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

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J.-C. Brachet, Matthieu Le Saux, C. Toffolon-Masclet. 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. Séminaire scientifique DEN sur la corrosion dans les REP - Corrosion in pressurized water reactors: phenomenology, mechanisms and modelling, Oct 2016, Saclay, France. cea-02438347

HAL Id: cea-02438347
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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)

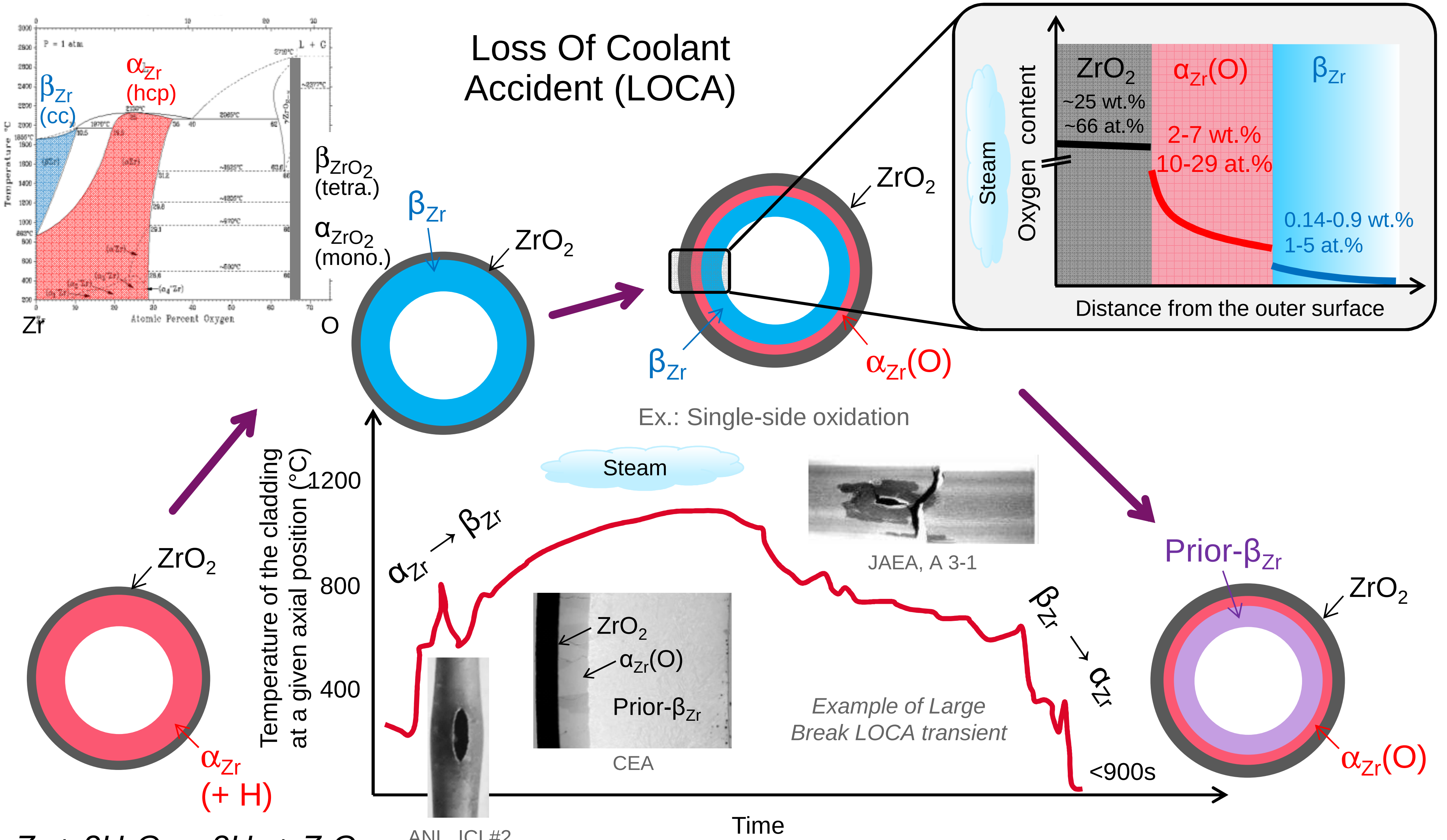
with the contribution of: Clara Desgranges (CEA-DPC), Valérie Vandenberghe, Laurence Portier and numerous colleagues & PhD students at CEA…

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

CORROSION IN PRESSURIZED WATER REACTORS:
PHENOMENOLOGY, MECHANISMS AND MODELLING
CEA/DEN 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...)



$$Zr + 2H_2O \rightarrow 2H_2 + ZrO_2$$

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 SLIGHLTY 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, µcrochemical) studies

- ✓ *$\alpha_{Zr} \leftrightarrow \beta_{Zr}$ transformation kinetics (dilatometry, resistivity, in-situ neutron diff...) (*)*
- ✓ Systematic and accurate phases thicknesses quantification (oxide, α(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 ») ⬄ Calphad/Thermocalc®
- ✓ Kinetics database for Zr alloys (« Zircomob ») ⬄ Dictra®
- ✓ HT Oxydation modelling « Ekinox-Zr » (collab. with CEA/DPC, 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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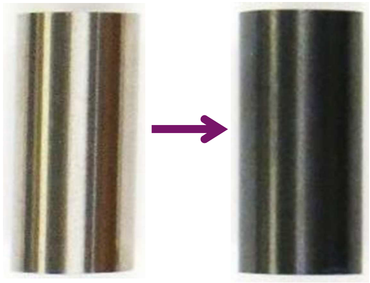
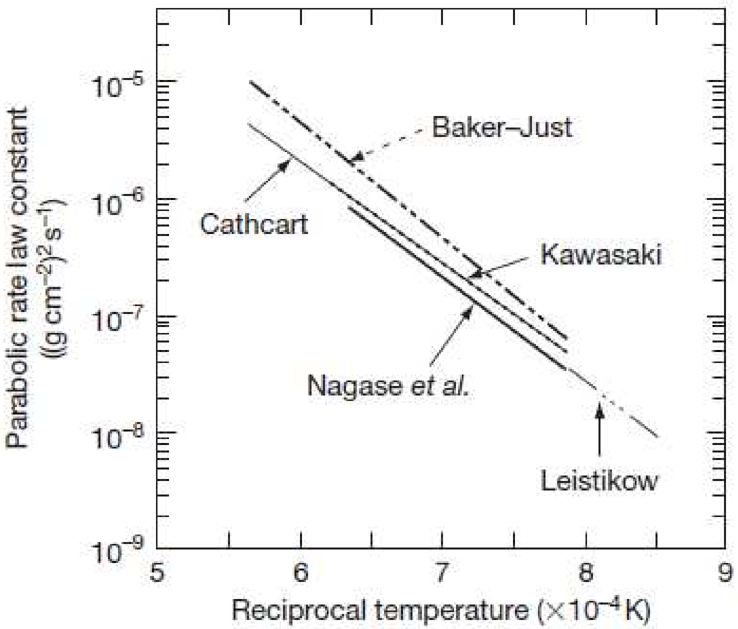
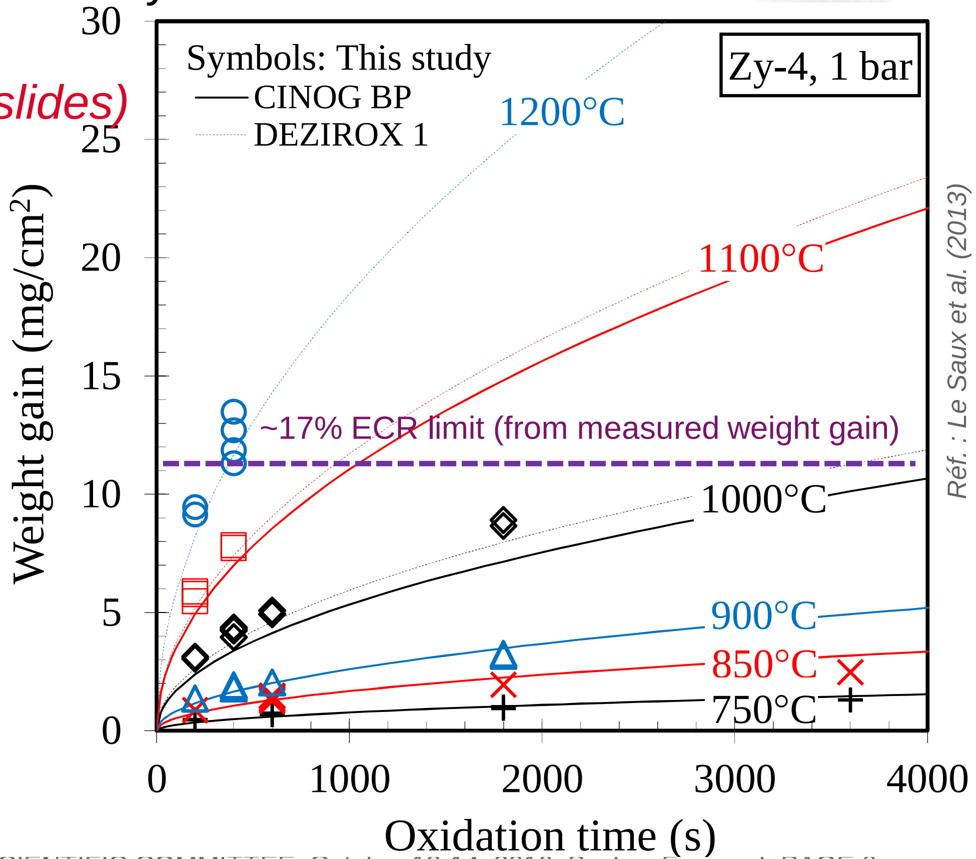
HT (1 BAR) STEAM OXIDATION - AS-RECEIVED MATERIALS

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°C
- No significant hydrogen uptake *(except for specific conditions – next 2 slides)*
- *CEA data consistent with the literature:*

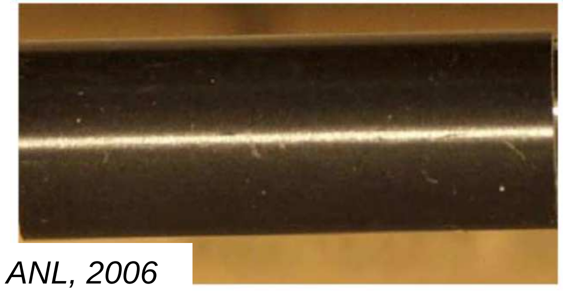




Réf. : Le Saux et al. (2013)

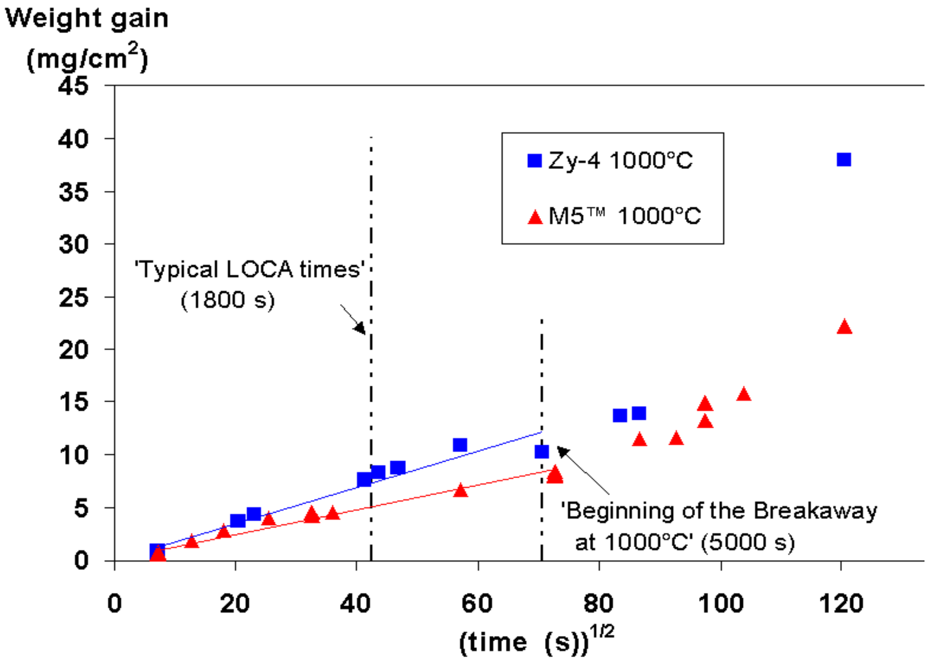
DEVIATION FROM THE HT OXIDATION PARABOLIC KINETICS: EX. N°1: « BREAKAWAY » PHENOMENA AT ~1000°C (*FOR BEYOND DBA-LOCA OXIDATION TIMES*)

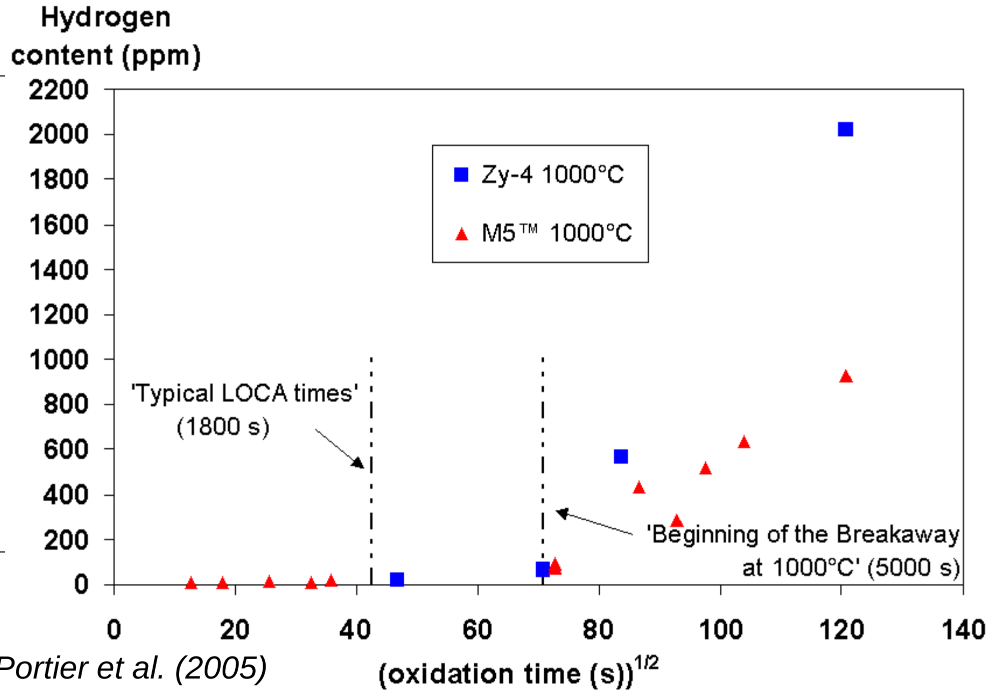
- *Early "breakaway" oxidation observed for old grade E110 alloy (russian Zr1Nb) - comparison with M5®*



