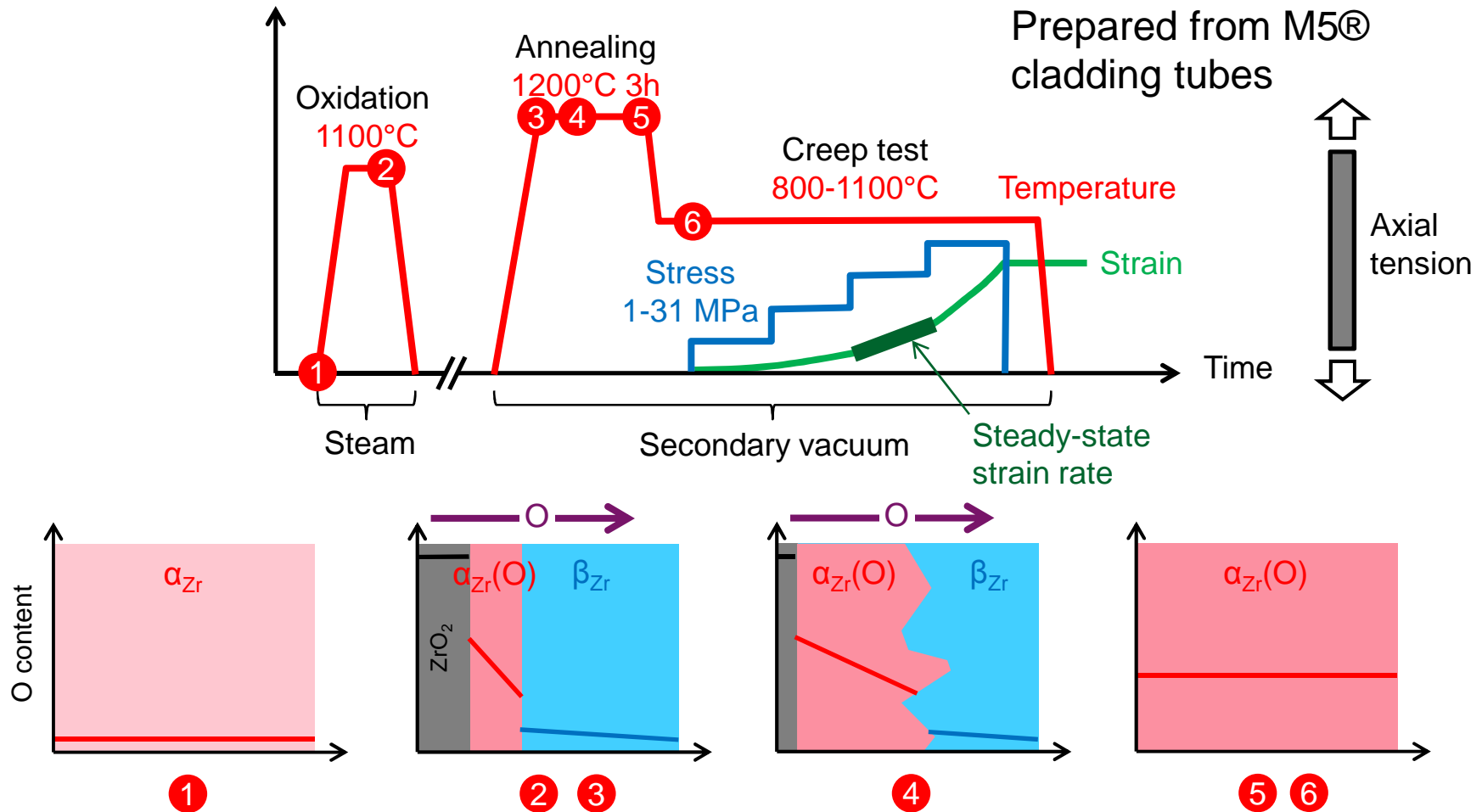
Mechanical behavior and integrity of the oxidized cladding during and after LOCA-like thermal-mechanical transients?

① Mechanical behavior at high temperature of the  $\alpha_{Zr}(O)$  phase containing more than 2 wt.% of oxygen?

② Mechanical behavior at high and low temperature of the (prior-)  $\beta_{Zr}$  phase containing up to 3000 wt.ppm of hydrogen?

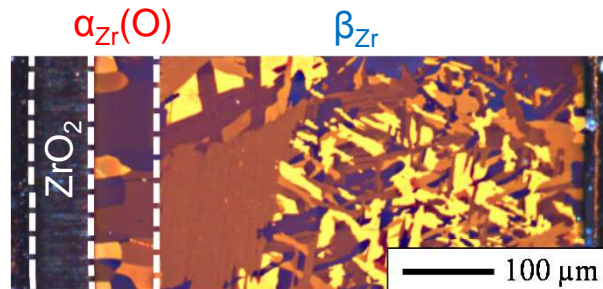
M5 is a registered trademark of AREVA NP in the USA or other countries

