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**CEA studies on High temperature oxidation and
hydriding of Zr based nuclear fuel claddings upon LOCA
transients phenomenology, mechanisms and modelling
=> consequences on mechanical properties**

J.-C. Brachet, Matthieu Le Saux, C. Toffolon-Masclat

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CEA STUDIES ON HIGH TEMPERATURE OXIDATION
AND HYDRIDING OF Zr BASED NUCLEAR FUEL
CLADDINGS UPON LOCA TRANSIENTS:
PHENOMENOLOGY, MECHANISMS AND MODELLING
=> *CONSEQUENCES ON MECHANICAL PROPERTIES*

J.-C. Brachet, M. Le Saux, C. Toffolon-Masclet
(Nuclear Materials Department / SRMA)

with the contribution of: Clara Desgranges (CEA-DPC),

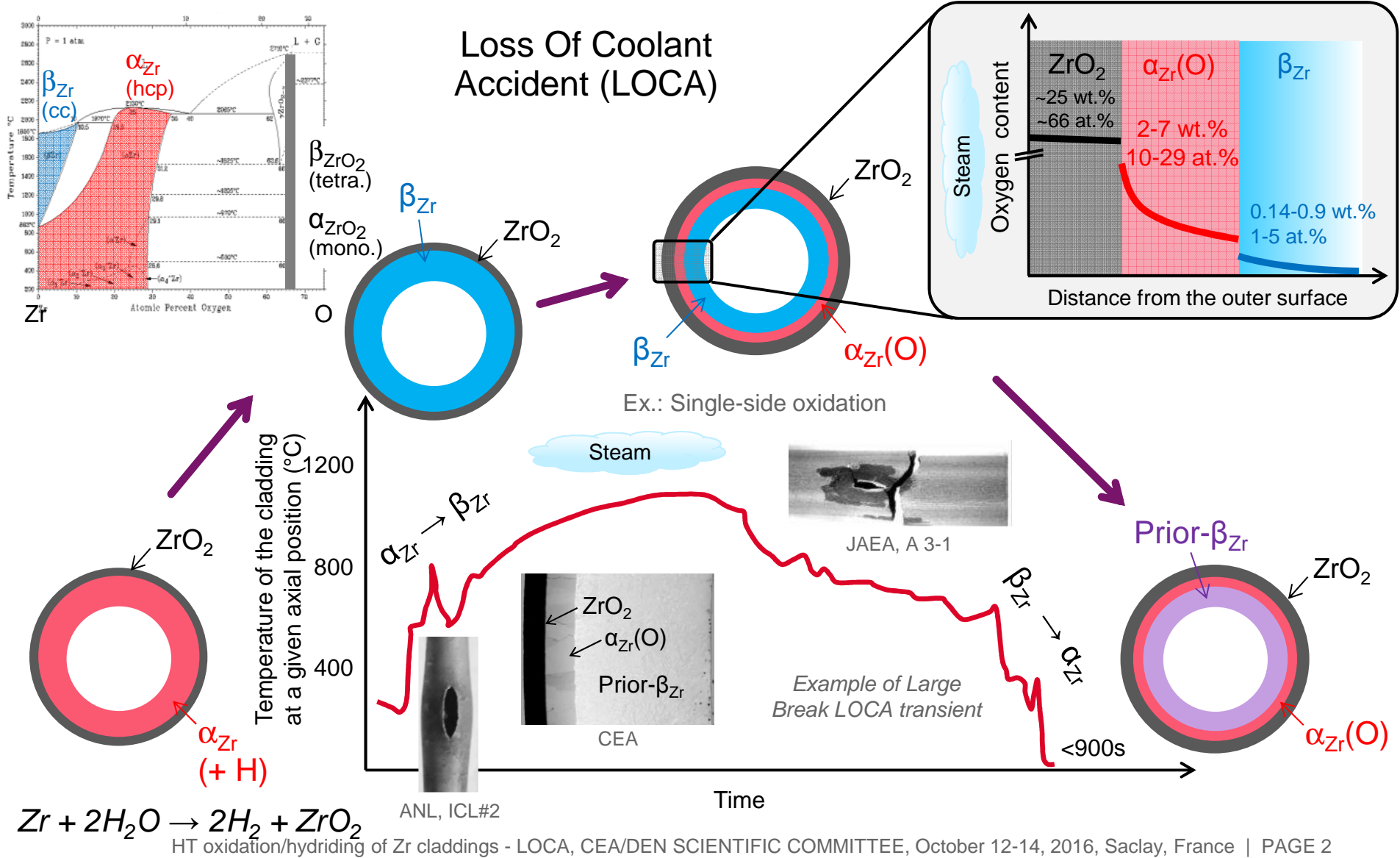
Valérie Vandenberghe, Laurence Portier

and numerous colleagues & PhD students at CEA...

+ scientific (informal) exchanges with ANL, KIT, JAEA...

CORROSION IN PRESSURIZED WATER REACTORS:
PHENOMENOLOGY, MECHANISMS AND MODELLING
CEADEN SCIENTIFIC COMMITTEE, OCTOBER 12-14, 2016,
SACLAY, FRANCE

INTRODUCTION (1/2) - DEEP METALLURGICAL EVOLUTIONS OF THE CLAD UPON HT INCURSION IN STEAM ENVIRONMENT (I.E., IN LOCA CONDITIONS)
=> STRONG INFLUENCE ON THE ACTUAL CLAD MECHANICAL PROPERTIES
(BALLOONING & BURST, WATER QUENCHING AND POST-QUENCHING RESISTANCE/DUCTILITY...)



INTRODUCTION (2/2) – OVERVIEW OF THE R&D PERFORMED AT CEA SINCE THE NINETIES ON THE NUCLEAR FUEL CLADDINGS BEHAVIOR UPON LOCA CONDITIONS (DBA AND SLIGHTLY BEYOND)

Oxidation and thermal-mechanical tests

- ✓ Creep and burst (upon fast heating, internal pressure), i.e., « EDGAR » tests...(*)
- ✓ High temperature oxidation in steam (700-1400°C)
- ✓ Final quenching resistance and Post-Quenching (PQ) residual ductility, i.e., Ring Compression (RCT), 3-Points-Bending (3-PBT), Impact, Tensile tests ...

Metallurgical multiscale (μstructural, μchemical) studies

- ✓ $\alpha_{Zr} \leftrightarrow \beta_{Zr}$ transformation kinetics (dilatometry, resistivity, in-situ neutron diff...) (*)
- ✓ Systematic and accurate phases thicknesses quantification (oxide, $\alpha(O)$ and prior- β)
- ✓ HT oxidation / oxygen diffusion quantifications (EPMA, O^{18} experiments...)
- ✓ Oxygen, hydrogen and alloying elements partitioning (EPMA, μ -ERDA, neutron radiography/tomography...)

Modelling

- ✓ Constitutive thermal-mechanical laws coupled with $\alpha_{Zr} \leftrightarrow \beta_{Zr}$ kinetics modelling (*)
- ✓ Thermodynamic database (« Zircobase ») \leftrightarrow Calphad/Thermocalc®
- ✓ Kinetics database for Zr alloys (« Zircomob ») \leftrightarrow Dictra®
- ✓ HT Oxidation modelling « Ekinox-Zr » (collab. with CEADPC, C. Desgranges)
- ✓ Finite Element (FE) calculation/modelling (ex.: application to PQ RCT), ...

Parameters studied:

- ✓ Materials: Low-Tin Zircaloy-4, M5®, model alloys and Cr coated Zr claddings (EATF)
- ✓ Pre-transient metallurgical conditions: pre-corroded / pre-oxidized, pre-hydrided, after burst occurrence (secondary hydriding), irradiated (*)
- ✓ Oxidation time-temperature (700-1400°C, 1 min up to a few hours), heating mode, outer steam pressure (1-80 bar, Small Break LOCA), final cooling scenario...

(*) Not presented here / out-of-topic

CONTENT:

- (1) HT steam oxidation and consequences on the Post-Quenching (PQ) mechanical properties of as-received materials
- (2) Effects of pre-transient oxide
- coming from in-service corrosion –
on HT oxidation mechanisms/kinetics and PQ mechanical properties
- (3) Effects of H - *simulating in-service hydriding* - on HT oxidation and PQ mechanical properties
- (4) HT secondary hydriding (*due to steam starvation conditions occurring upon HT steam oxidation into the pellet-clad gap after cladding burst*)
- (5) Conclusions and prospects: *on-going EATF / Cr-coated claddings R&D*

(1) HT steam oxidation and consequences on the Post- Quenching (PQ) mechanical properties of as-received materials

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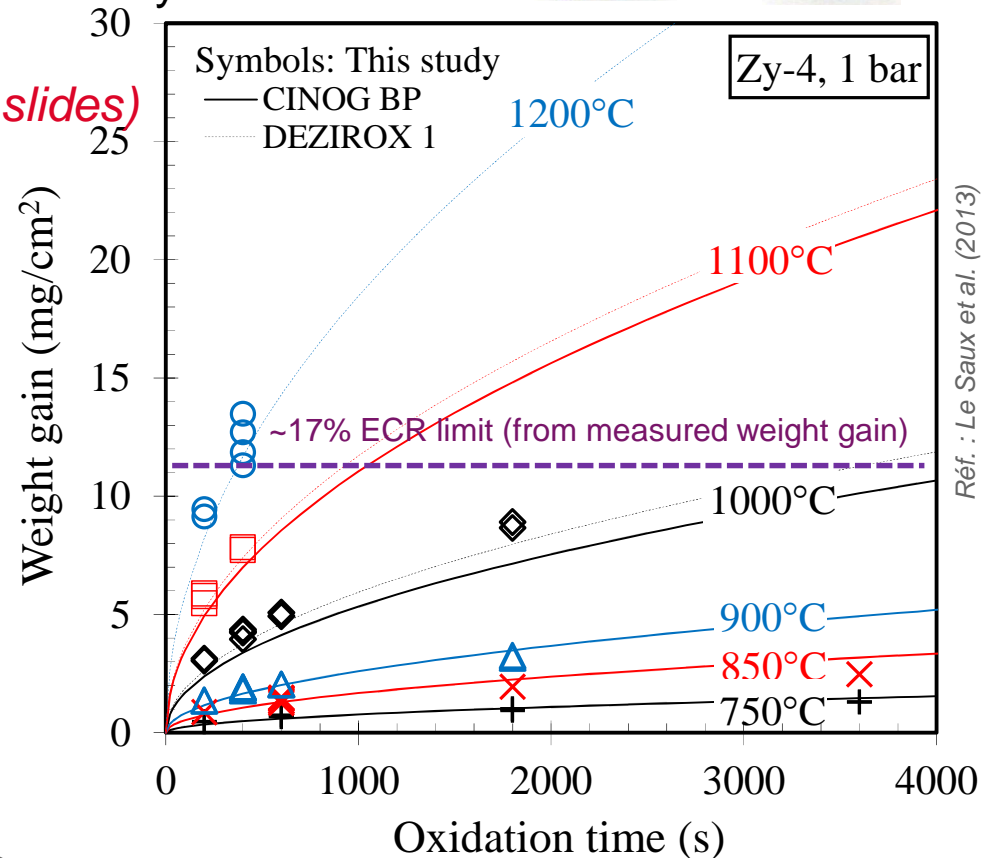
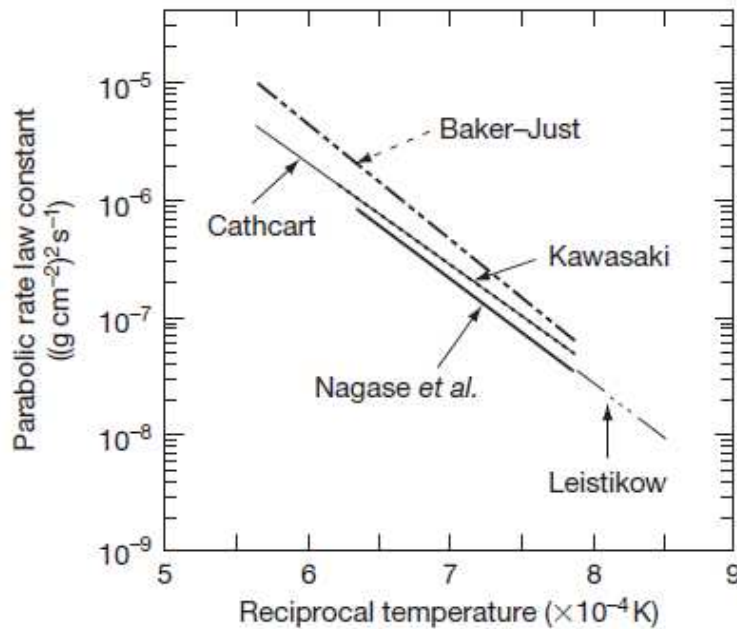
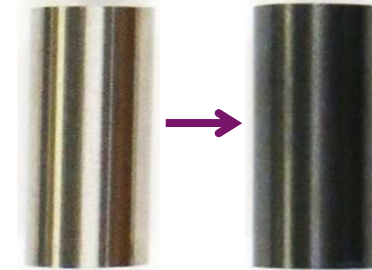
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HT (1 BAR) STEAM OXIDATION - AS-RECEIVED MATERIALS

OXIDATION KINETICS FOR TYPICAL DBA-LOCA OXIDATION TIMES:

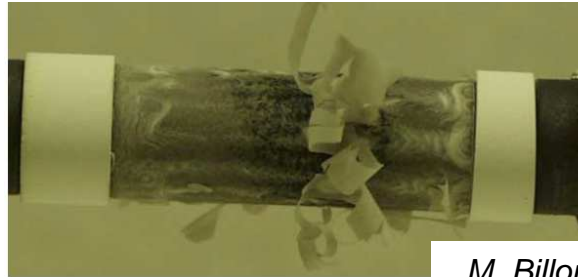
- At CEA, two main types of HT oxidation facilities used: “Dezirox” – furnace heating and “Cinog” – induction heating
- For modern cladding alloys: **oxidation kinetics ~parabolic** (except for specific conditions – next 2 slides)
- Oxidation kinetics not very sensitive to the alloy for $T > 1000^\circ\text{C}$
- No significant hydrogen uptake** (except for specific conditions – next 2 slides)
- CEA data consistent with the literature:



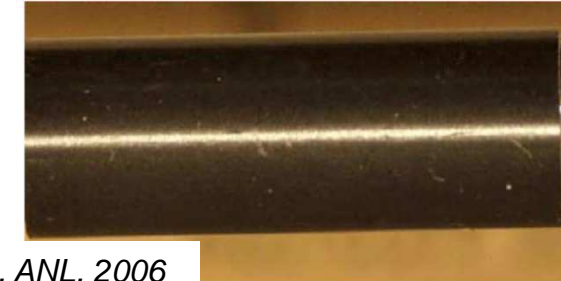
Réf. : Le Saux et al. (2013)

DEVIATION FROM THE HT OXIDATION PARABOLIC KINETICS: EX. N°1: « BREAKAWAY » PHENOMENA AT ~1000°C (FOR BEYOND DBA-LOCA OXIDATION TIMES)

- Early “breakaway” oxidation observed for old grade E110 alloy (russian Zr1Nb) - comparison with M5®

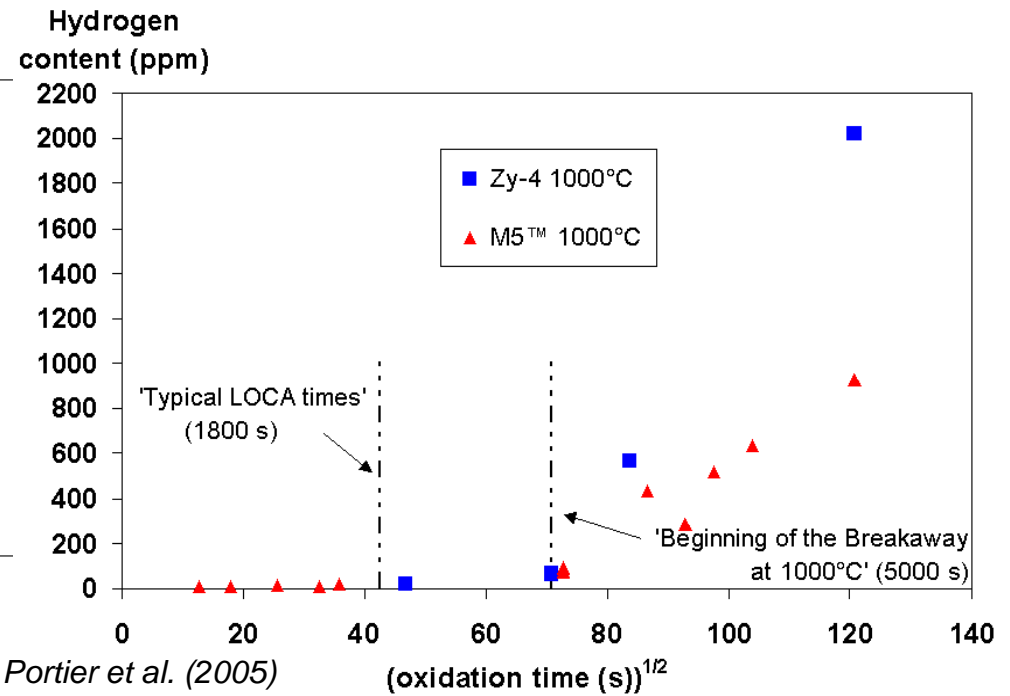
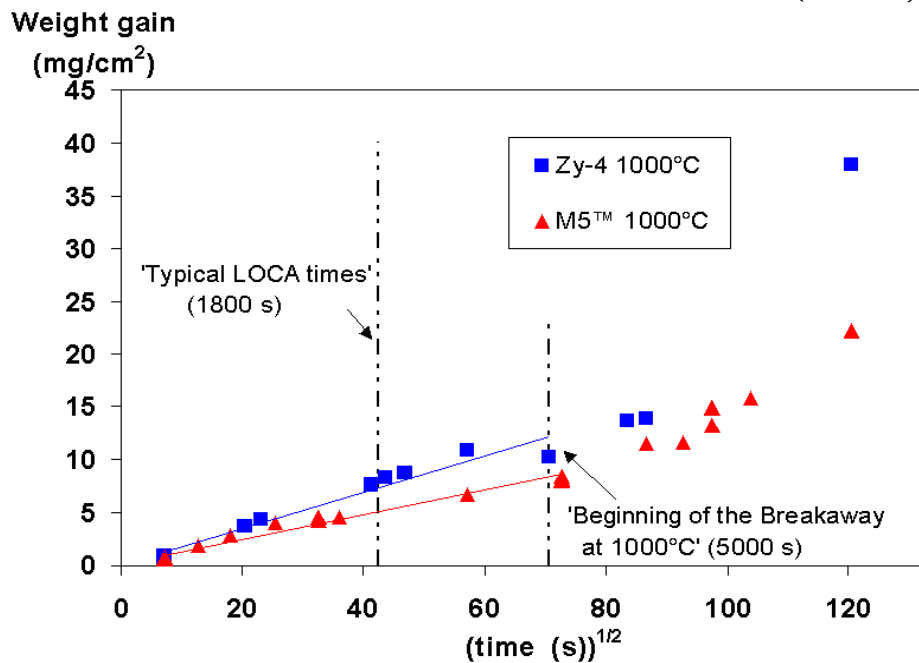


