

DE LA RECHERCHE À L'INDUSTRIE



*Université Paris-Saclay*



www.cea.fr

# OUT-OF-PILE R&D ON COATED NUCLEAR FUEL ZIRCONIUM BASED CLADDINGS FOR ENHANCED ACCIDENT TOLERANCE IN LWRS

*J.C. Brachet(\*), I. Idarraga(\*\*), M. Le Flem, M. Le Saux, F. Schuster, F. Lomello  
et al.*

*CEA-Saclay, Gif-Sur-Yvette, France*

*J. Bischoff, C. Delafoy  
AREVA NP, Lyon, France*

*E. Pouillier  
EDF R&D, MMC, Moret-Sur-Loing, France*

*Presented by Philippe BOSSIS (CEA-Saclay, France)*

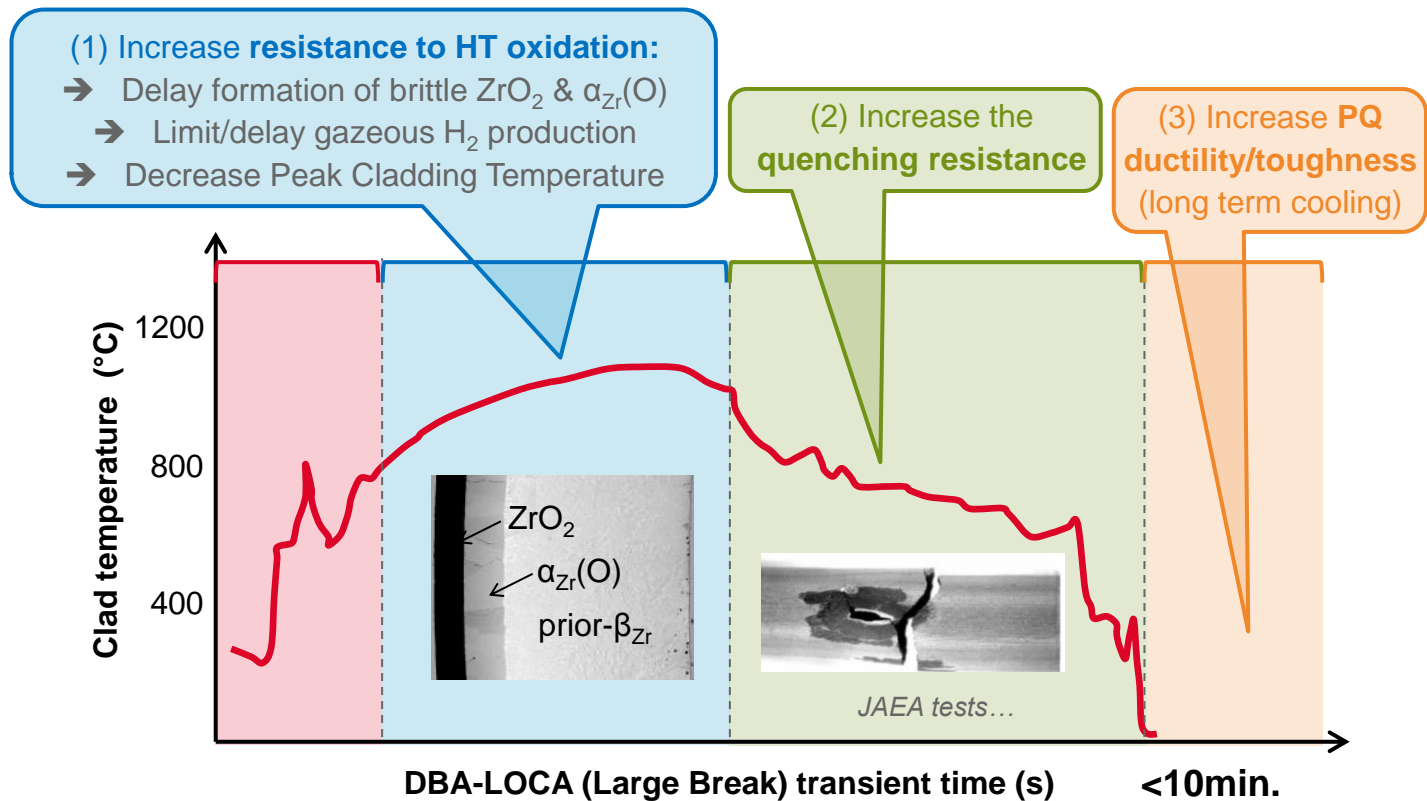
*(\*) corresponding author: [jean-christophe.brachet@cea.fr](mailto:jean-christophe.brachet@cea.fr)*

*(\*\*) now belonging to EDF R&D*

*18th International Symposium on Zirconium in the Nuclear Industry,  
Hilton Head, SC, USA, May 15-19 2016*

# INTRODUCTION / MAIN OBJECTIVES

Objective of R&D on coatings in the framework of the French CEA-EDF-AREVA Collaborative Program: to protect the cladding against corrosion and reduce hydrogen uptake during normal operating and accidental conditions and then to provide **additional margins on the nuclear fuel clad behavior in LWRs accidental conditions** such as LOCA by **decreasing the HT oxidation rate with steam at HT (and the associated heat production):**

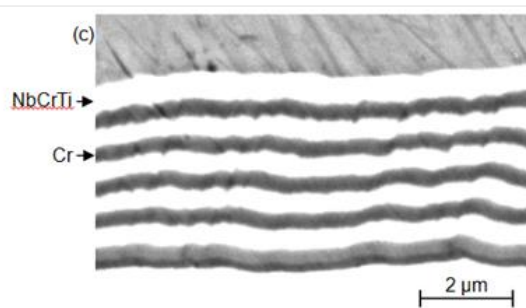
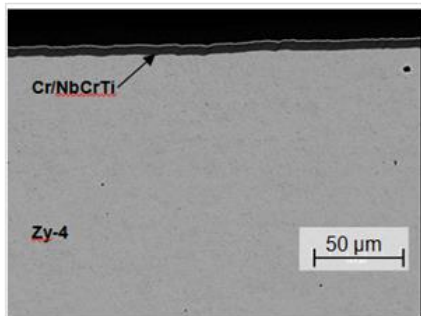


- (1) **Early studies - scoping tests on different types of coatings**  
including ceramic and metallic, mono or multilayered ones => chromium  
coatings have been selected as the most promising for next R&D steps
  - (2) **Improvement of the HT oxidation resistance of Cr coatings (DBA-LOCA)**
  - (3) **Cr-coated Zr nuclear fuel clad behavior upon nominal conditions:**
    - ⇒ as-received microstructure/properties
    - ⇒ corrosion resistance in PWR environment at 360°C & steam (100 bar) at 415°C
  - (4) **Cr-coated Zr nuclear fuel clad behavior upon steam oxidation at 1200°C:**
    - ⇒ numerous tests performed so far
    - ⇒ determination of the Cr-coating oxidation/consumption mechanism
    - ⇒ quantification/modélisation of the **overall coating consumption kinetics**
- (\* Remark: Additional studies/results for beyond LOCA conditions already published, including:*
- "post-breakaway " conditions, i.e., oxidation at 1000°C up to > 4 hours;
  - HT oxidation testing up to 1300°C, > 1 hour;
- => Assessment of the final quenching resistance and Post-Quenching (PQ) ductility...*