## Materials and experimental procedures

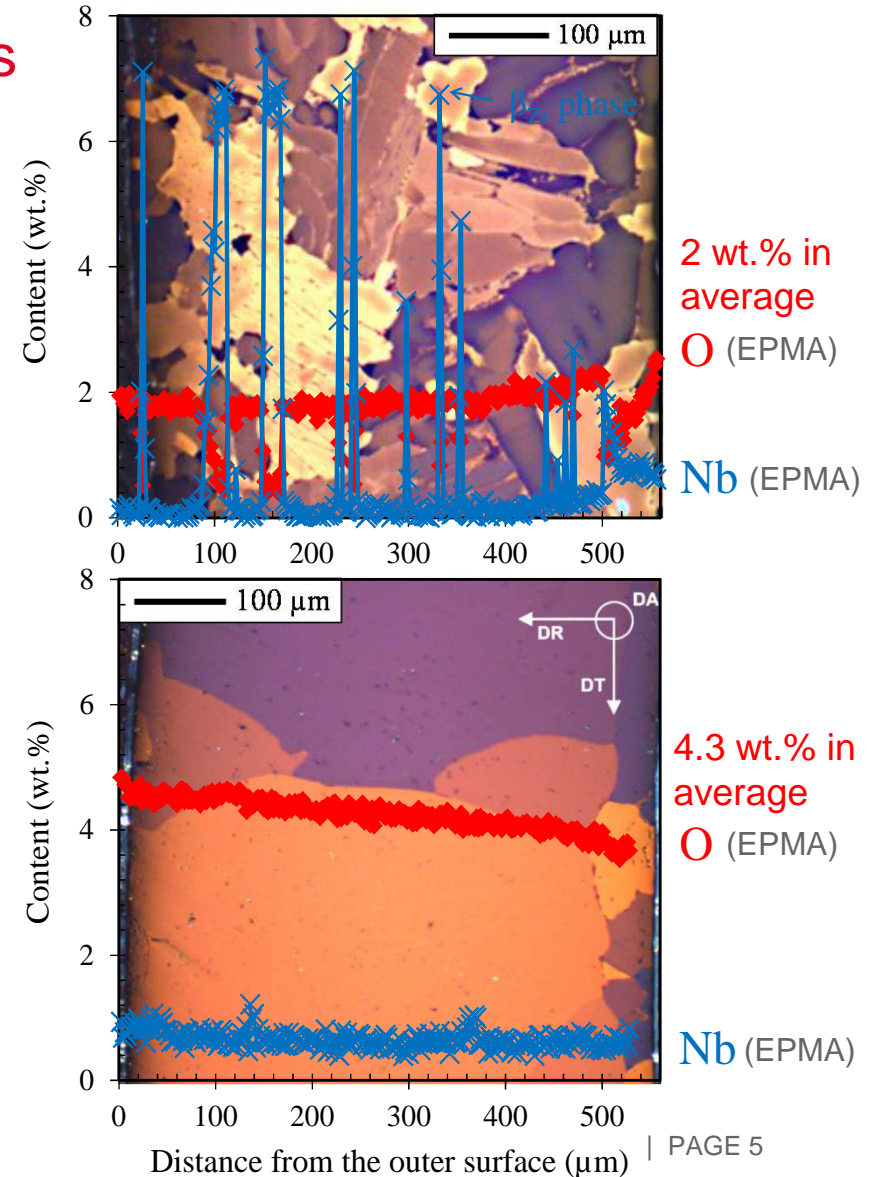


## Microstructure of model materials

- Average oxygen contents:  
2, 3.2, 4.3 and 5.8 wt.%
- Zirconia completely reduced and oxygen concentration rather homogeneous within the samples (with the exception of the one with 5.8 wt.% of O in average)
- Oxygen-enriched model materials mainly composed of  $\alpha_{Zr}(O)$  grains, enriched in O and depleted in Nb and Fe (0 to 15% of residual untransformed  $\beta_{Zr}$  phase)
- Coarse lamellae or large grains ( $\geq 100 \mu\text{m}$ )

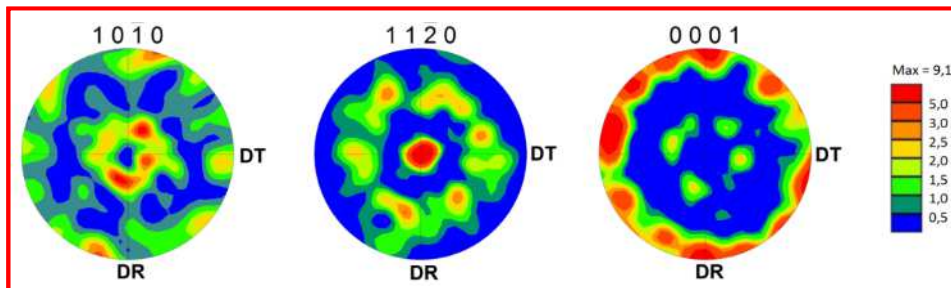


Zircaloy-4, oxidized 600s in steam at 1100°C



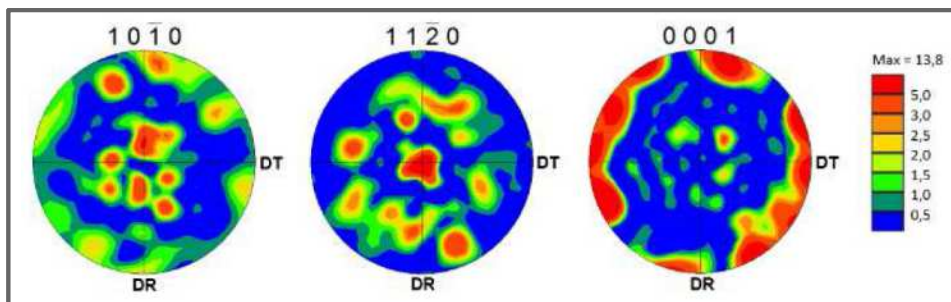
## Microstructure of model materials

- Texture (EBSD, neutron diffraction) comparable to that measured for the  $\alpha_{Zr}(O)$  phase formed during oxidation in steam at HT



Model  $\alpha_{Zr}(O)$  phase with 2 wt.% of O in average

≈

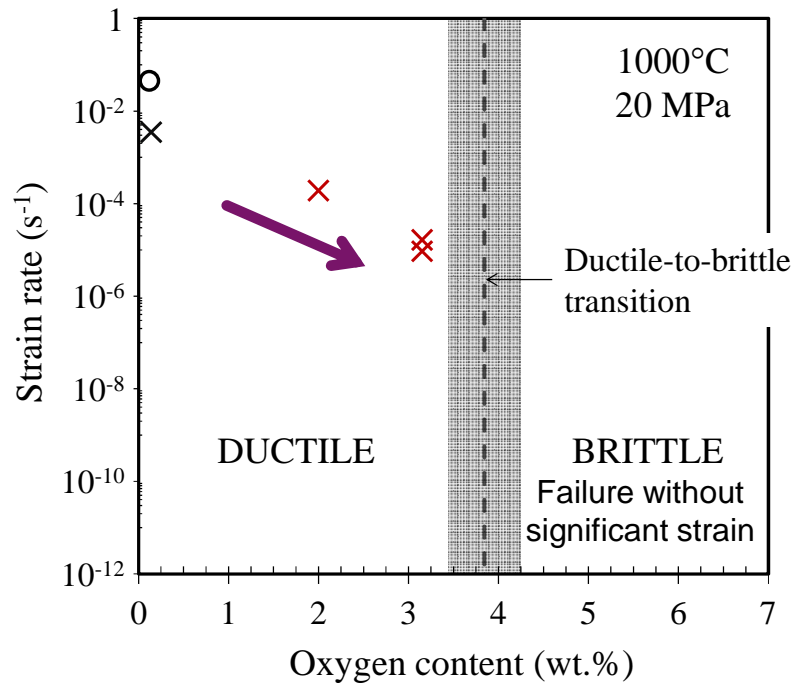


$\alpha_{Zr}(O)$  layer formed during oxidation in steam at 1100°C on a M5® cladding tube

- ➔ Model  $\alpha_{Zr}(O)$  phase reasonably representative of the  $\alpha_{Zr}(O)$  phase observed in claddings oxidized at HT