M. Billone, ANL, 2006



(E110, 1000°C, 1400 sec)

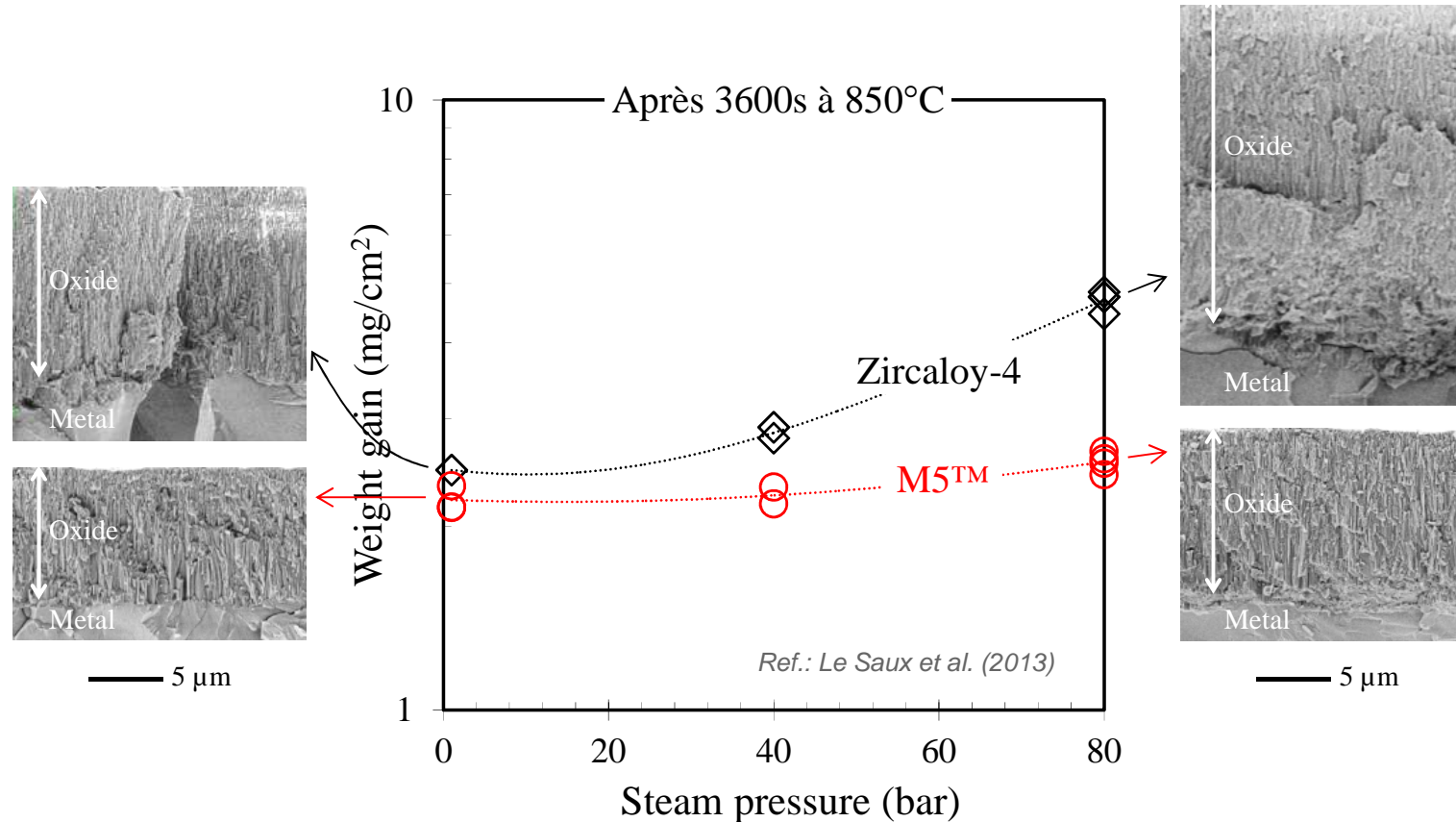
(M5, 1000°C, 2400 sec)



⇒ On-going work to understand more in depth the phenomena (+ further modelling)

DEVIATION FROM THE HT OXIDATION PARABOLIC KINETICS: EX. N°2: EFFECT OF STEAM PRESSURE (SMALL BREAK LOCA)

Specific HT oxidation device developed/used (« Cinog-HP ») allowing HT oxidation testing with steam pressure ranging from 1 to 80 bars (SB LOCA)



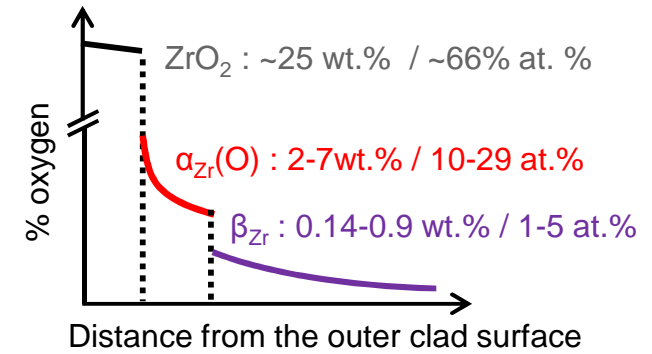
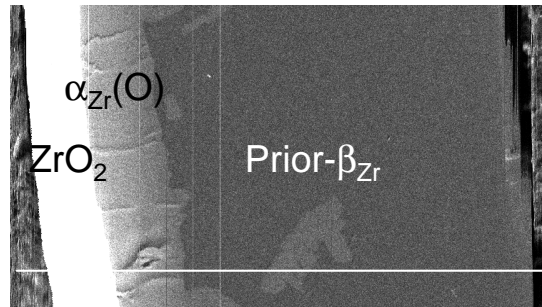
- ⇒ Sensivity of Zircaloy-4 – but not M5® – to the increase of steam pressure
- ⇒ *Further work needed to understand more in depth the phenomena (+ modelling)*

(1 BAR STEAM) OXIDATION PHENOMENOLOGY AND ANALYTICAL MODELLING:

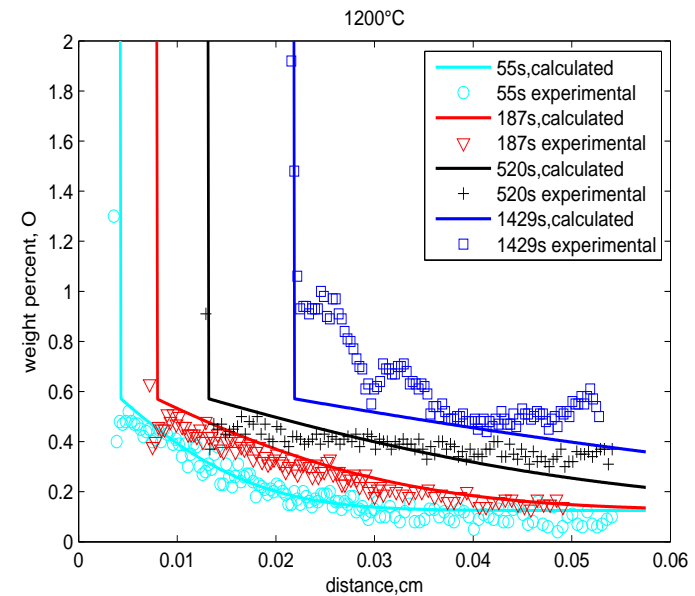
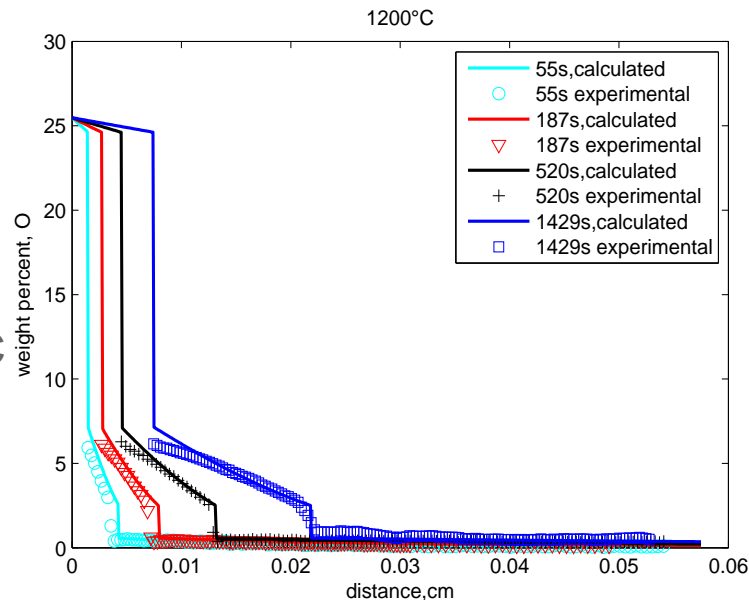
Oxygen ingress/diffusion into the sub-oxide residual metallic layer
=> ZrO_2 thickening and progressive transformation of β_{Zr} into $\alpha_{Zr}(O)$

EPMA oxygen mapping
Zircaloy-4 steam oxidized
for 1350s at 1100°C

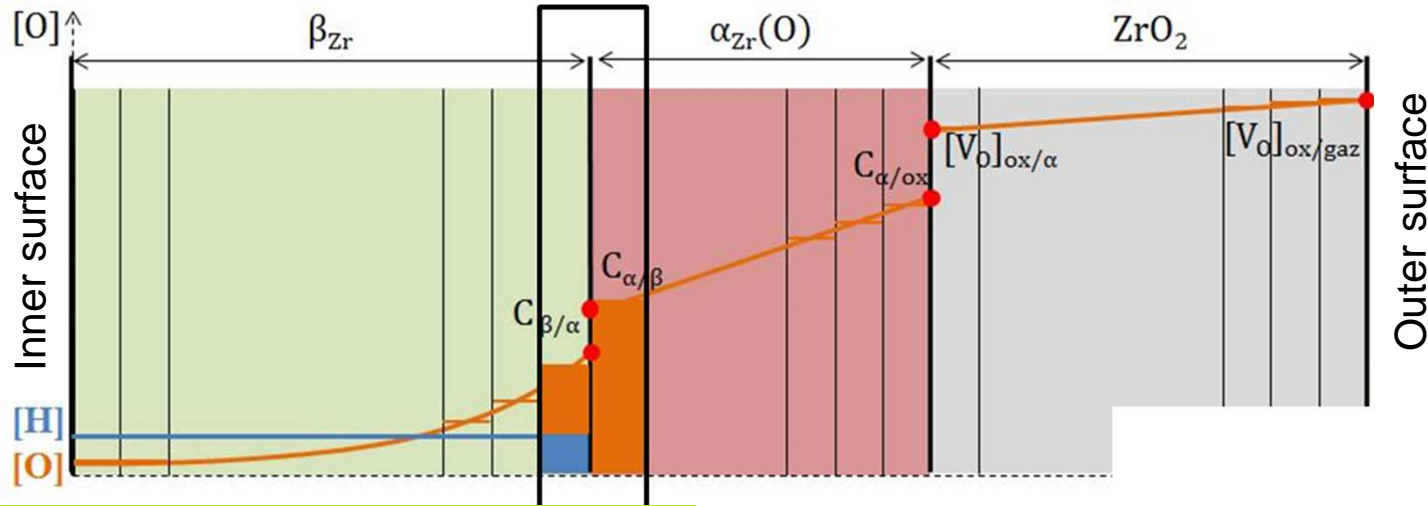
Réf. : Brachet et al. (2001)



Experimental
EPMA oxygen
diffusion profiles
measured on
Zircaloy-4
oxidized at 1200°C
for different times
and analytical
modelling



Réf. : Ma et al. (2008)



See also
C. Desgranges
& L. Martinelli
presentation on
« Ekinox / Ni alloys »
- this seminar
(Oct. 13th., 16h:45)

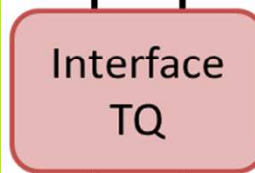
Development of the Zircobase (since 1998):


~10 elements: Cr, Fe, H, Nb, Ni, O, Sn, V, Zr,
(+Er, Gd)

~20 binary systems : Cr-Fe, Nb, Ni, Zr; Fe-
Nb, Ni, Sn, Zr; H-Nb, Ni, O, Sn, Zr ; Nb-O, Sn, Zr;
O-Sn, Zr ; Sn-Zr ; V-Zr ; (+ Er/Gd-Zr-O-H)

>10 ternary systems : Cr-Fe-Zr, Cr-Ni-Zr, Fe-
Nb-Zr, Fe-Ni-Zr, H-O-Zr, Nb-O-Zr, O-Sn-Zr...
(+ Zr-O-H, Zr-Er-O, Zr-Gd-O, Zr-Er-H...)

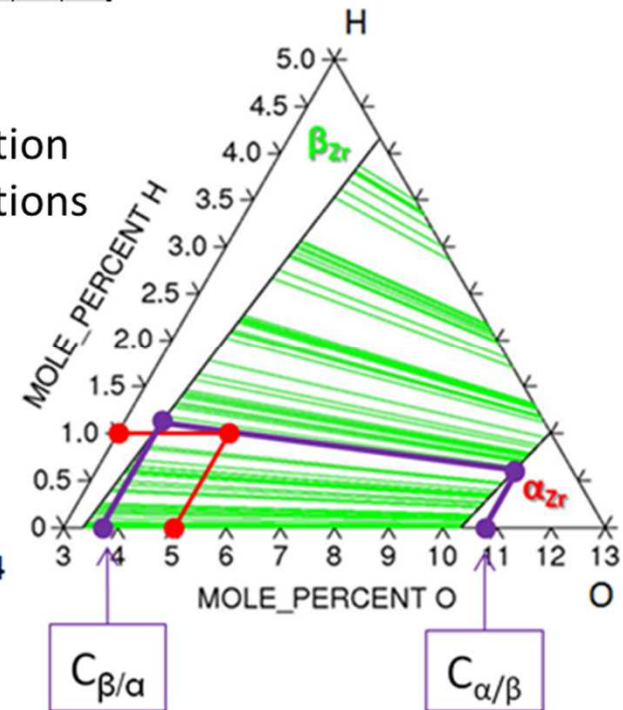
EKINOX numerical resolution
of diffusion equations



$C_{\alpha/\beta}, C_{\beta/\alpha}$ 

ThermoCalc® + Zircobase

Dupin et al, (1999), C. Toffolon-Masclet (2010)



Data for building « Zircomob » database:

- Thermodynamics (Zircobase)
- Diffusion experiments (unary, binary, ternary systems)
 - Tracer diffusivity,
 - Intrinsic diffusivity,
 - Interdiffusion coefficients/Marker motion

The mobilities \mathbf{M}_i are described for all binaries, using the following equations :

$$M_i = \frac{M_i^0}{RT} \exp\left(\frac{-\Delta Q_i}{RT}\right) \quad \text{where} \quad \Delta Q_i = f(c_i, T) \quad \text{and} \quad M_i^0 = 1$$

$$\Delta Q_i = \sum_{p=1}^n x_p Q_i^p(T) + \sum_{p>q}^n \sum_{q=1}^n x_p x_q {}^0 A_i^{pq}(T)$$

10 elements : Cr, Fe, H, Mo, Nb, Ni, O, Sn, V, Zr

9 binary systems :

Zr-Nb : HCP_A3, BCC_A2

Zr-Fe : HCP_A3, BCC_A2, FeZr₃, FeZr₂

Zr-O : HCP_A3, BCC_A2, FCC_C1 (ZrO₂_cubic), ZrO₂ Mono, ZrO₂ Tetra

Zr-H : HCP_A3, BCC_A2, ZrH₂_Epsilon, FCC_C1 (ZrH₂ Delta)