M. Billone, ANL, 2006

(E110, 1000°C, 1400 sec) **(M5, 1000°C, 2400 sec)**



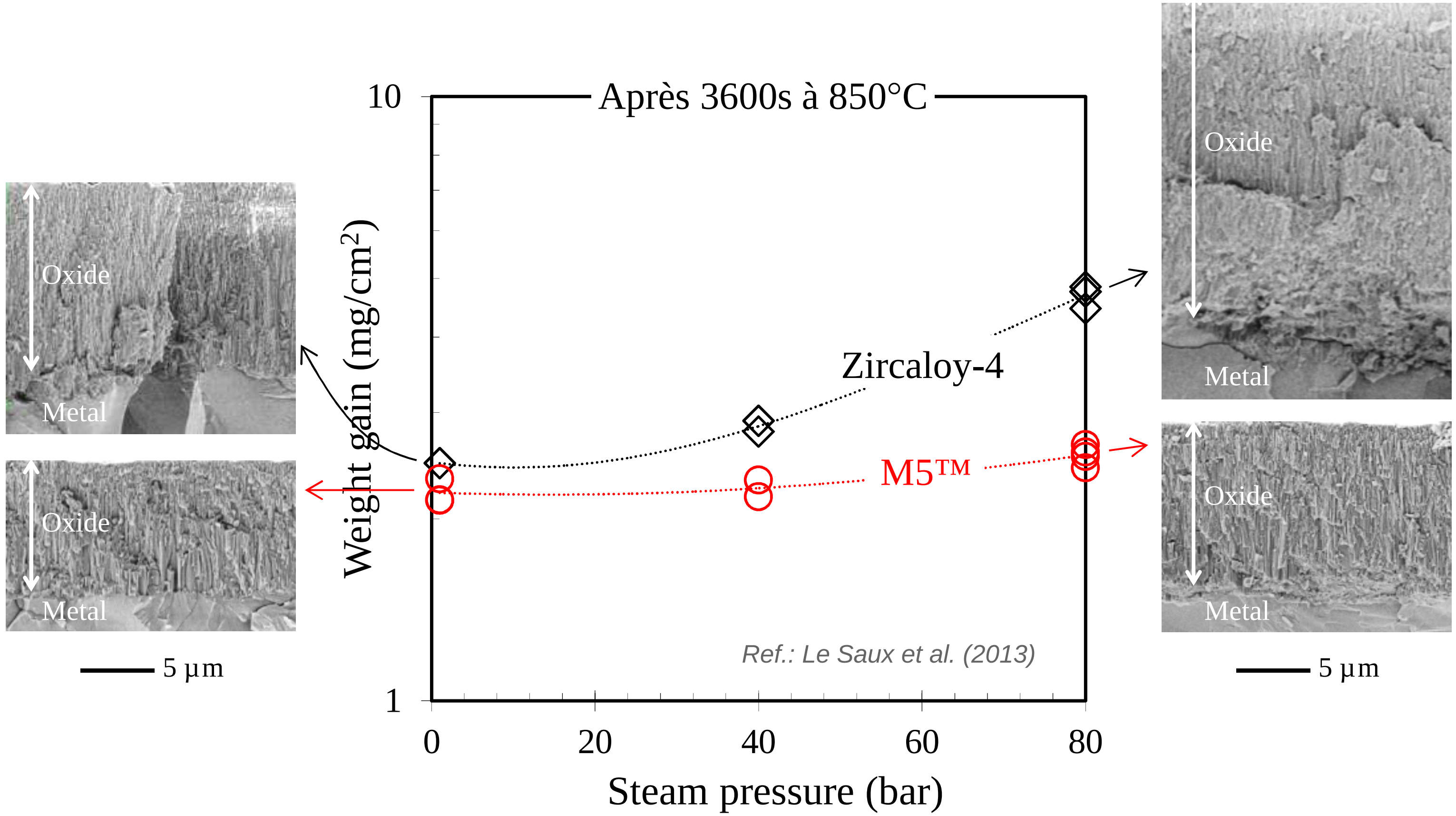


Réf. : Portier et al. (2005)

=> 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

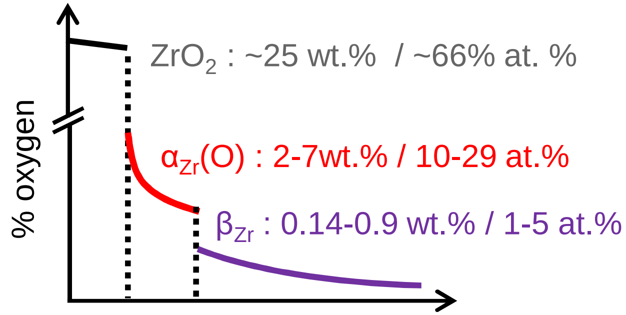
⇒ *Further work needed to understand more in depth the phenomena (+ modelling)*

(1 BAR STEAM) OXIDATION PHENOMENOLOGY AND ANALYTICAL MODELLING:

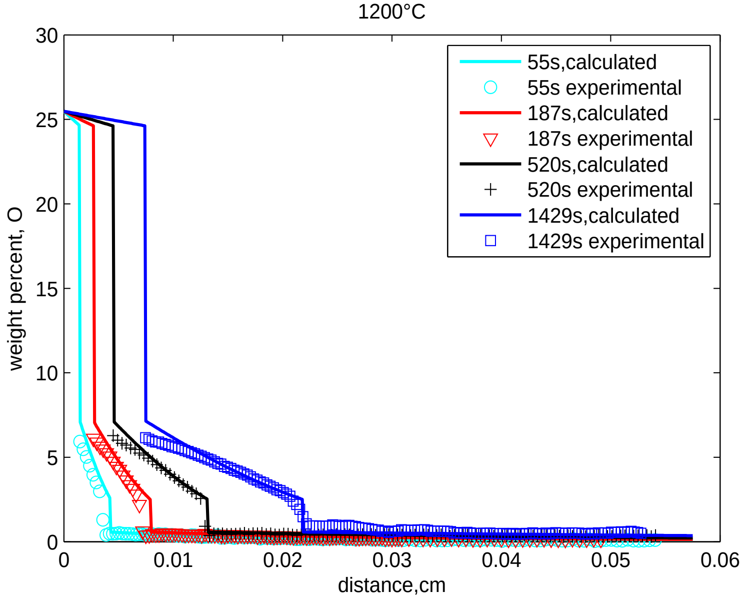
Oxygen ingress/diffusion into the sub-oxide residual metallic layer => ZrO_2 thickening and progressive transformation of β_{Zr} into $\alpha_{Zr}(O)$

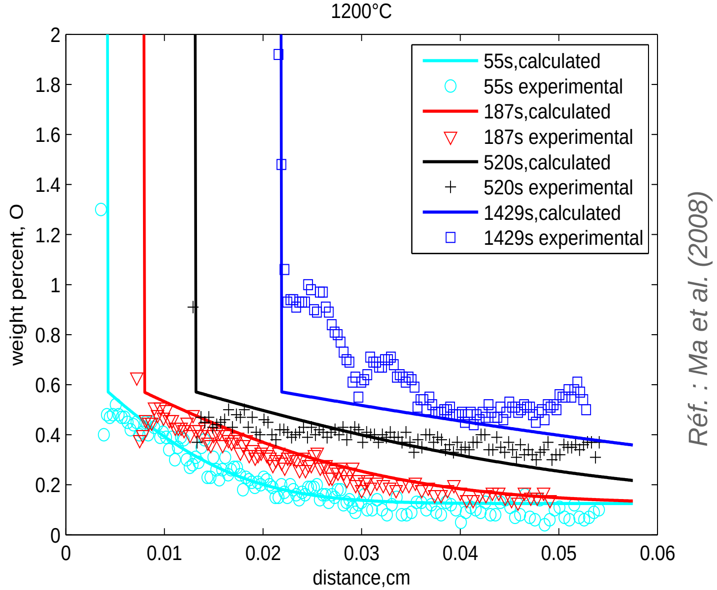
EPMA oxygen mapping Zircaloy-4 steam oxidized for 1350s at 1100°C

Réf. : Brachet et al. (2001)



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

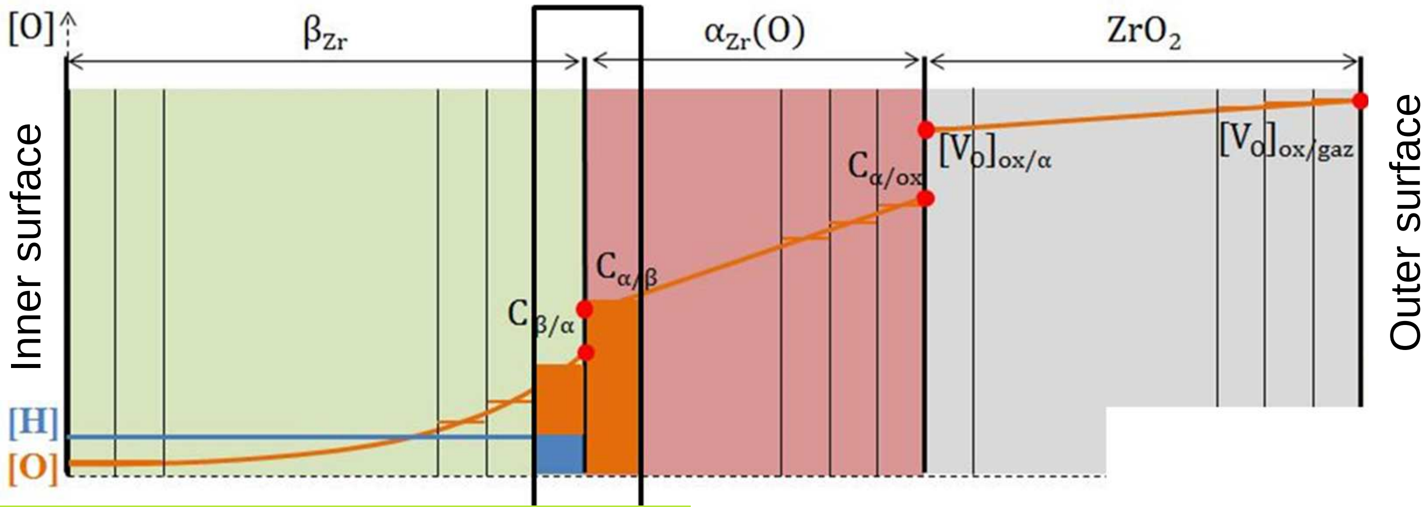




Réf. : Ma et al. (2008)

HT OXIDATION NUMERICAL MODELLING (1) « EKINOX-ZR »

(PHD OF B. MAZÈRES, IN COLLAB. WITH C. DESGRANGES, CEA/DEN/DPC AND D. MONCEAU – CIRIMAT)



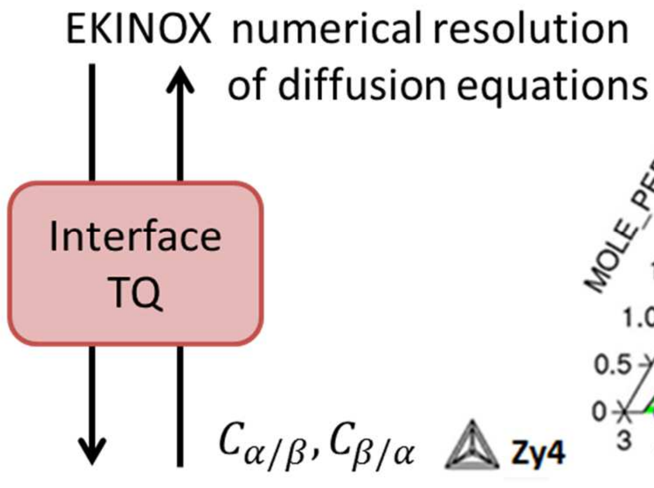
See also
C. Desgranges
& L Martinelli
presentation on
« Ekinox / Ni alloys »
- this seminar
(*Oct. 13th., 16h:45*)

Development of the Zircobase (since 1998):

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

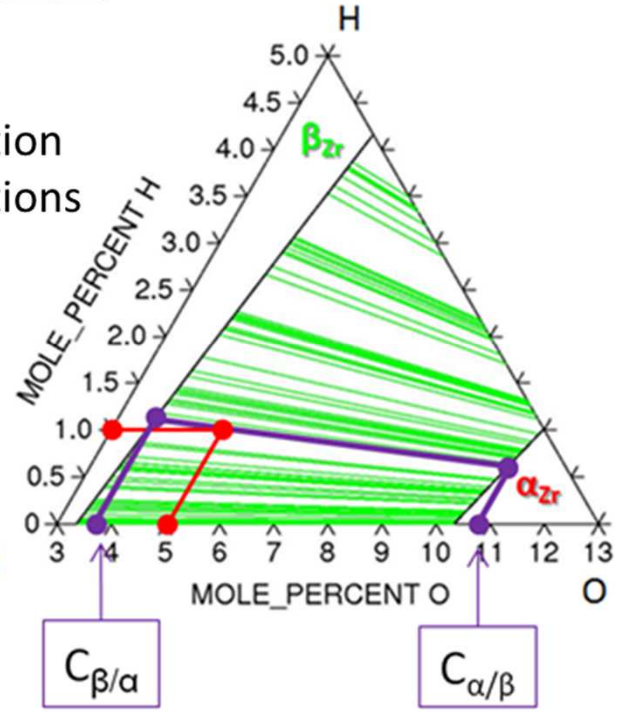
~20 binary systems : **Cr**-Fe,Nb,Ni,Zr; **Fe**-Nb,Ni,Sn,Zr; **H**-Nb,Ni,O,Sn,Zr ; **Nb**-O,Sn,Zr; **O**-Sn,Zr ; **Sn**-Zr ; **V**-Zr ; (+ Er/Gd-Zr-O-H)

>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...)



ThermoCalc® + Zircobase

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



HT OXIDATION NUMERICAL MODELLING (2) DICTRA® + « ZIRCOMOB »

(IN COLLAB. WITH M-H. MATHON, TCSAB, SWEDEN)

Data for building « Zircomob » database:

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

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, $FeZr_3$, $FeZr_2$

Zr-O : HCP_A3, BCC_A2, FCC_C1 (ZrO2_cubic),ZrO_2 Mono, ZrO_2 Tetra

Zr-H : HCP_A3, BCC_A2, ZrH_2_Epsilon, FCC_C1 (ZrH_2 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

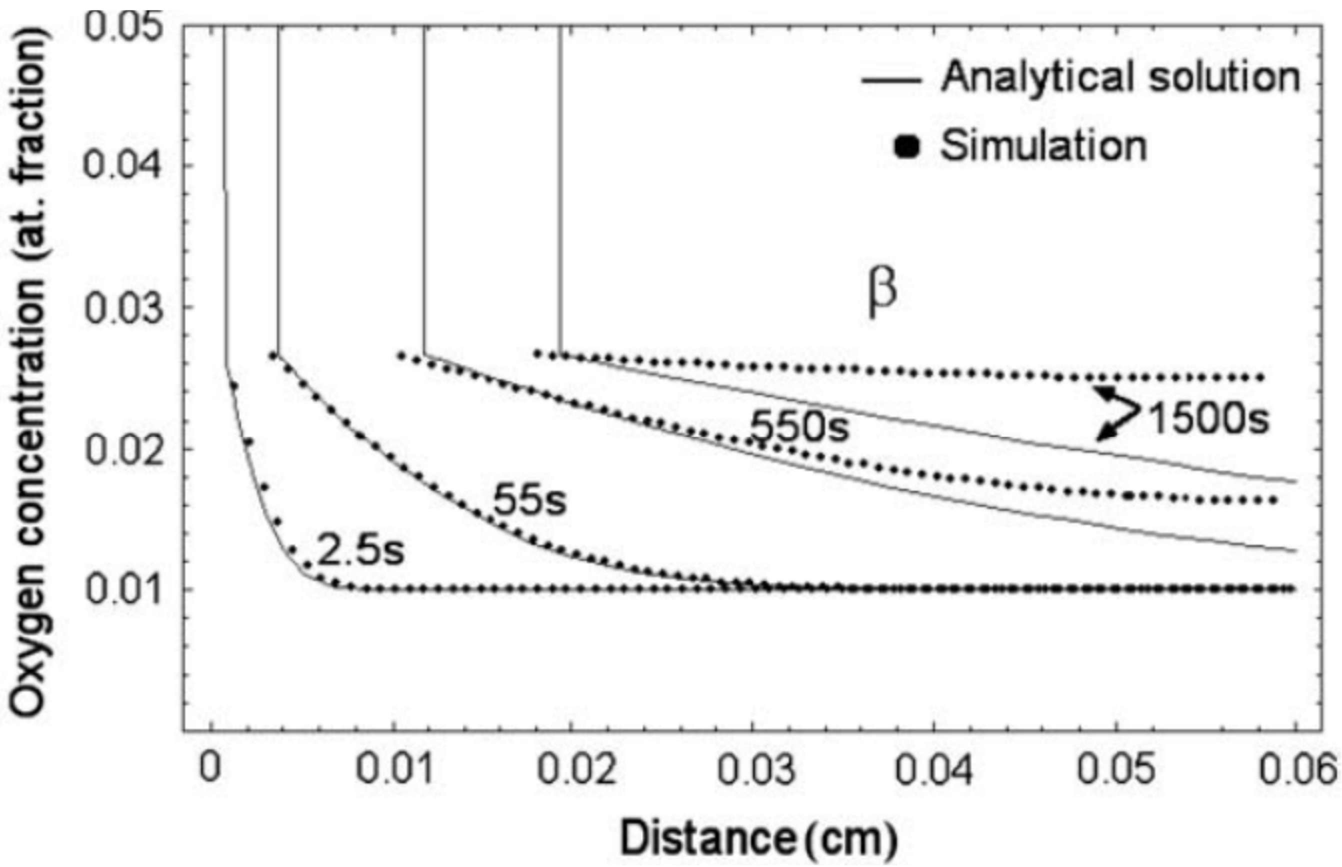
The mobilities $\mathbf{M_i}$ are described for all binaries, using the following equations :