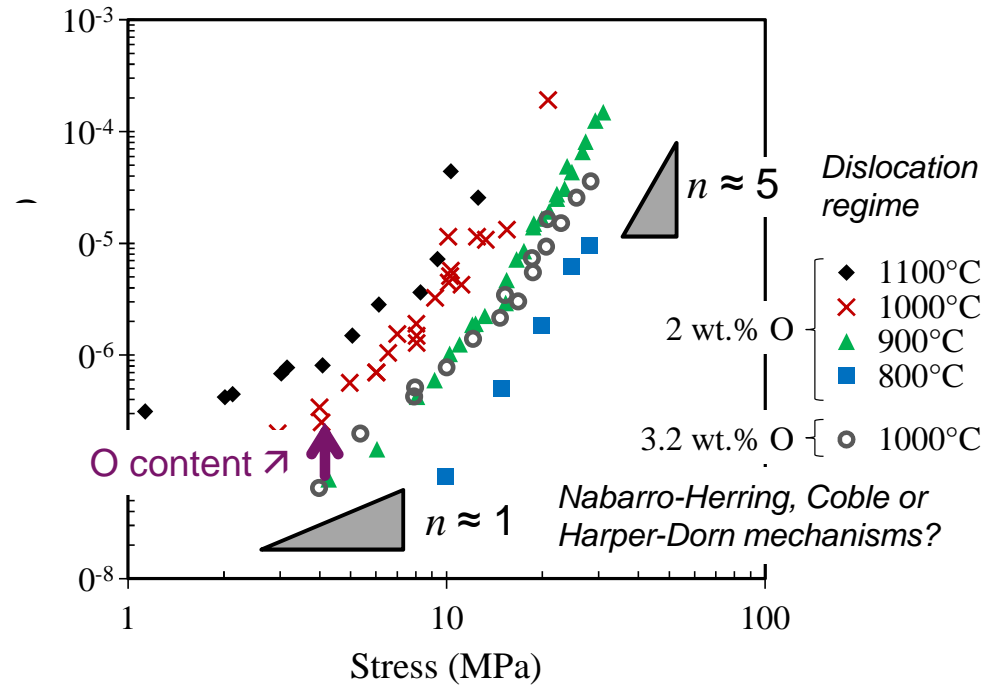
## Viscoplastic flow

- Two creep regimes, depending on stress level



Tests {  $\times$  Model  $\alpha_{Zr}(O)$  material (this study)

Extrapolated models {  $\times$  M5® (Kaddour *et al.*, 2004)  
 $\bullet$  Zircaloy-4 (Kaddour *et al.*, 2004)



- Creep resistance increases with increasing the oxygen content (e.g. strain rate of  $\alpha_{Zr}(2 \text{ wt.\% O})$  100-1000 times slower than that of  $\alpha_{Zr}$  phase without O addition)



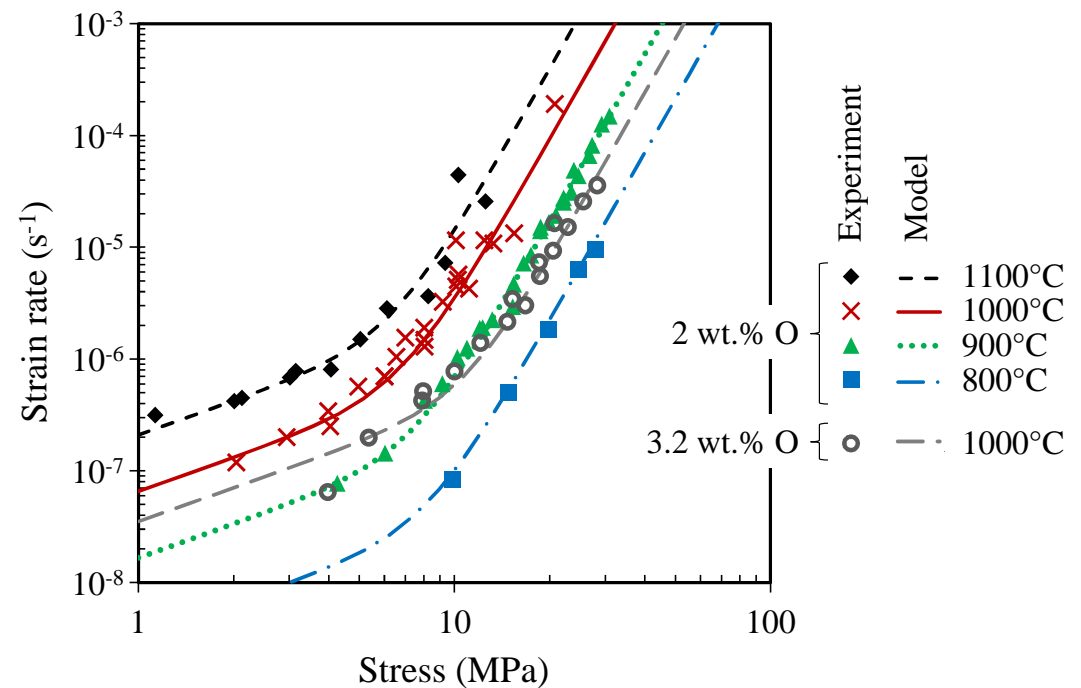
## Viscoplastic flow

### ■ Modeling:

$$\dot{\epsilon} = \frac{A}{T} \exp\left(-\frac{Q}{RT}\right) \sigma^n \exp(-BC_o)$$

strain rate  $\downarrow$  stress  $\downarrow$  oxygen content  $\downarrow$   
 $\uparrow$  temperature

Strain regime	$A$ (K.MPa <sup>-n</sup> .s <sup>-1</sup> )	$n$	$Q$ (kJ.mol <sup>-1</sup> )	$B$
Linear	$5.75 \cdot 10^3$	1	180	0.53
Power-law	$4.80 \cdot 10^3$	5	222	2.29



Effect of the residual  $\beta_{Zr}$  phase relatively small

## Viscoplastic flow

■ Modeling:

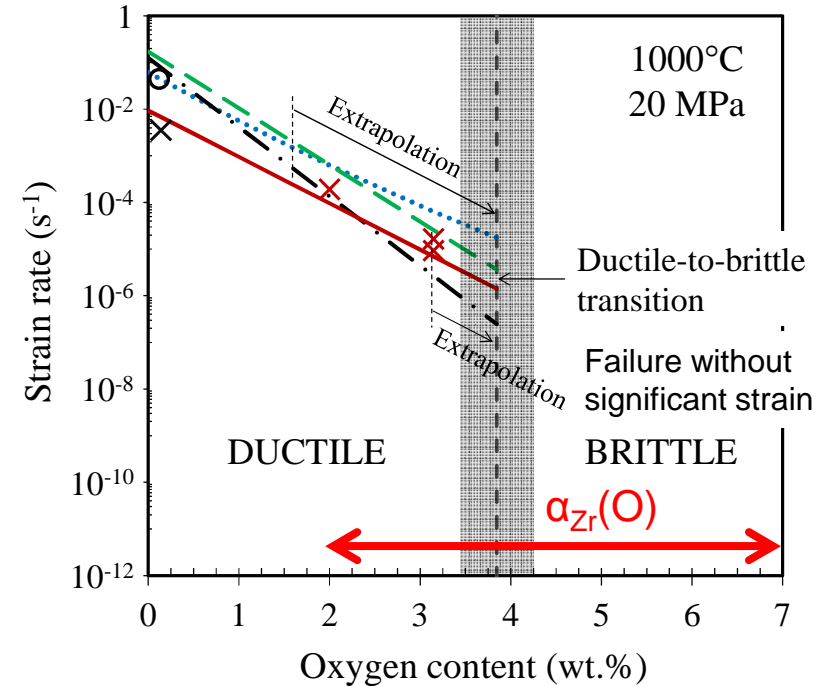
$$\dot{\epsilon} = \frac{A}{T} \exp\left(-\frac{Q}{RT}\right) \sigma^n \exp(-BC_o)$$

strain rate
stress
oxygen content  
↓
↓
↓  
 $\dot{\epsilon}$ 
 $=$ 
 $\frac{A}{T}$ 
 $\exp\left(-\frac{Q}{RT}\right)$ 
 $\sigma^n$ 
 $\exp(-BC_o)$   
↑