Zr-Sn : HCP_A3, BCC_A2

Zr-Cr : HCP_A3, BCC_A2

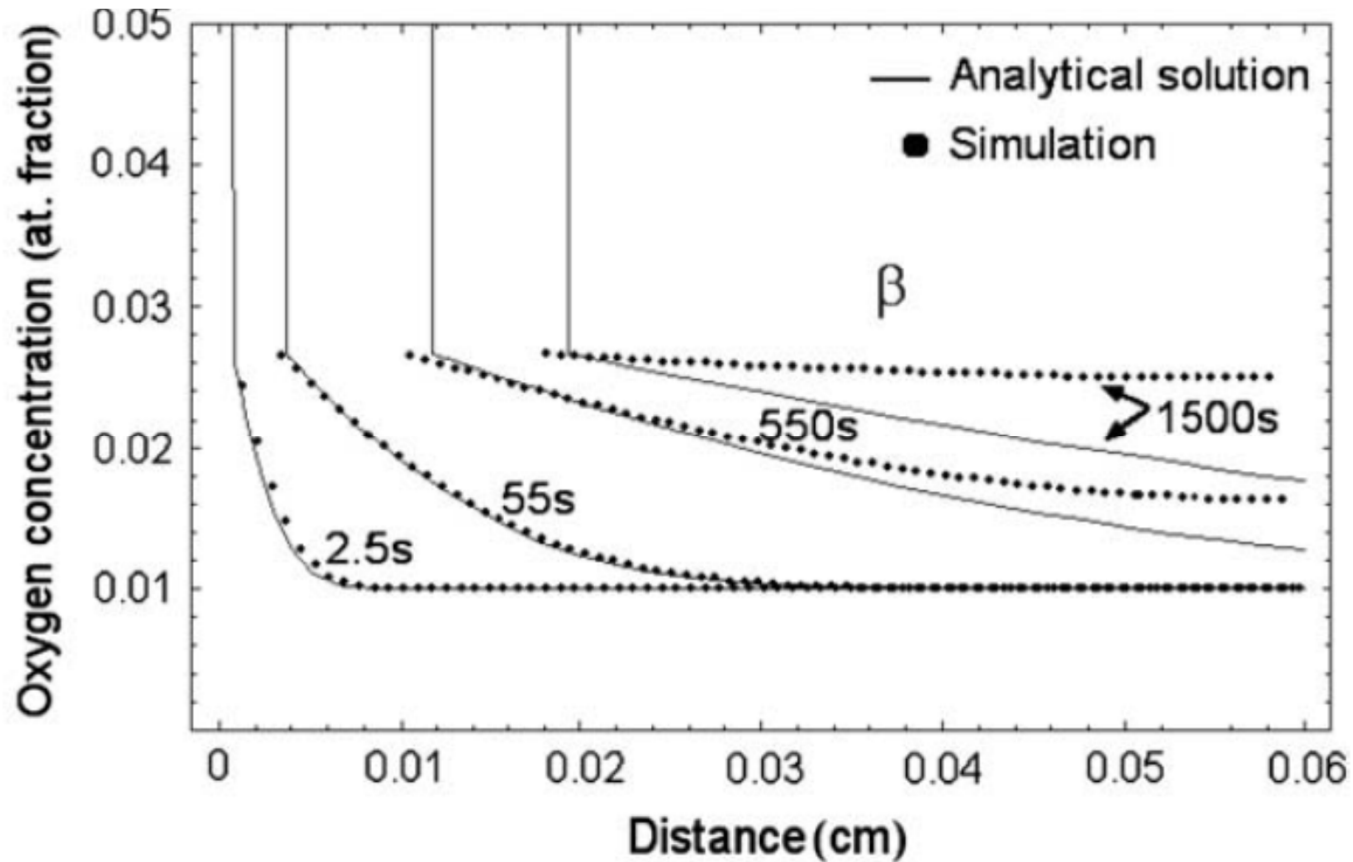
Zr-Ni : HCP_A3, BCC_A2

Zr-V : HCP_A3, BCC_A2

Zr-Mo : HCP_A3, BCC_A2

HT (1 BAR) STEAM OXIDATION - AS-RECEIVED MATERIALS

ANALYTICAL VS. NUMERICAL MODELLING

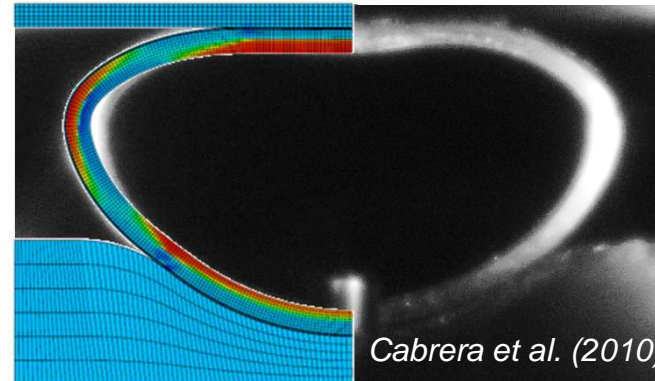


C. Corvalan-Moya et al., JNM, 2010

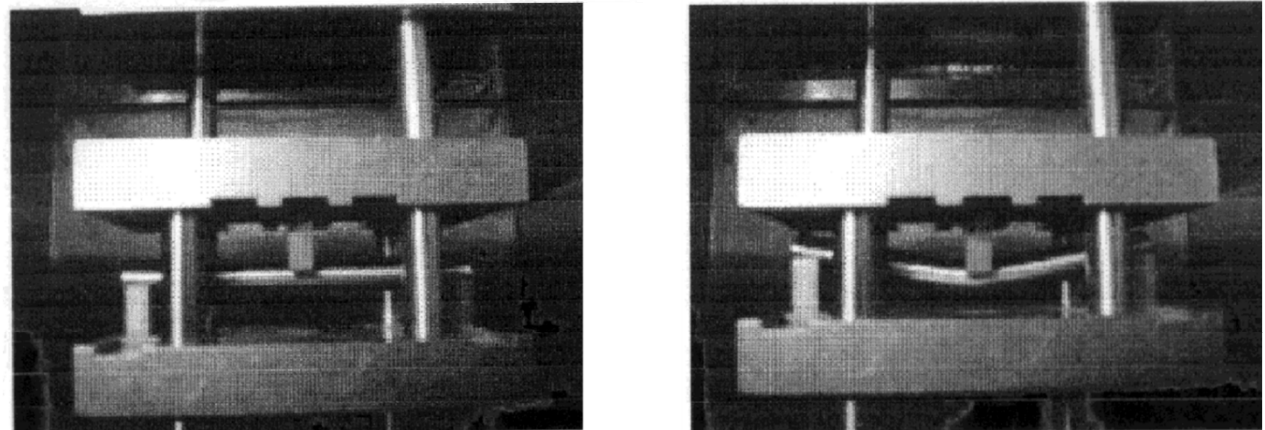
- *In the following, some additional case studies will be illustrated (effect of pre-hydriding, effect of pre-transient oxide...)*

Post-Quenching (PQ) mechanical tests performed at CEA:

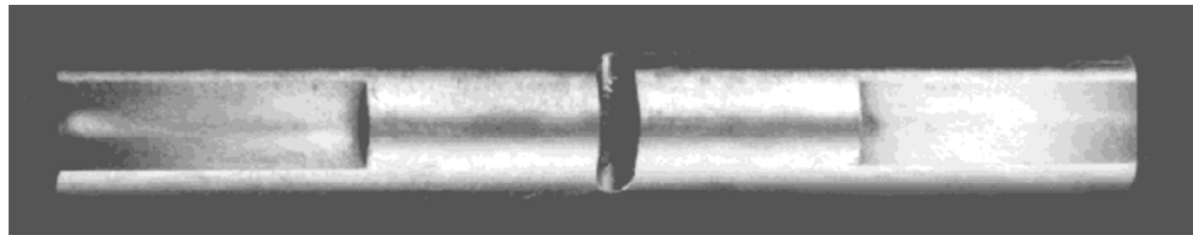
Ring Compression Testing (RCT)
at 20-135°C
+ FE modelling

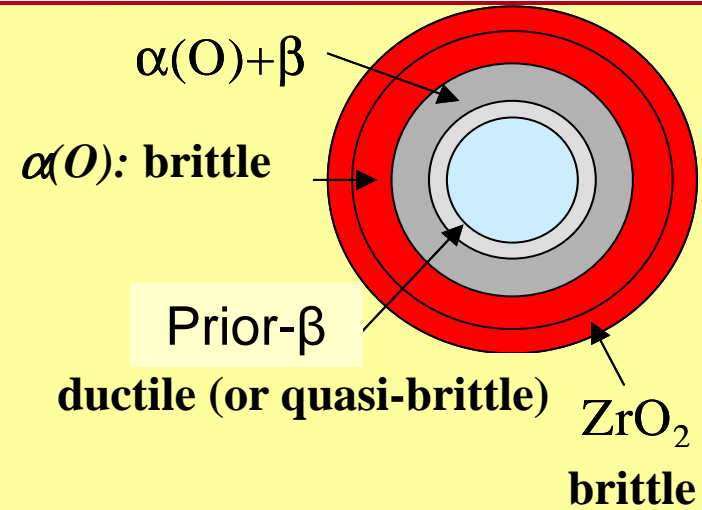


Three Points Bending Testing (3-PBT)
at 20-135°C

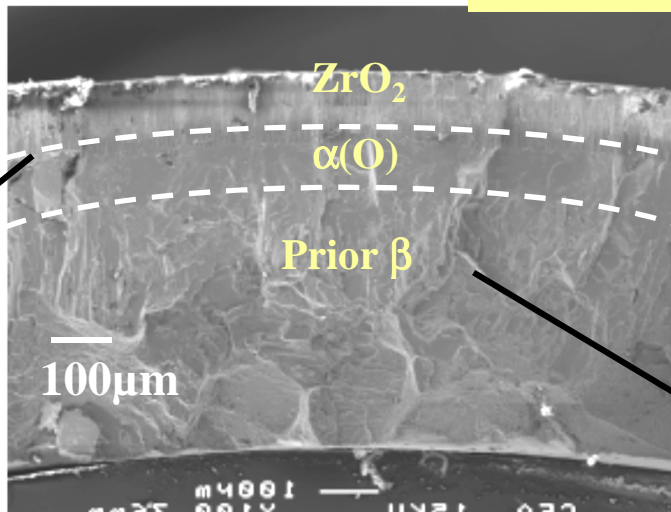


Room Temperature Impact Testing
(pre-notched clad sample)

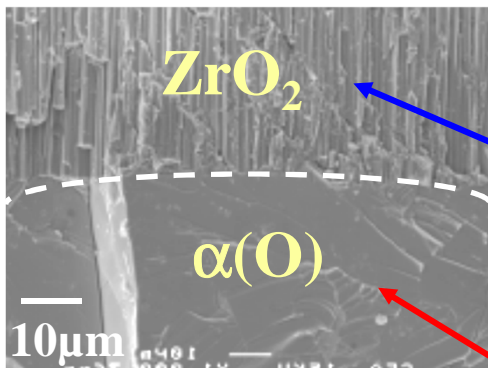




Typical PQ failure modes at RT:

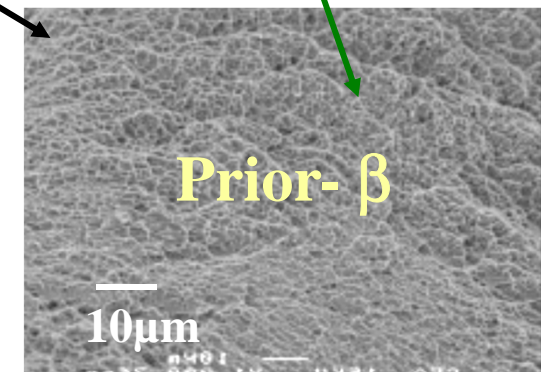


Prior- β layer: ductile (or nearly-brittle) failure mode (depending on the oxygen & hydrogen content)

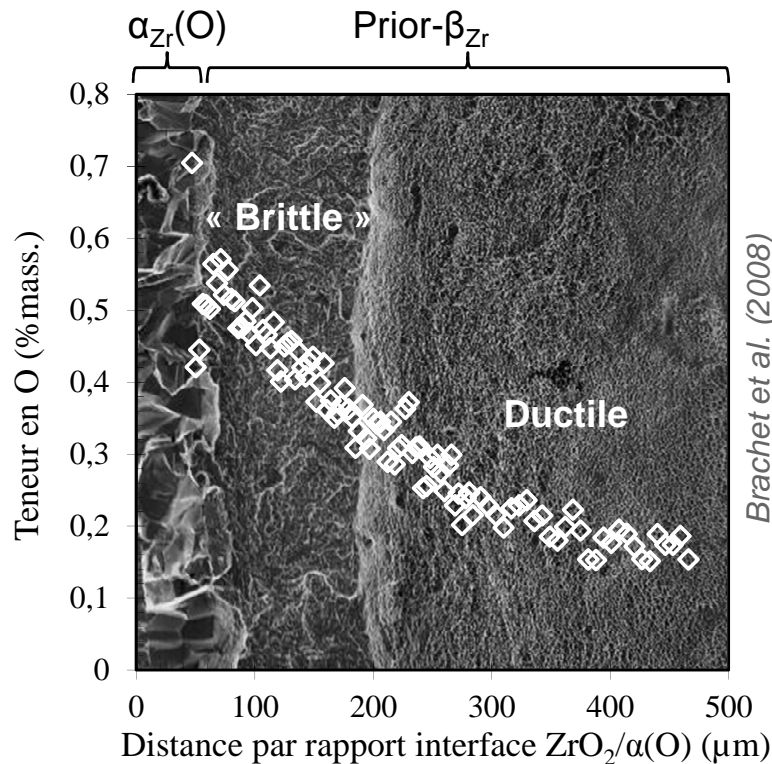


ZrO_2 : brittle (columnar) failure mode

$\alpha(O)$: pure brittle (cleavage and intergranular) failure mode

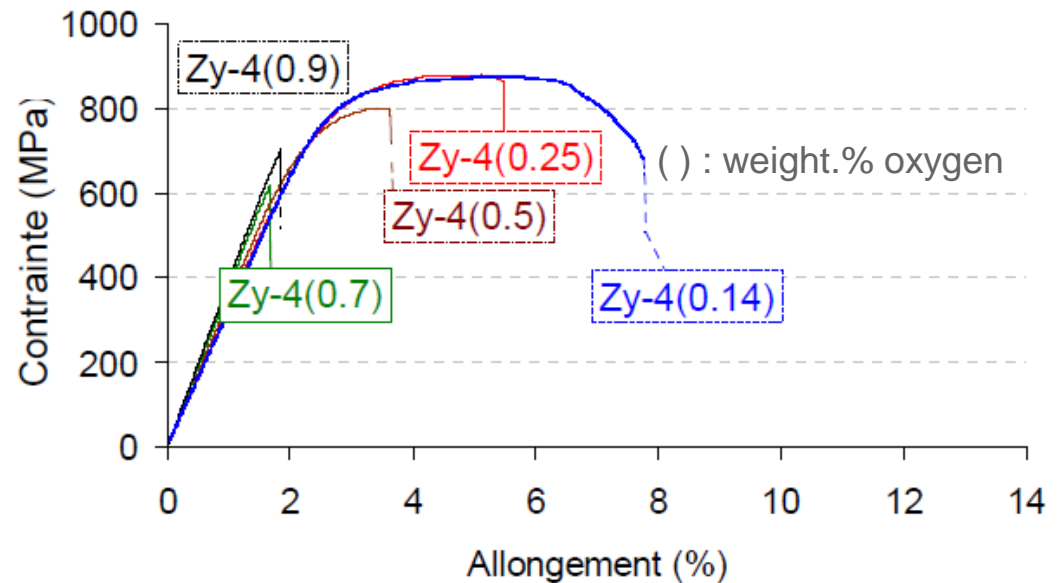


1st order influencing parameter = (local) oxygen content within the residual (quenched) prior- β phase layer => above a critical oxygen content value, ductile-to-brittle transition occurs - [O]%crit.~0,4-0,5 wt.% at RT



Brachet et al. (2008)

Fractograph of a Zircaloy-4 sample impact tested at RT after one-sided (steam) oxidation for 3 min at 1200°C + direct water quenching



(Quenched) prior- β model alloys charged homogeneously with different contents of oxygen and tensile tested at RT

Stern (2007)

- Huge experimental database
(~2 thousands HT oxidation tests performed these last 20 years at CEA + deep metallurgical examinations & PQ mechanical testing)
- Modelling effort (*analytical and numerical modelling: Ekinox/Zircobase, Dictra/Zircomob, Model alloys - FE calculations...*)
- For modern cladding alloys: oxidation kinetics ~parabolic and no significant hydrogen uptake (*except for specific conditions, i.e., “breakaway” oxidation at 1000°C for oxidation times > 5000s, increase of steam pressure (for Zircaloy-4, not for M5®)...*)
- Refined relationship with the PQ clad mechanical properties
=> critical prior- β oxygen content ~0,4 wt.% for DBTT at RT
- *Additional work needed to better understand “breakaway” oxidation and steam pressure effects + some potential oxidation modelling improvements (ex.: for application to dynamic anisothermal (heating/cooling) conditions)*

IN-SERVICE EXPOSURE CONSEQUENCES ON THE ZR BASE NUCLEAR FUEL CLAD MICROSTRUCTURE EVOLUTION (SEE M. TUPIN ET AL PRESENTATION)

- **Irradiation effects:** irradiation defects / formation of interstitial or vacancy loops, inducing significant hardening / loss of ductility of the irradiated clad
=> **not a concern at high temperature (LOCA)** due to fast thermal annealing

- **Outer/inner corrosion** (PWR environment): $Zr + 2H_2O \rightarrow 2H_2 + ZrO_2$

- **Outer oxide thickening**

(up to $\sim 25\mu\text{m} - 60\mu\text{m}$, depending of the alloy)

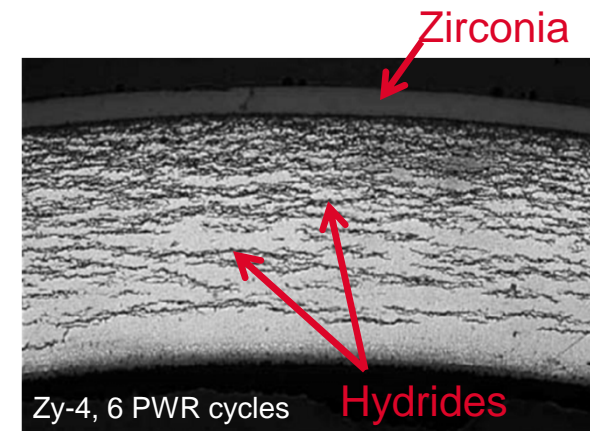
- **Hydrogen uptake**

(up to $\sim 100-700$ wt. ppm depending of the alloy)

- **Inner oxide formation**

(inner oxidation + clad-pellet chemical interaction)

=> thickness reaches $\sim 10-15\mu\text{m}$ at high BU



Bossis et al. (2005)

=> Question / pending issue: which consequences (if any?) of in-service corrosion on subsequent HT oxidation and PQ behavior of (high BU irradiated) cladding upon an hypothetical HT LOCA transient?