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

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

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

ANALYTICAL VS. NUMERICAL MODELLING



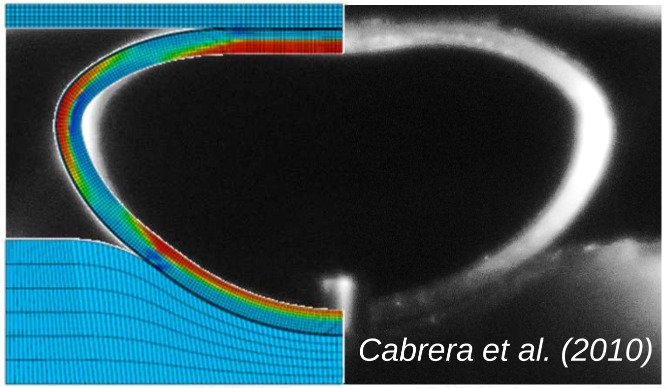
C. Corvalan-Moya et al., JNM, 2010

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

CONSEQUENCES OF THE HT OXIDATION ON THE POST-QUENCHING (PQ) CLAD MECHANICAL PROPERTIES (DUCTILITY, TOUGHNESS...) (1/3):

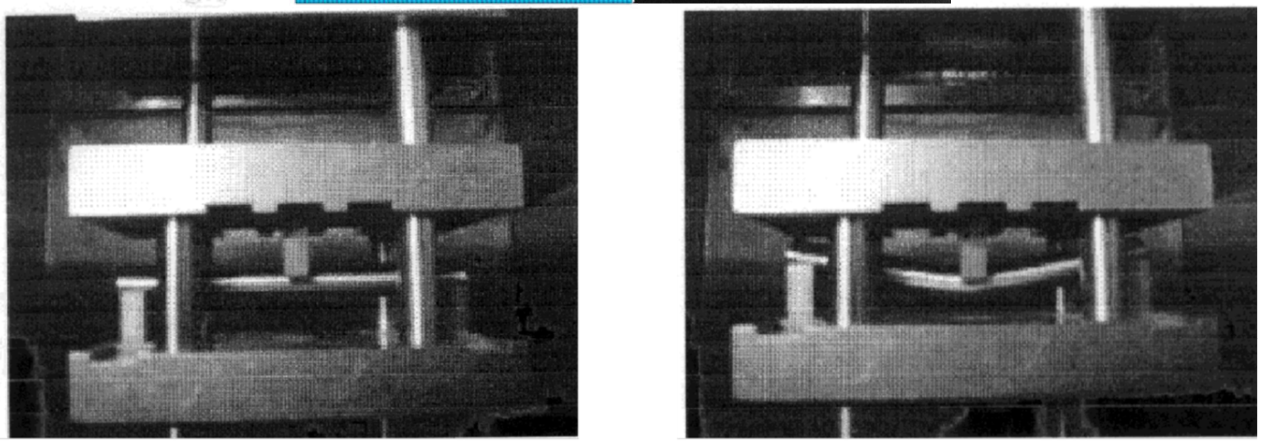
Post-Quenching (PQ) mechanical tests performed at CEA:

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

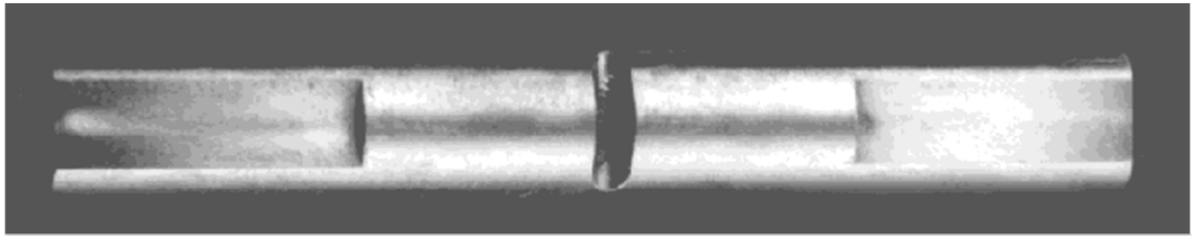


Cabrera et al. (2010)

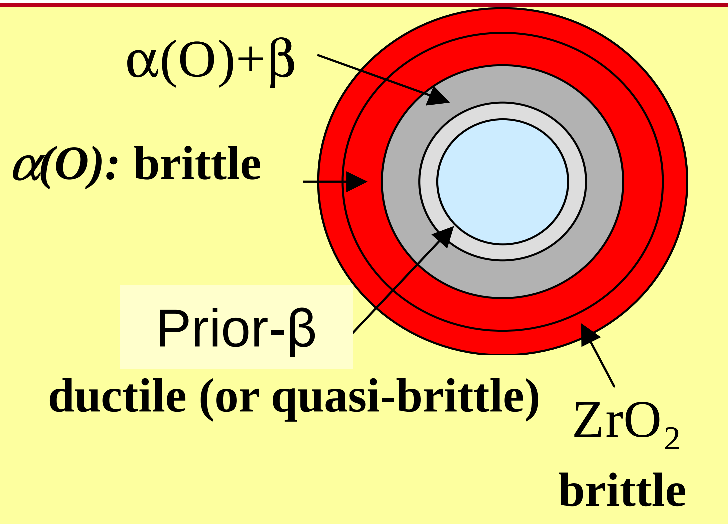
Three Points Bending Testing (3-PBT) at 20-135°C



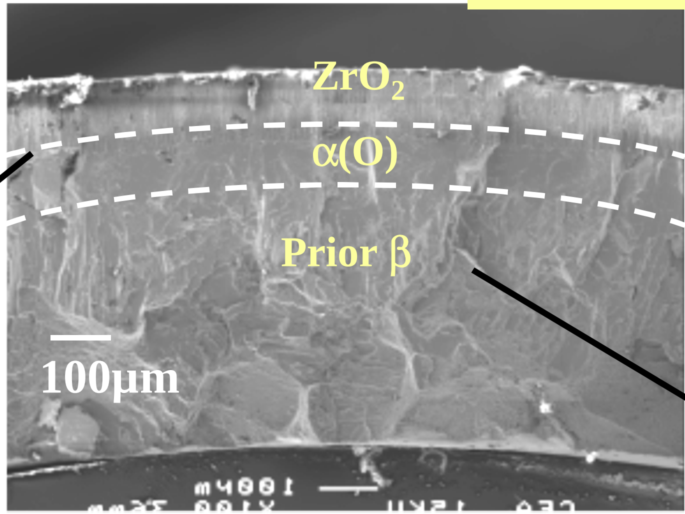
Room Temperature Impact Testing *(pre-notched clad sample)*

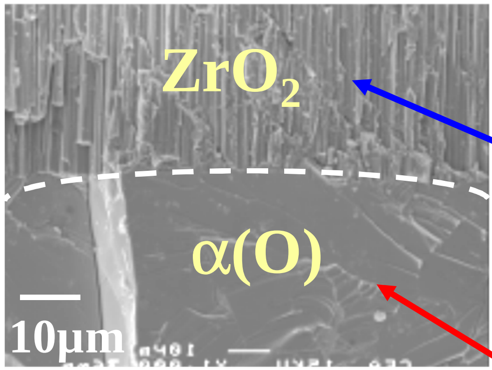


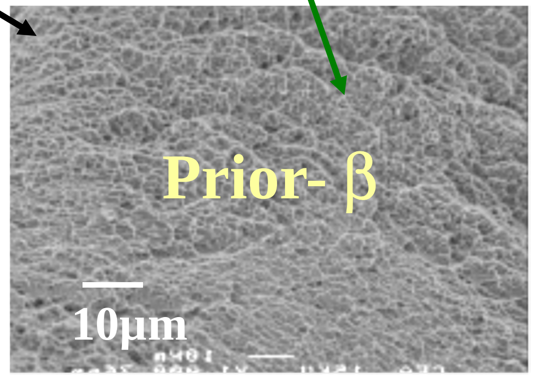
HT OXIDATION VS. PQ CLAD MECHANICAL PROPERTIES (2/3)



Typical PQ failure modes at RT:







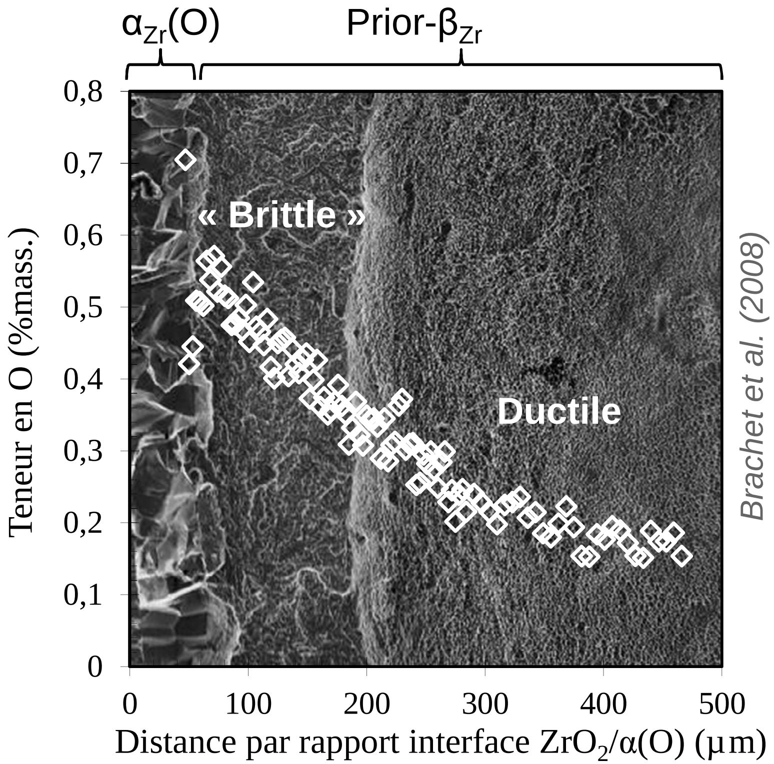
Prior-β layer: ductile *(or nearly-brittle)* failure mode *(depending on the oxygen & hydrogen content)*

ZrO_2 : brittle (columnar) failure mode

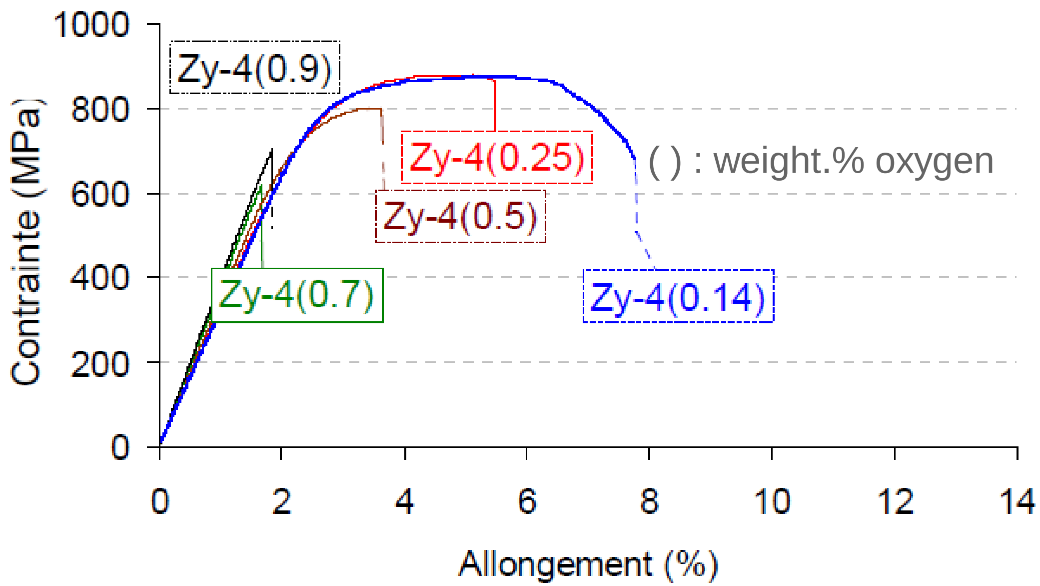
α(O) : pure brittle (cleavage and intergranular) failure mode

HT OXIDATION VS. PQ CLAD MECHANICAL PROPERTIES (3/3)

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



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)

HT STEAM OXIDATION AND CONSEQUENCES ON PQ MECHANICAL PROPERTIES OF AS-RECEIVED MATERIALS

CEA R&D / SUMMARY:

- 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®)…)*

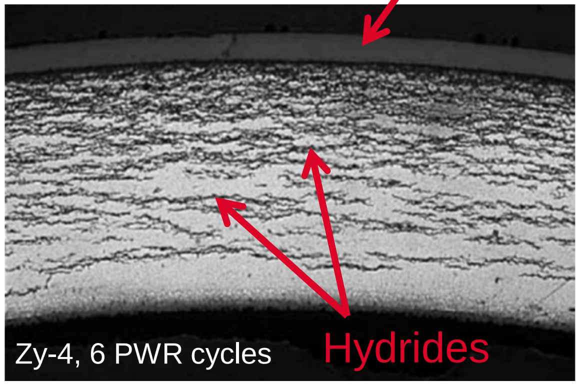
- Refined relationship with the PQ clad mechanical properties => critical prior-β oxygen content ~0,4 wt.% for DBTT at RT

- *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 ~25µm - 60µm, depending of the alloy)
  - Hydrogen uptake
    (up to ~100-700 wt. ppm depending of the alloy)
  - Inner oxide formation
    (inner oxidation + clad-pellet chemical interaction)
    => thickness reaches ~10-15µm 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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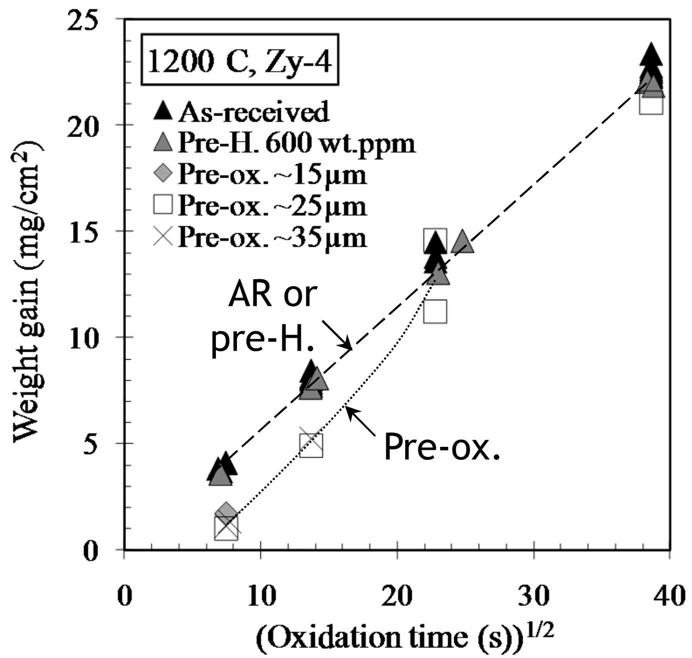
EFFECT OF PRE-TRANSIENT OXIDE ON HT STEAM OXIDATION (1/3)

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



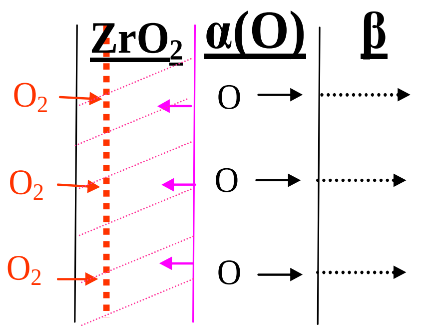
No H uptake ➔ both pre-ox. and HT ox. layers protective

❑ 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)

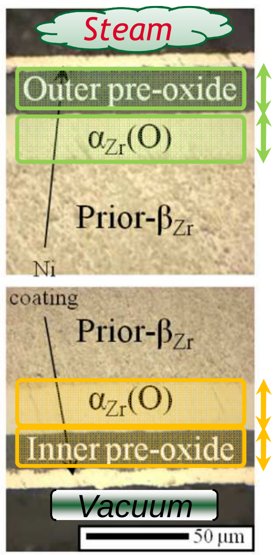
⇒ When looking (only) at the weight gain evolution, pre-transient oxide seems to have a "protective" effect on the overall HT oxidation kinetics.

