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# Secondary hydriding of zirconium-based fuel claddings at high temperature (LOCA conditions). Part 2: Effect of high hydrogen contents on metallurgical and mechanical properties. Part 1: Multi-scale study of hydrogen distribution

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23rd QUENCH workshop, October 17-19, 2017 Karlsruhe, Germany

## SECONDARY HYDRIDING OF ZIRCONIUM-BASED FUEL CLADDINGS AT HIGH TEMPERATURE (LOCA CONDITIONS)

### PART 2: EFFECT OF HIGH HYDROGEN CONTENTS ON METALLURGICAL AND MECHANICAL PROPERTIES

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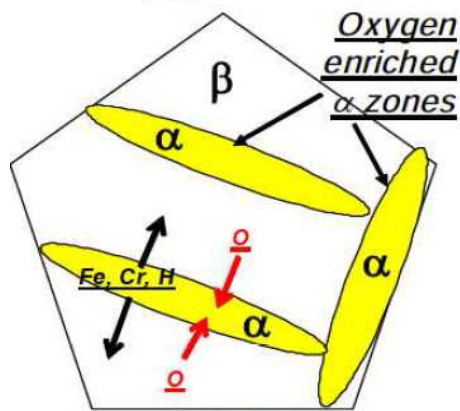
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<sup>2</sup> MINES ParisTech, PSL Research University, Centre des Matériaux, CNRS UMR 7633, BP 87, 91003 Evry, France

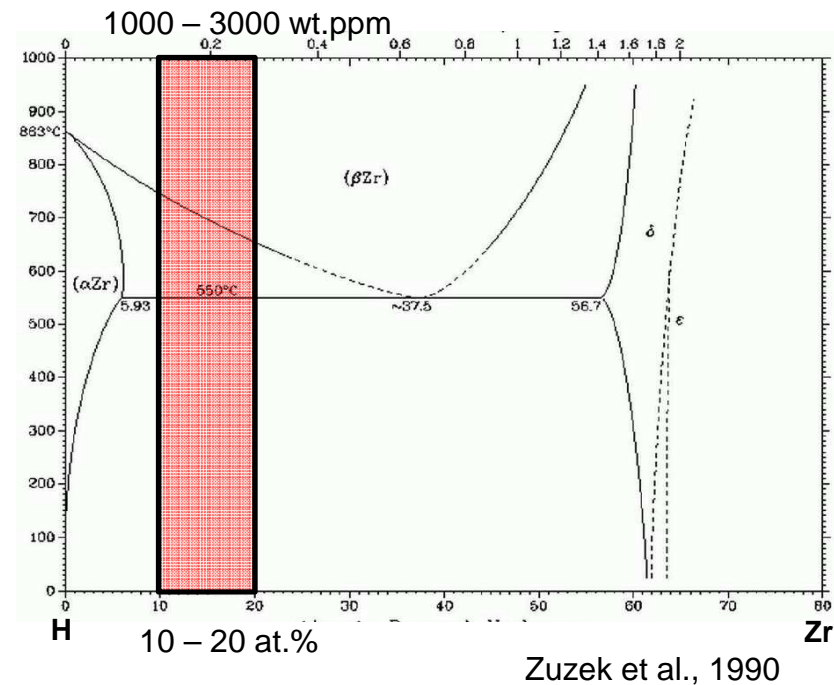
<sup>3</sup> Now at DEN-Service d'Etudes des Matériaux Irradiés (SEMI), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

- Scientific context of this work and motivation/challenges have been presented by J-C. Brachet in “Secondary hydriding of zirconium based fuel claddings at high temperature (LOCA conditions). Part 1: Multi-scale study of hydrogen distribution”

- Study the coupled effects of oxygen (0,14-0,9wt.%) and high hydrogen contents (1000-3000 wt.ppm) on the metallurgical and mechanical properties of fuel claddings in zirconium based alloys, Zircaloy-4 and M5, during and after cooling/quenching from high temperature ( $\beta_{Zr}$  domain), *i.e.* LOCA conditions



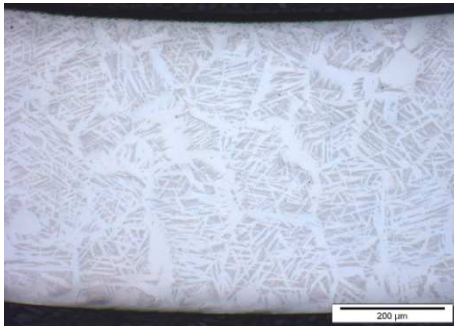
Heterogeneous “micro-composite” prior- $\beta$  microstructure



This presentation : Effects of high hydrogen contents (up to 3000 wt.ppm)

Model materials homogeneously charged in hydrogen at 1000-3000 wt.ppm under hydrogenated Ar at 800°C, prepared from Zircaloy-4 and M5™\* fuel cladding tube specimens

- ❖ Heat-treatment in the  $\beta$  phase temperature domain (1000°C)
- ❖ Cooling down to RT, water quenching or slow cooling, for studying the effects of cooling scenario



Microstructure of a tube in M5 prehydrogenated at 2000 wt.ppm under hydrogenated Ar at 800°C

**Metallurgical characterizations** (phase fractions, phase transition temperatures and evolution of lattice parameters) :