(2) Effects of pre-transient oxide
- *coming from in-service corrosion* -
on HT oxidation
mechanisms/kinetics and PQ
mechanical properties

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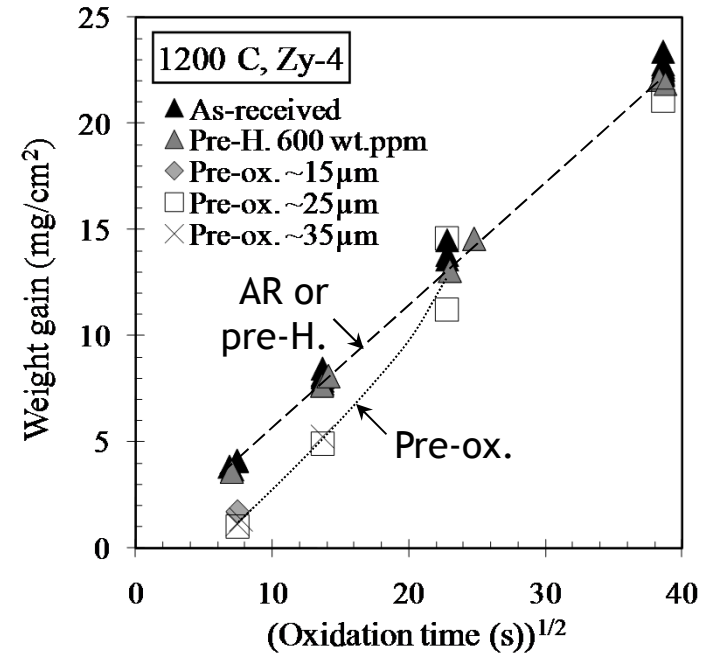
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EFFECT OF PRE-TRANSIENT OXIDE ON HT STEAM OXIDATION (1/3)

Samples **pre-corroded at 340-360°C / PWR chemistry** (out-of-pile) and then subjected to HT steam oxidation

Materials	Pre-oxidation conditions	OD / ID preoxide thickness (µm)	Hydrogen content (wt. ppm)
Zy-4	Autoclave 340° C 1060d	~10 / 10	~200-380
	Autoclave 360° C 1010d	~25 / 25	~500-600
	Autoclave 360° C 1370d	~35 / 35	~750
	Reggae loop 350° C (*)	~15 / 5	~150-200
M5™	Autoclave 350° C 1112d	~10 / 10	~200
	Autoclave 360° C ~1000d	~15 / 15	~140-240
	Autoclave 360° C 1250d	~35 / 35	~180-280
	Reggae loop 350° C (*)	~15 / 5	~150-200

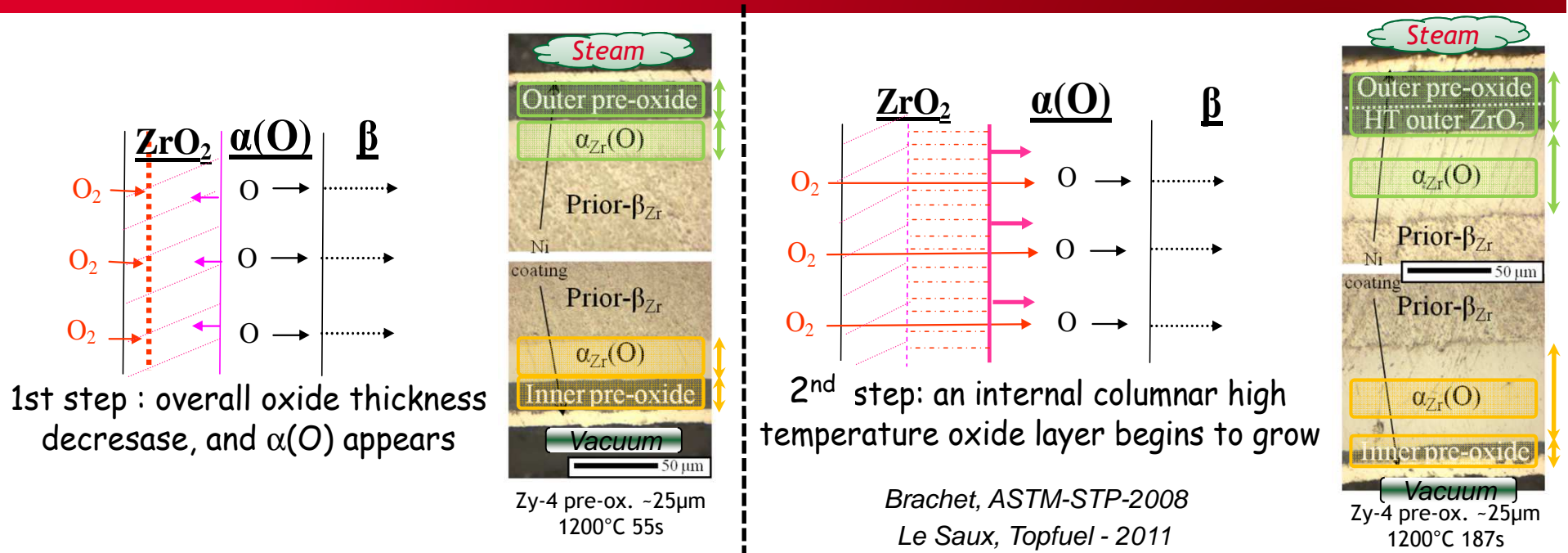
Le Saux, Topfuel - 2011



No H uptake → both pre-ox. and HT ox. layers protective

□ **Weight gains (Wg) of the pre-ox. samples lower** than those of the non pre-ox. materials exposed to the same HT ox. conditions **for short ox. times** (from 1 to ~3 min at 1200°C) and **similar for longer ox. times** (>8 min at 1200°C)

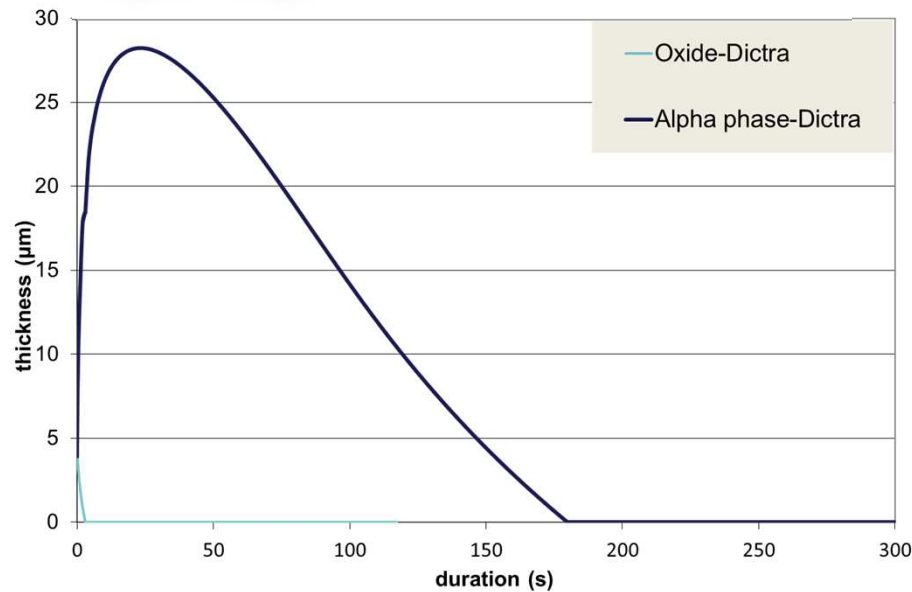
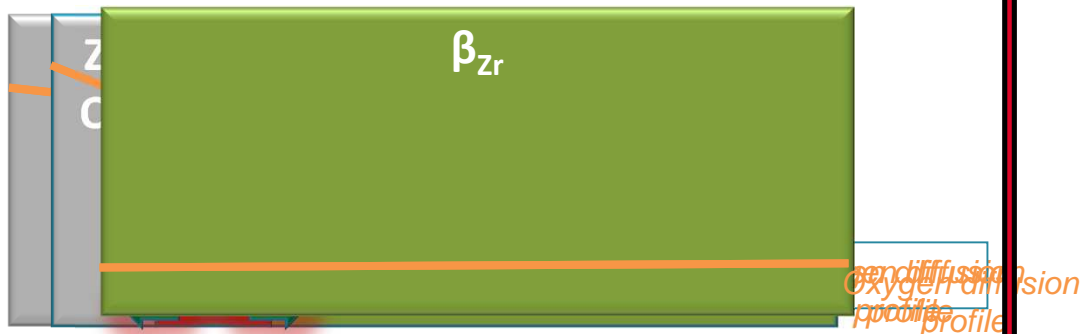
- ⇒ When looking (only) at the weight gain evolution, pre-transient oxide seems to have a **“protective” effect on the overall HT oxidation kinetics.**
- ⇒ **but is it true for sub-oxide oxygen diffusion / resultant PQ mechanical properties?**



- ⇒ **For the OD**, the overall quantity oxygen diffusing into the substrate is the same with/without pre-transient oxide for any given oxidation time => no “protective effect / grace time” due to the pre-transient oxide regarding PQ mechanical properties
- ⇒ **For the ID**, (not subjected to the outer steam oxidation but with potential pre-transient inner oxide formation, depending on the BU), only reduction of the pre-transient oxide takes place, however, inducing oxygen diffusion into the β_{Zr} sub-oxide substrate => α_{Zr} layer formation/thickening => oxygen diffusion comparable to the outer oxidation one for short oxidation times

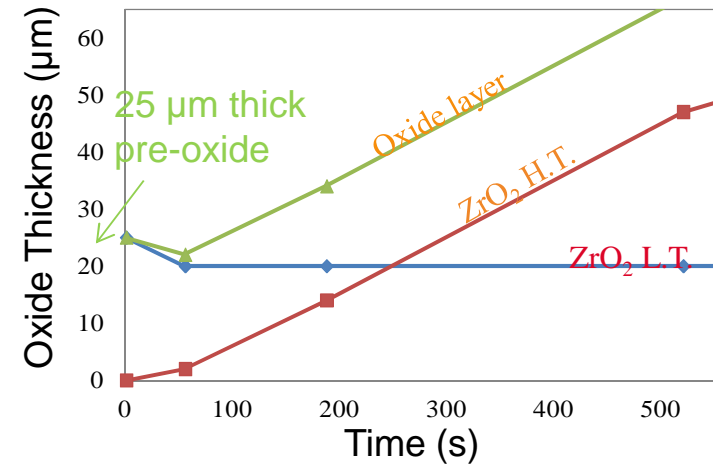
Inner oxide (neutral environment)

DICTRA/ZIRCOMOB simulation of the Zirconia layer dissolution at HT (C. Toffolon-Masclat, 2012)

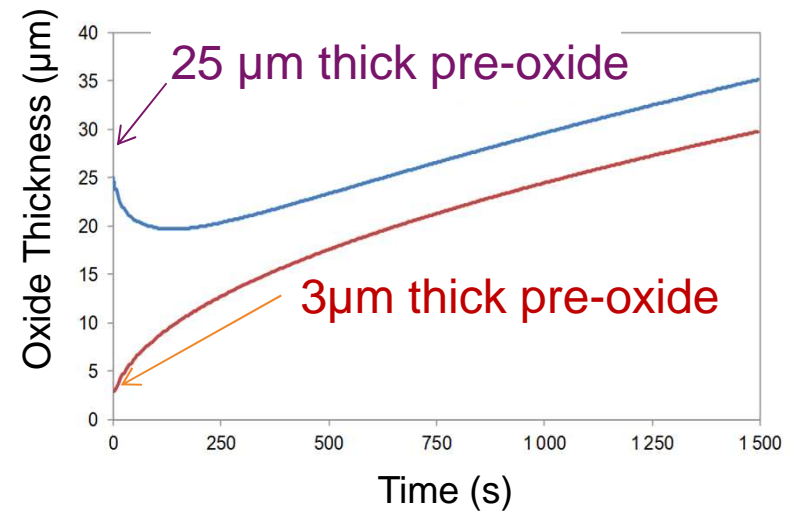


Outer oxide (steam environment)

Experimental results (Le Saux, 2011)



EKINOX Calculations (C. Desgranges, 2014)



PRE-TRANSIENT OXIDE EFFECT (SIMULATING THE IN-SERVICE OXIDATION CONTRIBUTION) ON THE HT STEAM OXIDATION SUMMARY:

- From the overall time evolution of weight gain / oxide thickness
=> apparent “protective effect” (delay) on HT oxidation
- In fact, the overall quantity of O that diffuses into the prior- β substrate is the same whether there is a pre-ox. or not
(pre-transient zirconia as efficient as the outer steam as an oxygen source)
=> **No “protective effect / grace time” regarding PQ mechanical properties**
- Numerical modelling (Ekinox/Zircobase, Dictra/Zircomob) able to reproduce complex (non-monotonous) evolution as a function of oxidation time of the:
(1) respective ZrO_2 , $\alpha_{Zr}(O)$ and prior- β_{Zr} layer thicknesses;
(2) oxygen diffusion profiles within the different layers
=> *refinement of the modelling necessary to take into account the specific pre-transient oxide behavior (oxygen diffusivity) at HT*
- *Residual question: same behavior at HT of the pre-transient oxide formed out-of-pile (autoclave) vs. the one formed under irradiation in PWR?*

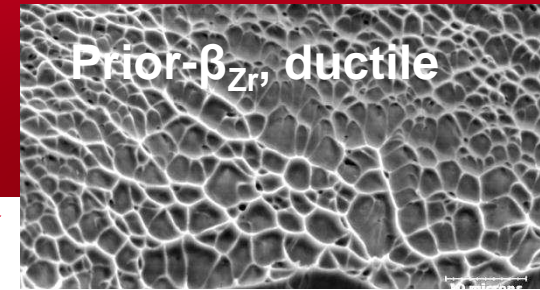
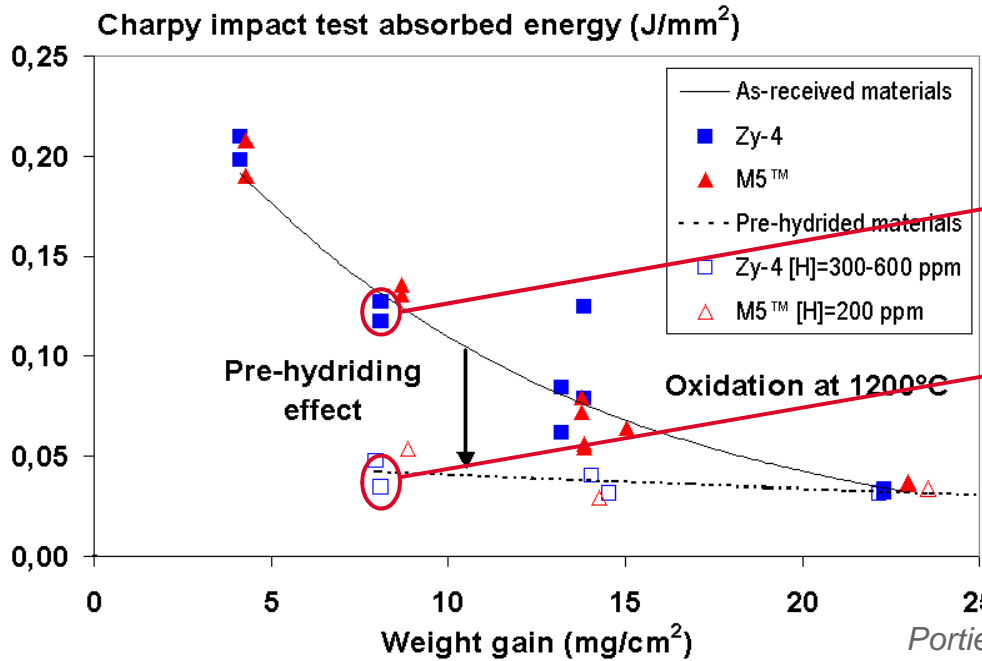
(3) Effects of pre-hydridding
- *simulating in-service hydridding* -
on HT oxidation
and PQ mechanical properties

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Direction de l'Energie Nucléaire
Département des Matériaux pour le Nucléaire
Service de Recherches Métallurgiques Appliquées

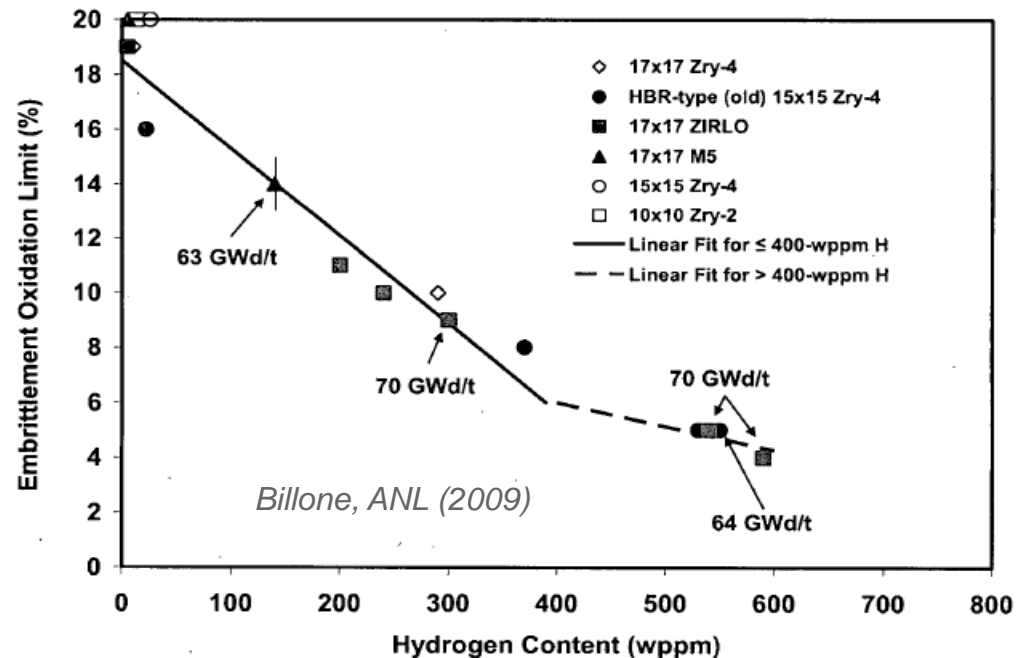
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EFFECTS OF PRE-HYDRIDING (1/5)



Portier et al. (2005)

Recent NRC recommendation for regulatory (LOCA) criteria revision: New LOCA criteria should take into account the influence of the hydrogen content (typical of high « BU » materials) on the « critical ECR » for retention of cladding PQ ductility



Billone, ANL (2009)