  
temperature

Strain regime	A (K.MPa <sup>-n</sup> .s <sup>-1</sup> )	n	Q (kJ.mol <sup>-1</sup> )	B
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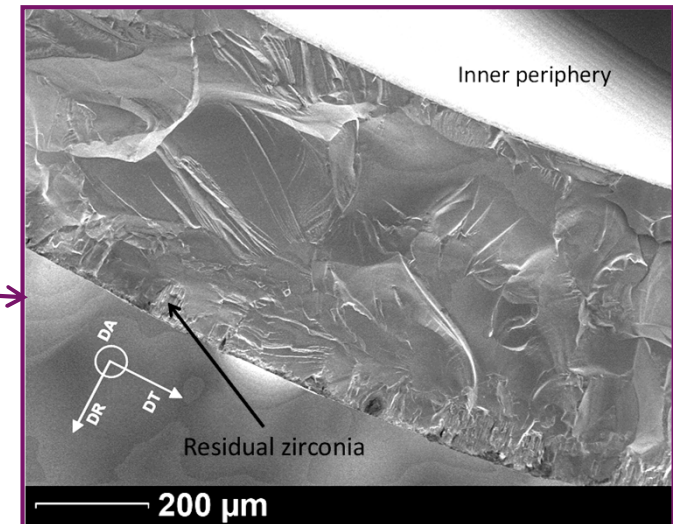
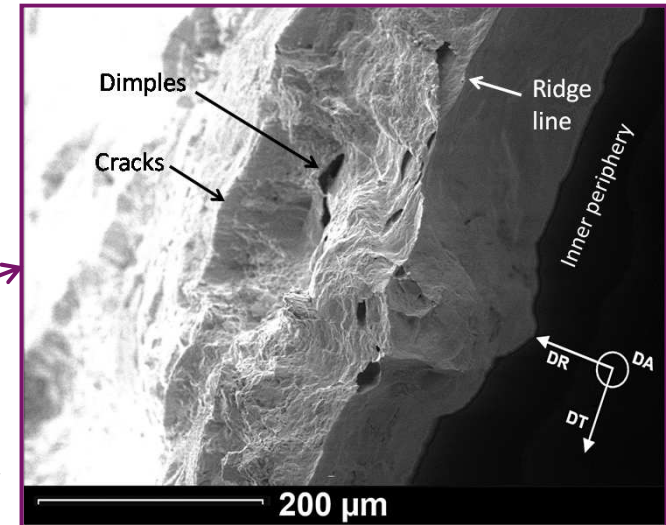
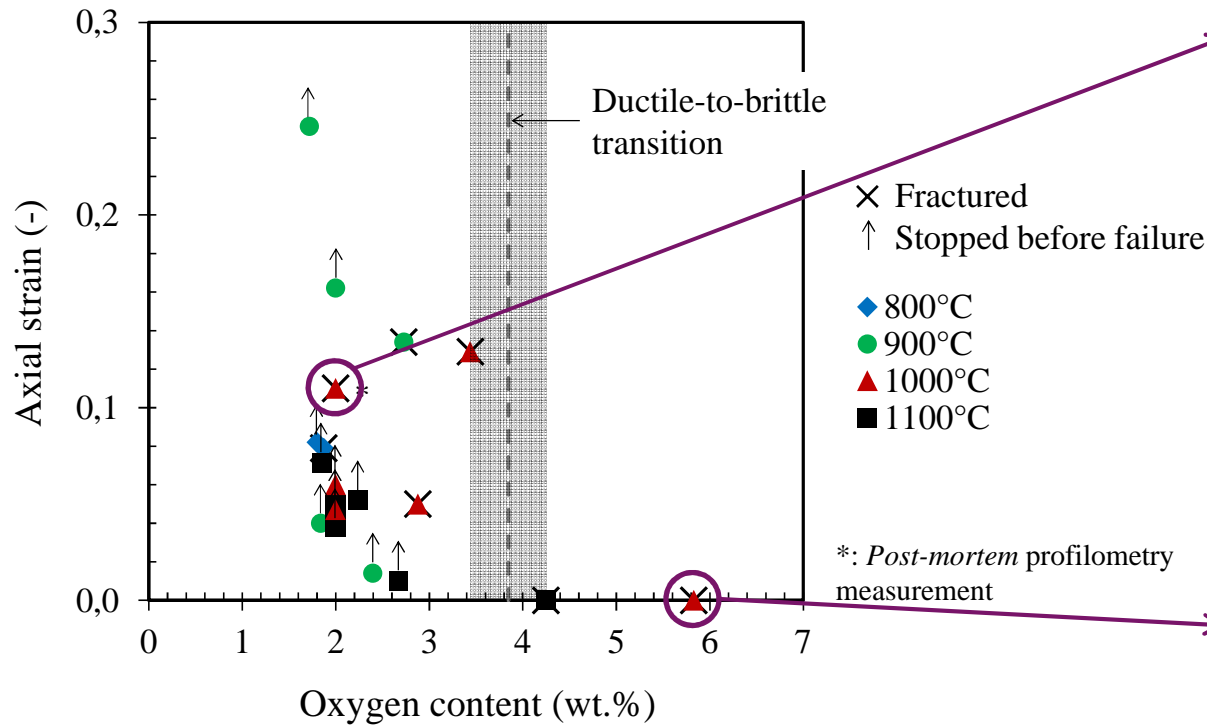


Tests { × Model  $\alpha_{Zr}(O)$  material (this study)

Models {

- $\alpha_{Zr}(O)$  (this study)
- × M5® (Kaddour *et al.*, 2004)
- Zircaloy-4 (Kaddour *et al.*, 2004)
- ⋯ Zircaloy-2 (Donaldson and Evans, 1981)
- · Zircaloy-2 (Burton *et al.*, 1979)
- · Zircaloy-4 (Chow *et al.*, 1982)