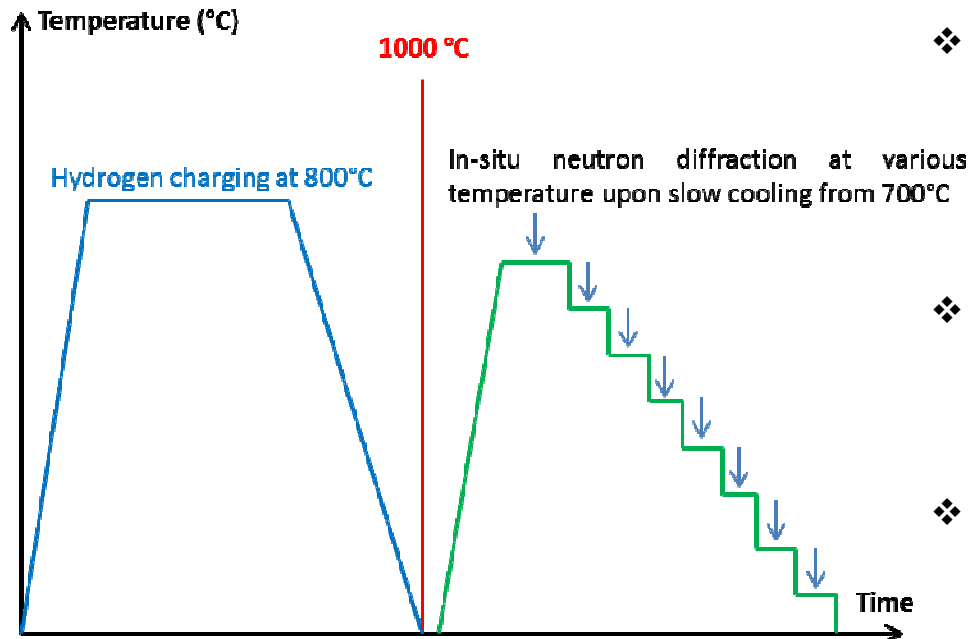
- ❖ In situ neutron diffraction during cooling from 700°C down to 20°C
- ❖ Neutron and X-ray diffraction at RT
- ❖ Comparison to thermodynamic equilibrium prediction obtained by Thermo-Calc and Zircobase thermodynamic database

**Mechanical characterizations :**

- Uniaxial tensile tests at various temperatures (700°C-30°C) during cooling from high temperatures