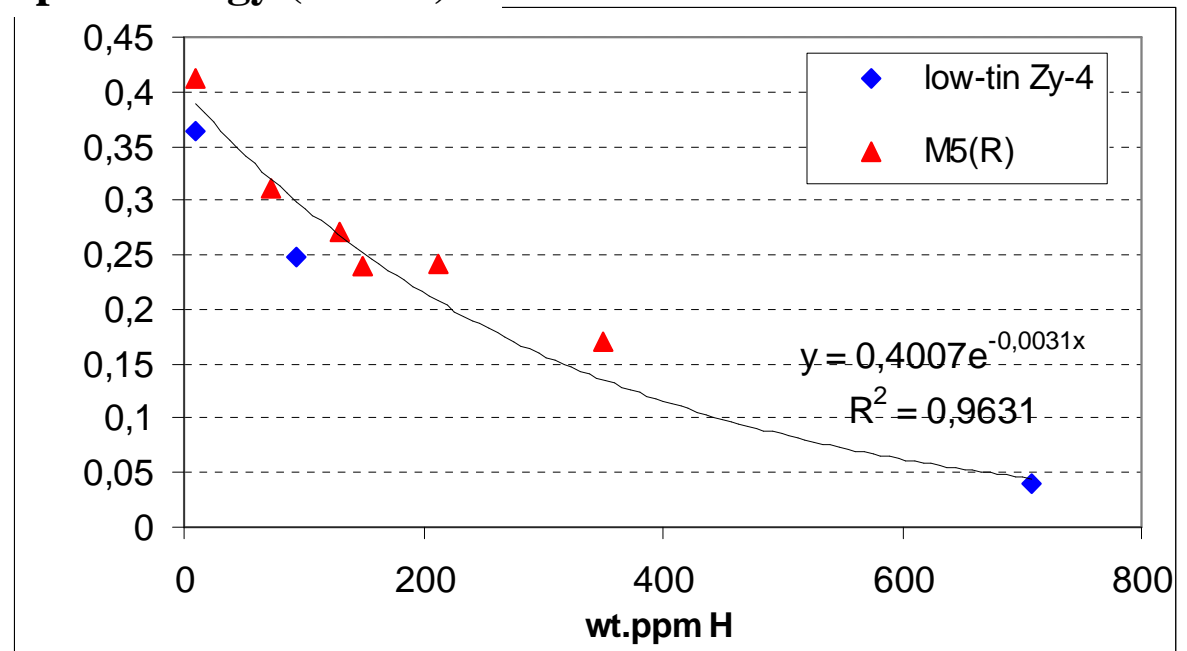
Two basic mechanisms for the [H] influence on PQ properties:

(1) « intrinsic » effect

(1) « Intrinsic » hydrogen embrittling effect highlighted by « flash » oxidation test (50s) at 1000°C => negligible ECR

=> Sharp decrease of the impact Energy at RT as H content increases

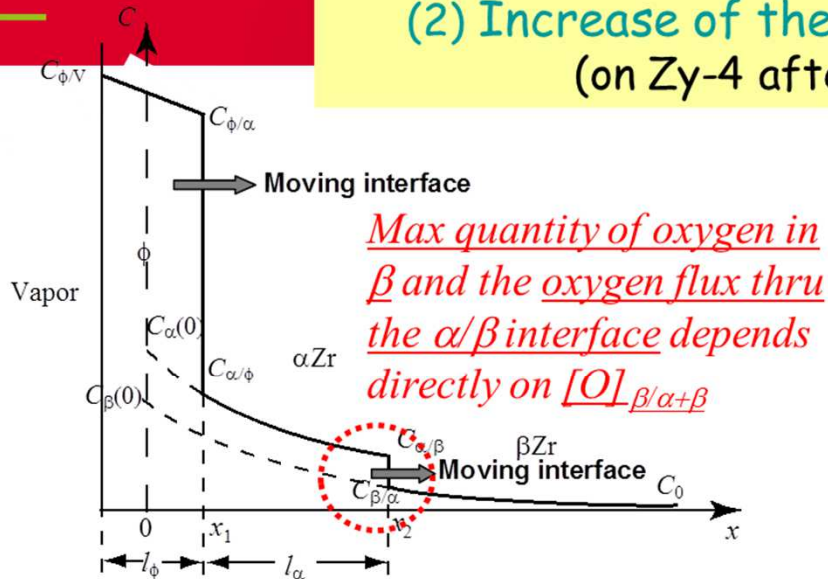
Impact energy (J/mm²)



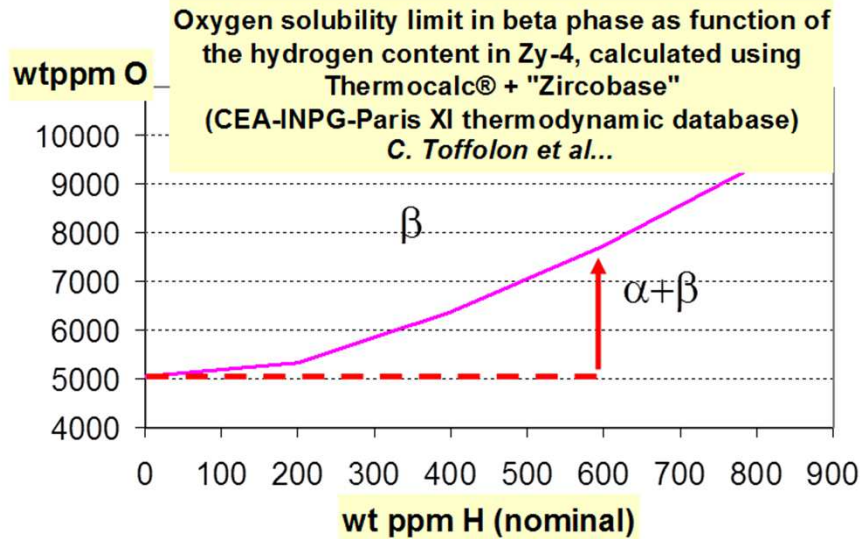
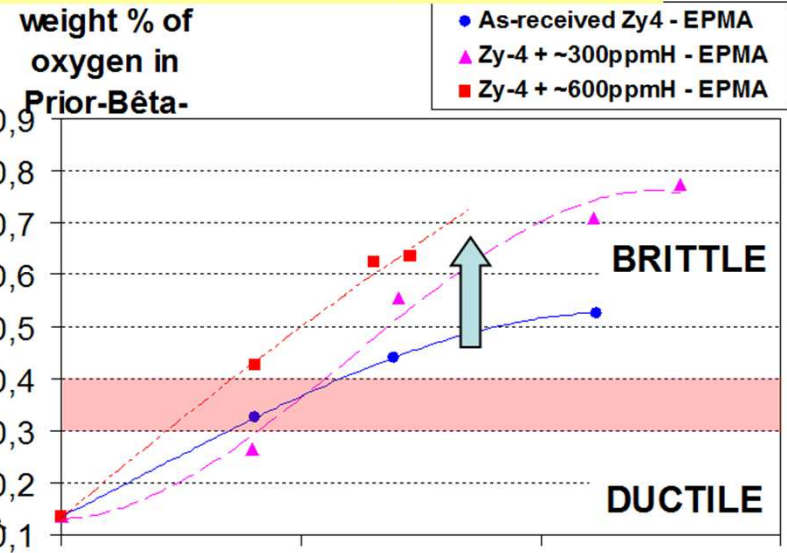
Brachet et al. (2008)

EFFECTS OF PRE-HYDRIDING (3/5)

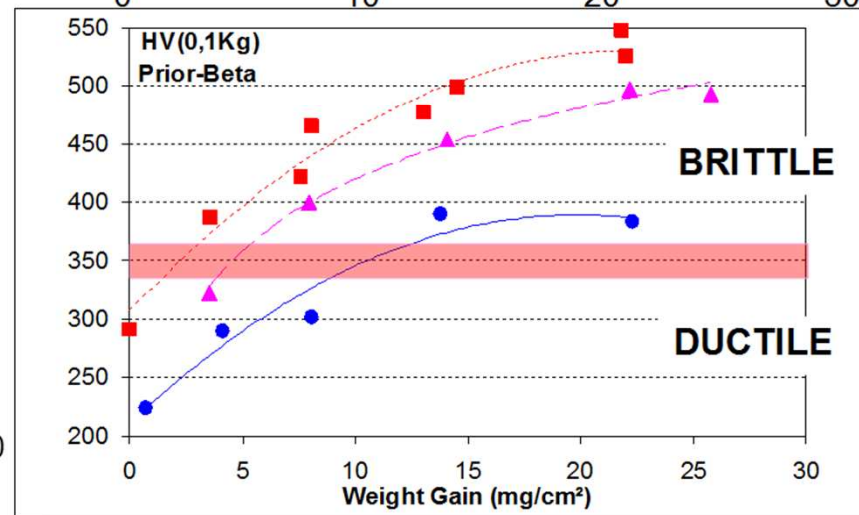
(2) Increase of the oxygen solubility in β effect (on Zy-4 after oxidation at 1200°C)



Schematic diagram of Zy-4 oxidized at temperature above the α/β transition temperature



Oxygen solubility limit in beta phase as function of the hydrogen content in Zy-4, calculated using Thermocalc® + "Zircobase" (CEA-INPG-Paris XI thermodynamic database) C. Toffolon et al...

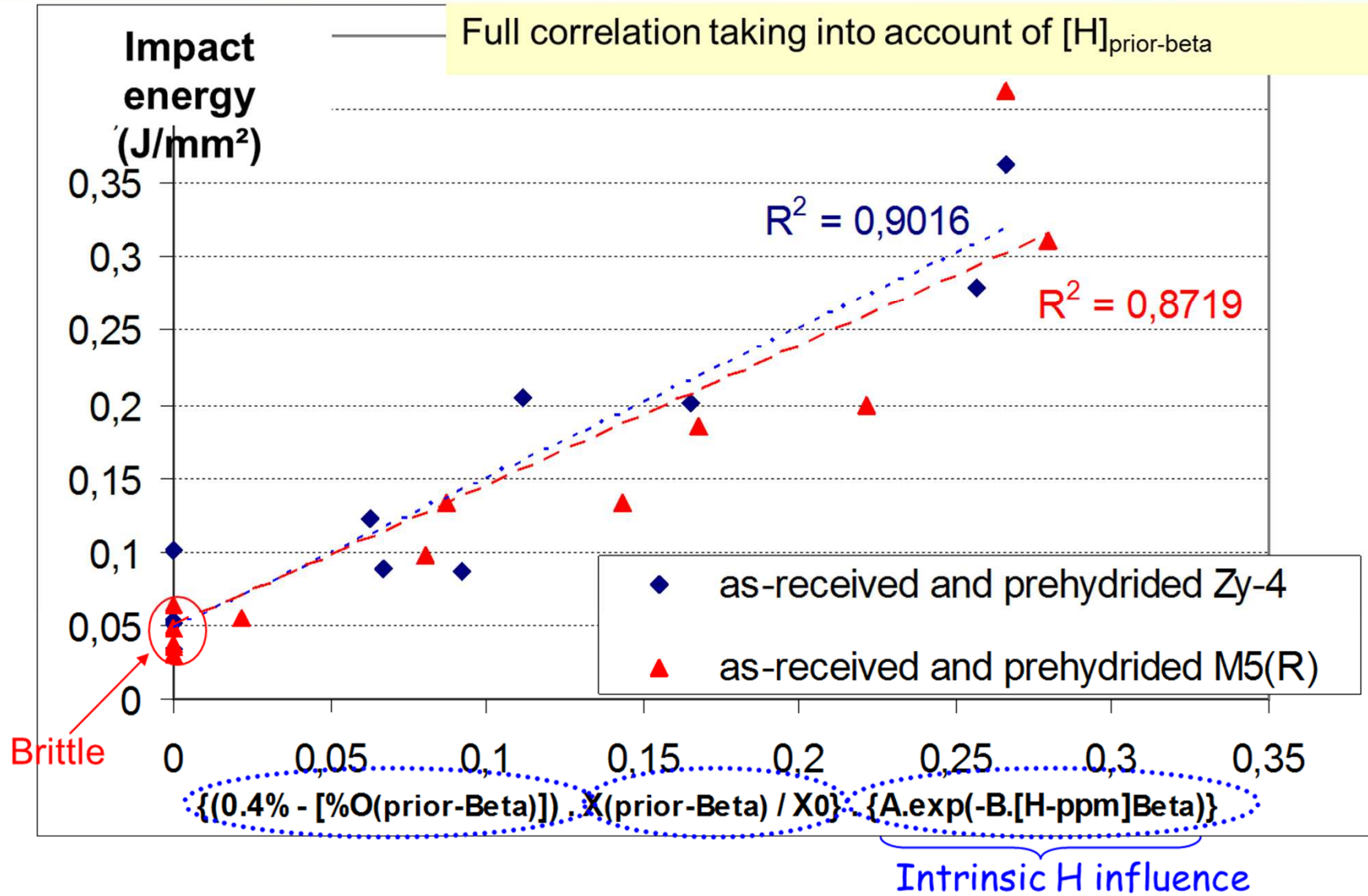


Brachet et al. (2008)



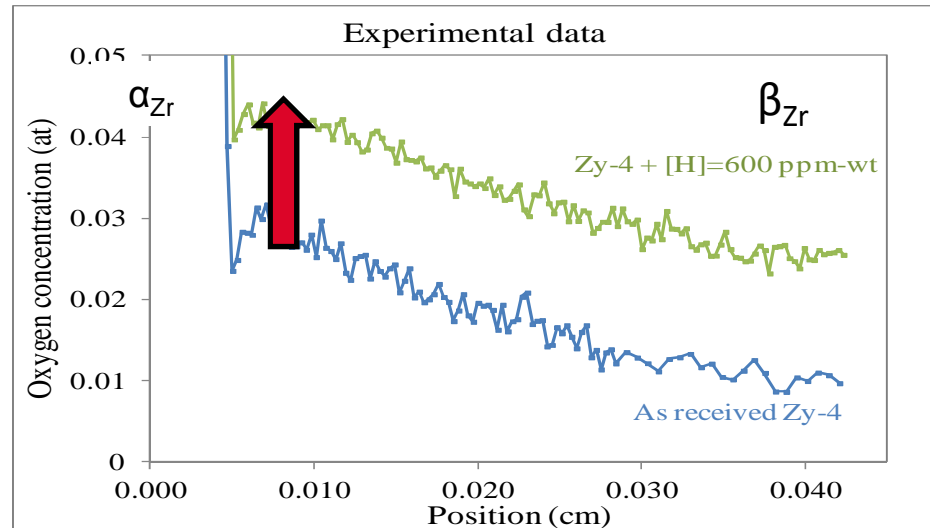
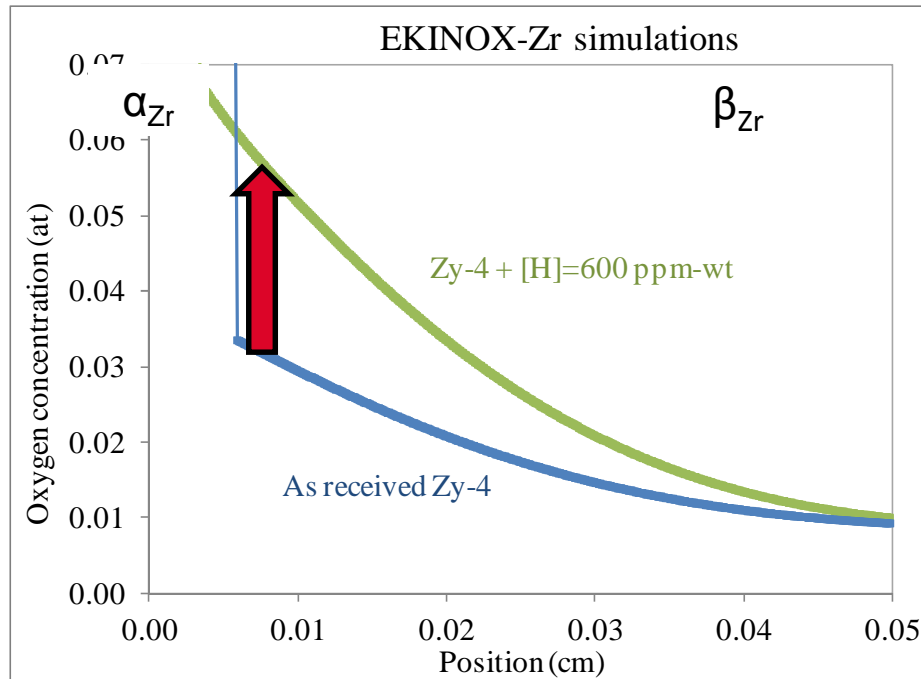
EFFECTS OF PRE-HYDRIDING (4/5)

=> REFINED CORRELATION BETWEEN PQ MECHANICAL PROPERTIES VS. RESIDUAL PRIOR-β : THICKNESS, %O AND %H



Brachet et al. (2008)

EFFECTS OF PRE-HYDRIDING (5/5) OXYGEN DIFFUSION MODELLING



As received and pre-hydrided (600 wt.ppm) Zircaloy-4 oxidized for 200s at 1200°C

⇒ Effect of H on the increase of oxygen solubility in β (assuming local thermodynamic equilibrium close to α/β interface) **correctly described** thanks to the coupling between Ekinox and Thermocalc®/Zircobase

⇒ *Further diffusion modelling improvement is necessary to fully describe the oxygen diffusion into the β layer upon HT steam oxidation*