⇒ but is it true for sub-oxide oxygen diffusion / resultant PQ mechanical properties?

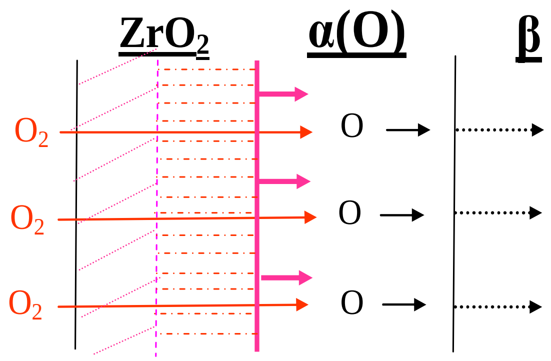
EFFECT OF PRE-TRANSIENT OXIDE ON HT STEAM OXIDATION (2/3)



1st step : overall oxide thickness decresase, and α(O) appears

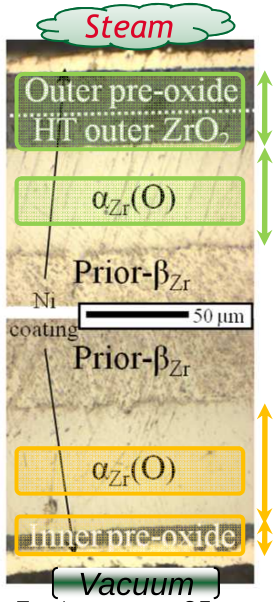


Zy-4 pre-ox. ~25µm
1200°C 55s



2nd step: an internal columnar high temperature oxide layer begins to grow

Brachet, ASTM-STP-2008
Le Saux, Topfuel - 2011



Zy-4 pre-ox. ~25µm
1200°C 187s

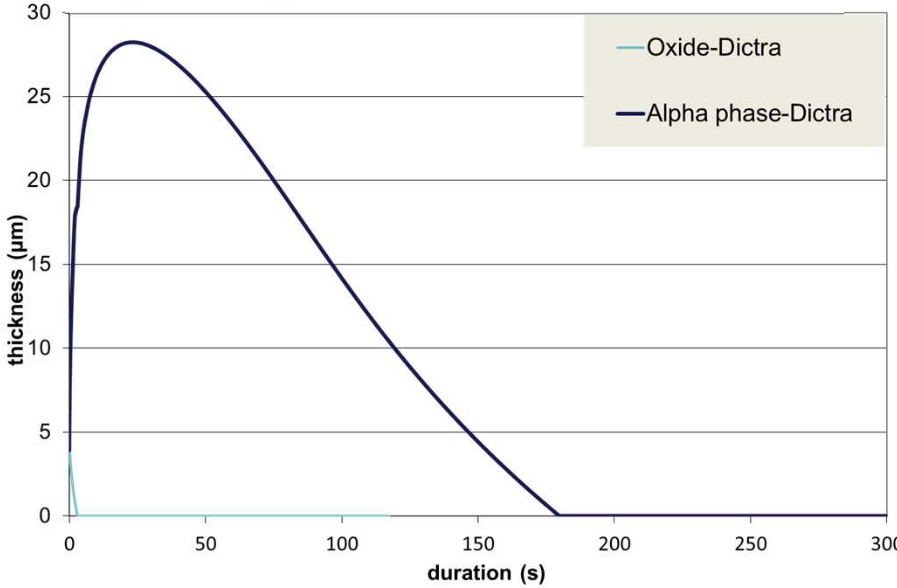
⇒ **For the OD**, the overall quantity oxygen diffusing into the substrate is the same with/without pre-transient oxide for any given oxidation time => no "protective effect / grace time" due to the pre-transient oxide regarding PQ mechanical properties

⇒ **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

EFFECT OF PRE-TRANSIENT OXIDE – MODELLING (3/3)

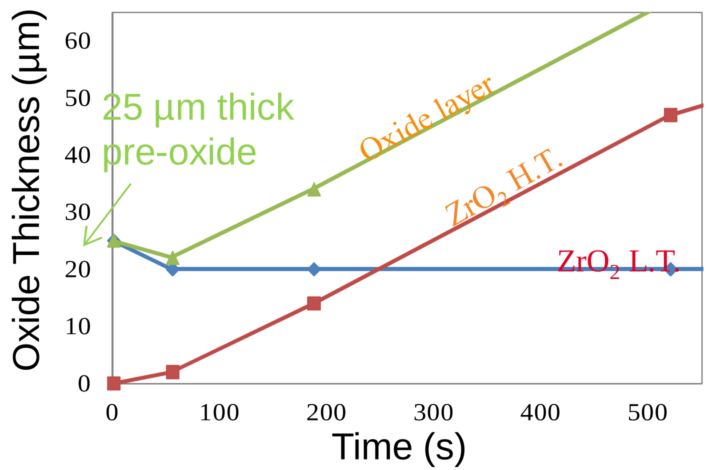
Inner oxide (neutral environment)

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

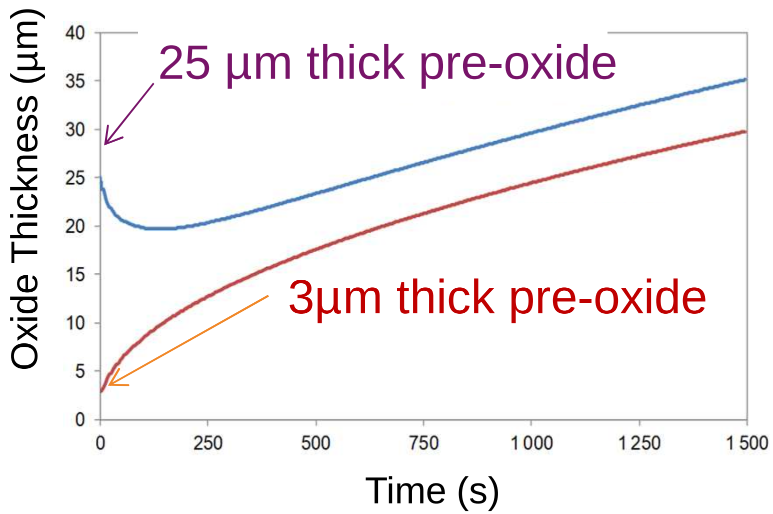


Outer oxide (steam environment)

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-hydriding *- simulating in-service hydriding -* on HT oxidation and PQ mechanical properties

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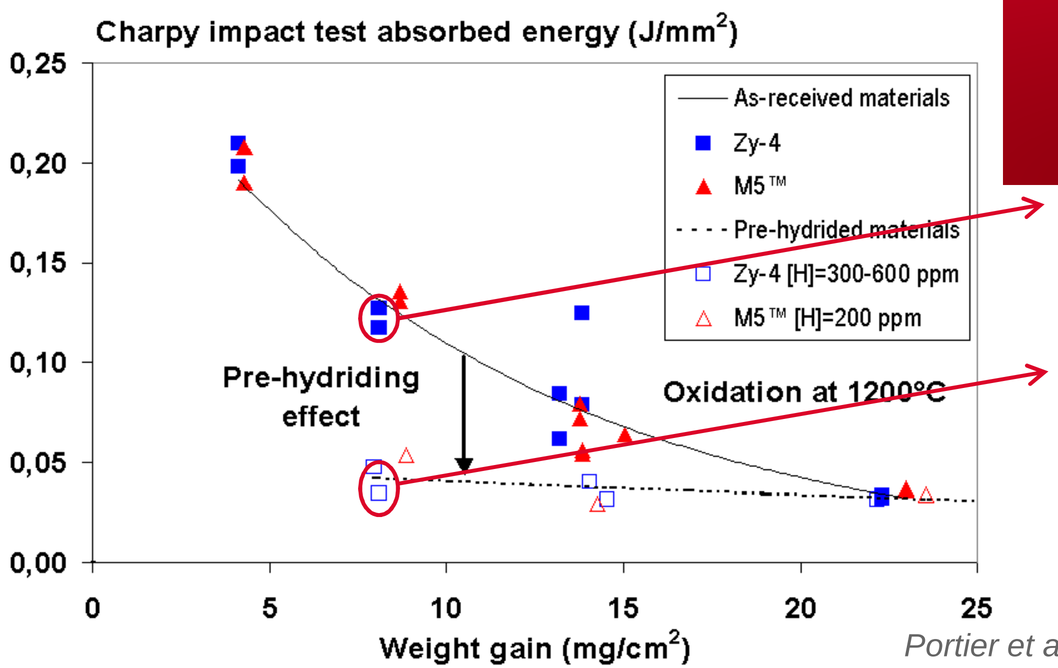
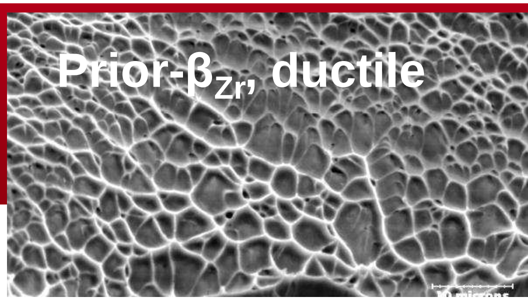
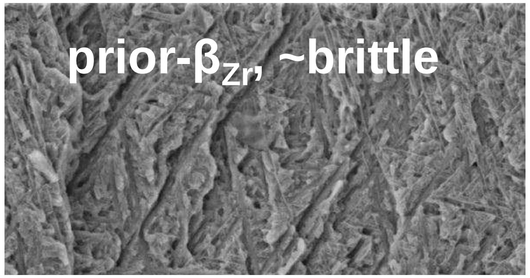
EFFECTS OF PRE-HYDRIDING (1/5)

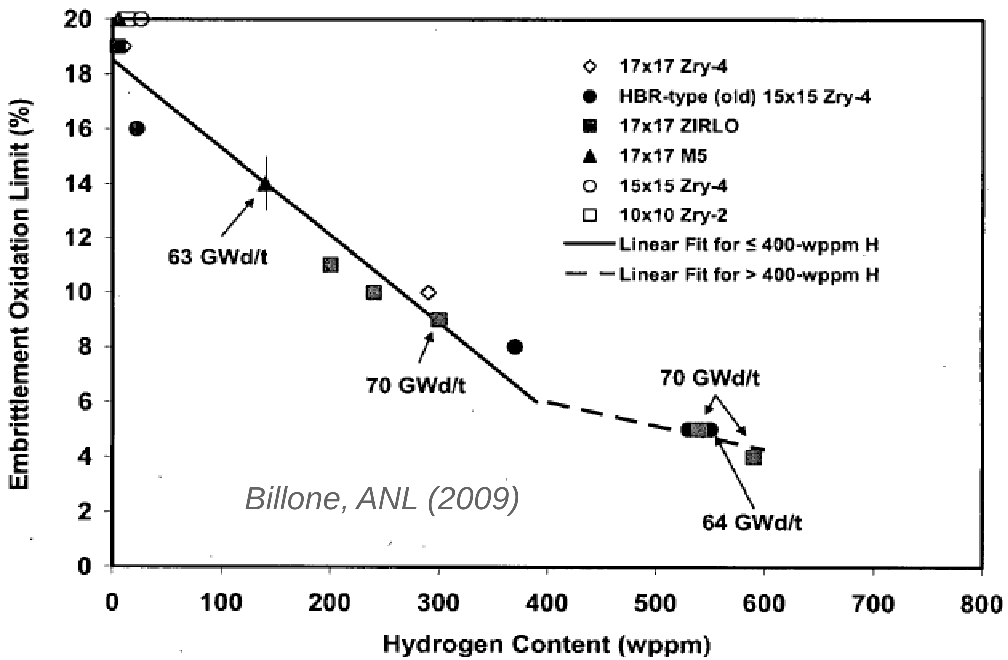






Portier et al. (2005)

Recent NRC recommandation 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



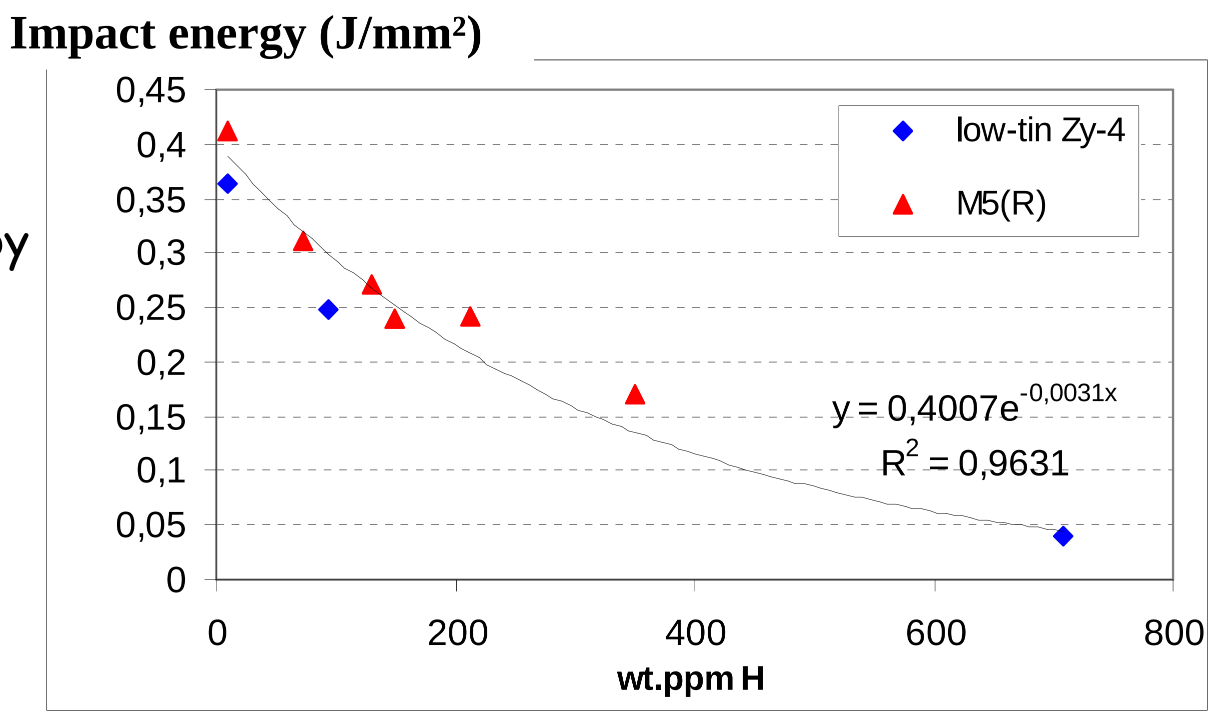
Billone, ANL (2009)