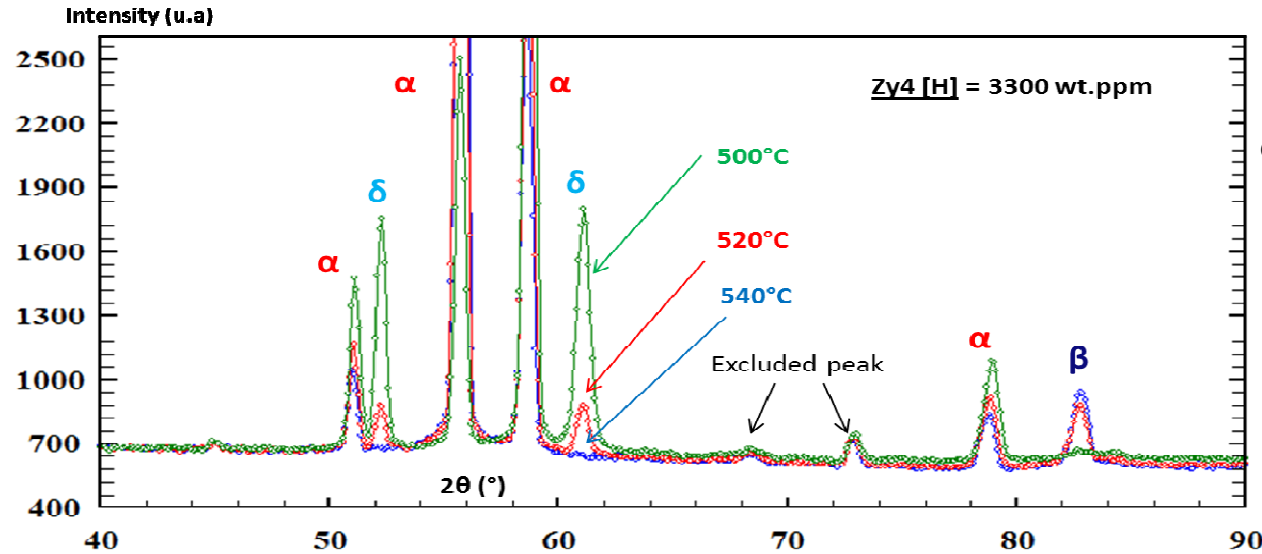
**METALLURGICAL PROPERTIES OF  
PREHYDRIDED MATERIALS**

## In situ neutron diffractions



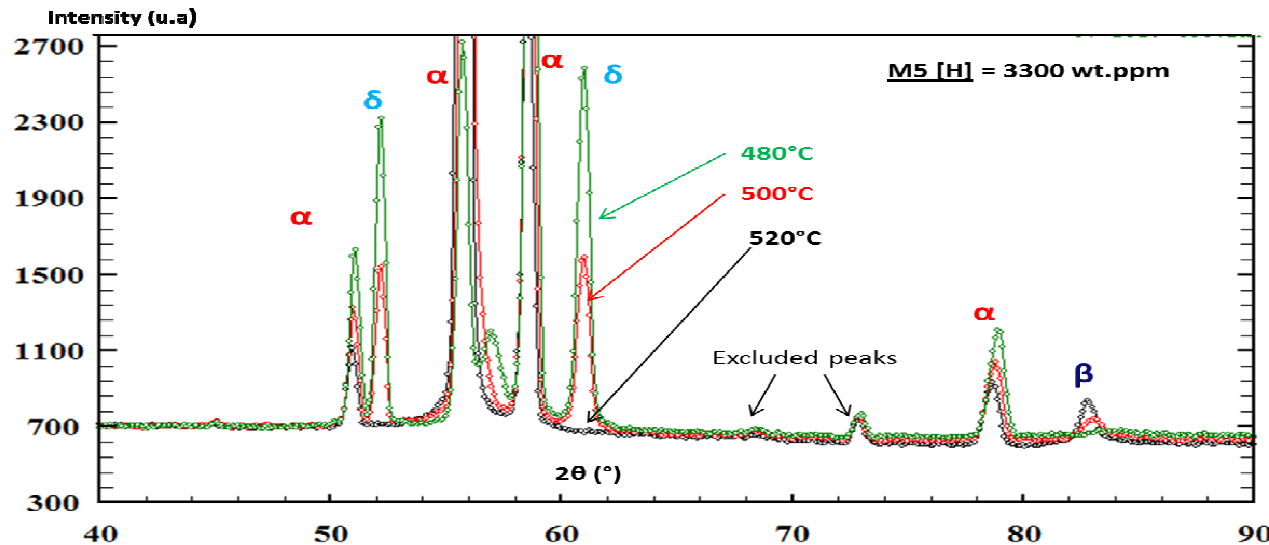
- ❖ **Experimental conditions:** Data acquisition at various temperatures during slow cooling from 700°C (near-equilibrium conditions) to RT
- ❖ **Objectives:** Phase transition temperatures and metallurgical evolutions
- ❖ **Refinement method:** Rietveld refinement and Fullprof software

## Eutectoid transformation temperature



Neutron diffraction diagrams obtained for prehydrided Zy4 and M5 at 3300 wt.ppm, during slow cooling from 700°C after heat-treatment at 1000°C in steam

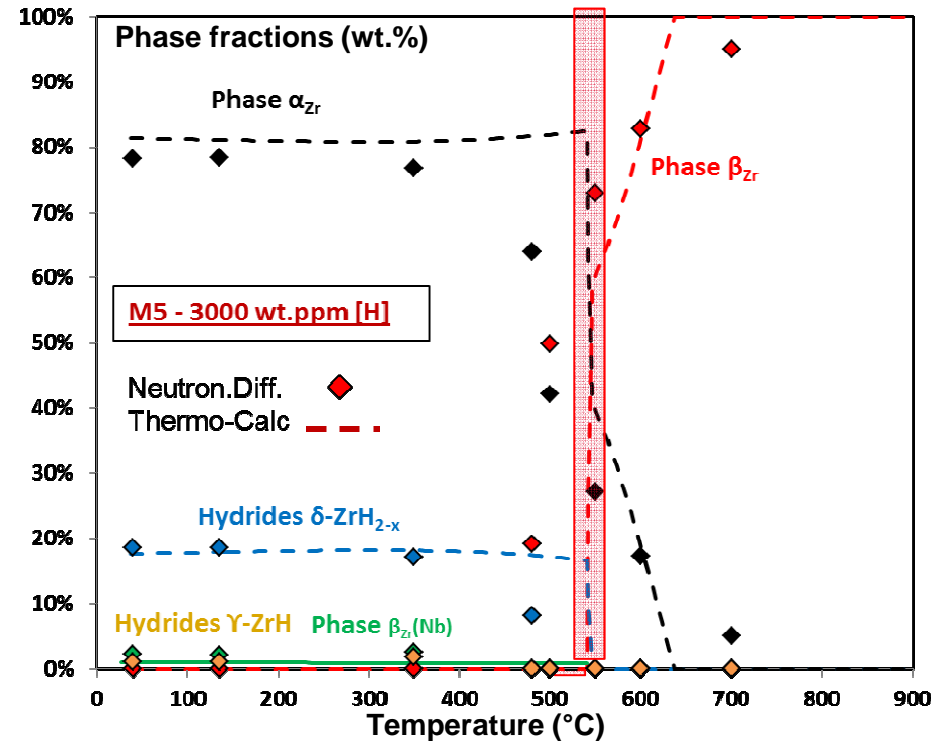
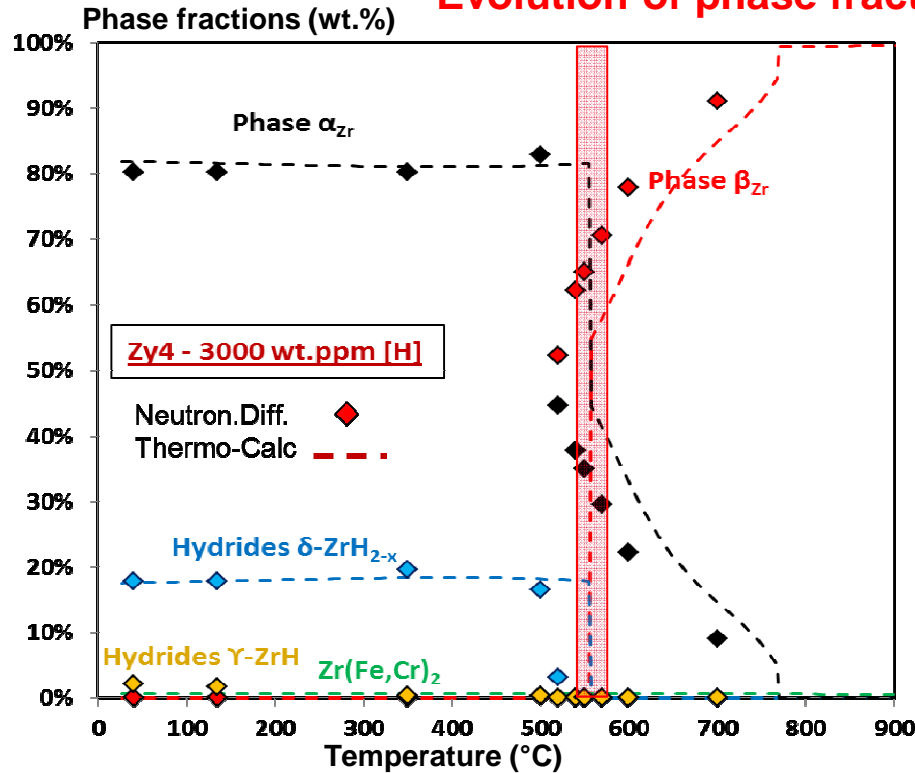
- ❖  $\delta$ -ZrH<sub>2-x</sub> starts to precipitate in Zy4-3300H at ~ 540°C
- ❖ Temperature range of co-existence  $\alpha + \beta + \delta$  : 520°C-540°C