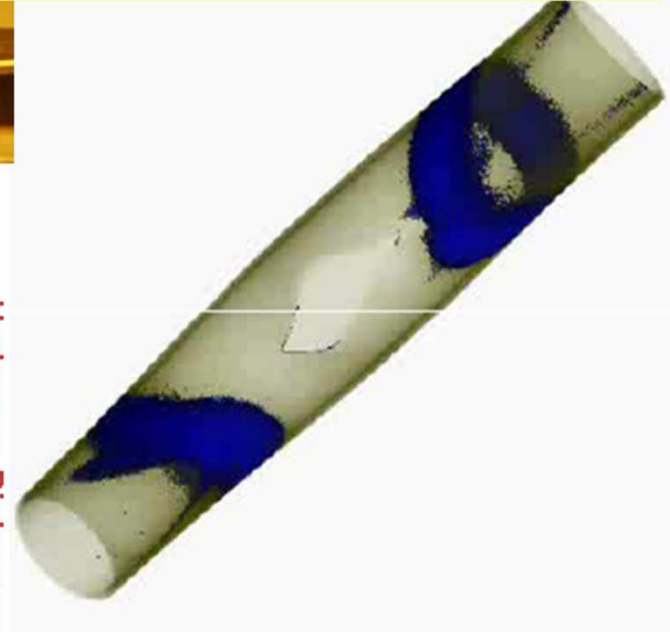
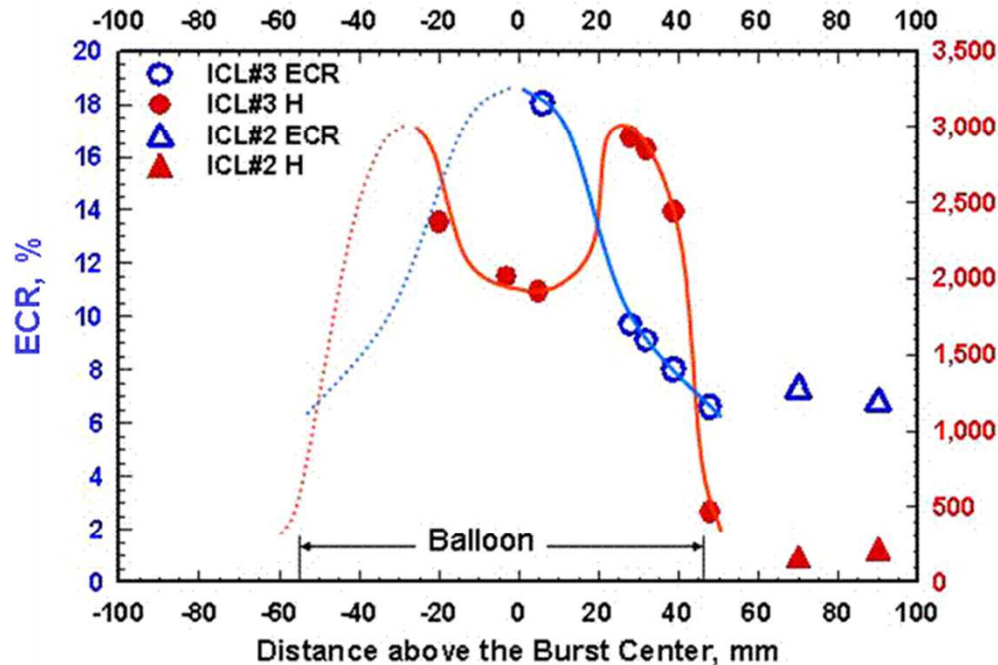
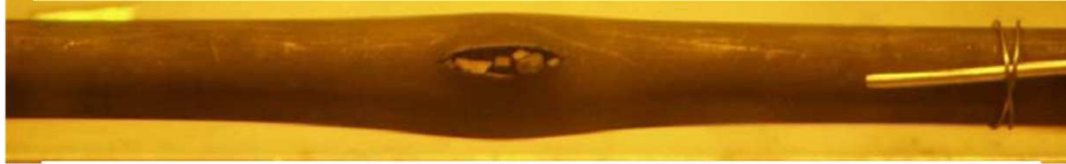
EFFECTS OF PRE-HYDRIDING ON HT OXIDATION AND PQ MECHANICAL PROPERTIES SUMMARY

- Pre-hydridding – simulating in-service hydridding (corrosion) - induces a decrease of the PQ ductility (for any given HT oxidation time and temperature)
- Two basics mechanisms:
 - (1) intrinsic « embrittlement » effect (*further studies needed to better understand this effect*)
 - (2) thermodynamic effect (*i.e., increase of the oxygen solubility in β_{Zr}*)
- Preliminary modelling (Ekinox/Thermocalc®Zircobase) able to reproduce the « thermodynamic » effect
=> *additional refinement of the diffusion modelling needed*
- “Final cooling scenario” observed on pre-hydrided zircaloy-4 assumed to be due to O and H partitioning upon the on cooling $\beta \rightarrow \alpha$ transformation => *further “micromechanical” approach/modelling...*

(3) HT secondary hydriding
(*due to steam starvation conditions
occurring upon HT steam oxidation into
the pellet-clad gap after cladding burst*)

HT SECONDARY HYDRIDING (1/3) - INTRODUCTION

Secondary hydriding in the vicinity of the burst location



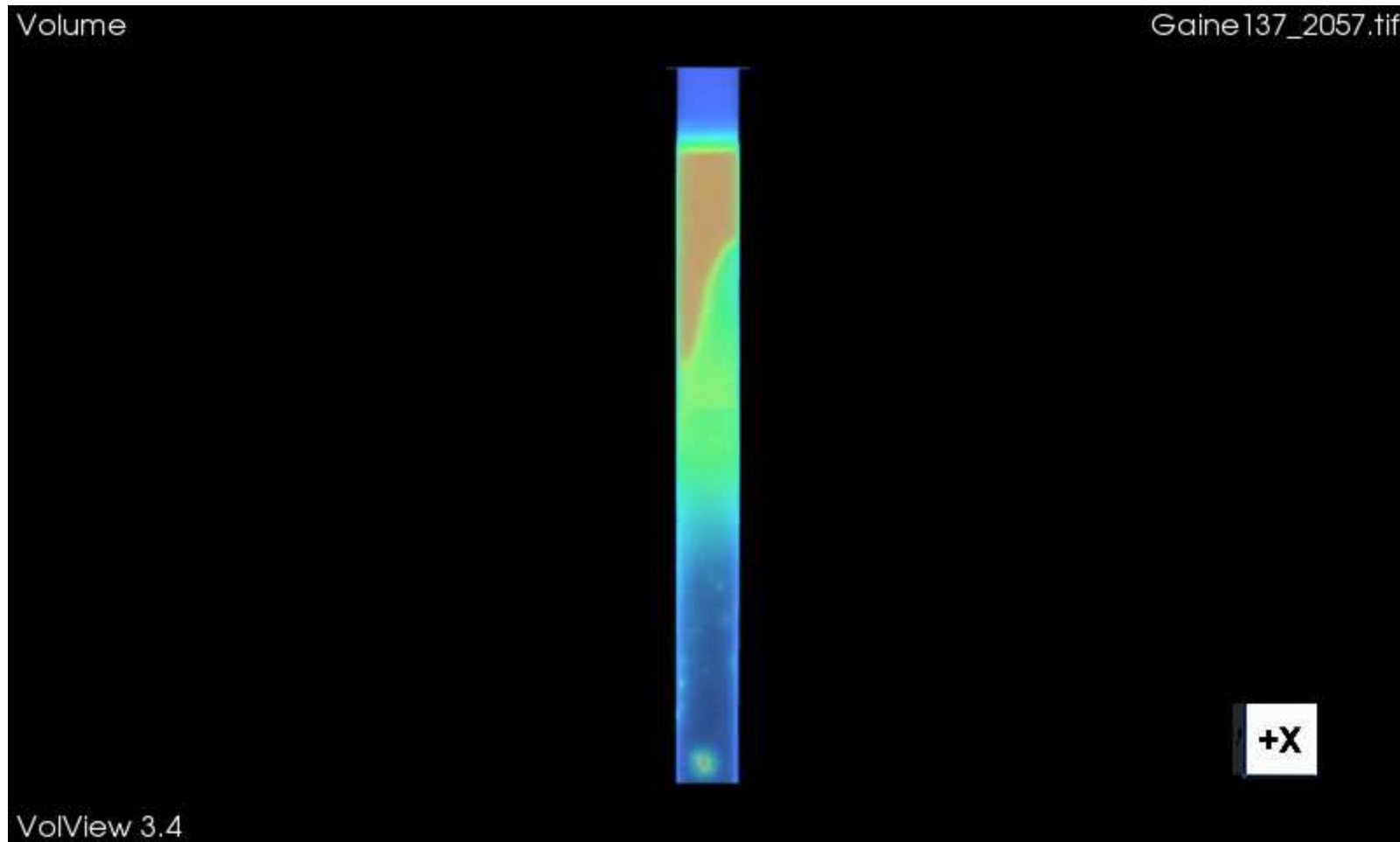
Hydrogen distribution into a LOCA tested clad due to secondary hydriding

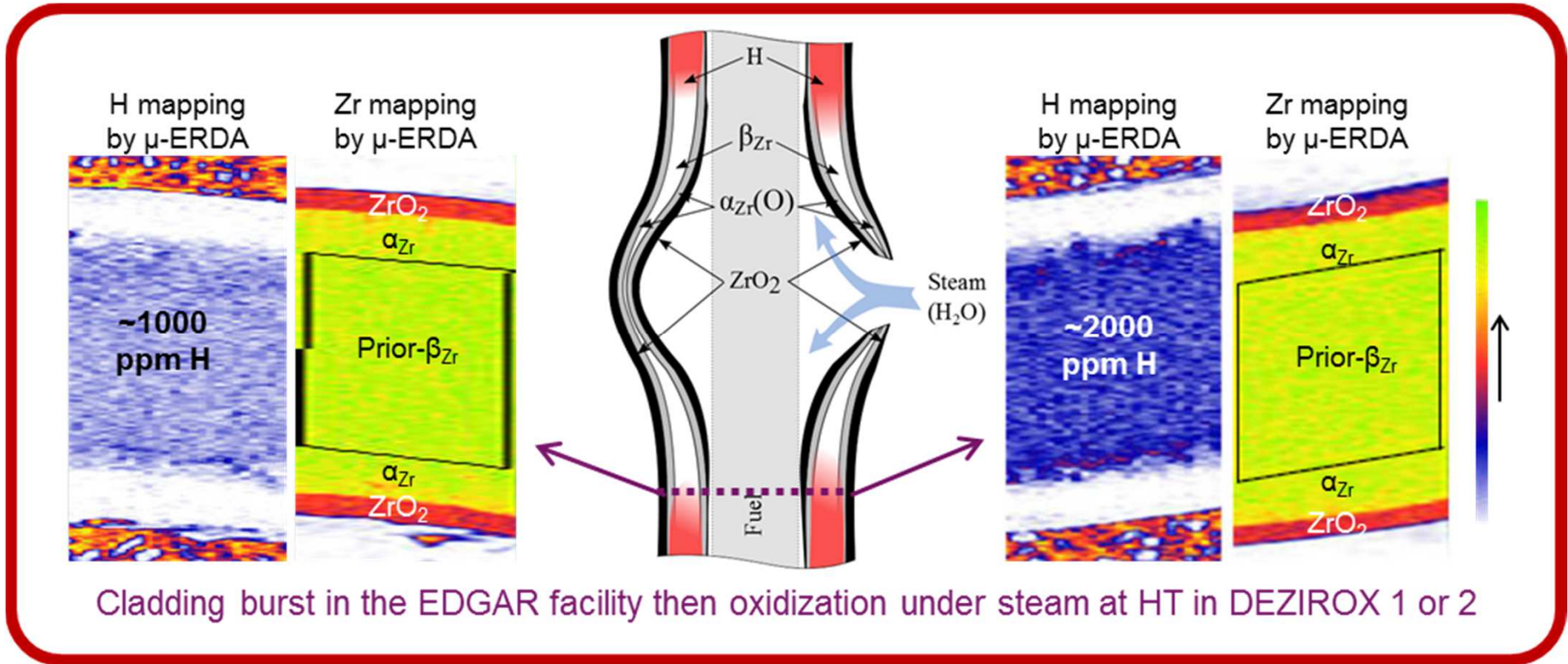
(Neutron Tomography, M. Grosse et al., Quench meeting, KTI, 2010)

*ANL integral one-rod LOCA test on high BU Zy-4
(M. Billone et al, ANL, 2005)*

Rem.: First observations in the early 80ties by JAEA (Uetsuka)...

Neutron-tomography performed on a clad segment having experienced HT burst and subsequent HT steam oxidation (collab. with CEA/DSM/LLB, lab., “Orphée” reactor





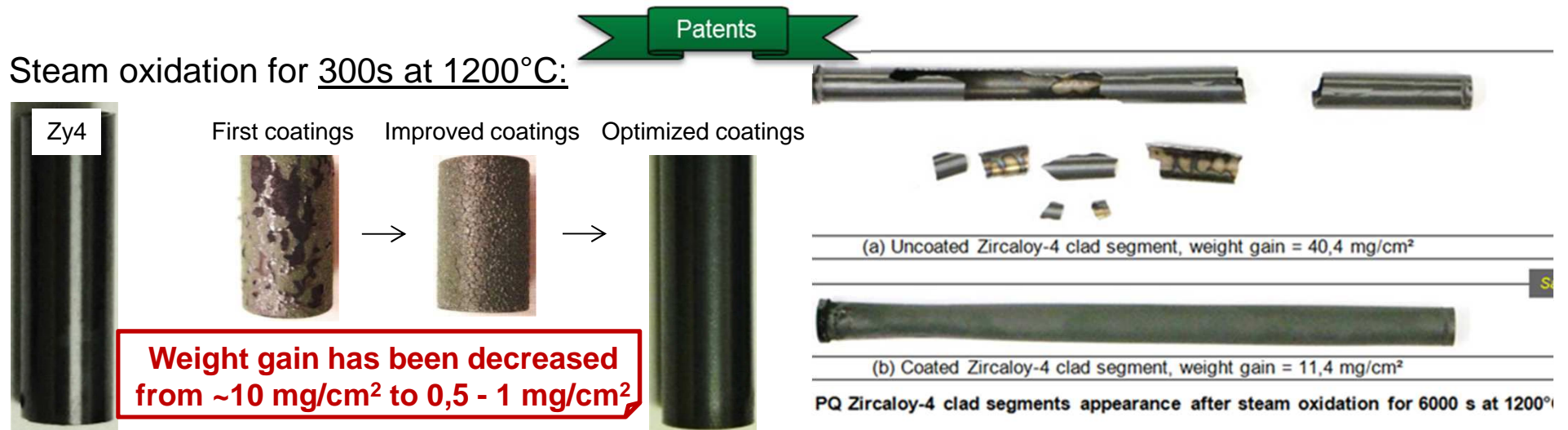
(Brachet, Le Saux et al... To be published)

On-going (PhD) work at CEA using model alloys with controlled (homogeneous) hydrogen and oxygen contents to reproduce the different local conditions of a clad that has experienced semi-integral LOCA testing - including 2nd hydriding phenomena => relationship with the PQ mechanical strength and ductility...

- Huge experimental database developed at CEA and associated deep (multi-scale) metallurgical analysis & PQ mechanical testing
- 1st order influence of oxygen and hydrogen diffusion/partitioning (into the residual prior- β layer)
- Modelling effort (analytical & numerical modelling: Ekinox/Zircobase, Dictra/Zirconob, FE calculations...) + refined relationship with the PQ clad mechanical properties taking into account both oxygen and hydrogen diffusion contributions
- *Additional work on-going, further oxidation modelling refinements...*
- *CEA expertise now used for development of “Enhanced Accident Tolerant Fuel for LWRs” (next slides)*

Expected Benefits :

- Decrease oxidation rate in service and with steam water at high temperature
- Reduce in service hydriding and hydrogen release during accidental sequence
- Improve LOCA behavior (Peak clad T ↓, post quench ductility ↗)
- Improve long term coolability - procure grace time in the early stage of SA



Brachet et al., 2014

On-going ions irradiation simulations and neutron irradiations planned (Halden...)

Continue evaluation experiments dedicated to the consolidation of the viability of the concept

- Autoclave testing
- Mechanical testing and impact on the tightness
- Tightness of caps ends



Optimization of the concept for LWRs application

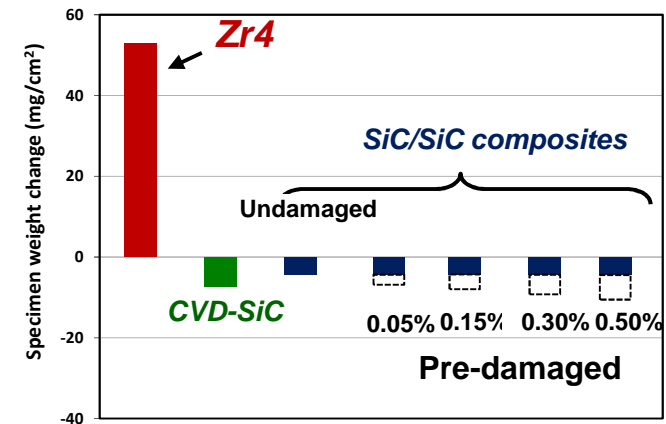
Patents

- Normal conditions: Secure resistance in water environment

SiC recession needs to be mitigated surface from reaction with water

Positive mechanical/thermal behavior
SiC/SiC in LWR conditions (Out of pile)

- Off-normal conditions: Oxidation of SiC/SiC under high temperature steam (up to 1400 °C)
=> Confirmation of the protective function by silica in these conditions



Forgeron et al., 2016

Thank you for your attention

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Back slides



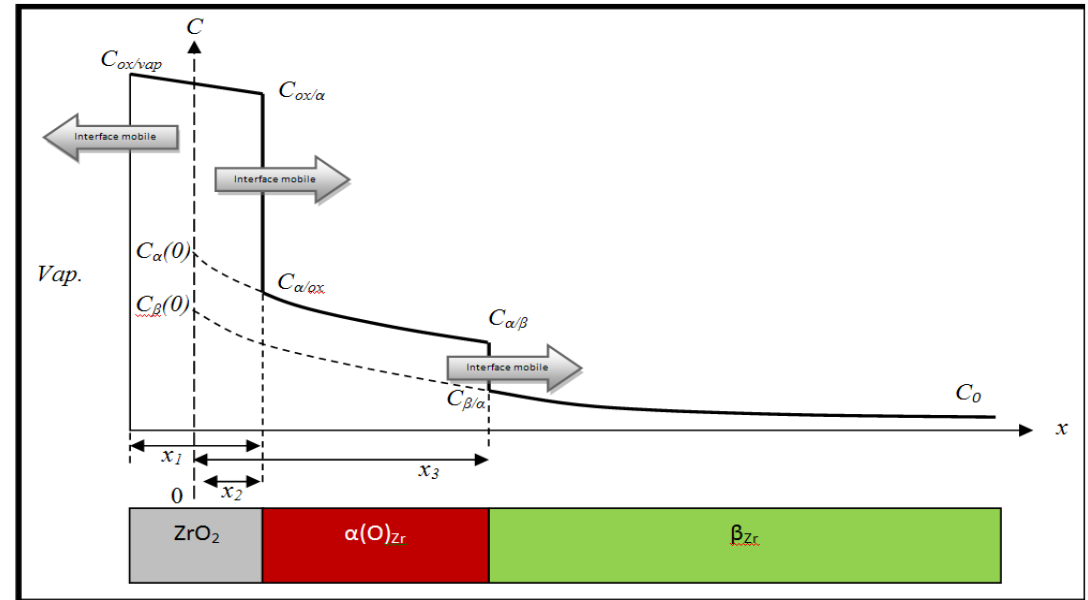
HT OXIDATION ANALYTICAL MODELLING (1) DEBUIGNE'S MODEL (1966)

Boundary conditions:

$$Ox : \begin{cases} C_{ox} = C_{ox/vap} & \text{for } x = x_0, t > 0 \\ C_{ox} = C_{ox/\alpha}(\infty) & \text{for } x = x_1, t = 0 \end{cases}$$

$$\alpha_{Zr} : \begin{cases} C_{\alpha} = C_{\alpha}(0) & \text{for } x = 0, t > 0 \\ C_{\alpha} = C_{\alpha}(\infty) & \text{for } x > 0, t = 0 \end{cases}$$

$$\beta_{Zr} : \begin{cases} C_{\beta} = C_{\beta}(0) & \text{for } x = 0, t > 0 \\ C_{\beta} = C_{\beta}(\infty) & \text{for } x > 0, t = 0 \end{cases}$$



Oxygen diffusion equations at the interfaces ox/α and α/β :

$$D_{ox} \times \frac{\partial C_{ox/\alpha}}{\partial x} \Big|_{x=x_1} - D_{\alpha} \times \frac{\partial C_{\alpha/ox}}{\partial x} \Big|_{x=x_2} = -C_{ox/\alpha} \frac{dx_1}{dt} + C_{\alpha/ox} \frac{dx_2}{dt}$$

$$D_{\alpha} \times \frac{\partial C_{\alpha/\beta}}{\partial x} \Big|_{x=x_3} - D_{\beta} \times \frac{\partial C_{\beta/\alpha}}{\partial x} \Big|_{x=x_3} = -C_{\alpha/\beta} \frac{dx_3}{dt} + C_{\beta/\alpha} \frac{dx_3}{dt}$$

Steady-state hypothesis:

$$\frac{C_0 - C_{\Phi}(x)}{C_0 - C_{\Phi}(0)} = 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{\Phi}t}} \right)$$

J. DEBUIGNE. PhD thesis, Université de Paris, May the 25th 1966.
X. MA et al. Journal of Nuclear Materials, 2008, vol. **377**. p. 359-369.