# (1.1) EARLY STUDIES / SCOPING TESTS OF DIFFERENT TYPES OF COATINGS ON ZIRCALOY-4 SHEET SUBSTRATE

The different coatings studied (PVD - DC Magnetron sputtering):

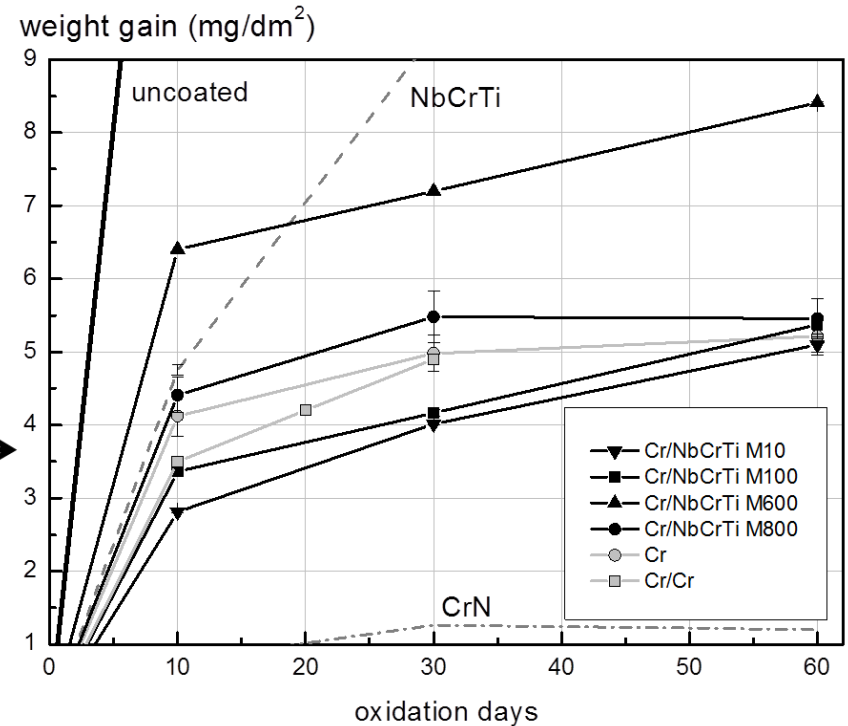
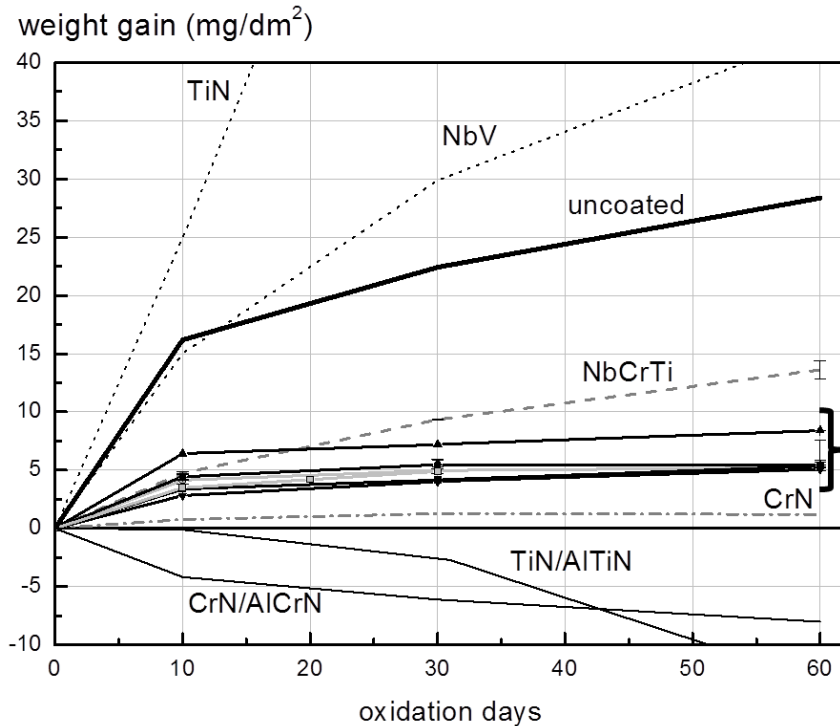
Coating type	notation	Architecture / period ( $\lambda^*$ )	Period number	Total thickness $\pm 0,2 \mu\text{m}$
TiN	TiN	Singlelayered	/	2,6
CrN	CrN	Singlelayered	/	3
TiN and AlTiN	TiN/AlTiN	Multilayered, $\lambda = 2 \times 8 \text{ nm}$	>200	3,4
CrN and AlTiN	CrN/AlTiN	Multilayered, $\lambda = 2 \times 8 \text{ nm}$	>200	3,2
Nb <sub>82%</sub> V <sub>18%</sub> (at%)	NbV	Singlelayered	/	5
Nb <sub>67%</sub> Cr <sub>10%</sub> Ti <sub>23%</sub> (at%)	NbCrTi	Singlelayered	/	4
Cr	Cr	Singlelayered	/	1 and 5
	Cr/Cr	Multipass, $\lambda = 500 \text{ nm}$	14	7
Cr and Nb <sub>67%</sub> Cr <sub>10%</sub> Ti <sub>23%</sub> (at%)	Cr/NbCrTi M10	Multilayered, $\lambda = 2 \times 5 \text{ nm}$	>500	6
	Cr/NbCrTi M100	Multilayered, $\lambda = 2 \times (50 \text{ to } 80) \text{ nm}$	40	5,5
	Cr/NbCrTi M600	Multilayered, $\lambda = 2 \times 300 \text{ nm}$	10	6
	Cr/NbCrTi M800	Multilayered, $\lambda = 2 \times 400 \text{ nm}$	5	4



\* The period corresponds to the number of "layers", i.e. 1 layer of Cr in the case of Cr/Cr coating and 2 successive layers of different materials for TiN/AlTiN, CrN/AlCrN and Cr/NbCrTi coatings

# (1.2) EARLY STUDIES / SCOPING TESTS OF DIFFERENT TYPES OF COATINGS ON ZIRCALOY-4 SHEET SUBSTRATE

Autoclave tests, 360°C, pressurized water, PWR chemistry (M. Tupin, P. Billaud et al., CEA):