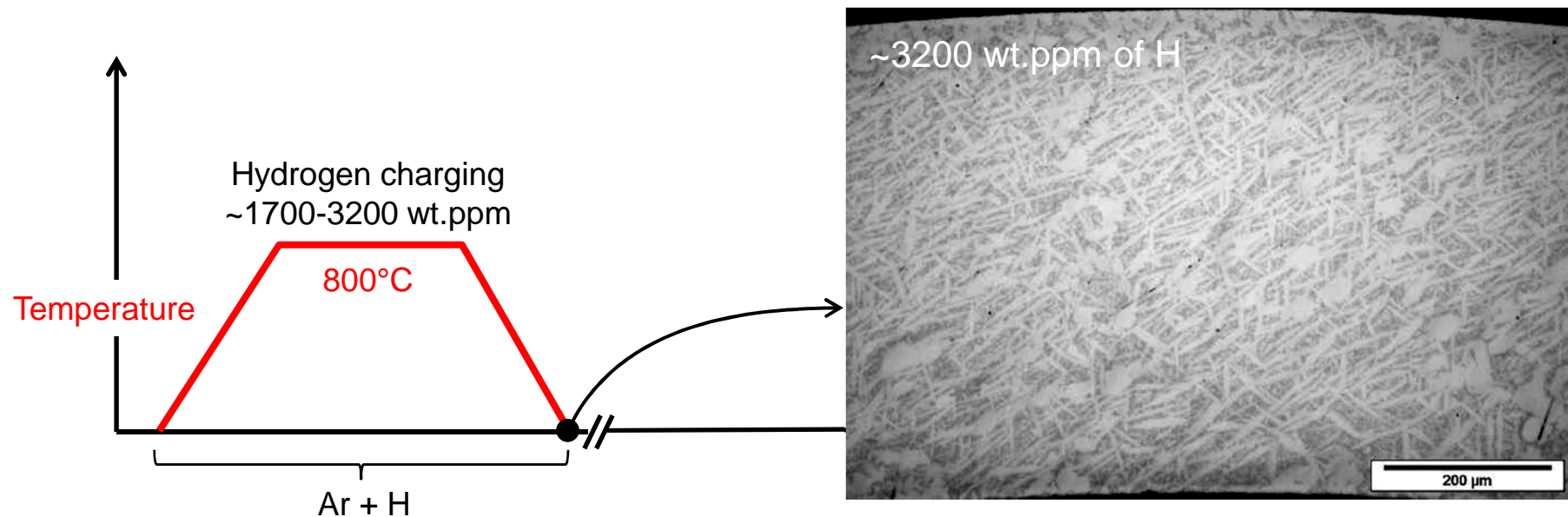
## Fracture



② Mechanical behavior between et low ad high temperature of the (prior-)  $\beta_{Zr}$  phase containing up to 3000 wt.ppm of hydrogen?

## Materials and experimental procedures

Prepared from low-tin Zircaloy-4 cladding tubes

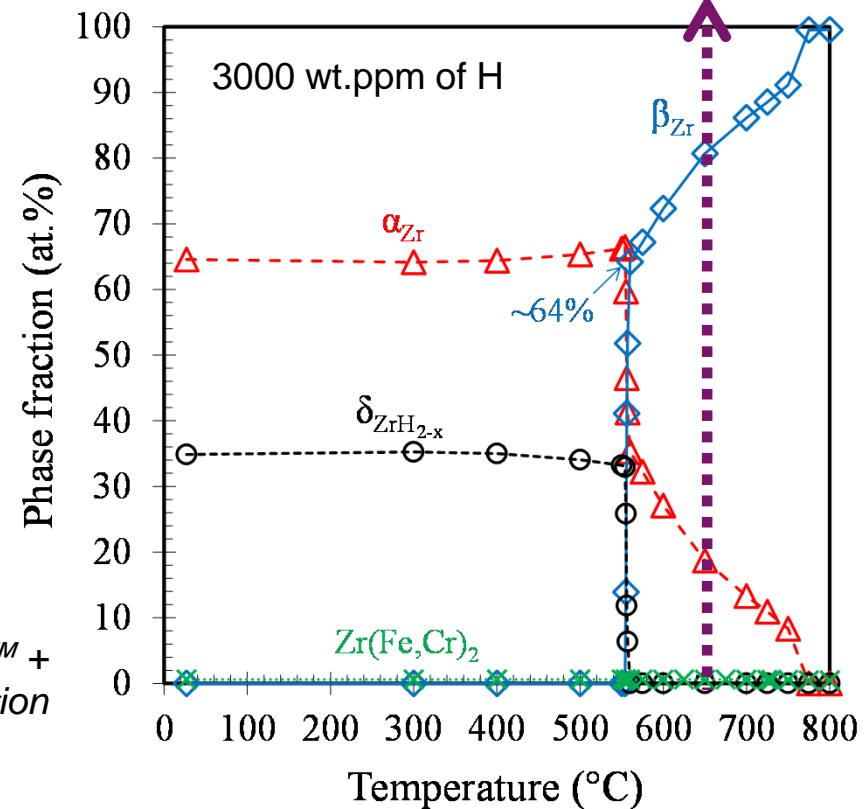
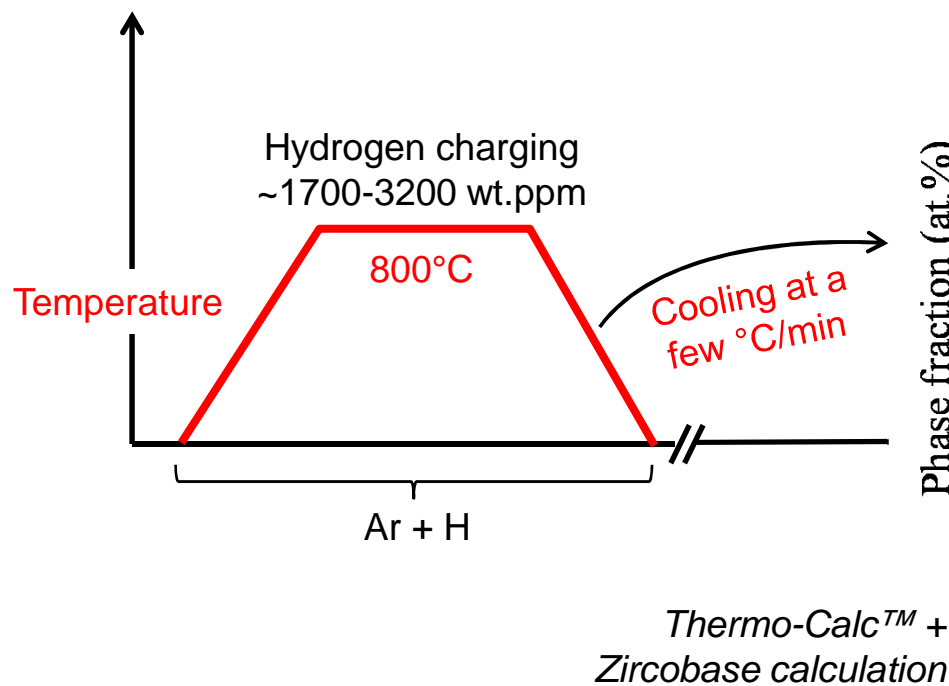
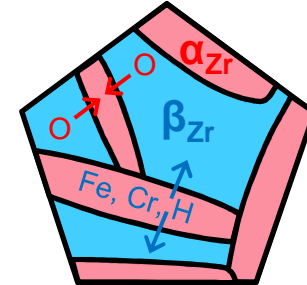


Hydrogen content measured for each sample by using an inert gas fusion thermal conductivity technique (+ DSC,  $\mu$ -ERDA and neutron radiography on a selected number of samples)