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

(1) « intrinsic » effect

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

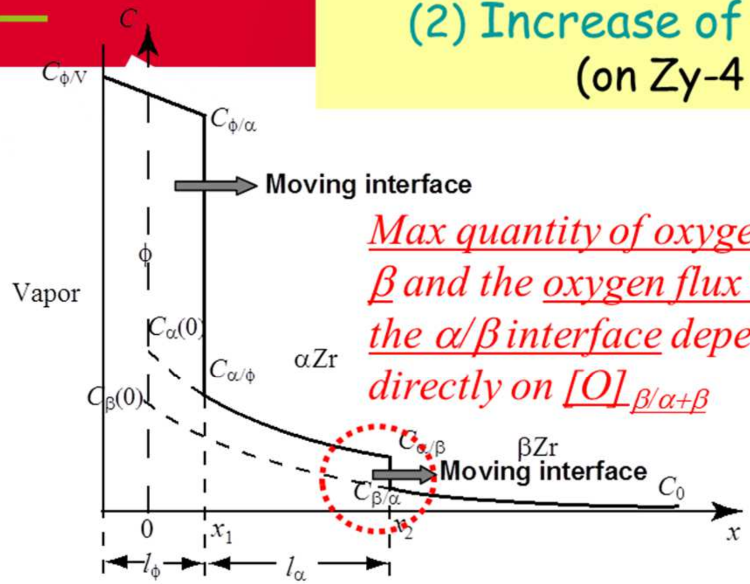
=> Sharp decrease of the impact Energy at RT as H content increases



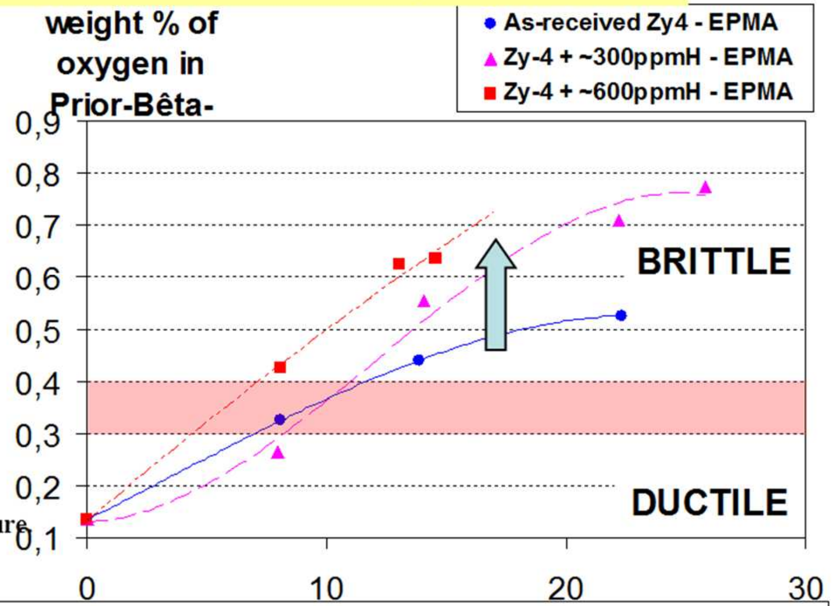
Brachet et al. (2008)

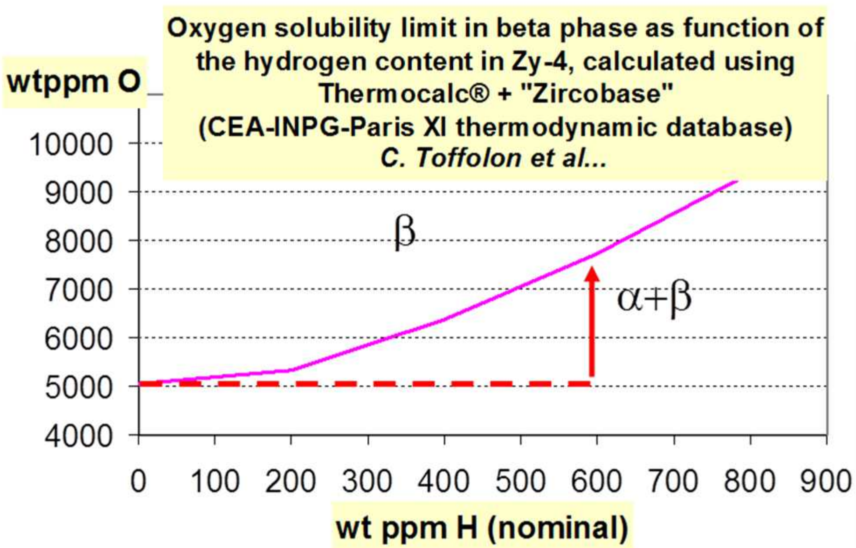
EFFECTS OF PRE-HYDRIDING (3/5)

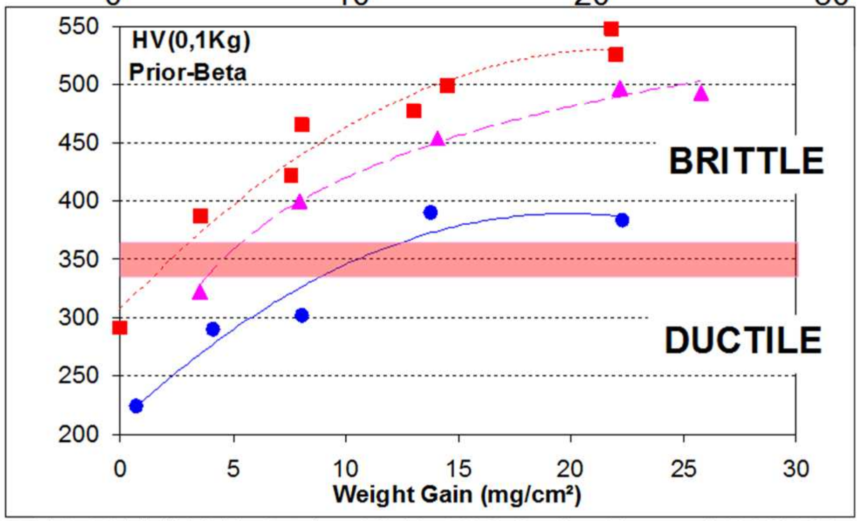
(2) Increase of the oxygen solubility in β effect
(on Zy-4 after oxidation at 1200°C)



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



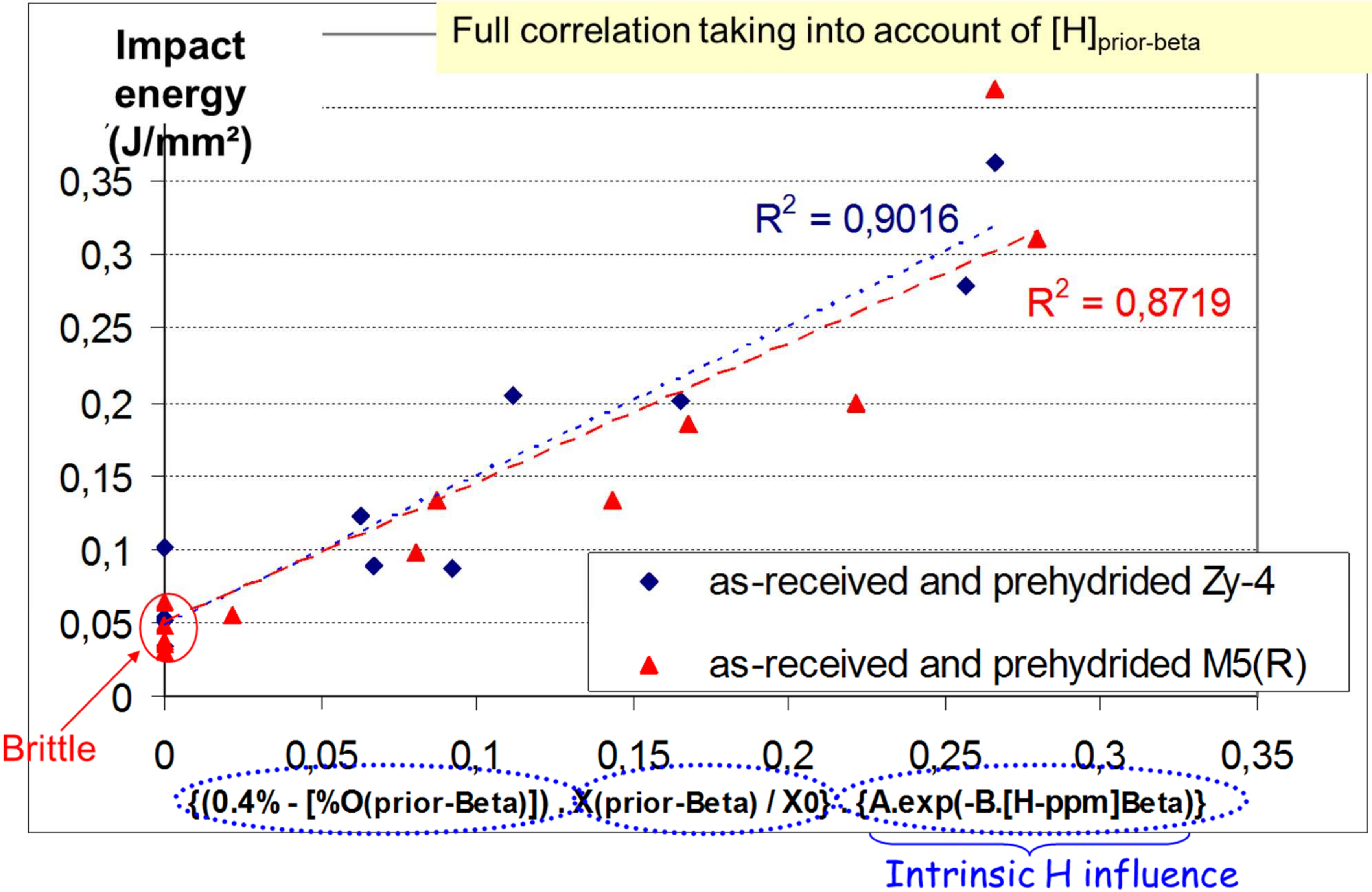




Brachet et al. (2008)

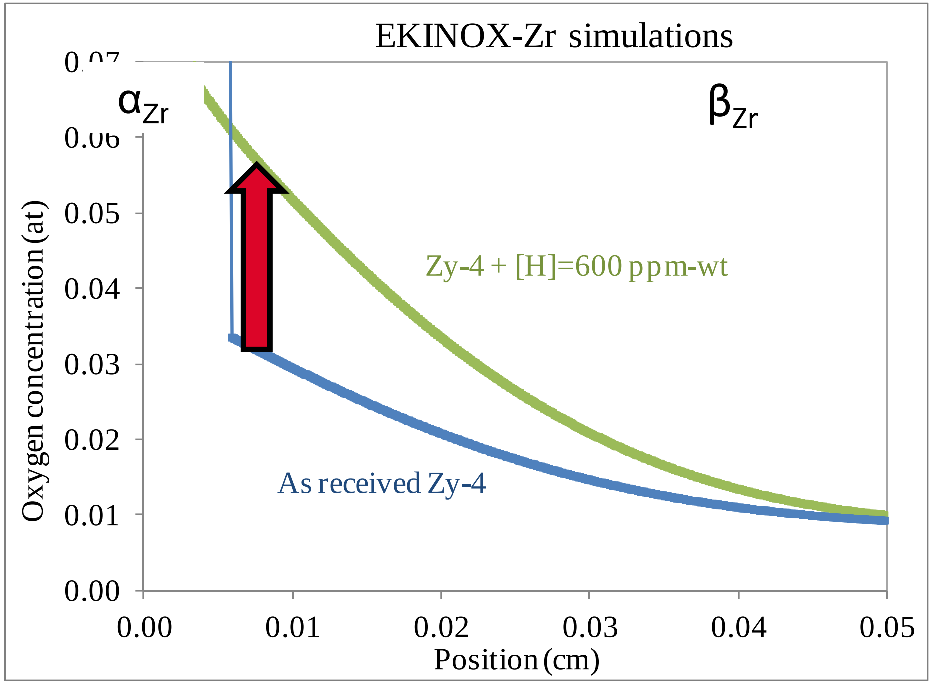
EFFECTS OF PRE-HYDRIDING (4/5)
=> REFINED CORRELATION BETWEEN PQ MECHANICAL PROPERTIES VS. RESIDUAL PRIOR-β : THICKNESS, %O AND %H

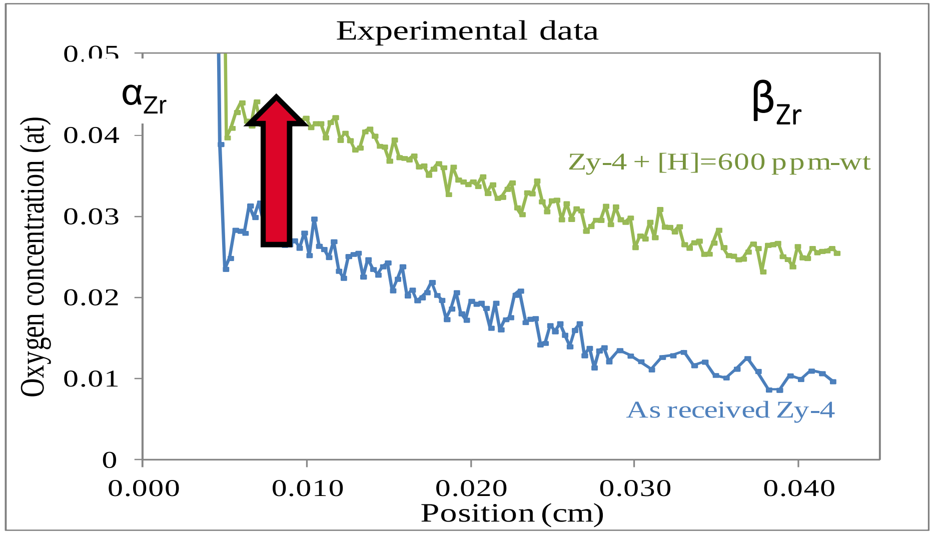
Full correlation taking into account of $[H]_{prior-beta}$



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*

SUMMARY

- Pre-hydriding – simulating in-service hydriding (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 β→α 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)

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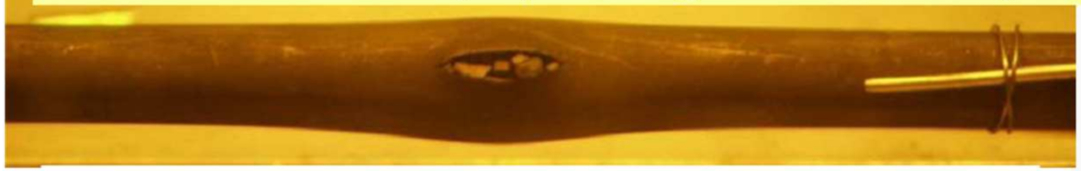
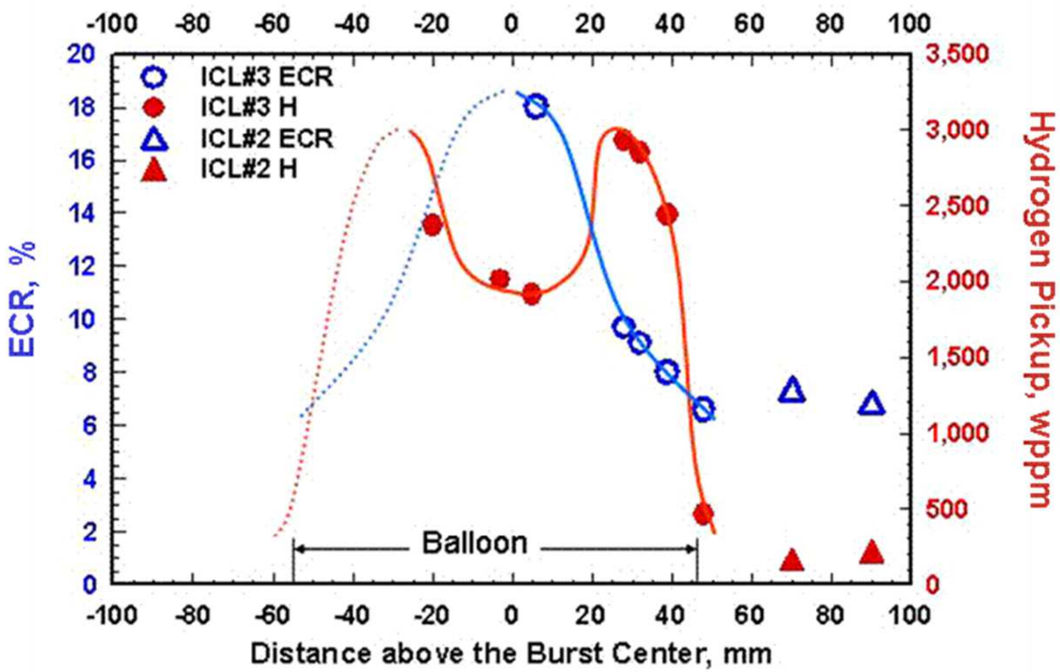
HT SECONDARY HYDRIDING (1/3) - INTRODUCTION