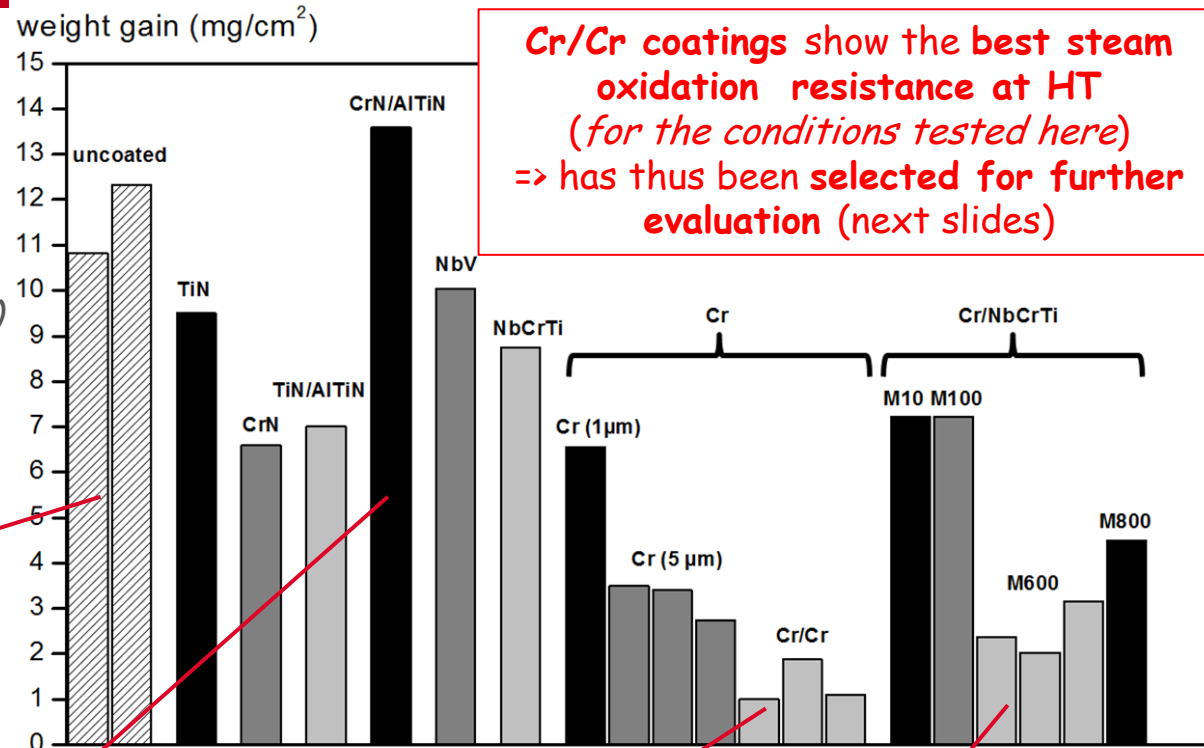
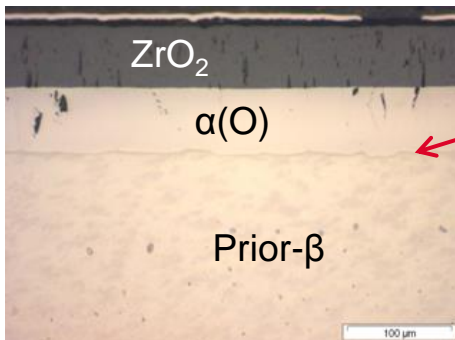
- Poor behavior of TiN and NbV coatings

- Loss of weight gain observed for Al containing multilayered coatings, probably due to outward migration of aluminum and potential release in the pressurized water as observed by some other authors (Alat et al. - 2015, R. Van Nieuwenhove - this conference, etc...)

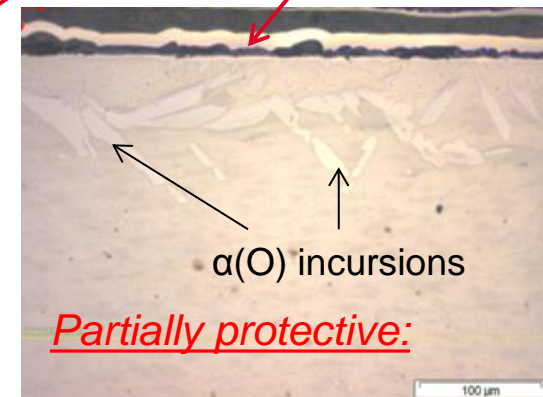
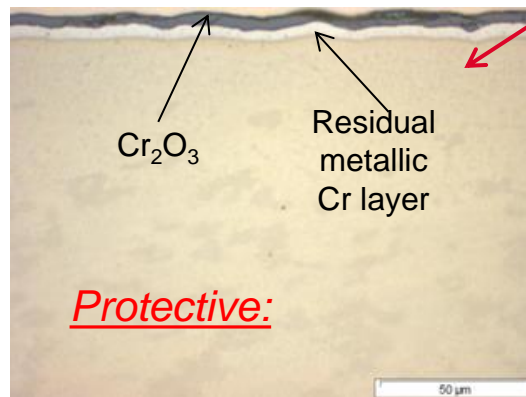
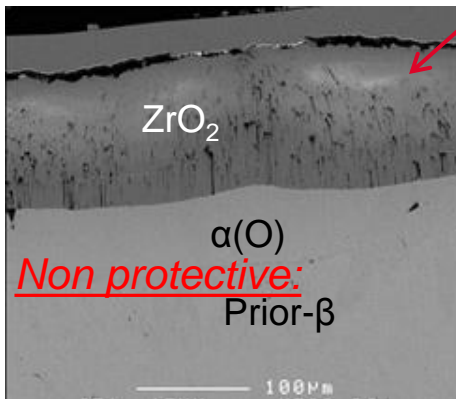
- Best behavior observed for CrN, Cr, Cr/Cr and multilayered Cr/NbCrTi coatings

# (1.3) EARLY STUDIES / SCOPING TESTS OF DIFFERENT TYPES OF COATINGS ON ZIRCALOY-4 SHEET SUBSTRATE

Coatings resistance to HT steam oxidation in DBA-LOCA conditions - Ex. = Steam oxidation for 850s at 1100°C (ECR<sub>measured-weight-gain</sub> ~10% for uncoated Zry-4 - one sided oxidation) + direct water quenching



**Cr/Cr coatings show the best steam oxidation resistance at HT (for the conditions tested here) => has thus been selected for further evaluation (next slides)**



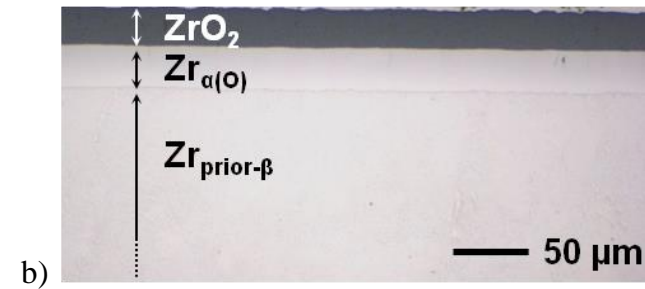
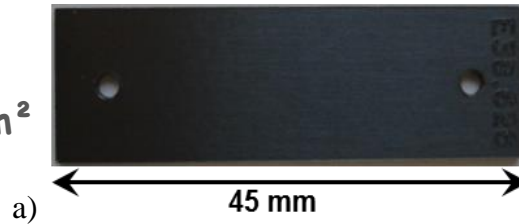