→ Satisfactory homogeneity of hydrogen content within the samples

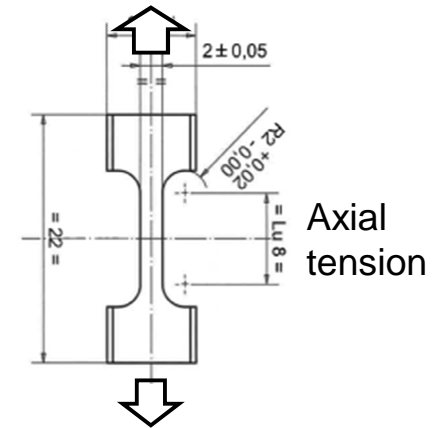
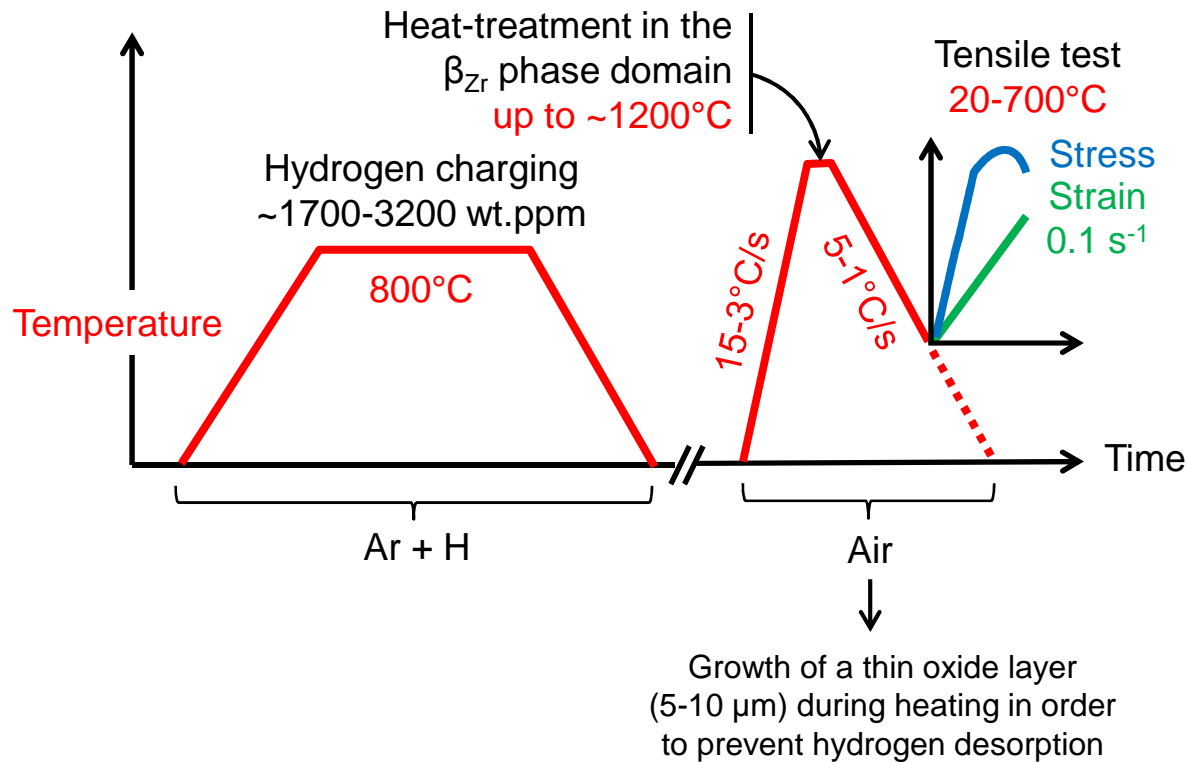
## Materials and experimental procedures

Partitioning of chemical elements between  $\beta_{Zr}$  and  $\alpha_{Zr}$  (prior- $\beta_{Zr}$ ) phases during cooling and  $\beta_{Zr}$  to  $\alpha_{Zr}$  phase transformation



## Materials and experimental procedures

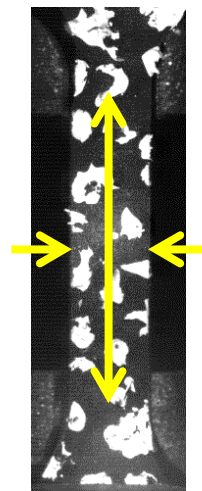
Prepared from low-tin Zircaloy-4 cladding tubes



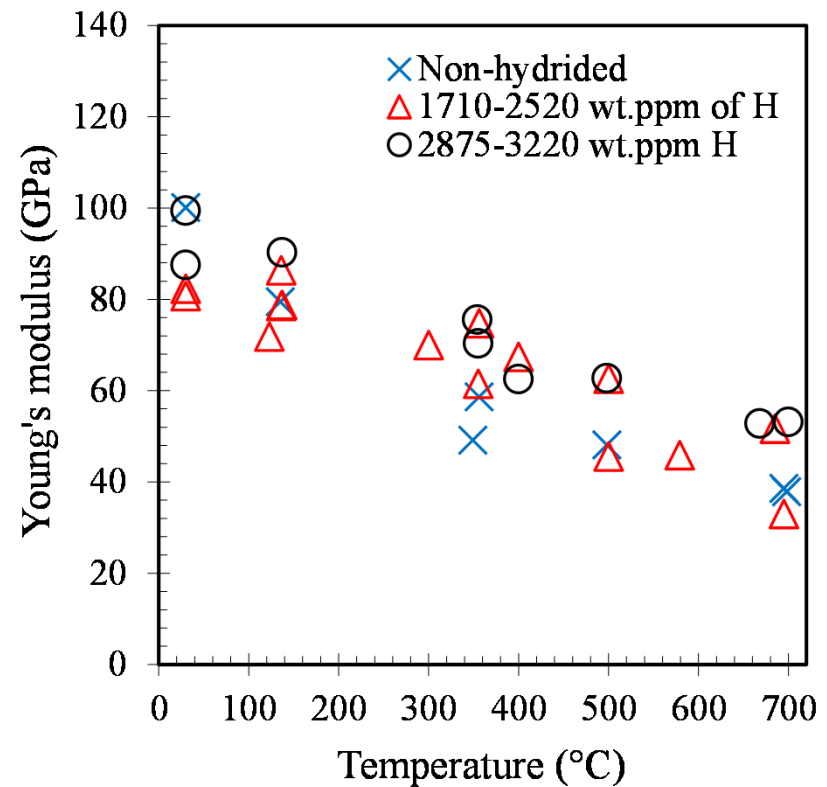
fast strain rate in order to minimize metallurgical evolutions and oxidation of the material during the test (faster than the rates at which the cladding can be subjected during a LOCA transient)

## Elasticity and plastic isotropy

- Young's modulus and plastic isotropy not significantly modified by the presence of high H contents