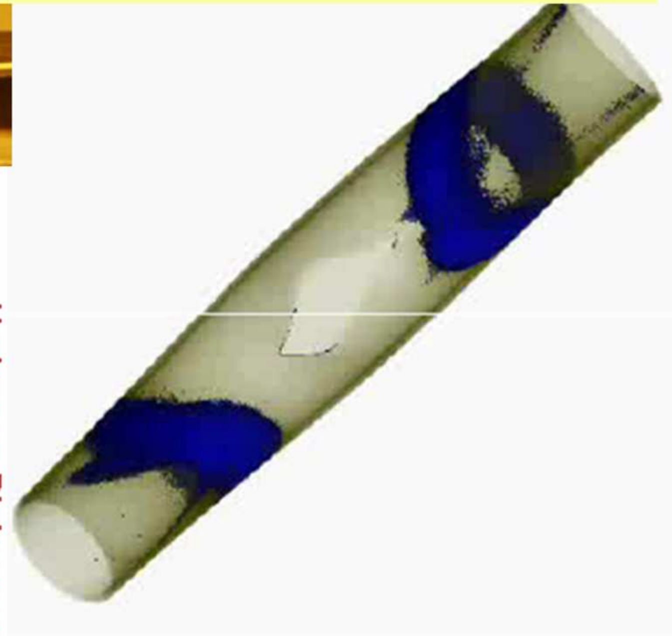
Secondary hydriding in the vicinity of the burst location





ANL integral one-rod LOCA test on high BU Zy-4

(M. Billone et al, ANL, 2005)



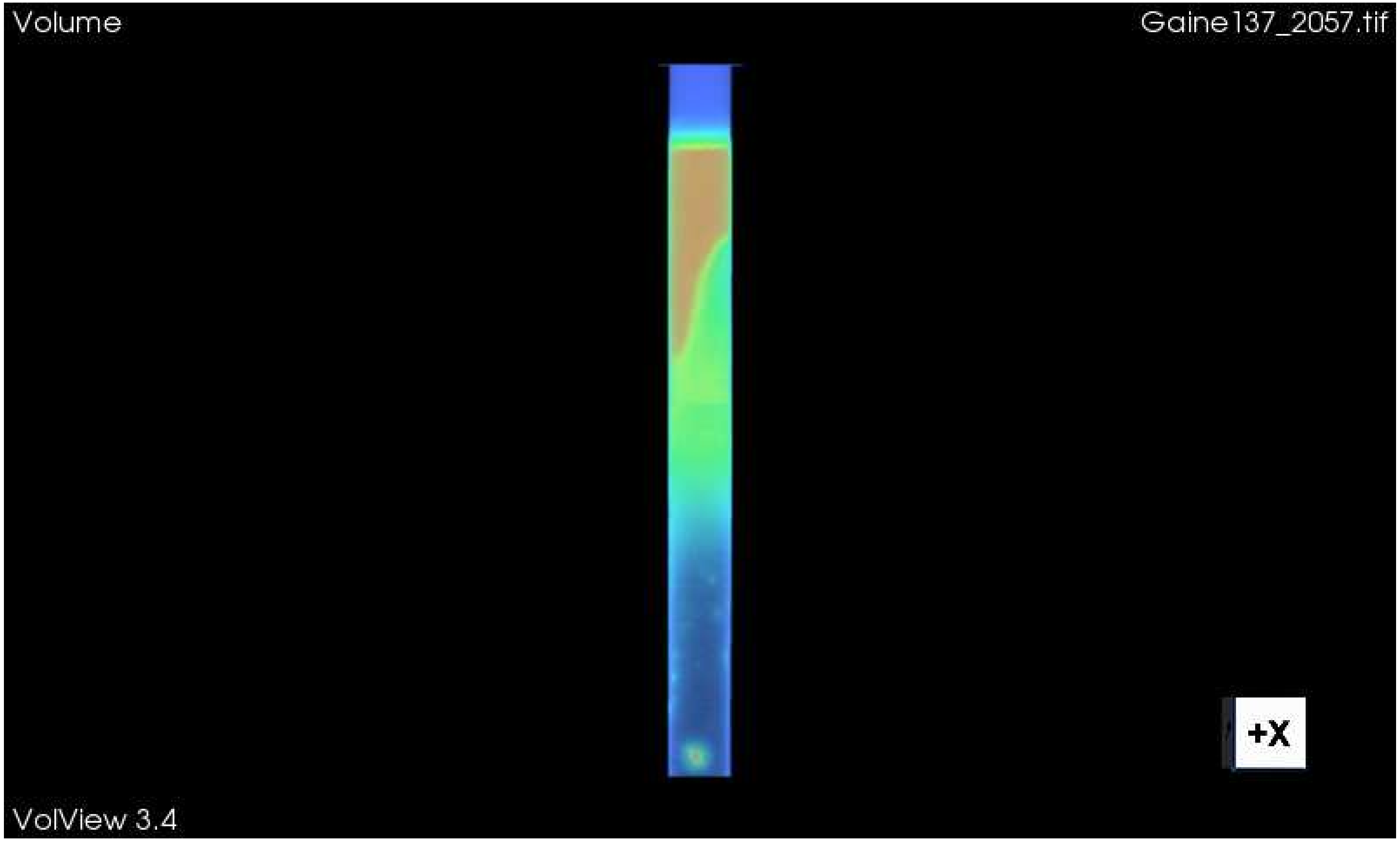
Hydrogen distribution into a LOCA tested clad due to secondary hydriding

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

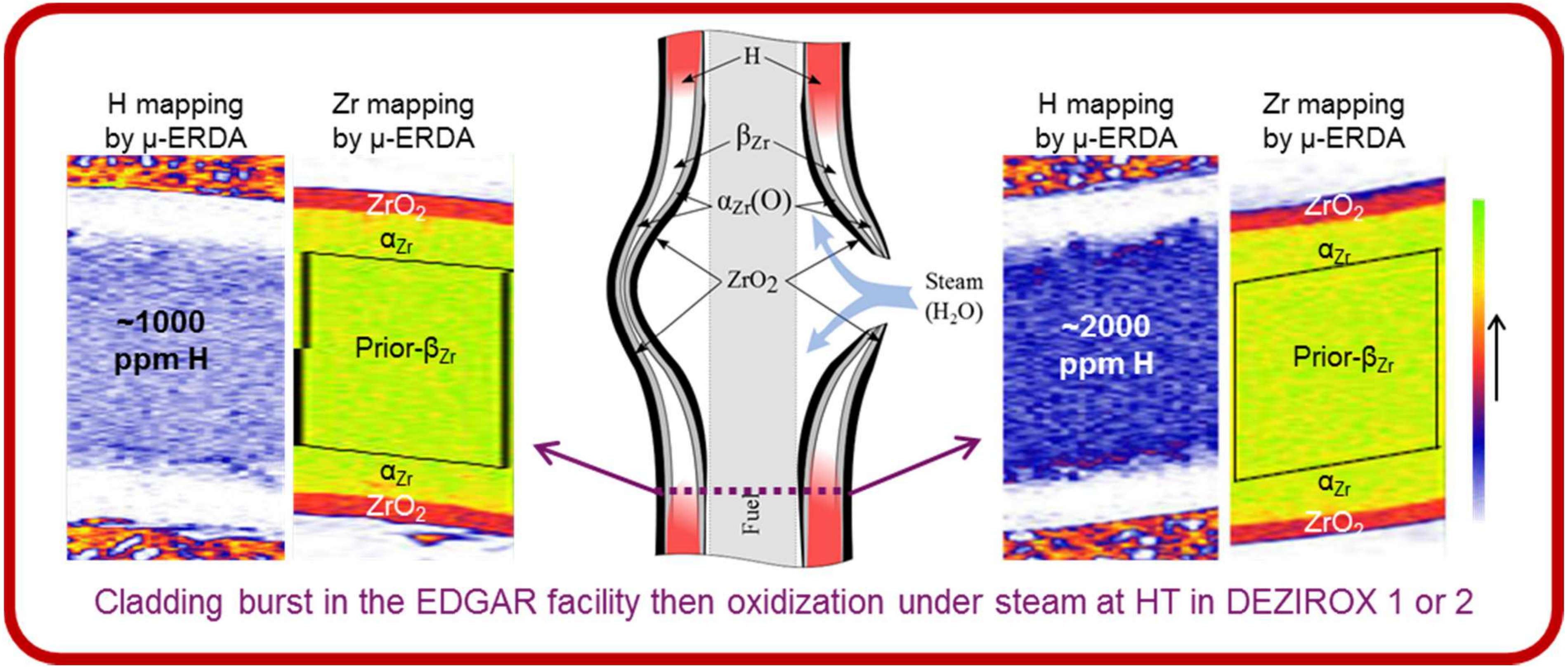
Rem.: First observations in the early 80ties by JAEA (Uetsuka)…

HT SECONDARY HYDRIDING (2/3) – ON-GOING CEA MULTISCALE STUDY

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



HT SECONDARY HYDRIDING (3/3) – ON-GOING CEA MULTISCALE STUDY



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

On-going (PhD) work at CEA using model alloys with controled (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...

HT oxidation in LOCA / Conclusions and prospects:
On-going R&D on EATF Cr-coated Zr base & "sandwich" SiCSiC

- Huge experimental database developed at CEA and associated deep (multi-scale) metallurgical analysis & PQ mechanical testing
- 1^{st} order influence of oxygen and hydrogen diffusion/partitioning (into the residual prior-β layer)
- Modelling effort (analytical & numerical modelling: Ekinox/Zircobase, Dictra/Zircomob, 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)*

CR COATED ZR BASE NUCLEAR FUEL CLADDINGS R&D

Expected Benefits :

→Decrease oxidation rate in service and with steam water at high temperature

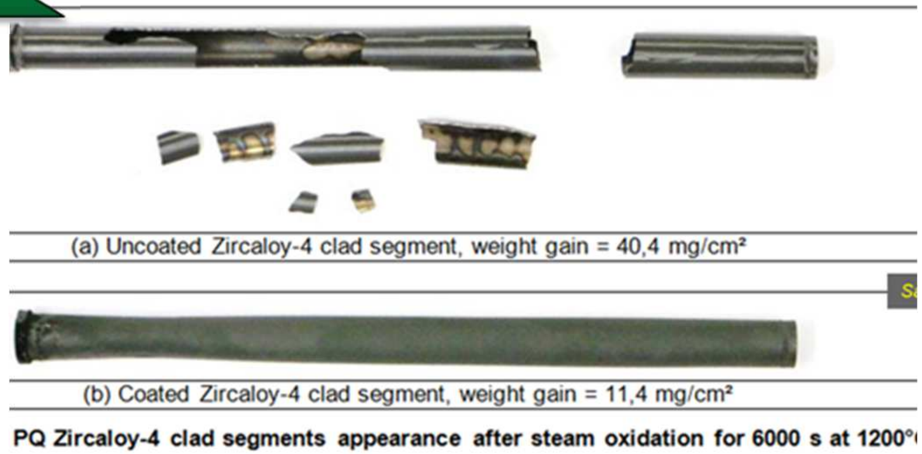
→Reduce in service hydriding and hydrogen release during accidental sequence

→Improve LOCA behavior (Peak clad T ↘, post quench ductility ↗)

→Improve long term coolability - procure grace time in the early stage of SA

Patents

Steam oxidation for 300s at 1200°C:



Brachet et al., 2014

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

R&D ON SIC-SIC SANDWICH CLADDINGS FOR LWRS

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

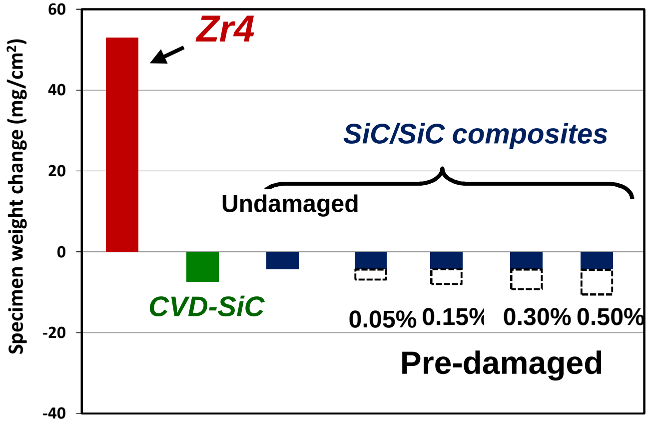
Optimization of the concept for LWRs application

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

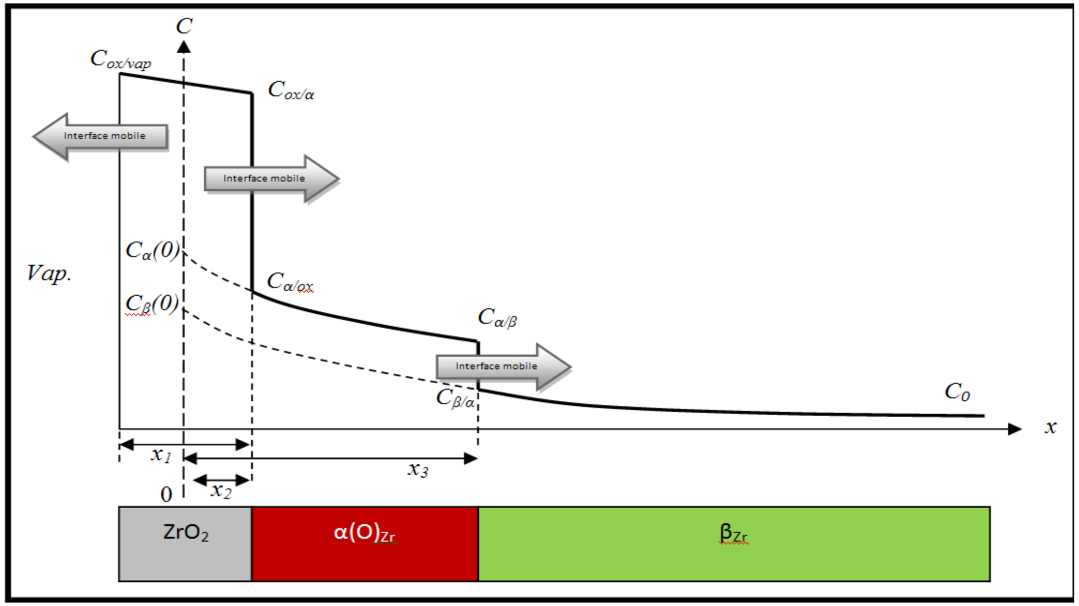
HT OXIDATION ANALYTICAL MODELLING
(1) DEBUIGNE'S MODEL (1966)

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 :

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

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

Steady-state hypothesis:

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

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.