- ❖ Apparition of  $\delta$ -ZrH<sub>2-x</sub> hydrides in M5-3300H at ~520°C
- ❖ Temperature range of co-existence  $\alpha + \beta + \delta$  : 480°C-520°C



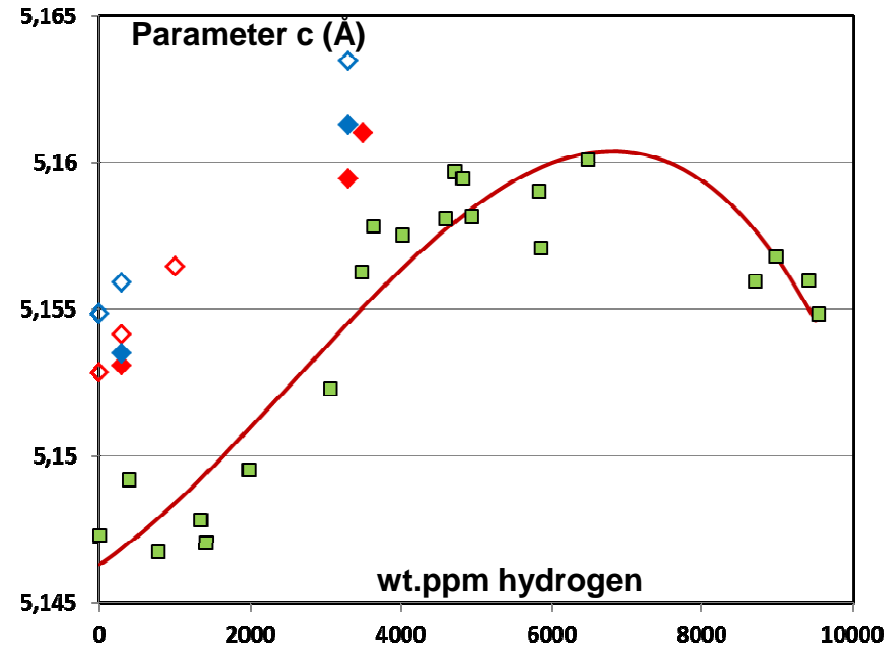
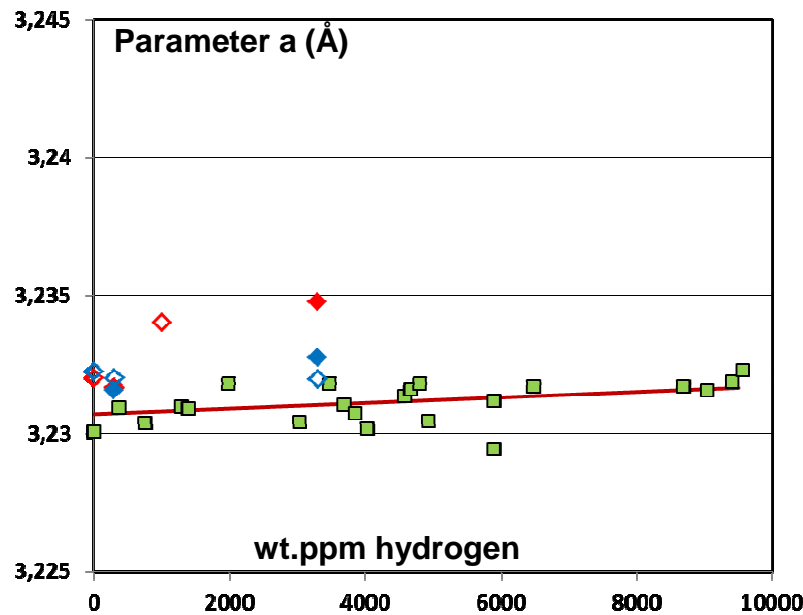
## Evolution of phase fractions with temperature



- ❖ Good agreement between Thermo-Calc prediction and neutrons diffraction data
- ❖ Phase transition temperature of M5 < Zy4 because of the presence of Nb
- ❖ Apparition of  $\gamma-ZrH$  hydrides (~2 wt.%) (potentially metastable) at the end of cooling in both cases
- ❖ Not shown here but presence of metastable  $\gamma-ZrH$  hydrides also observed at room temperature in the materials heat-treated at high temperature containing lower quantities of hydrogen (~300 wt.ppm)