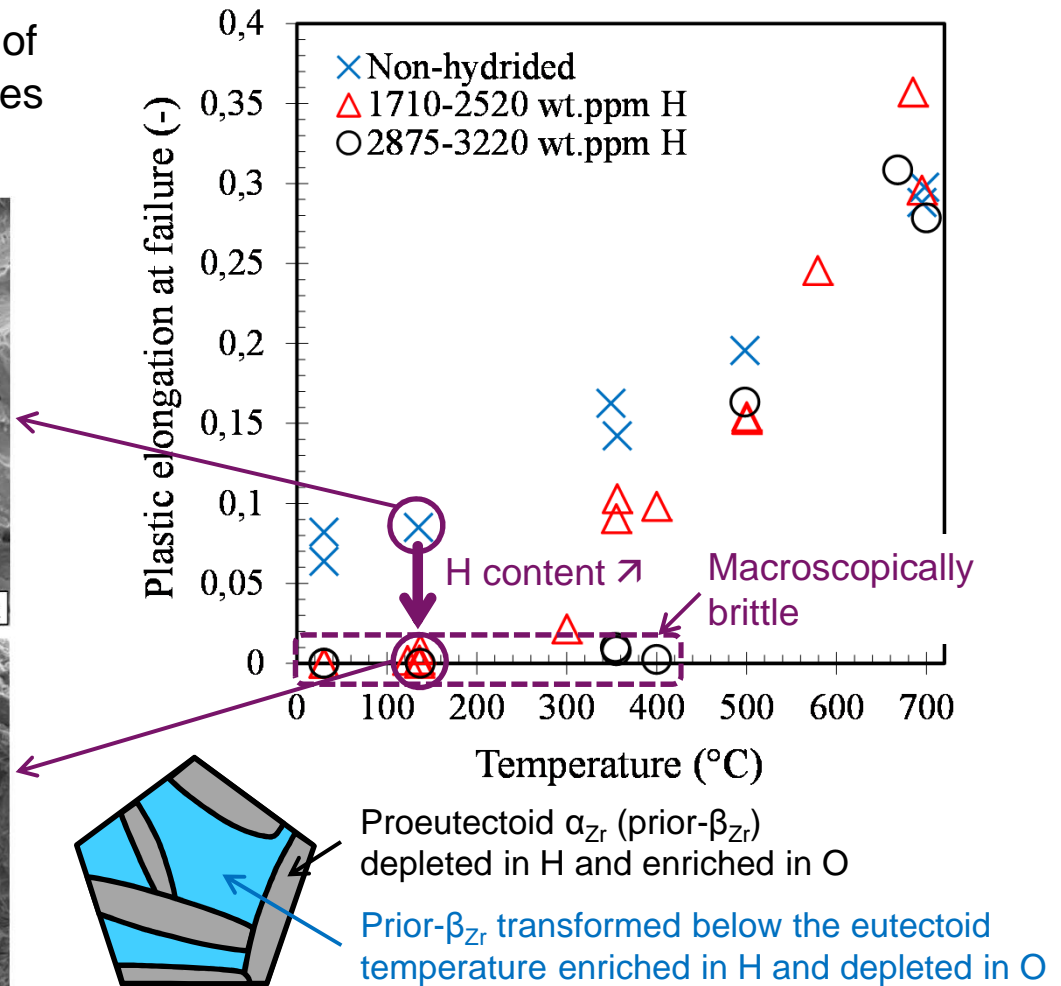
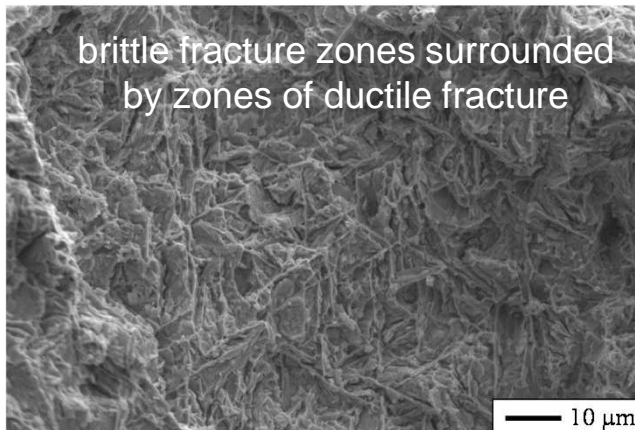
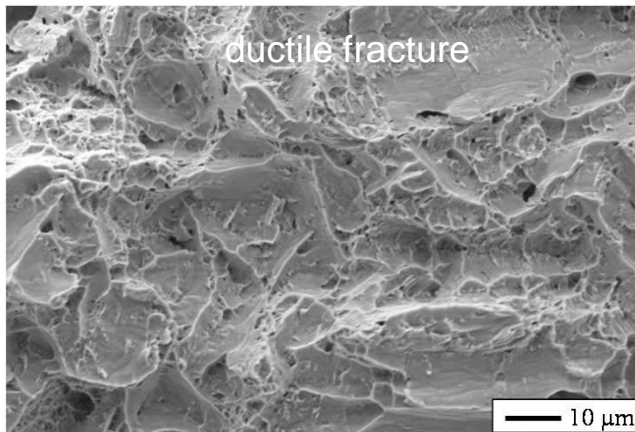
2D digital image correlation  
→ Young's modulus and plastic strain anisotropy





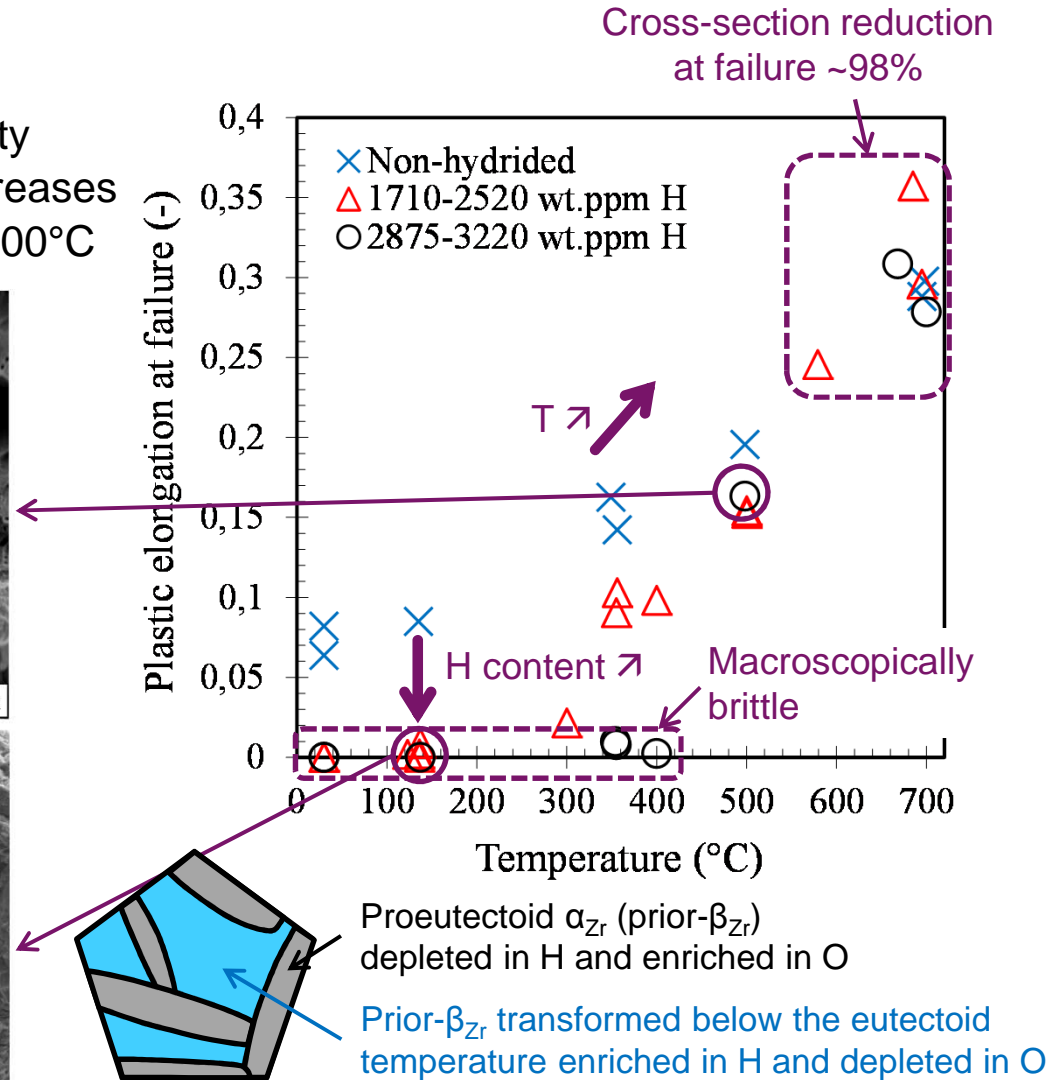
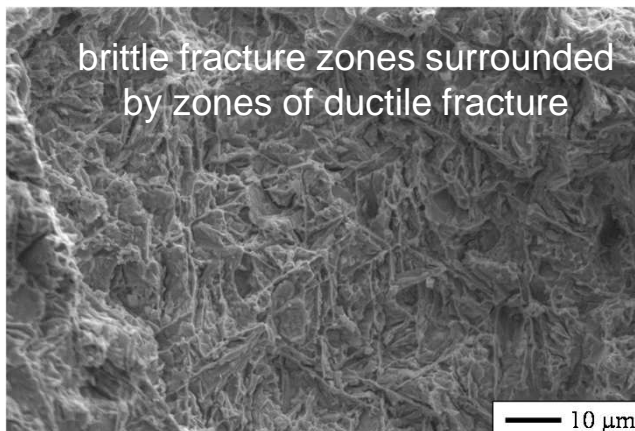
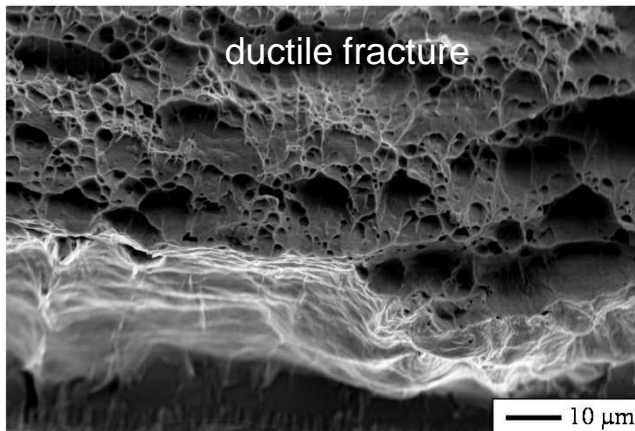
## Fracture