## (2.1) IMPROVEMENT OF THE HT OXIDATION RESISTANCE OF CR BASED COATINGS (DBA-LOCA):

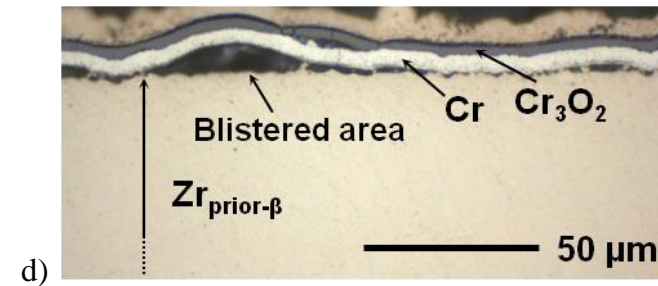
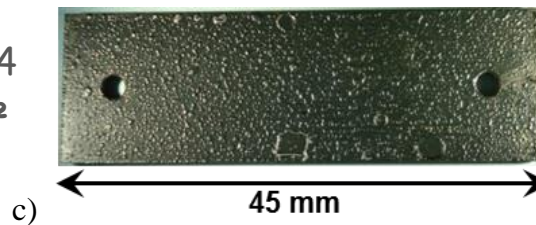
1<sup>st</sup> R&D step: improvement of the HT steam oxidation resistance of Cr-coated materials conducted on Zircaloy-4 sheet samples and focusing on **DBA-LOCA** conditions at first (i.e., max. PCT = 1200°C, max. ECR (BJ) = 17% => oxidation time <600s for one-sided oxidation)

One-sided steam oxidation at 1200°C for 300s ( ECR (BJ) ~ 10%):

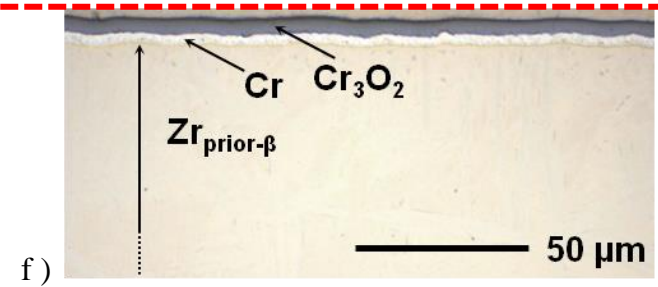
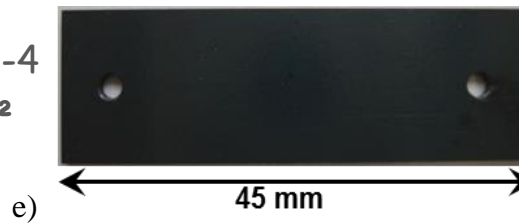
Reference uncoated Zircaloy-4  
Weight Gain = 10,5 - 11,0 mg/cm<sup>2</sup>



1<sup>st</sup> generation of Cr-coated Zirc-4  
Weight Gain = 1,5 - 2,0 mg/cm<sup>2</sup>



Last generation of Cr-coated Zirc-4  
Weight Gain = 0,4 - 0,9 mg/cm<sup>2</sup>

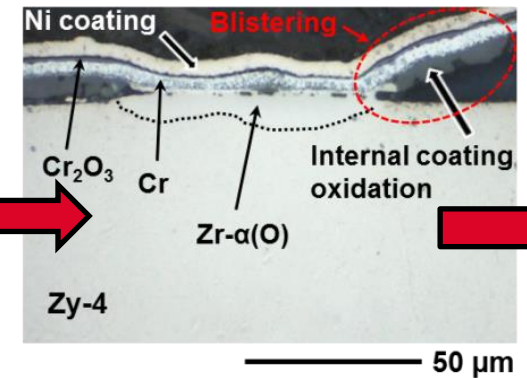
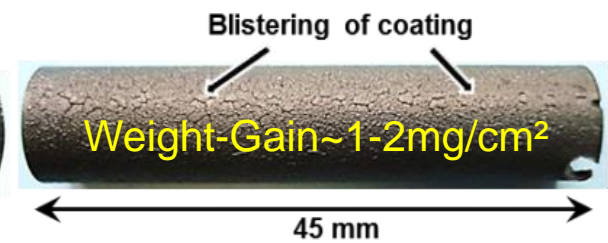
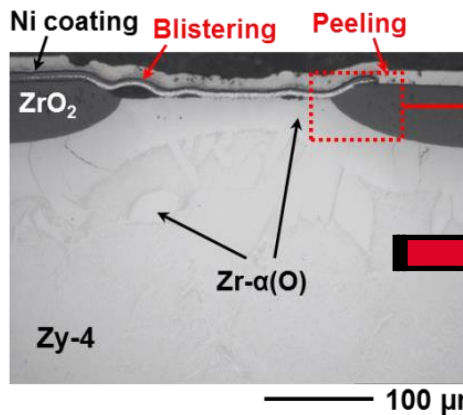
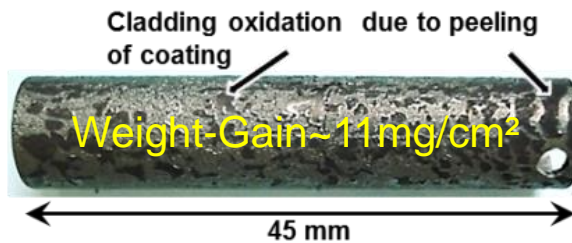
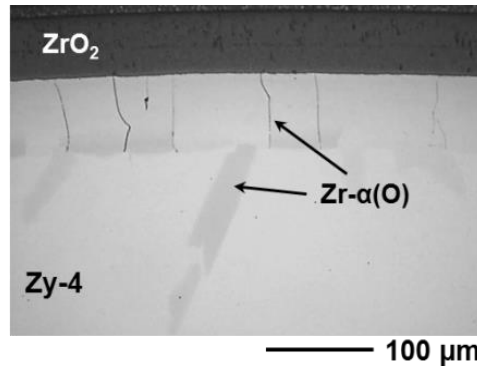
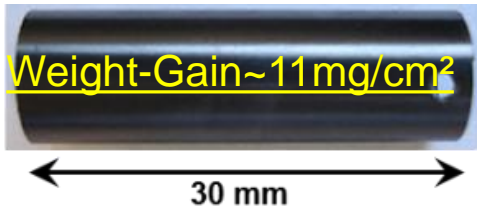