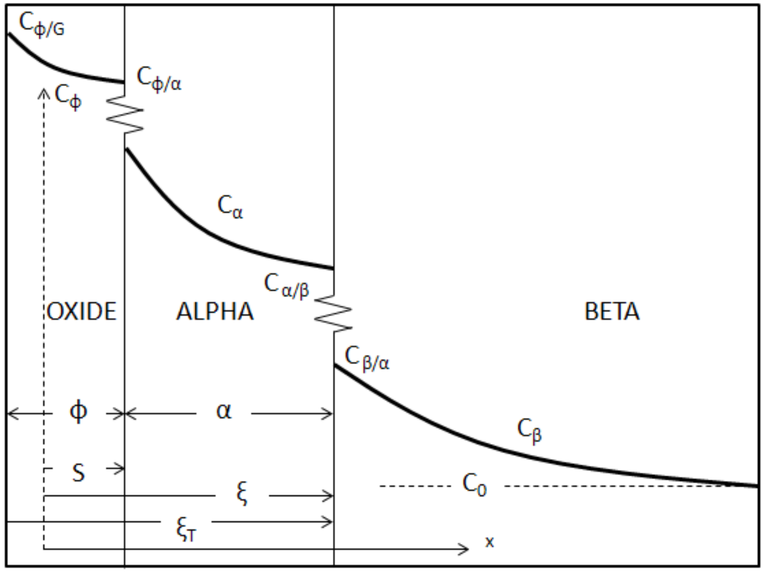
HT OXIDATION ANALYTICAL MODELLING
(2) PAWEL'S MODEL (1979)

Oxide growth kinetic:

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

Interface motion ox/α and α/β :

$$\frac{d\xi}{dt} = \frac{-D_\alpha \left.\frac{\partial C_\alpha}{\partial x}\right|_{x=\xi} + D_\beta \left.\frac{\partial C_\beta}{\partial x}\right|_{x=\xi}}{C_{\alpha/\beta} - C_{\beta/\alpha}} \qquad \frac{dS}{dt} = \frac{-D_\varphi \left.\frac{\partial C_\varphi}{\partial x}\right|_{x=S} + D_\alpha \left.\frac{\partial C_\alpha}{\partial x}\right|_{x=S}}{VC_{\varphi/\alpha} - C_{\alpha/\varphi}}$$



Steady-state hypothesis:

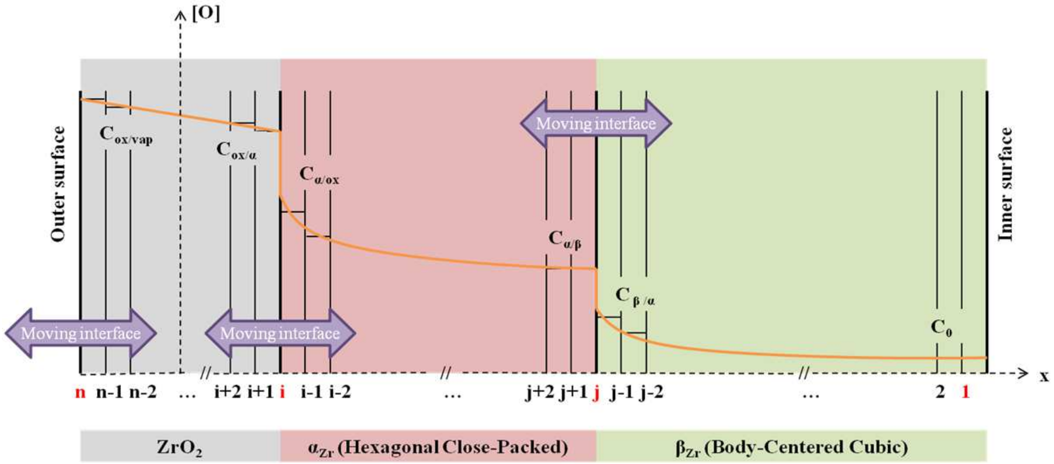
$$C_\varphi = C_{\varphi/G} - \frac{(C_{\varphi/G} - C_{\varphi/\alpha})}{erf\left(\frac{VS}{2\sqrt{D_\varphi t}}\right)} erf\left(\frac{x + (V-1)S}{2\sqrt{D_\varphi t}}\right)$$

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

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

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

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



- EKINOX-Zr :
  - Boundary conditions:

$$C_{ox}(n,t) = C_{ox/vap} \qquad C_\alpha(j,t) = C_{\alpha/\beta}$$
$$C_{ox}(i,t) = C_{ox/\alpha} \qquad C_\beta(j,t) = C_{\beta/\alpha}$$
$$C_\alpha(i,t) = C_{\alpha/ox} \qquad C_\beta(1,t) = C_0$$

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

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

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

$$\left(C_{\alpha/\beta} - C_{\beta/\alpha}\right)\frac{\partial x_j}{\partial t} = D_\alpha \left.\frac{\partial C_\alpha}{\partial x}\right|_j - D_\beta \left.\frac{\partial C_\beta}{\partial x}\right|_j \qquad \left(C_{ox/\alpha} - C_{\alpha/ox}\right)\frac{\partial x_i}{\partial t} = D_{ox}\left.\frac{\partial C_{ox}}{\partial x}\right|_i - D_\alpha\left.\frac{\partial C_\alpha}{\partial x}\right|_i$$

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

$$J^p_{V_O} = -\frac{D^p_{V_O}}{\Omega^p} \times \frac{X^{p+1}_{V_O} - X^p_{V_O}}{\frac{e^p - e^{p+1}}{2}}$$

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

$$\dot{X}^p_{V_O} = \frac{dX^p_{V_O}}{dt} = -\Omega^p \times \frac{J^p_{V_O} - J^{p+1}_{V_O}}{e^p}$$

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

$$\frac{de^{j+1}}{dt} = \Omega^{p+1} \times \frac{J^{j-1}_{V_O} - J^{j+1}_{V_O}}{C_O^{\alpha/\beta} - C_O^{\beta/\alpha}} \qquad \frac{de^{i+1}}{dt} = \frac{\Omega^{i+1}}{\gamma} \times \frac{J^{i-1}_{V_O} - J^{i+1}_{V_O}}{C_O^{ox/\alpha} - C_O^{\alpha/ox}}$$

Epaisseur finie de la gaine

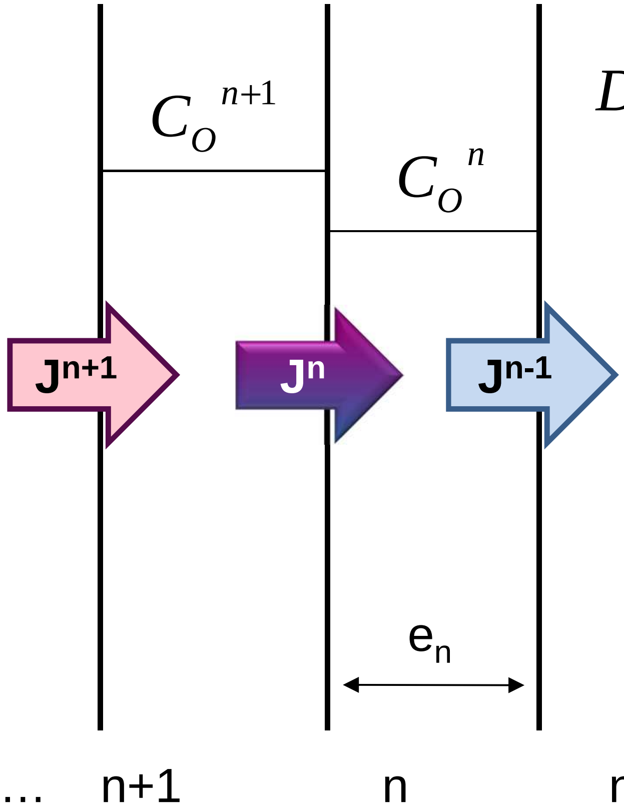
ÈLE NUMÉRIQUE

PRINCIPE DU CODE IZOX

Extérieur de la gaine (ZrO_2)

Cœur de la gaine (β_{Zr})

Sens de diffusion de O^{2-}



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

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

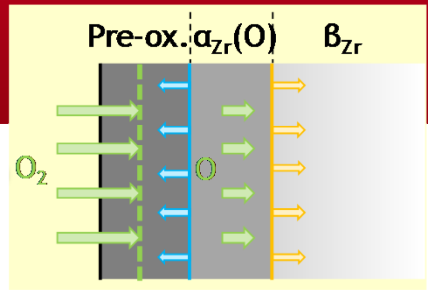
$$\frac{dC_O^{n}}{dt} = -\frac{J_O^{n} - J_O^{n-1}}{e_n}$$

$$C_O^{n}(t+dt) = C_O^{n}(t) + \frac{dC_O^{n}}{dt} \times \Delta t$$

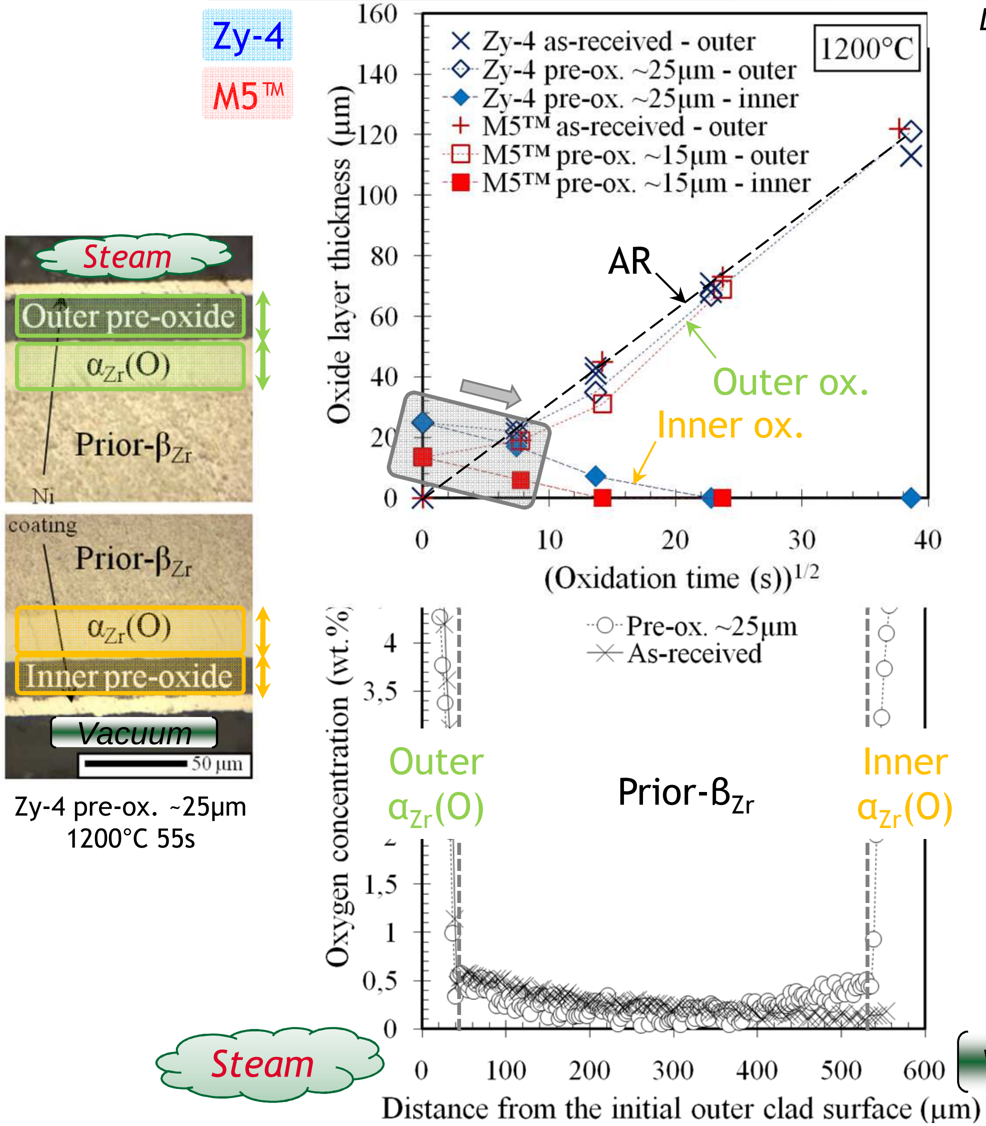
Reproduction et/ou diffusion interdite sans

EFFECT OF PRE-TRANSIENT OXIDE

For short oxidation times…



Le Saux, Topfuel - 2011



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

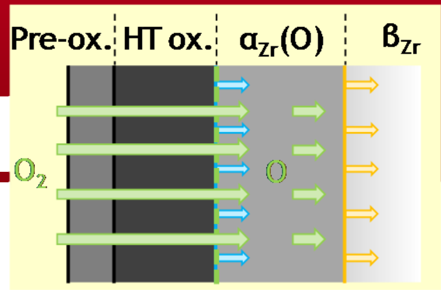
- ❑ Diffusion of the O coming from the reduction of the pre-ox. into the cladding metallic part

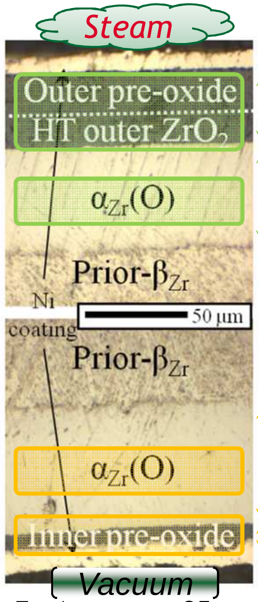
The overall quantity of O that diffuses is the same whether there is a pre-ox. or not

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

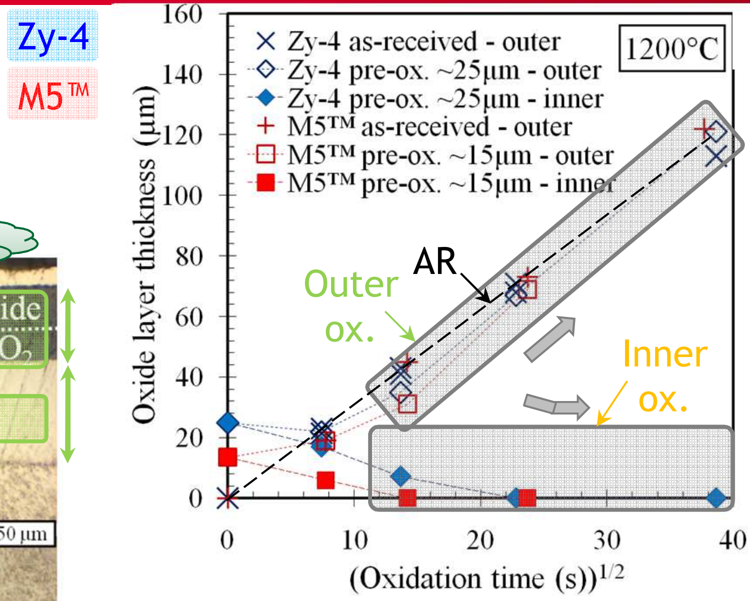
EFFECT OF PRE-TRANSIENT OXIDE (2)