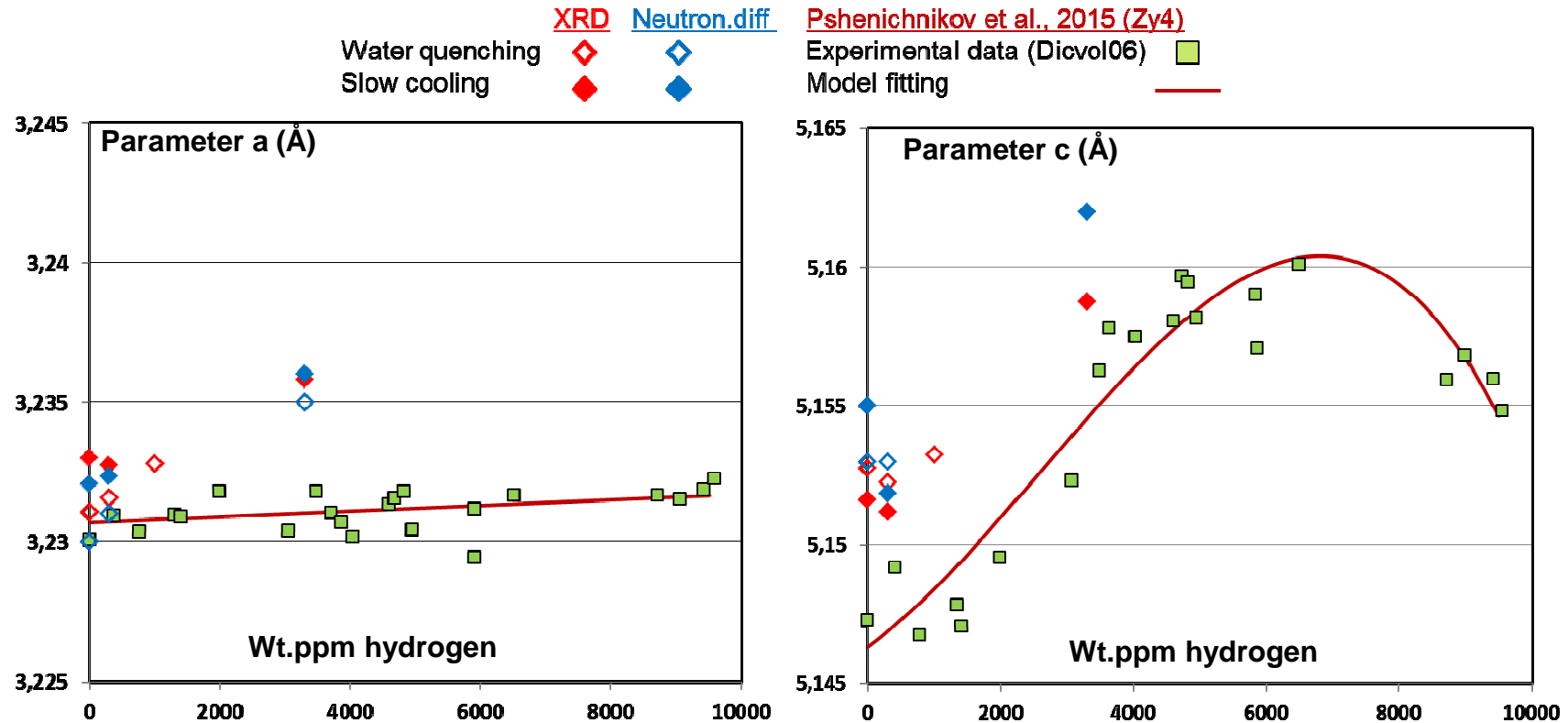
Evolution of lattice parameters – Diffraction at RT (case Zy4)

◇ XRD Water quenching  
◇ Neutron.diff Slow cooling  
■ Pshenichnikov et al., 2015 (Zy4) Experimental data (Dicvol06)  
— Model fitting



The results of both CEA XRD and neutrons diffraction at room temperature show a relative a and c parameters increase as a function of the mean H content, as already observed by KIT for Zy4

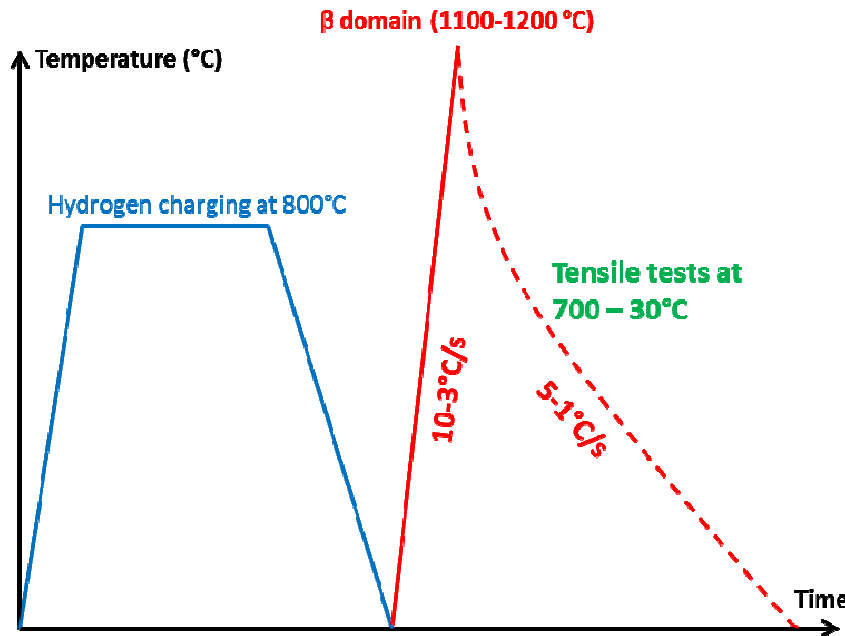
Evolution of lattice parameters – Diffraction at RT (case M5)



Similar results obtained for M5

*Pshenichnikov et al., 2015. Microstructure and mechanical properties of Zircaloy-4 cladding hydrogenated at temperature typical for loss-of-coolant accident (LOCA) conditions. Nuclear Engineering and Design 238, 33-39.*

**MECHANICAL BEHAVIOR OF THE HIGHLY  
HYDROGEN-CHARGED (PRIOR-)  $\beta$  PHASE  
DURING COOLING FROM  $\beta$  DOMAIN  
TEMPERATURES**