## (2.2) IMPROVEMENT OF THE HT OXIDATION RESISTANCE (DBA-LOCA)

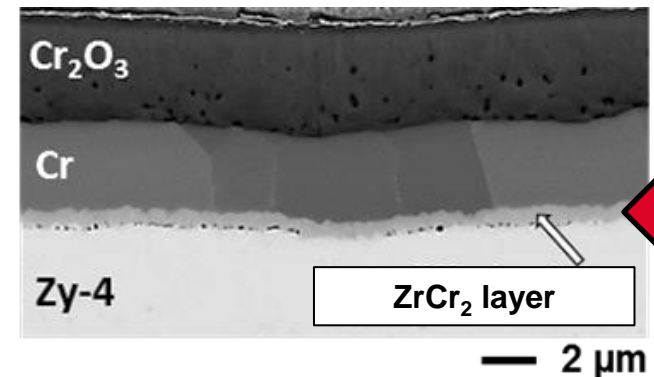
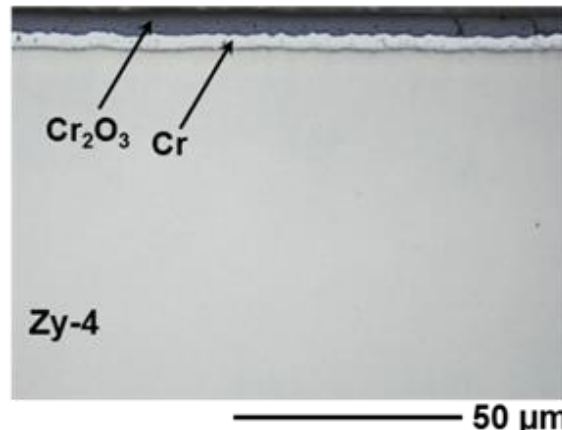
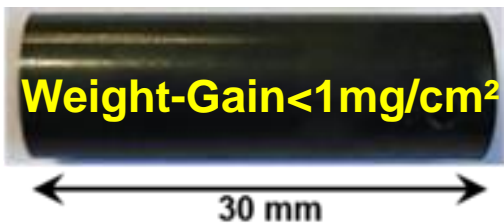
2<sup>nd</sup> R&D step: Cr-coatings on tubular geometry

(One-sided steam oxidation at 1200°C for 300s - ECR (BJ) ~ 10%):

Uncoated-reference Zircaloy-4:



Last generation Cr-coated Zircaloy-4:





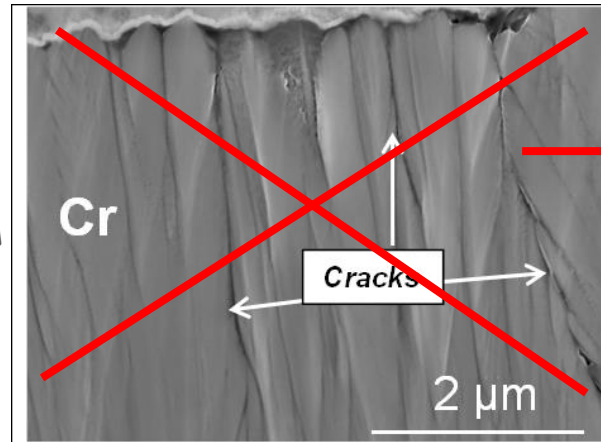
# (3.1) (OUT-OF-PILE) NOMINAL BEHAVIOR OF (LAST GENERATION) CR-COATED ZR:

## As-received $\mu$ structure:

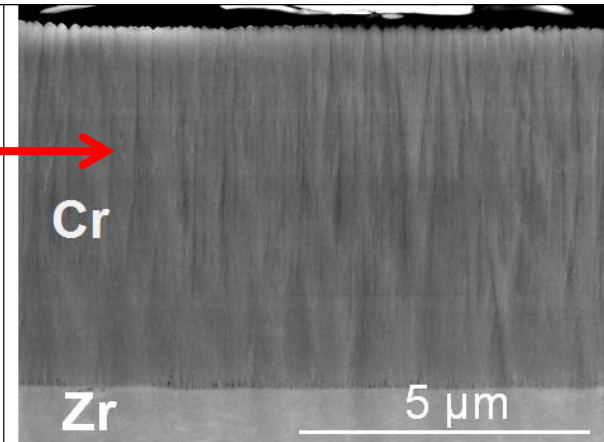
- Thicknesses studied: 1-20  $\mu\text{m}$
- Multi-scale characterization: Optical microscopy, XRD, SEM-EBSD, EPMA, TEM (High resolution mode) on thin foils (FIB)...

## Last generation of Cr-coatings:

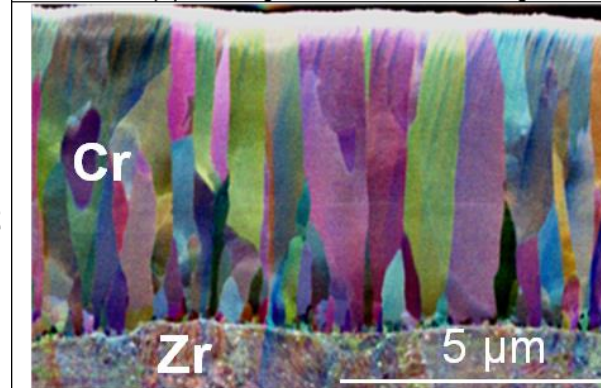
**=> Dense coatings, with no cracks, good Zr-Cr bonding with no interfacial defects**



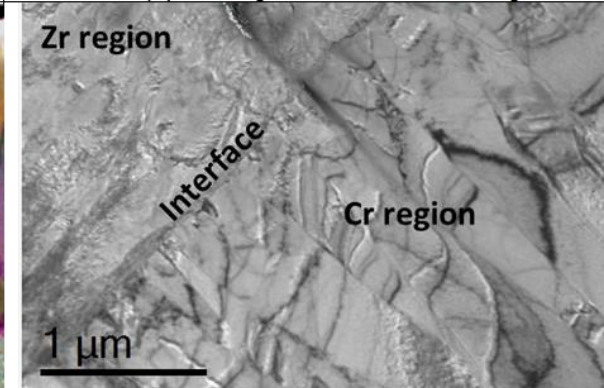
(a) First generation of coating



(b) Last generation of coating



(c) Forward Scattered Detectors Imaging (Field Emission Gun Scanning Electron Microscopy, FEG-SEM)



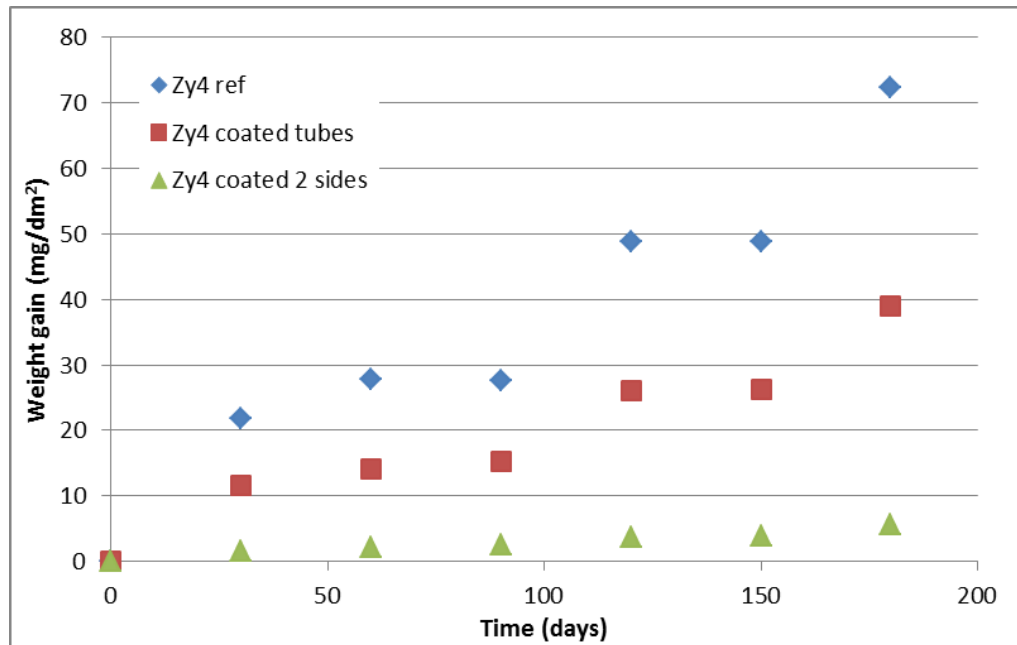
(d) Zircaloy-4/chromium interface as observed by TEM (J. Ribis, B. Arnal, CEA)