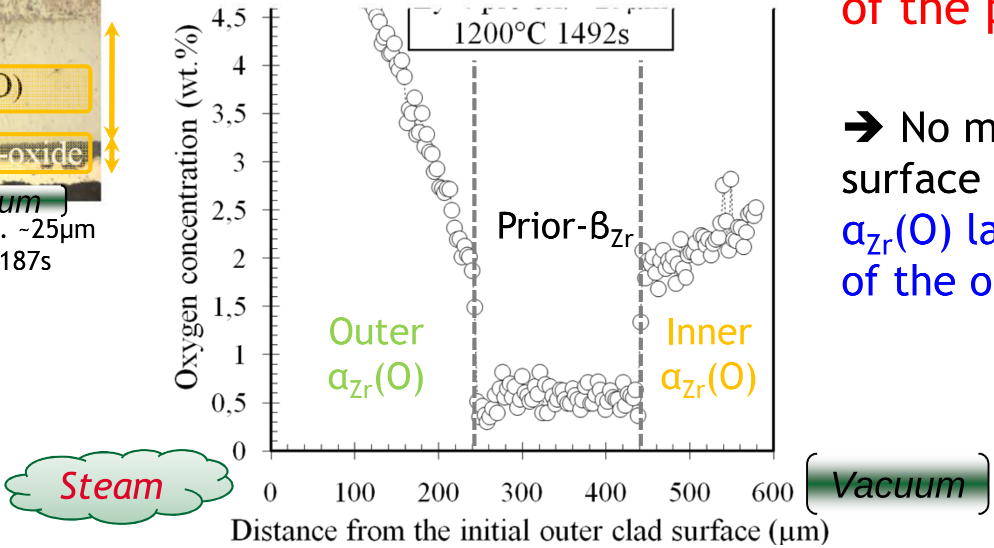
Later…





Zy-4 pre-ox. ~25µm
1200°C 187s





Le Saux, Topfuel - 2011

- ❑ 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

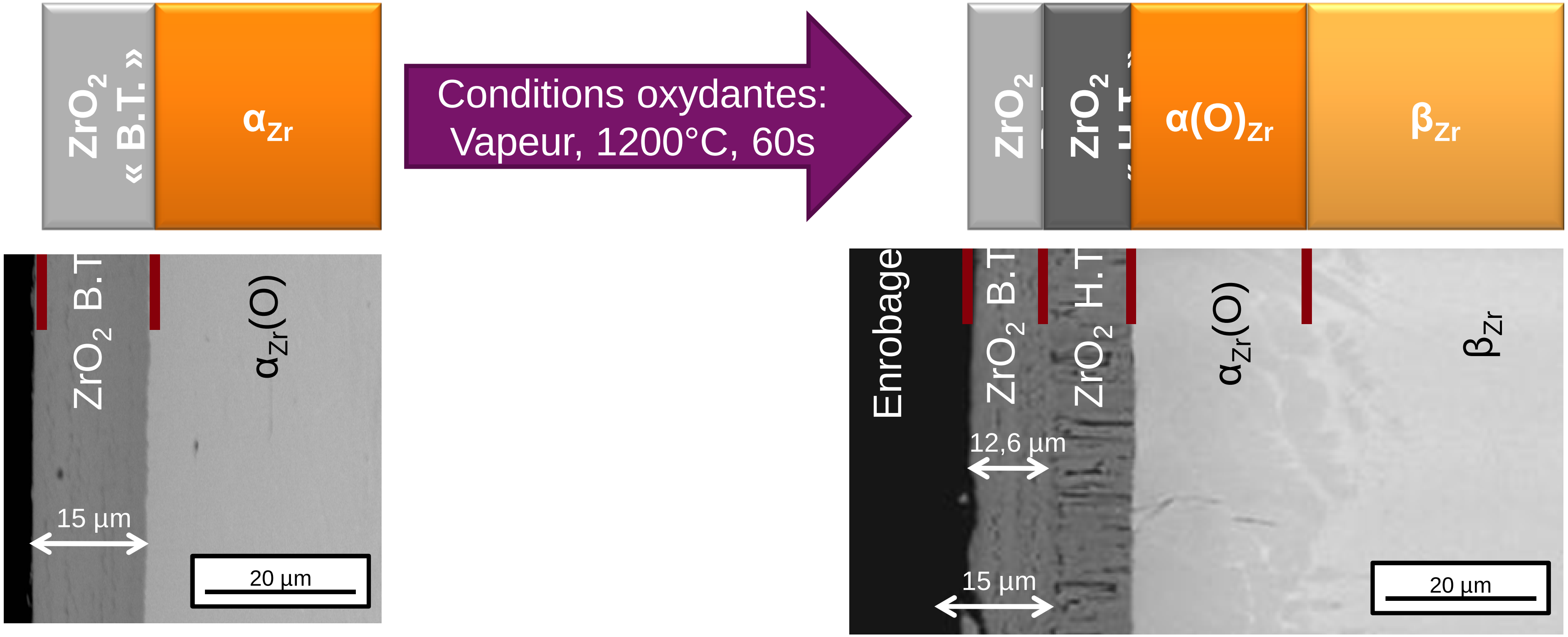
Similar results at 1000°C

Effet d'un pré-oxyde

ÈLE NUMÉRIQUE
CAS DE LA DISSOLUTION-RECROISSANCE

Phénomène de la dissolution-recroissance :

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



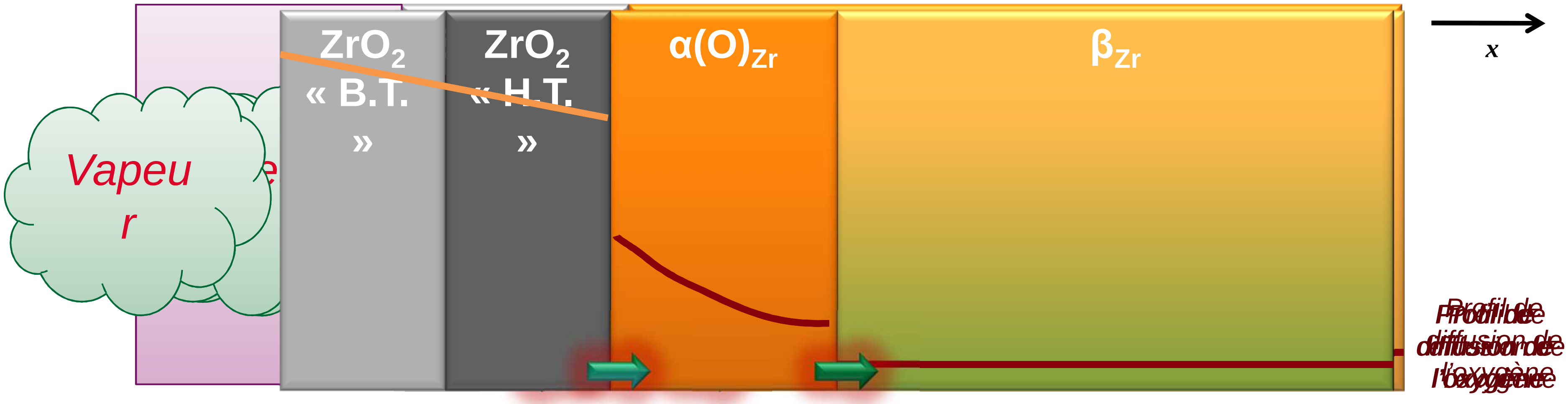
J.-C. BRACHET et al. *Hydrogen content, preoxidation and cooling scenario. Effects on post-quench microstructure and mechanical properties of Zircaloy-4 and M5™ alloys in LOC*
Journal of ASTM Internatonal. Vol 5, N°5. 2008. Paper ID JAI101116

Reproduction et/ou diffusion interdite sans

Effet d'un pré-oxyde ÈLE NUMÉRIQUE
CAS DE LA DISSOLUTION-RECROISSANCE

Phénomène de la dissolution-recroissance

Echantillons de Zy-4 pré-oxydés 15 µ



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

T ≈ 1200°C

T ≈ 360°C

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

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

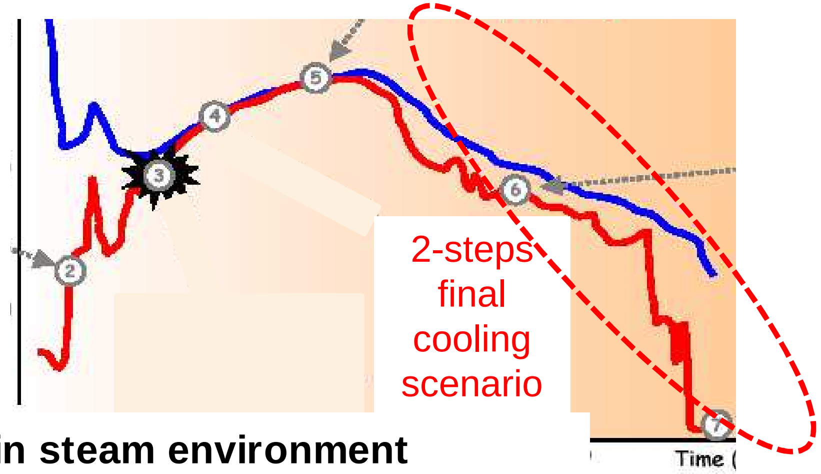
Reproduction et/ou diffusion interdite sans

EFFECTS OF PRE-HYDRIDING
=> « FINAL COOLING SCENARIO » EFFECT ON PQ DUCTILITY

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

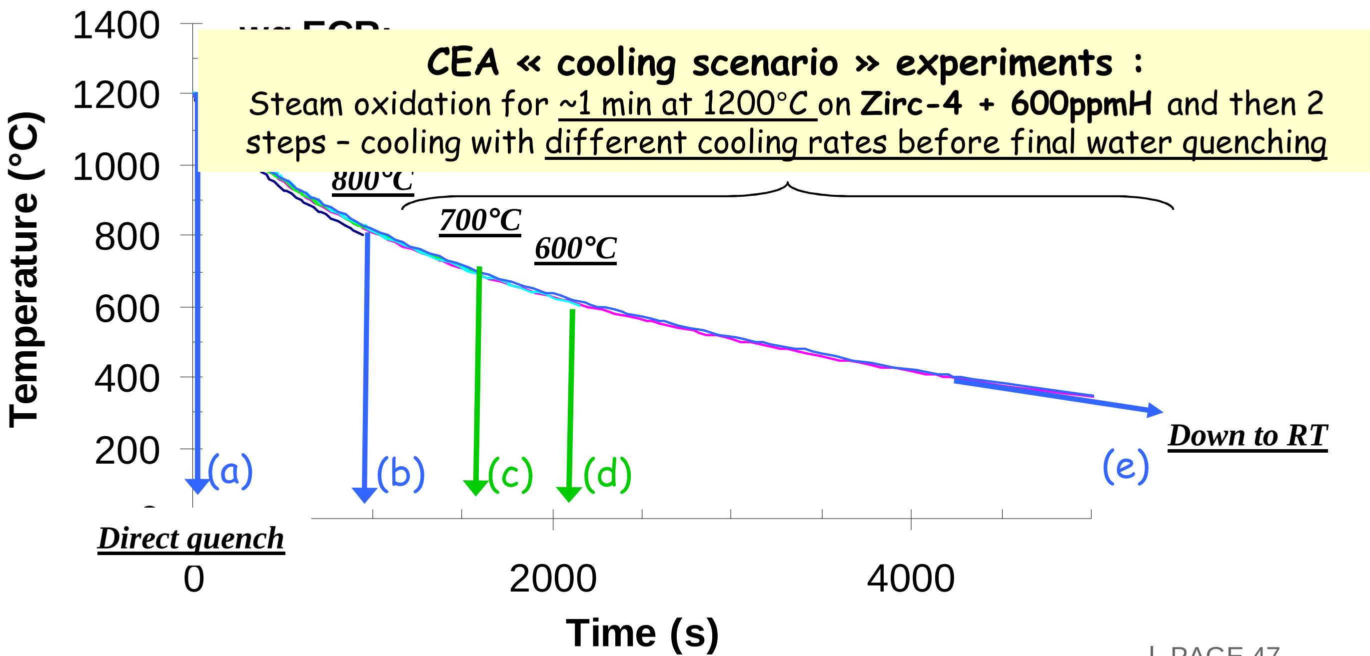
(2) and then **final water**



Cooling in steam environment

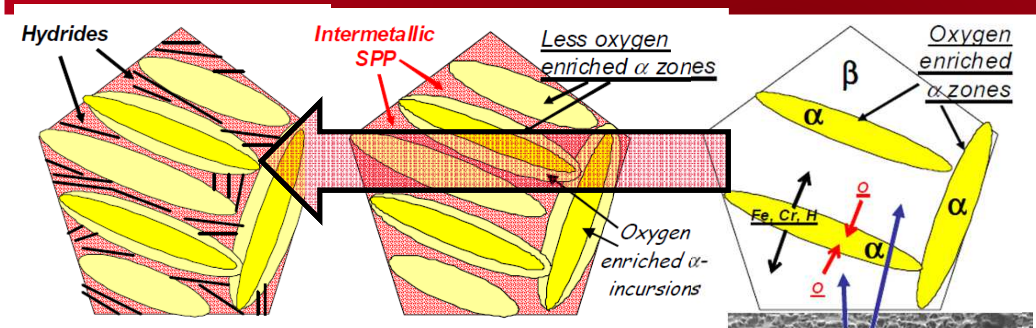
Depending on the LOCA transient type (SB, LB...) typical final quenching (wetting) temperatures range from ~1000°C down to ~400°C

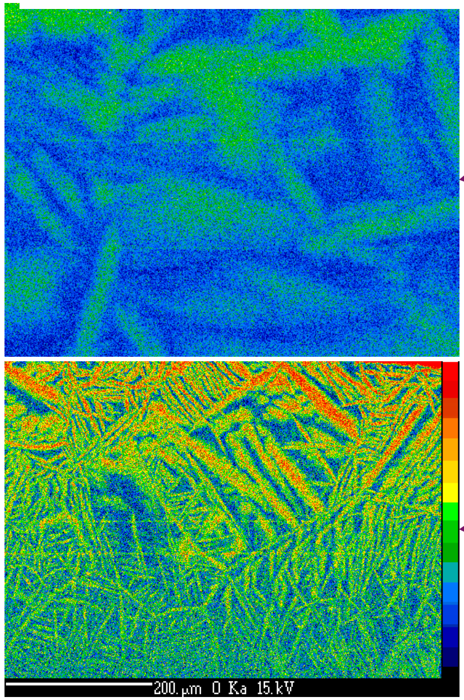
CEA « cooling scenario » experiments :
Steam oxidation for ~1 min at 1200°C on **Zirc-4 + 600ppmH** and then 2 steps – cooling with different cooling rates before final water quenching



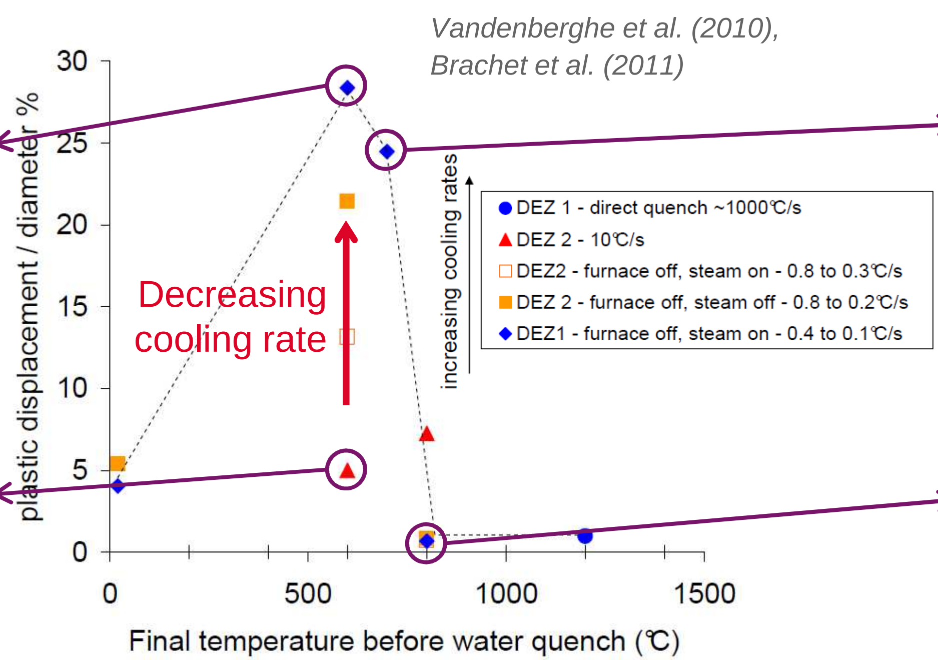
EFFECTS OF PRE-HYDRIDING
=> « FINAL COOLING SCENARIO » EFFECT ON PQ DUCTILITY

=> strong influence of O and H partitioning upon the on cooling β⟶α transformation ⇔ « microcomposite » mechanical behavior

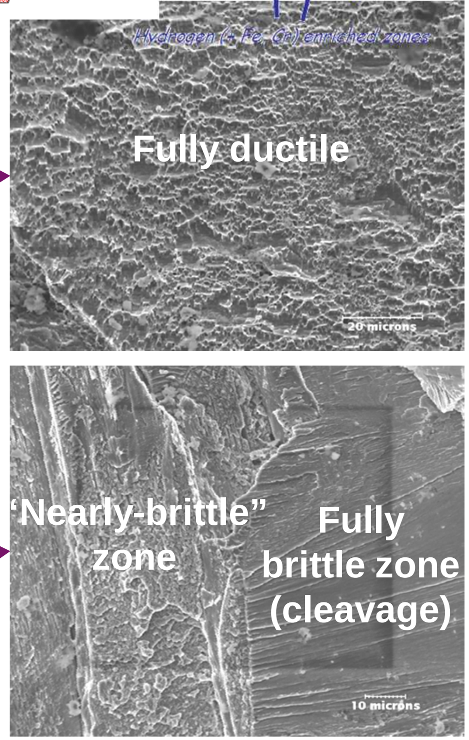




EPMA oxygen map within prior-β layer



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