- Material embrittled by H contents of 2000-3000 wt.ppm for temperatures below 500°C



## Fracture

- Effect of H on macroscopic ductility diminishes when temperature increases and becomes negligible beyond 500°C

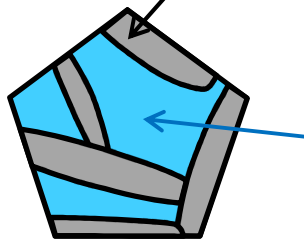


## Plasticity

- When the behavior is macroscopically ductile, the flow stress of the (prior-)  $\beta_{Zr}$  phase containing between 1700 and 3200 wt.ppm of H is, compared to the one of the non-hydrided material

— higher at 500°C and below

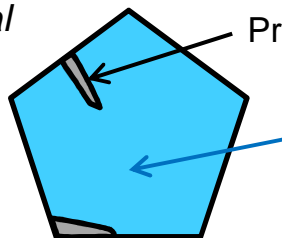
Proeutectoid  $\alpha_{Zr}$  enriched in O and depleted in H



Prior- $\beta_{Zr}$  transformed below the eutectoid temperature, depleted in O but containing a very large amount of H at least partially precipitated under the form of strengthening nano-hydrides

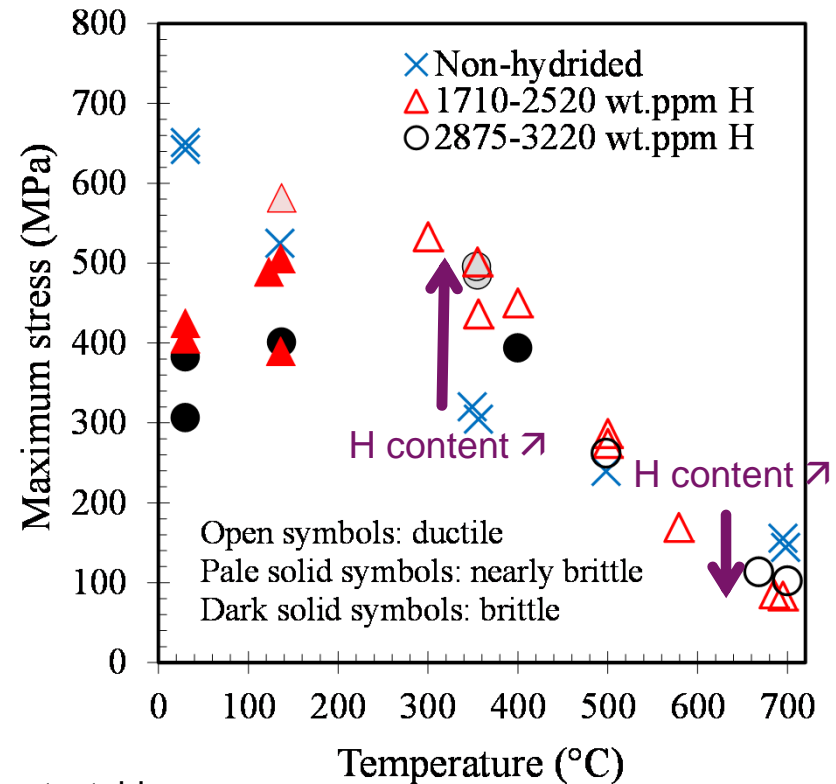
Figure: Highly hydrided material

— lower at 700°C



Proeutectoid  $\alpha_{Zr}$

$\beta_{Zr}$  with all H in solid solution



Oxygen and hydrogen are known to be the main parameters responsible for embrittlement of zirconium alloys

① Mechanical behavior **between 800 and 1100°C** of the  $\alpha_{\text{Zr}}(\text{O})$  phase containing **between 2 and 5.8 wt.% of oxygen?**

- Creep resistance of the oxygen-enriched  $\alpha_{\text{Zr}}(\text{O})$  material increases with increasing O content, significantly higher than the creep resistance of the as-received material without additional O
- Two creep regimes observed: power-law regime for stresses higher than 15 MPa and nearly linear regime for lower stresses (further investigation needed to identify the mechanisms that drive the linear creep regime)
- Model  $\alpha_{\text{Zr}}(\text{O})$  materials ductile between 800 and 1100°C for O contents between 2 and 3.2 wt.%, brittle, even at 1100°C, for O contents higher than 4 wt.%

② Mechanical behavior between 20 and 700°C of the (prior-)  $\beta_{Zr}$  phase containing between 1700 and 3200 wt.ppm of hydrogen?

- Young's modulus and plastic isotropy not substantially modified by H
- Material embrittled by H contents of 1700-3200 wt.ppm for temperatures below 500°C: macroscopically brittle at 135°C and below for average H content of ~2000 wt.ppm and at 350-400°C for ~3000 wt.ppm of H (further work to be done to determine the underlying mechanisms responsible for the effects of high H contents)
- Effect of H on macroscopic ductility diminishes when temperature increases and becomes negligible beyond 500°C
- When the behavior is macroscopically ductile, the flow stress of the material containing between 1700 and 3200 wt.ppm of H is higher than the one of the non-hydrided material at 500°C and below, and lower at 700°C

# Thank you for your attention

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