**Additionally, nano-hardness, scratch and preliminary fretting/wear tests have been done => Good adhesion properties and good resistance to fretting for as-received conditions**

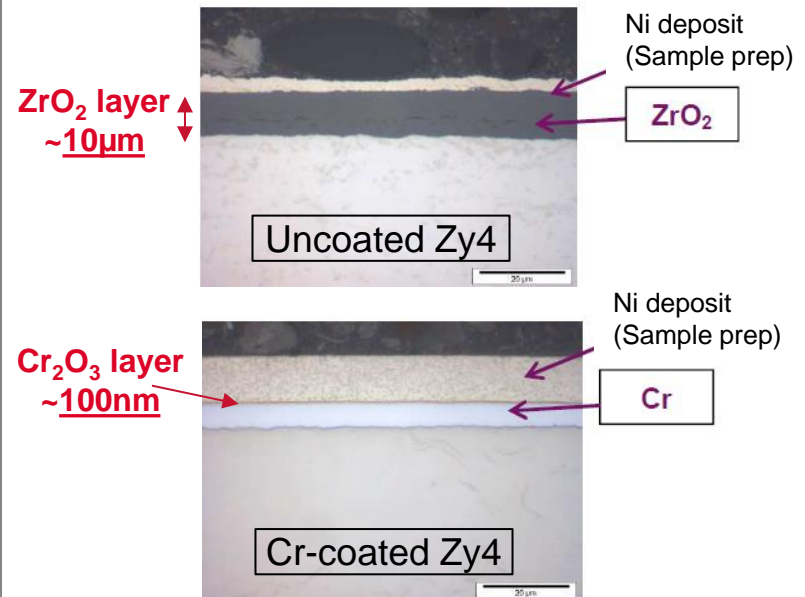
## (3.2) (OUT-OF-PILE) NOMINAL BEHAVIOR OF (LAST GENERATION) CR-COATED ZR:

### Corrosion properties

360°C PWR pressurized water



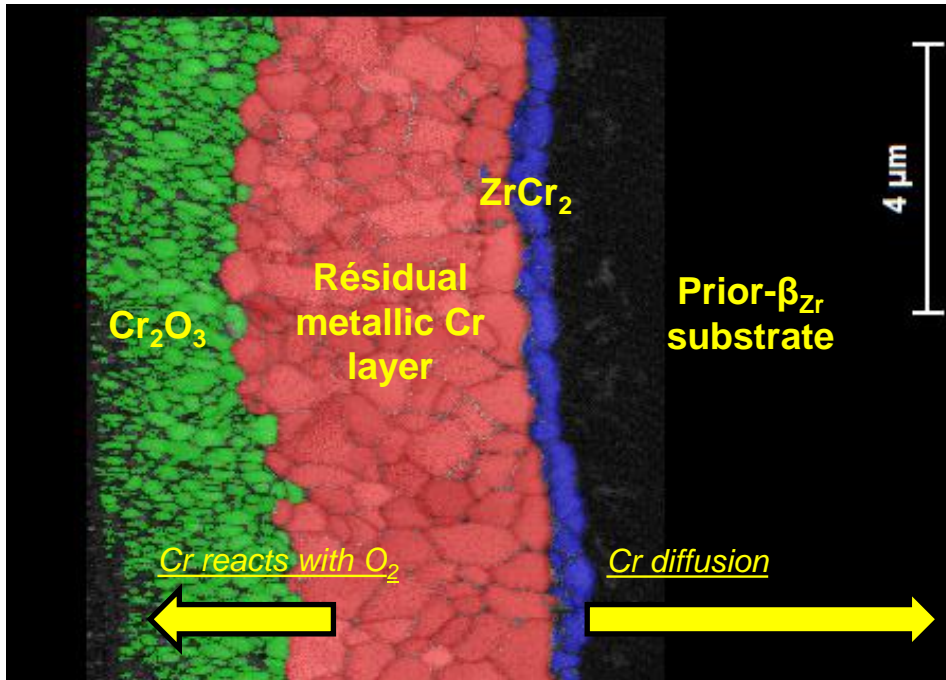
415°C pressurized steam (100 days)



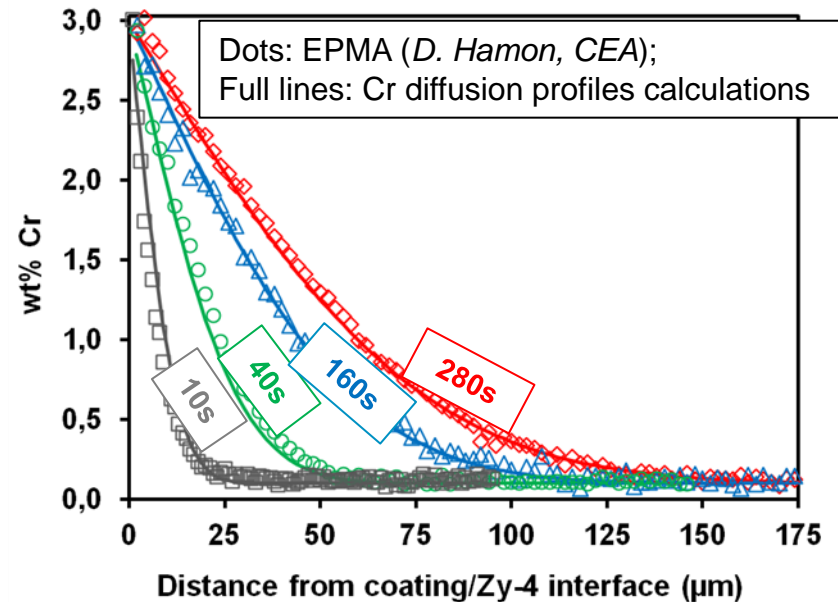
- Cr-coated samples exhibit significantly reduced weight gain in autoclave (1-3 mg/dm<sup>2</sup>) with very little variation with time
- No dissolution or delamination of Cr-coating observed
- No ZrO<sub>2</sub> « pockets » formed under the Cr-coating = coating is **very protective**

# (3.3) HT STEAM OXIDATION BEHAVIOR CR-COATED ZR => CHROMIUM COATING EVOLUTION/CONSUMPTION KINETICS UNDER STEAM ENVIRONMENT AT HT:

SEM-EBSD map in phase contrast imaging mode of Cr-coated Zircaloy-4 after steam oxidation for 300s at 1200°C (E. Rouesne, CEA):