Thermal cycles for tensile tests

## Uniaxial tensile tests in air

Temperatures: 700 °C – 20°C on cooling from  $\beta$  domain (1100-1200°C)

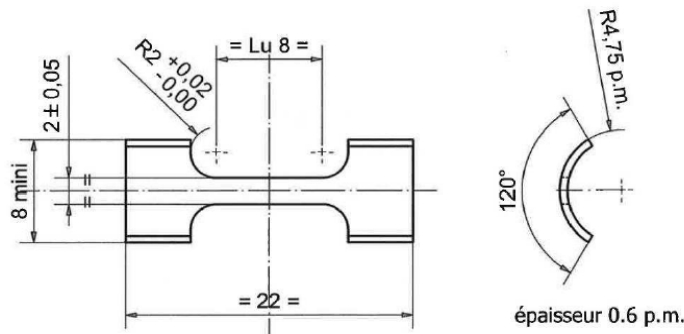
Geometry: Specimens were fabricated from the cladding tubes

Materials: Zy4 et M5™

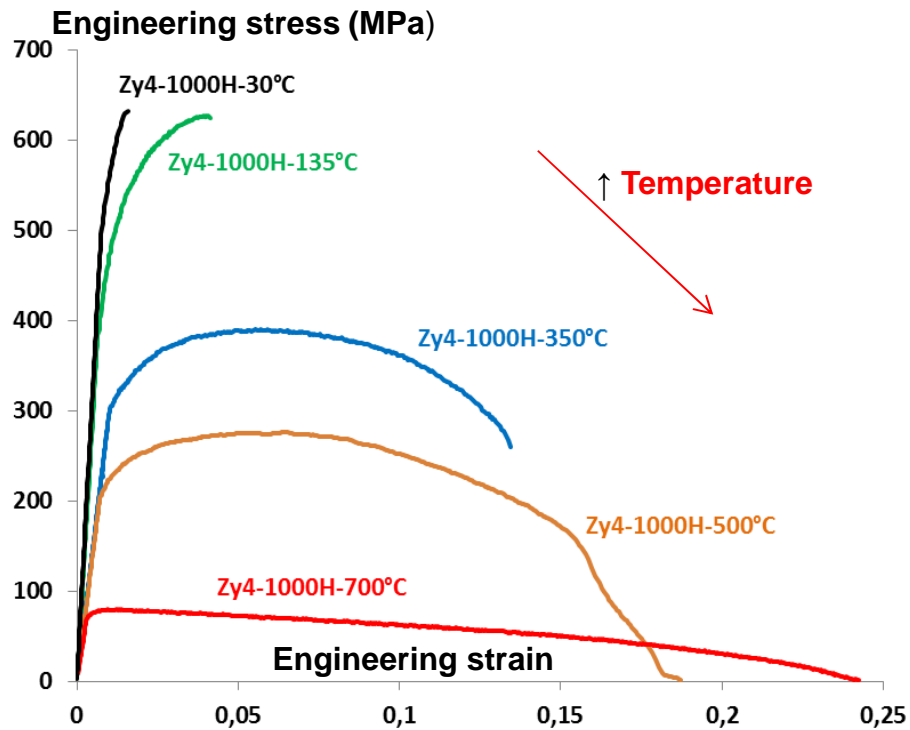
- ❖ as-received
- prehydrided at 1000, 2000 and 3000 wt.ppm