HT OXIDATION ANALYTICAL MODELLING (2) PAWEL'S MODEL (1979)

Oxide growth kinetic:

$$\frac{dk}{dt} = \frac{\delta_k}{2k} \quad k = 0, t = 0 \Rightarrow k = \delta_k \sqrt{t}$$

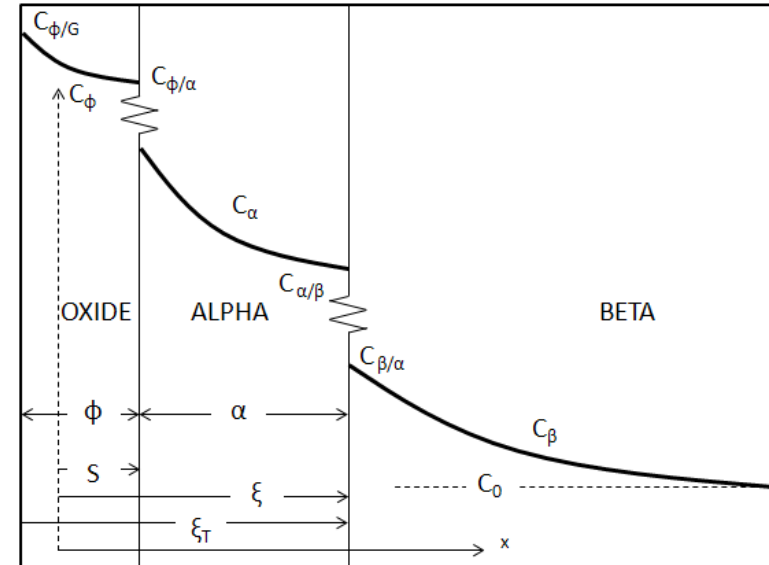
Interface motion ox/ α and α/β :

$$\frac{d\xi}{dt} = \frac{-D_\alpha \frac{\partial C_\alpha}{\partial x} \Big|_{x=\xi} + D_\beta \frac{\partial C_\beta}{\partial x} \Big|_{x=\xi}}{C_{\alpha/\beta} - C_{\beta/\alpha}} \quad \frac{dS}{dt} = \frac{-D_\phi \frac{\partial C_\phi}{\partial x} \Big|_{x=S} + D_\alpha \frac{\partial C_\alpha}{\partial x} \Big|_{x=S}}{VC_{\phi/\alpha} - C_{\alpha/\phi}}$$

Steady-state hypothesis:

$$C_\phi = C_{\phi/G} - \frac{(C_{\phi/G} - C_{\phi/\alpha}) \operatorname{erf}\left(\frac{x + (V-1)S}{2\sqrt{D_\phi t}}\right)}{\operatorname{erf}\left(\frac{VS}{2\sqrt{D_\phi t}}\right)}$$

$$C_\alpha = C_{\alpha/\phi} - \frac{(C_{\alpha/\phi} - C_{\alpha/\beta}) \times \left[\operatorname{erf}\left(\frac{x}{2\sqrt{D_\alpha t}}\right) - \operatorname{erf}\left(\frac{S}{2\sqrt{D_\beta t}}\right) \right]}{\left[\operatorname{erf}\left(\frac{\xi}{2\sqrt{D_\alpha t}}\right) - \operatorname{erf}\left(\frac{S}{2\sqrt{D_\alpha t}}\right) \right]}$$



$$C_\beta = C_0 + \frac{(C_{\beta/\alpha} - C_0) \times \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D_\beta t}}\right) \right]}{\left[1 - \operatorname{erf}\left(\frac{\xi}{2\sqrt{D_\beta t}}\right) \right]}$$

R.E. Pawel, J. Electrochim. Soc. 126 (1979) 1111.

HT OXIDATION NUMERICAL MODELLING (1) CEA « EKINOX » MODEL (2012)

- EKINOX-Zr :

- Boundary conditions:

$$\begin{aligned} C_{Ox}(n, t) &= C_{Ox/vap} & C_{\alpha}(j, t) &= C_{\alpha/\beta} \\ C_{Ox}(i, t) &= C_{Ox/\alpha} & C_{\beta}(j, t) &= C_{\beta/\alpha} \\ C_{\alpha}(i, t) &= C_{\alpha/ox} & C_{\beta}(1, t) &= C_0 \end{aligned}$$

- First and second Fick's laws, oxide growth:

$$J = -D \frac{\partial c}{\partial x} \quad \frac{\partial J}{\partial x} = -\frac{\partial c}{\partial t} \quad \frac{\partial e}{\partial t} = PBR \frac{\partial x_i}{\partial t}$$

- Interface motion is linked to the oxygen flux which crosses the interface:

$$(C_{\alpha/\beta} - C_{\beta/\alpha}) \frac{\partial x_j}{\partial t} = D_{\alpha} \frac{\partial C_{\alpha}}{\partial x} \Big|_j - D_{\beta} \frac{\partial C_{\beta}}{\partial x} \Big|_j \quad (C_{Ox/\alpha} - C_{\alpha/ox}) \frac{\partial x_i}{\partial t} = D_{Ox} \frac{\partial C_{Ox}}{\partial x} \Big|_i - D_{\alpha} \frac{\partial C_{\alpha}}{\partial x} \Big|_i$$

- In the oxide, oxygen diffuses thanks to anionic vacancies:

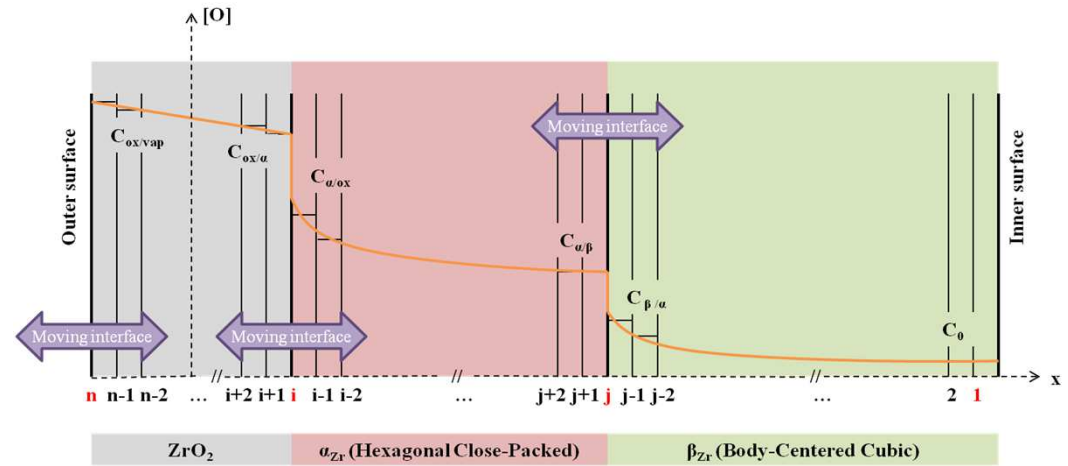
$$J_{V_O}^p = -\frac{D_{V_O}^p}{\Omega^p} \times \frac{X_{V_O}^{p+1} - X_{V_O}^p}{2}$$

- The evolution of oxygen concentration in one slab is linked to the flux balance of in the slab:

$$\dot{X}_{V_O}^p = \frac{dX_{V_O}^p}{dt} = -\Omega^p \times \frac{J_{V_O}^p - J_{V_O}^{p+1}}{e^p}$$

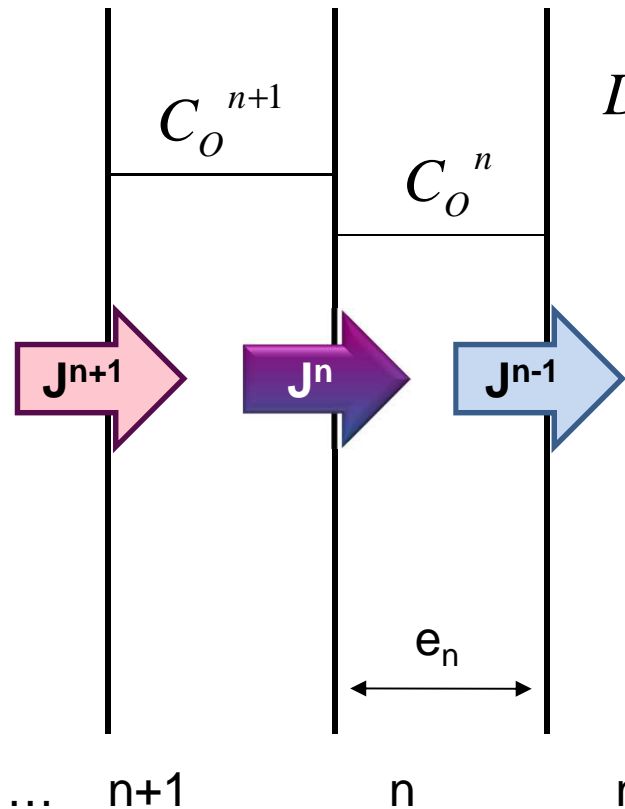
- Interface motion is calculated by thickness variations of the two slabs close to the interface:

$$\frac{de^{j+1}}{dt} = \Omega^{p+1} \times \frac{J_{V_O}^{j-1} - J_{V_O}^{j+1}}{C_0^{\alpha/\beta} - C_0^{\beta/\alpha}} \quad \frac{de^{i+1}}{dt} = \frac{\Omega^{i+1}}{\gamma} \times \frac{J_{V_O}^{i-1} - J_{V_O}^{i+1}}{C_0^{Ox/\alpha} - C_0^{\alpha/Ox}}$$



Extérieur de la gaine (ZrO_2)
Cœur de la gaine (β_Zr)

Sens de diffusion de O^{2-}



$$D(T, \Phi) = D_0(T, \Phi) \times e^{-\frac{E_A(n, \Phi)}{RT}}$$

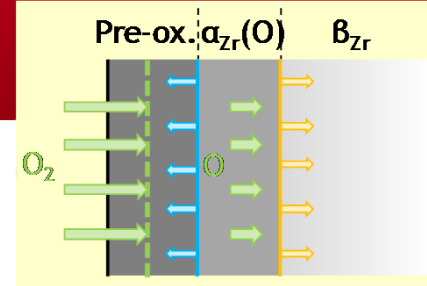
$$J^n = D(T, \Phi) \times \frac{C_o^{n+1} - C_o^n}{\frac{e_{n+1} + e_n}{2}}$$

$$\frac{dC_o^n}{dt} = -\frac{J_o^n - J_o^{n-1}}{e_n}$$

$$C_o^n(t + dt) = C_o^n(t) + \frac{dC_o^n}{dt} \times \Delta t$$

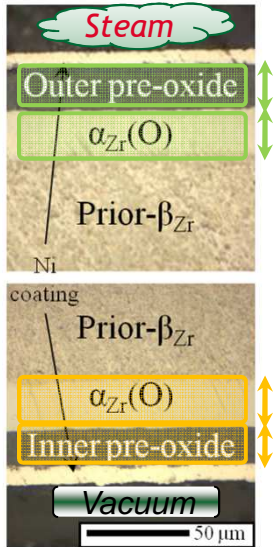
EFFECT OF PRE-TRANSIENT OXIDE

For short oxidation times...

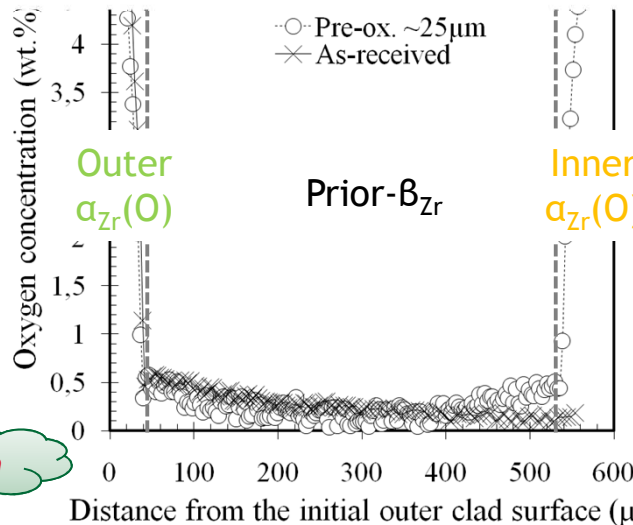
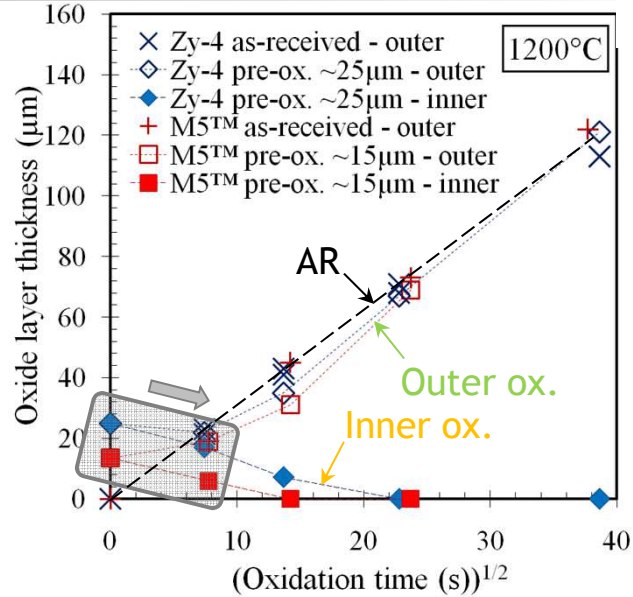


Le Saux, Topfuel - 2011

Zy-4
M5™



Zy-4 pre-ox. ~25µm
1200°C 55s



Reduction of the pre-transient ox. at the $ZrO_2/\alpha_{Zr}(O)$ interface without formation of new “fresh” HT ox.

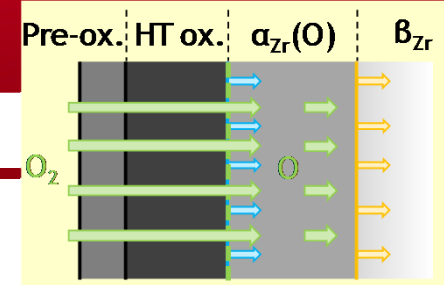
→ Lower weight gains compared to those of the non pre-ox. specimens

Diffusion of the O coming from the reduction of the pre-ox. into the cladding metallic part

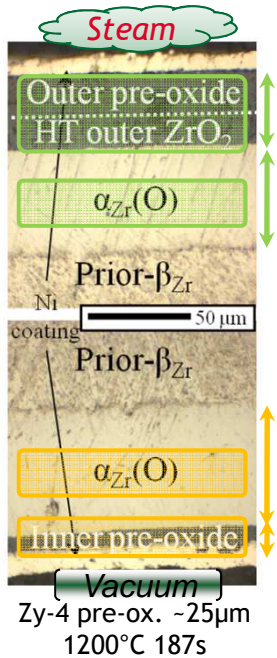
The overall quantity of O that diffuses is the same whether there is a pre-ox. or not

→ The pre-ox. layers are not protective regarding PQD !

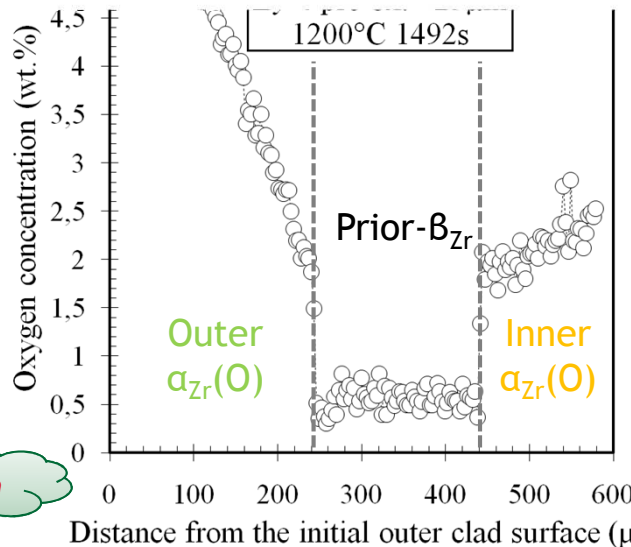
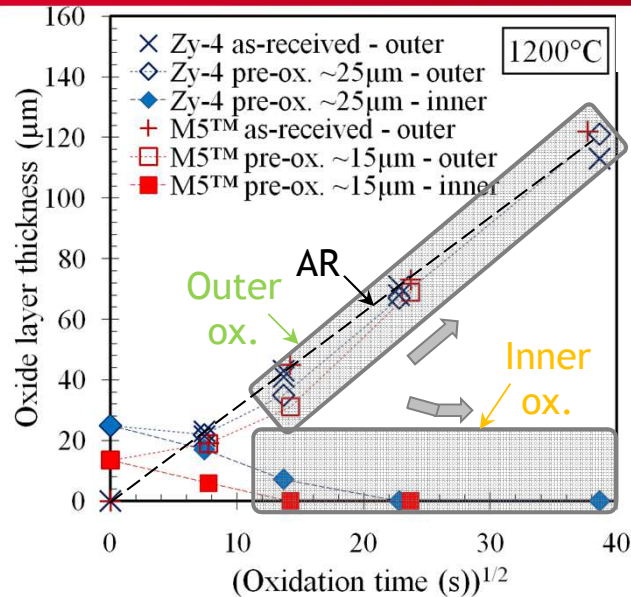
Later...