Cr diffusion profiles into the prior-β substrate from Zr/Cr interface after oxidation at 1200°C:



1D diffusion calculation performed (semi-infinite volume assumption):  $C(x, t) - C_0 = (C_s - C_0)(1 - \text{erf}(x/(2\sqrt{Dt})))$

- $D$  : thermal (volumic) diffusion coefficient in prior- $\beta_{Zr}$  (from the litterature) =  $6,29 \mu\text{m}^2/\text{s}$  at  $1200^\circ\text{C}$ ,
- $C(x, t)$  is the Cr concentration diffusing into prior- $\beta_{Zr}$  at distance  $x$  from Zr-Cr interface, and for diffusion time  $t$ ,
- $C_0$  is the initial Cr concentration in the Zircaloy-4 substrate ( $\sim 0.1 \text{ wt}\%$ )
- $C_s$  the concentration at the Cr/Zr interface assuming local thermodynamic equilibrium  
=> calculated thanks to CEA-"Zircobase" thermodynamic database =>  $\sim 3 \text{ wt}\%$  at  $1200^\circ\text{C}$  (solubility limit of Cr in  $\beta_{Zr}$ )

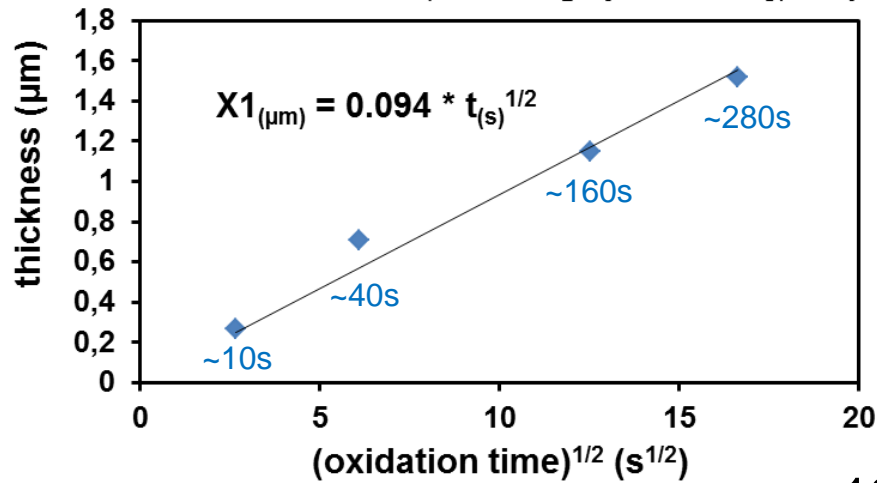
## Cr coating consumption mechanism during steam oxidation at HT

Two main contributions:

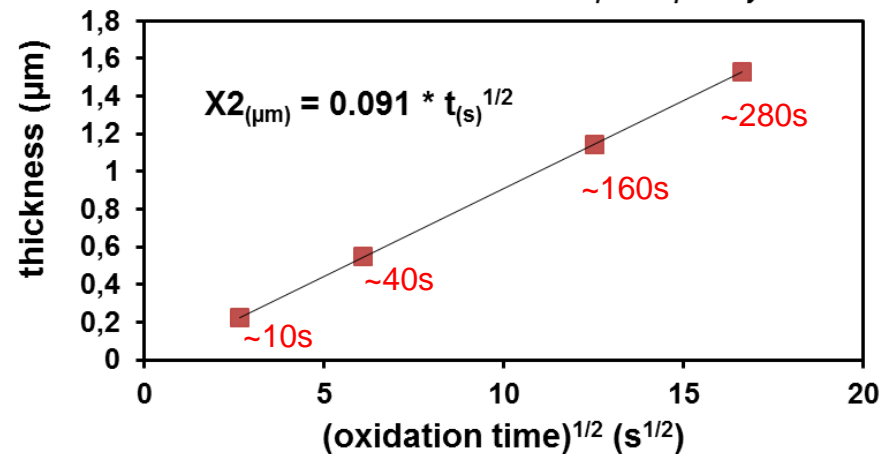
- (1) Growth/thickening of outer  $\text{Cr}_2\text{O}_3$  scale;
- (2) Diffusion of Cr from the Zr/Cr interface into the prior- $\beta$  substrate.

*For coating thicknesses of at least a few micrometers and as far as DBA-LOCA oxidation times are considered, the two basic kinetics are parabolic:*

Cr coating thickness consumption kinetics due to oxidation (outer  $\text{Cr}_2\text{O}_3$  thickening) only:



Cr coating thickness consumption kinetics due to Cr diffusion into the prior- $\beta$  only:

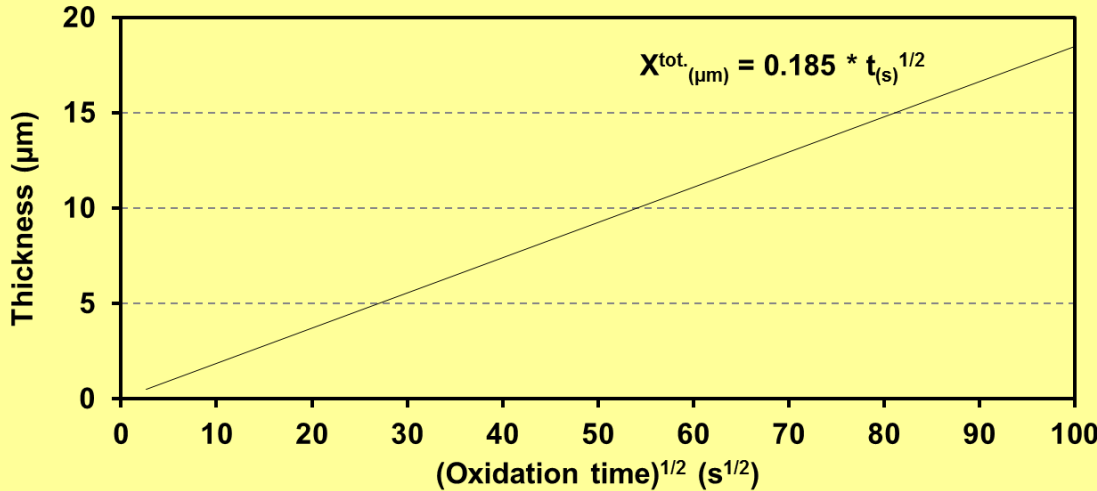


1200°C



# (3.5) HT STEAM OXIDATION BEHAVIOR OF CR-COATED ZR:

Overall Cr coating consumption due to steam oxidation at 1200°C



Consistent with previously published results  
(J.C. Brachet et al., Fontevraud 8, 2014):

Ex.: One-sided steam oxidation for 6000s at 1200°C  
(beyond DBA-LOCA conditions):