Strain rate :  $\dot{\epsilon} = 10^{-1} \text{ s}^{-1}$

Fast camera (250 images/second) → Digital Images Correlation

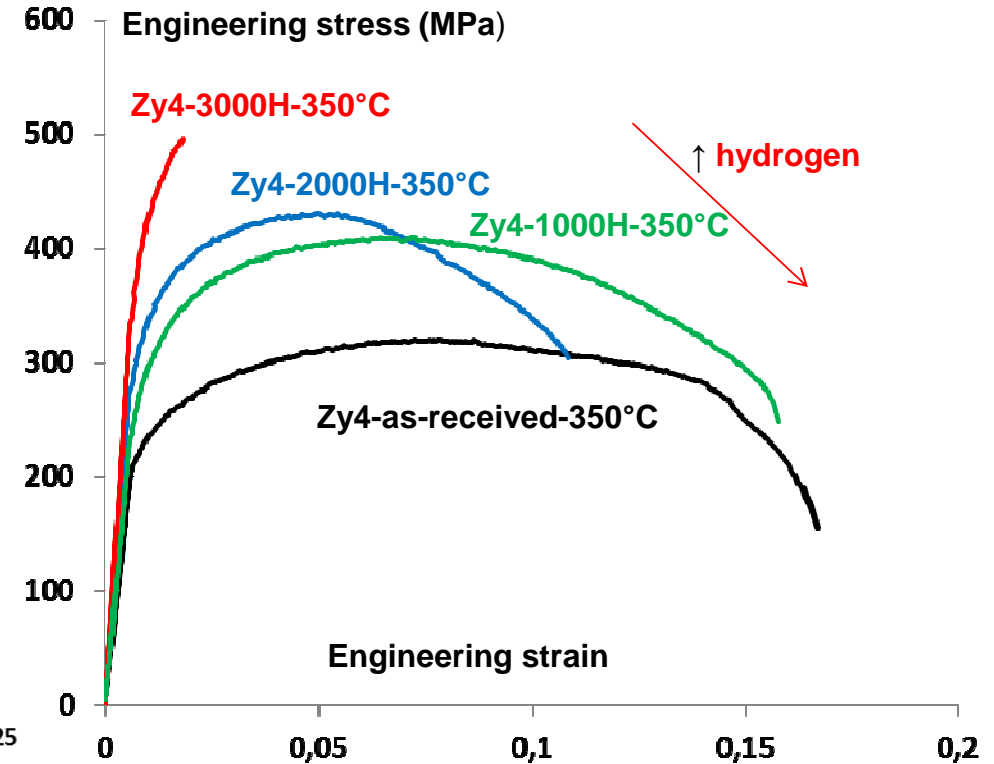


## Temperature effect



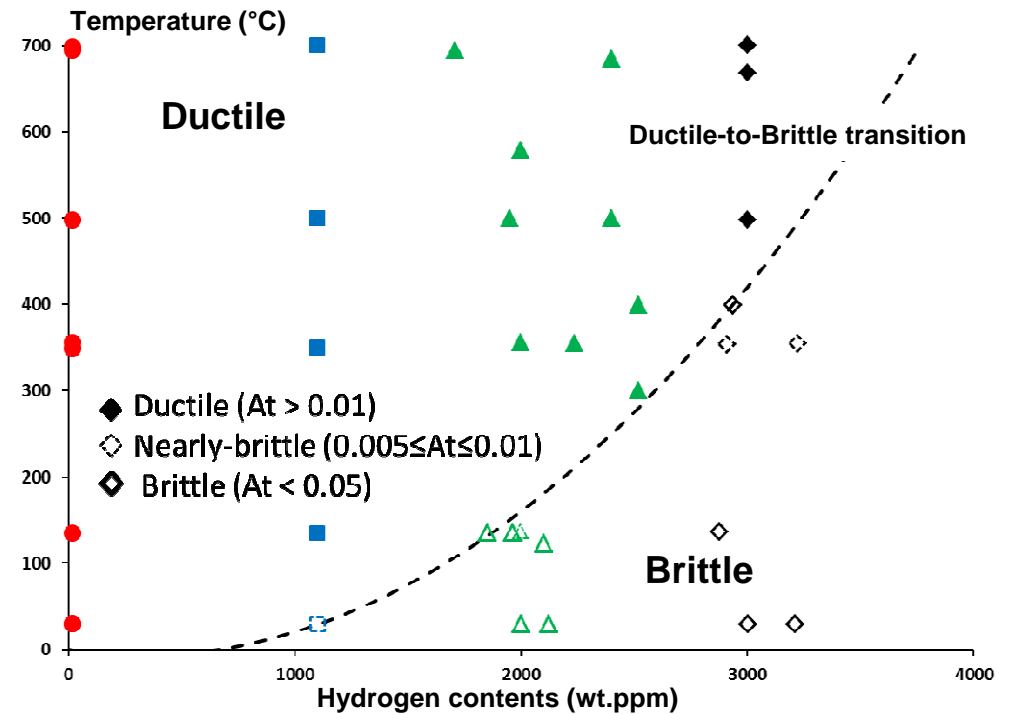
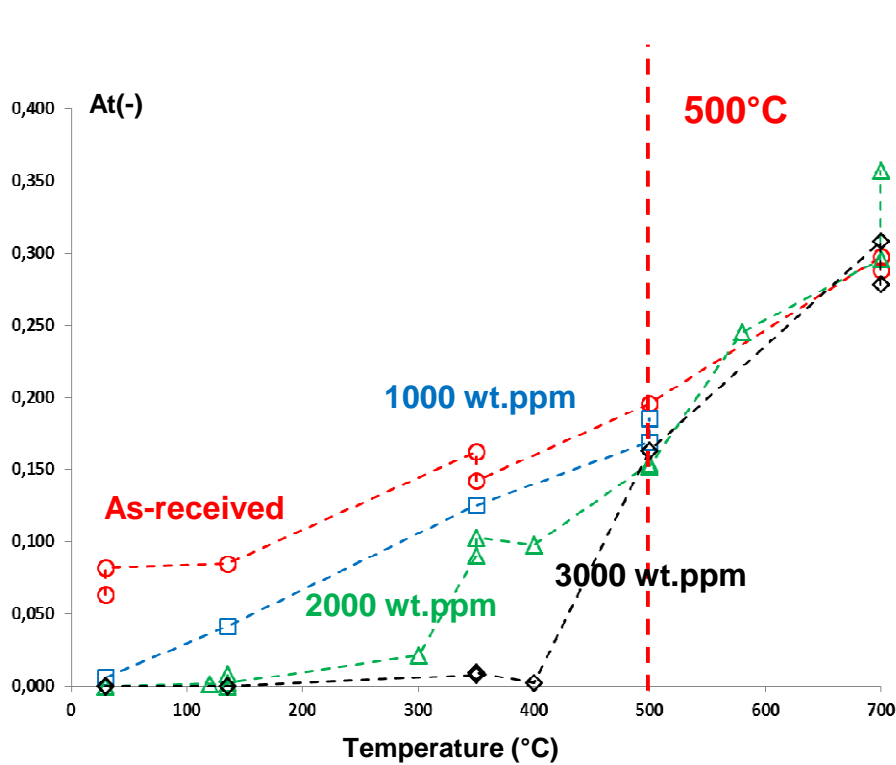
Engineering stress-strain curves of tensile tests on prehydrided Zy4 at 1000 wt.ppm