Le Saux, Topfuel - 2011



Zy-4
M5™



□ OD (steam) : Growth of a “fresh” columnar HT oxide beneath the residual pre-ox. when O atoms coming from the outer steam have reached the moving $ZrO_2/\alpha_{Zr}(O)$ interface (the thicker the pre-ox., the later it occurs)

□ ID (vacuum): Complete reduction of the pre-ox.

➔ No more O is available on the inner surface and growth kinetics of the inner $\alpha_{Zr}(O)$ layer slows down compared to that of the outer $\alpha_{Zr}(O)$ layer

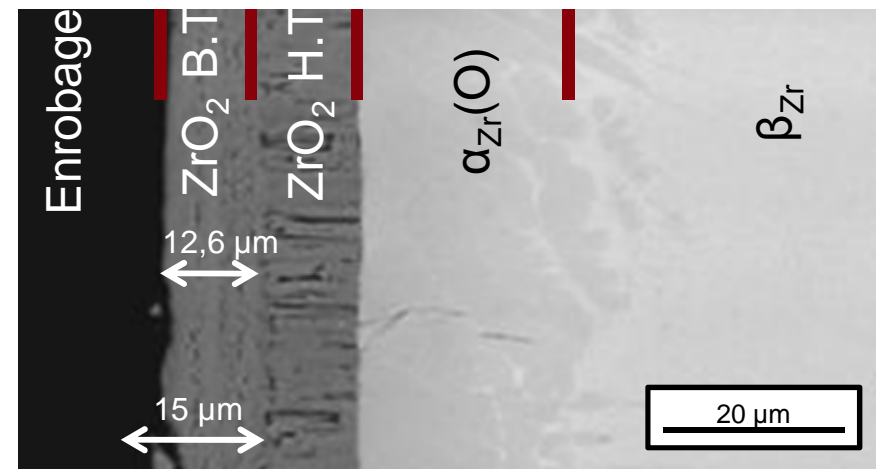
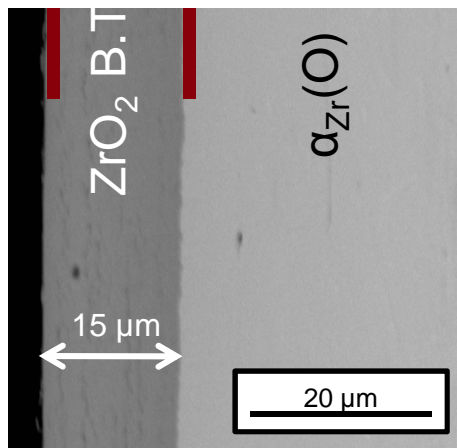
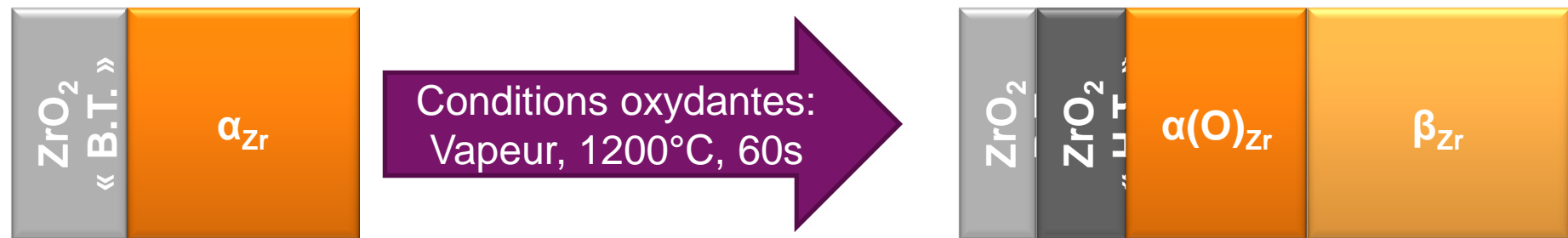
Similar results at 1000°C

Steam

Vacuum

Phénomène de la dissolution-recroissance :

M5™ pré-oxydé 15 µm, oxydé sous vapeur à 1200°C pendant 60s

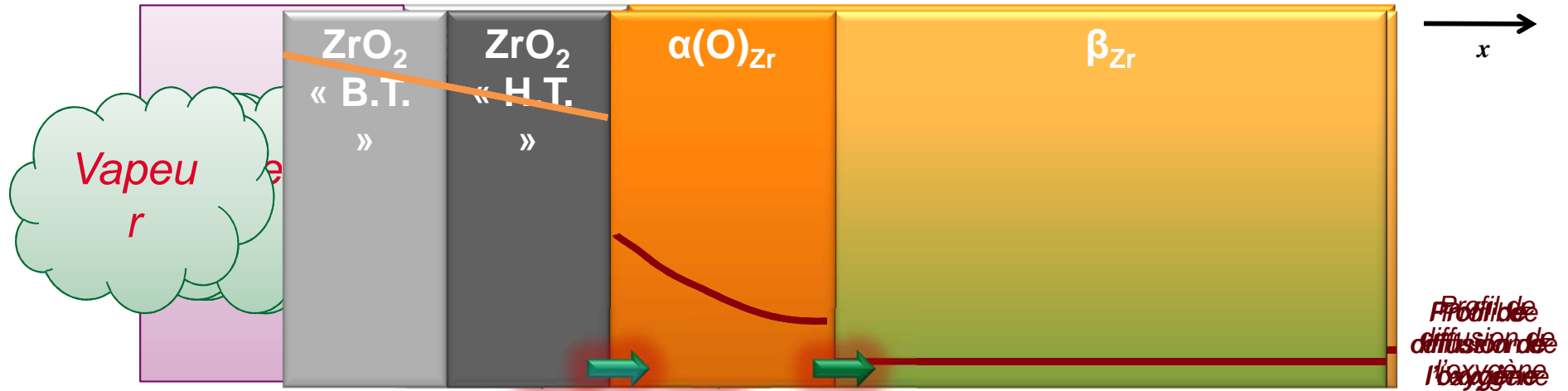


J.-C. BRACHET et al. *Hydrogen content, preoxidation and cooling scenario. Effects on post-quench microstructure and mechanical properties of Zircaloy-4 and M5™ alloys in LOCA*. Journal of ASTM International. Vol 5, N°5. 2008. Paper ID JAI101116

ÉLÉMENT NUMÉRIQUE

CAS DE LA DISSOLUTION-RECROISSANCE

Phénomène de la dissolution-recroissance Echantillons de Zy-4 pré-oxydés 15 μ



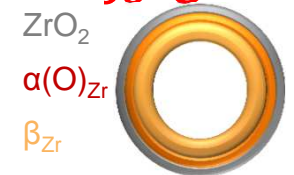
$$J_{ox} = J_{\alpha} < 0$$

$$\frac{dx_2}{dt} = \frac{\overbrace{-D_{ox} \times \frac{\partial C_{ox/\alpha}}{\partial x}}^{J_{ox}} \Big|_{x=x_2} + \overbrace{+D_{\alpha} \times \frac{\partial C_{\alpha/ox}}{\partial x}}^{J_{\alpha}} \Big|_{x=x_2}}{\frac{1}{P} C_{ox/\alpha} - C_{\alpha/ox}} < 0$$

$$\frac{dx_3}{dt} = \frac{-D_{\alpha} \times \frac{\partial C_{\alpha/\beta}}{\partial x} \Big|_{x=x_3} + D_{\alpha} \times \frac{\partial C_{\beta/\alpha}}{\partial x} \Big|_{x=x_3}}{C_{\alpha/\beta} - C_{\alpha/\beta}} > 0$$

$T \approx 1200^{\circ}\text{C}$

$T \approx 360^{\circ}\text{C}$



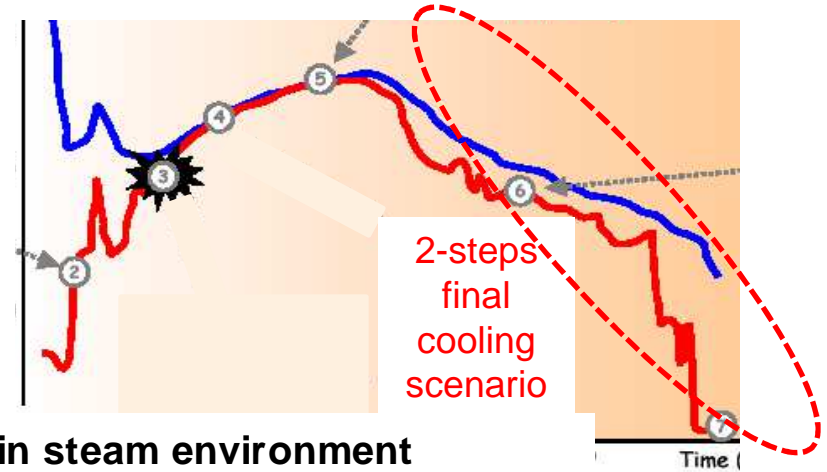
Numerous CEA HT oxidation tests were performed with **direct water quenching** at the end of the isothermal HT steam oxidation process

But, for « real » LOCA transient

=> **two steps final cooling** of the clad :

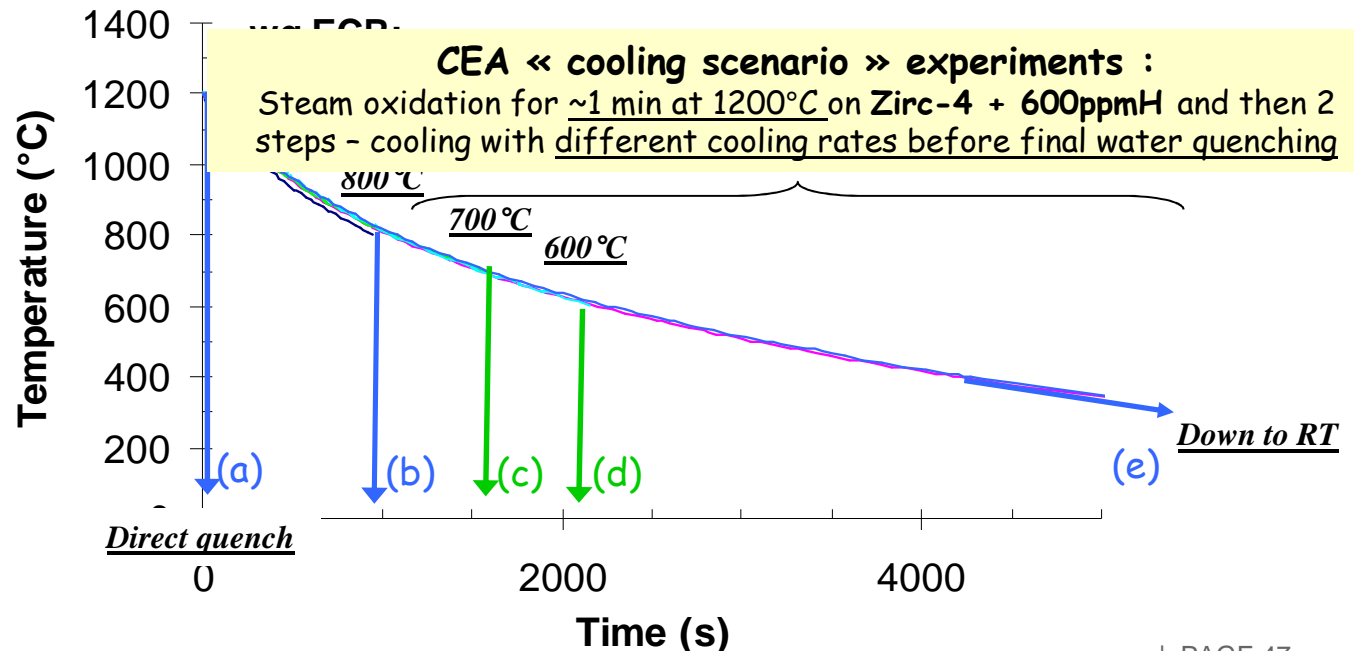
(1) **cooling first at 1-10°C/s** down to a certain « wetting » temperature

(2) and then **final water**



Cooling in steam environment

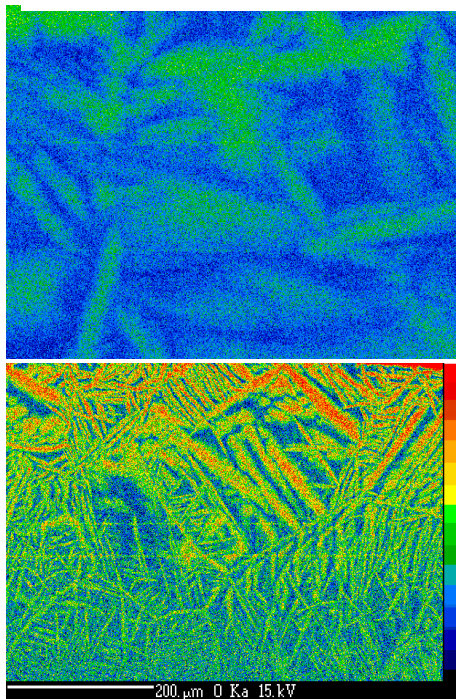
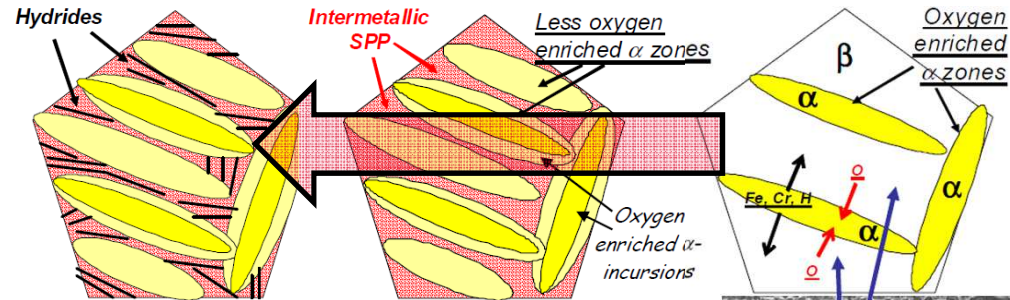
Depending on the LOCA transient type (SB, LB...) typical final quenching (wetting) temperatures range from ~1000°C down to ~400°C



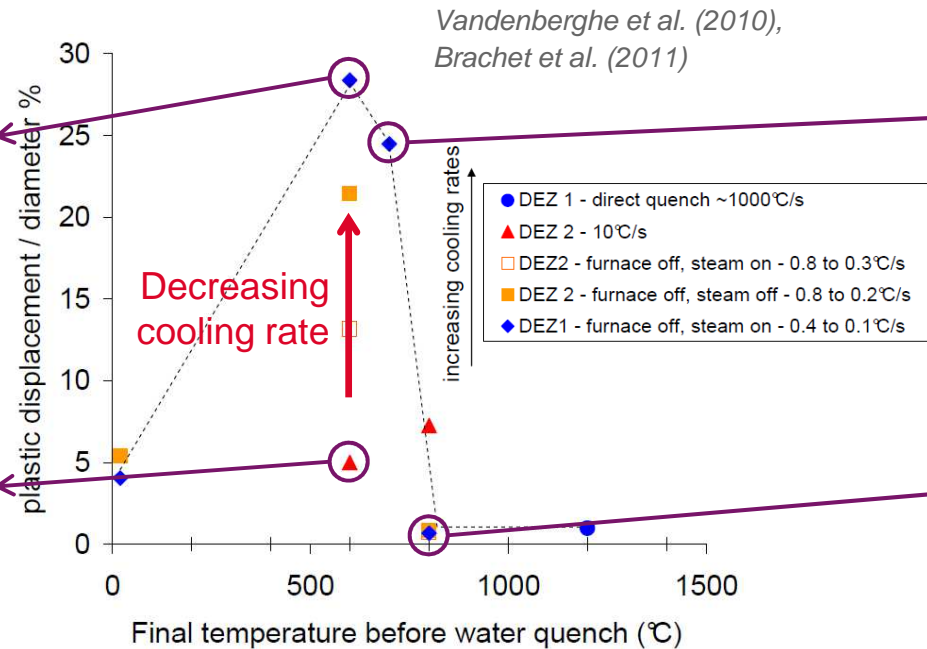
EFFECTS OF PRE-HYDRIDING

=> « FINAL COOLING SCENARIO » EFFECT ON PQ DUCTILITY

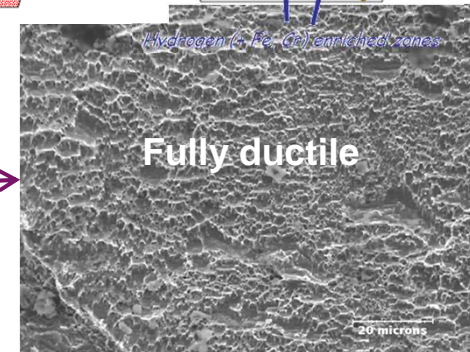
=> strong influence of O and H partitioning upon the on cooling $\beta \rightarrow \alpha$ transformation
 ⇔ « microcomposite » mechanical behavior



EPMA oxygen map within prior- β layer



Pre-hydrided (600 ppm) zircaloy-4 after HT oxidation for 1 min at 1200°C and tested (3-point bending) at 135°C



Fractographs of prior- β_{Zr} zones