## Hydrogen effect

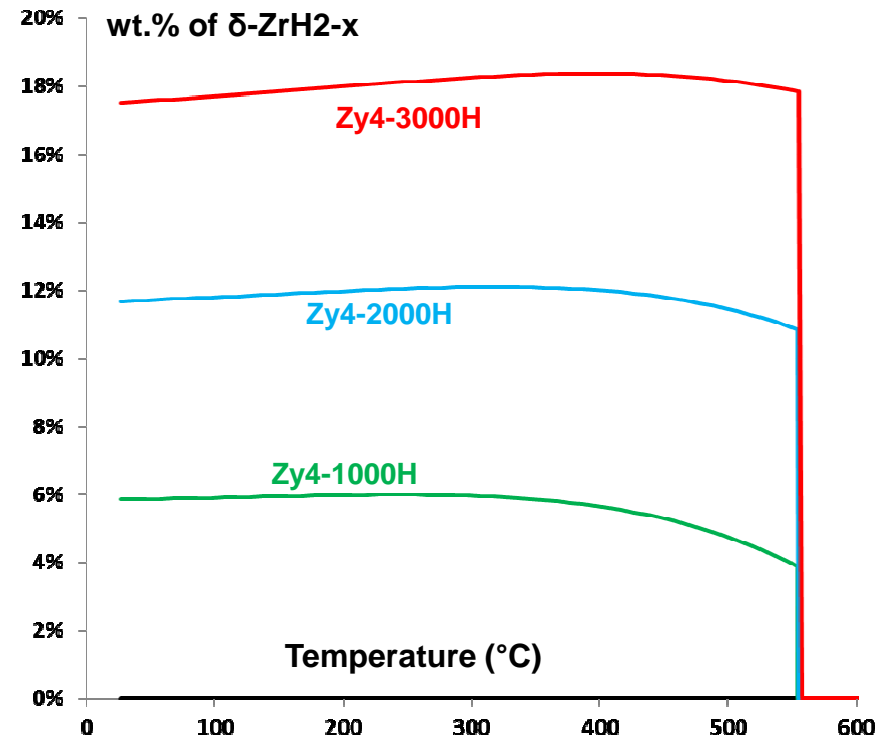
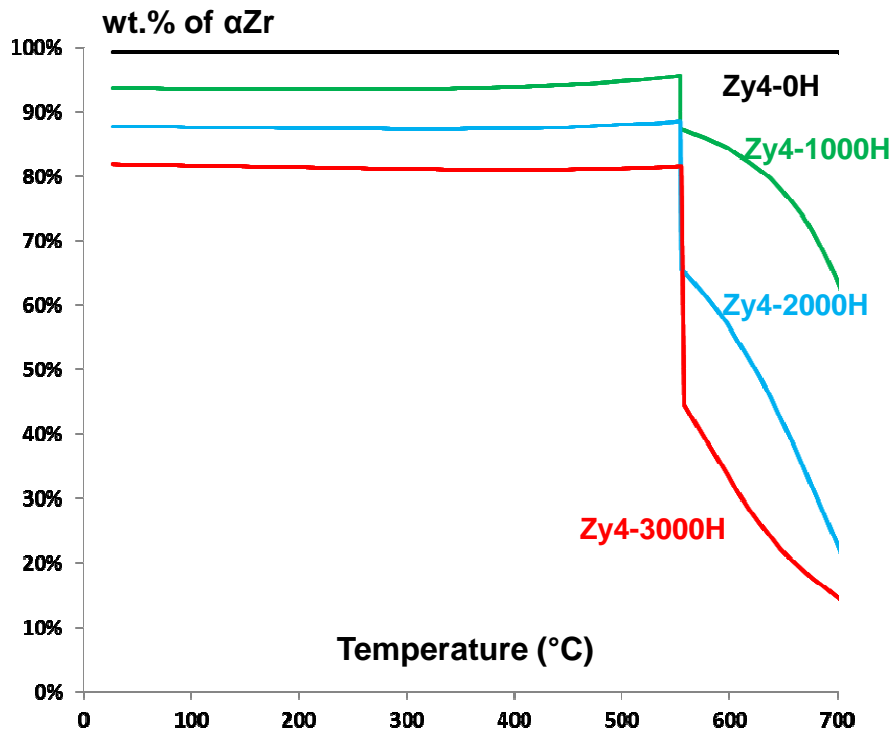


Engineering stress-strain curves of tensile tests on as-received and prehydrided Zy4 at 1000, 2000 and 3000 wt.ppm, tested at 350°C

Plastic elongation of as-received and prehydrated Zy4 at 1000, 2000 and 3000 wt.ppm, tested in tension on cooling after heat-treatment in the  $\beta$  domain



- $T > 500^{\circ}\text{C}$ , no effects of hydrogen and all materials are ductile
- $T < 500^{\circ}\text{C}$ , significant embrittlement effect of hydrogen



Evolution of phase weight fractions obtained by thermodynamic calculation at equilibrium by ThermoCalc and thermodynamic database Zircobase



### Metallurgical behavior :

- ❖ Concerning the evolution of phase weight fractions with temperatures, good agreement between neutron diffraction data and thermodynamic prediction obtained by Thermo-Calc software and thermodynamic database Zircobase of CEA. No significant difference between Zy4 and M5
- ❖ The precipitation of metastable  $\gamma$ -ZrH hydrides was observed at low temperatures in materials containing high (1000 and 3000 wt.ppm) and lower (300 wt.ppm) hydrogen contents
- ❖ Same observations made by KIT (Pshechnikov et al., 2015) for the evolution of lattice parameters (a and c) at room temperature as a function of mean hydrogen content.
- ❖ X-rays diffraction will be performed on materials (Van Arkel Zirconium) containing a low content of oxygen (100 wt.ppm) heat-treated in the  $\beta$  domain followed by  $\neq$  cooling scenarios. Try to understand the effects of hydrogen on the lattice parameter and to decorrelate from the effects of oxygen

### Mechanical behavior :

- ❖ Embrittlement effect of hydrogen for temperatures below 500°C
- ❖ Ductile-to-Brittle transition map as a function of temperature and hydrogen content was established from experimental data

# Thank you for your attention

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