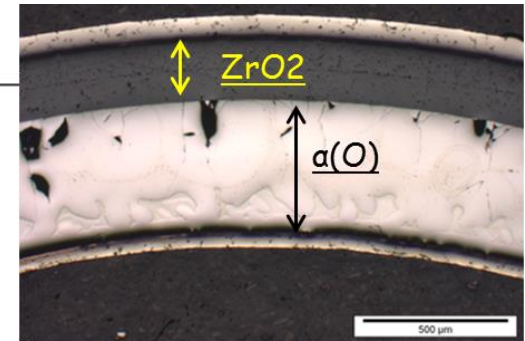


(a) Uncoated Zircaloy-4 clad segment, weight gain = 40,4 mg/cm<sup>2</sup>

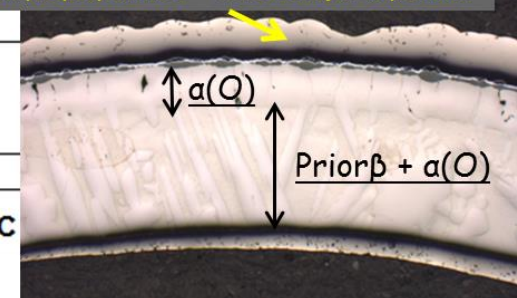


(b) Coated Zircaloy-4 clad segment, weight gain = 11,4 mg/cm<sup>2</sup>

PQ Zircaloy-4 clad segments appearance after steam oxidation for 6000 s at 1200°C



Sample preparation => outer Ni layer deposition





## CONCLUSION, ON-GOING AND FURTHER WORK:

- In the framework of the French CEA-EDF-AREVA Collaborative Program, **zirconium based coated claddings** are developed as potential Enhanced Accident Tolerant Fuels (EATF) materials for LWRs applications:
    - => **Mid-term (~10 years) R&D** with negligible/limited impact on the geometry, mechanical, neutronic and thermal properties of the nuclear fuel assembly => **Easier/faster licensing**
  - From the early scoping tests performed on different types of coatings (including metallic, ceramics, multi-layered...), **chromium coatings have been selected and further improvement of its HT oxidation resistance has been conducted;**
  - **Last generation of chromium coated zirconium based nuclear fuel clad behavior shows:**
    - (1) **very good nominal corrosion resistance (PWR environment at 360°C & steam at 415°C)**
    - (2) **attractive HT steam oxidation resistance for DBA-LOCA and beyond (up to 1300°C);**
- => for prototypical DBA-LOCA oxidation times, Cr-coating coating consumption mechanism and kinetics established at 1200°C (*can be extended at other oxidation temperatures*);
- *Ballooning & burst tests under internal pressure at HT (LOCA) are on-going showing encouraging behavior (protective effect maintained, no peeling ... cf. Topfuel 2016)*
  - *Ions and neutron irradiation experiments are on-going/planned (cf. poster A. Wu - this conference, Halden-IFA-796 project...)*

# THANK YOU FOR YOUR ATTENTION

## *Some CEA references:*

*[1] I. Idarraga et al., "Assessment at CEA of coated nuclear fuel cladding for LWRs with increased margins in LOCA and beyond LOCA conditions", in proceedings of 2013 LWR Fuel Performance Meeting/TopFuel, Charlotte, USA, (Sept. 15-19, 2013)*

*[2] J.C. Brachet, Ch. Lorrette, et al., "CEA studies on advanced nuclear fuel claddings for enhanced Accident Tolerant LWRs Fuel (LOCA and beyond LOCA conditions)", Proceedings of the 8th. Int. Symposium "Fontevraud 8" on "Contribution of Materials Investigations and Operating Experience to LWRs' Safety, Performance and Reliability", Avignon, France, (Sept. 14-18 2014)*

*[3] "J.C. Brachet, et al., "On-going studies at CEA on chromium coated zirconium based nuclear fuel claddings for enhanced tolerant LWRs fuel", proceeding of TopFuel 2015, (13-19 Sept. 2015), Zurich, Switzerland*

---

French alternative energies and atomic energy commission  
Saclay center | F91191 Gif-sur-Yvette Cedex  
T. +33 (0)1 69 08 51 66 | F. +33 (0)1 69 08 82 52

Nuclear Energy Division  
Nuclear Materials Department  
Section for Applied Metallurgy Research

# *Additional/back slides*

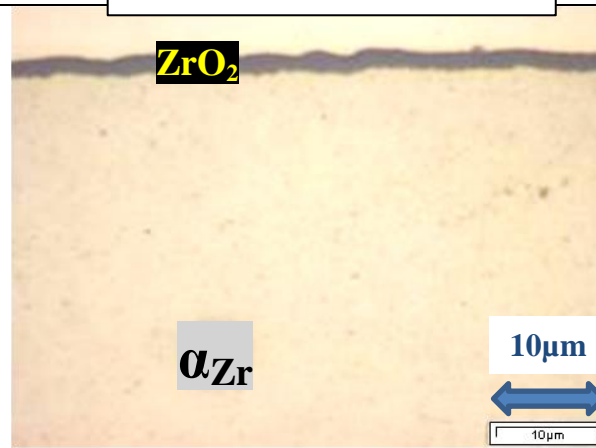
# IMPACT OF PRE-EXISTING CR COATING DEFECTS

*The potential negative impact of a pre-existing defect (i.e., as-received crack) within the Cr coating on the subsequent coated clad oxidation is an important issue:*

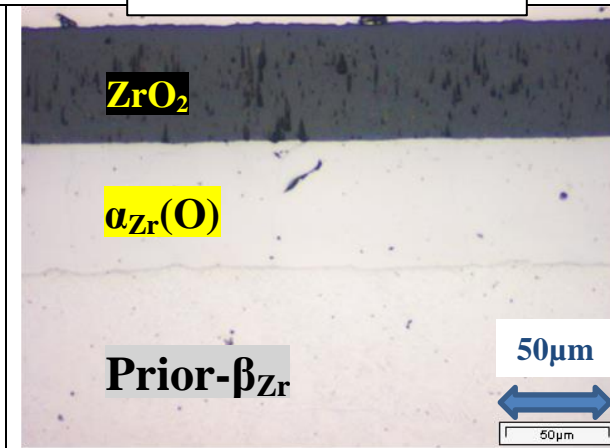
*⇒ Results obtained so far show only a limited and very localized impact of a pre-existing thru-wall Cr layer crack on the subsequent oxidation behavior for both nominal and accidental (LOCA) conditions (i.e., neither local accelerated corrosion, nor coating spallation)*

*⇒ However, further work is necessary: longer oxidation times...*

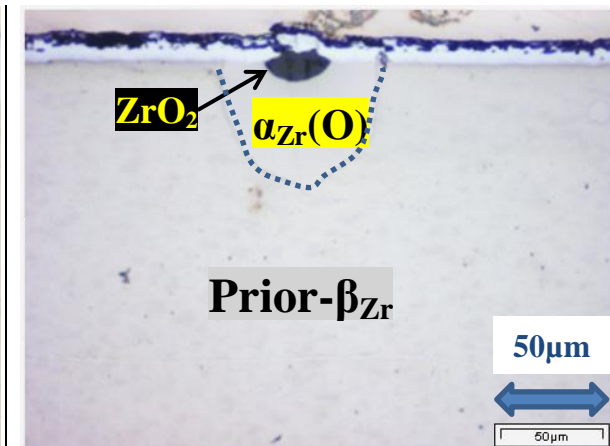
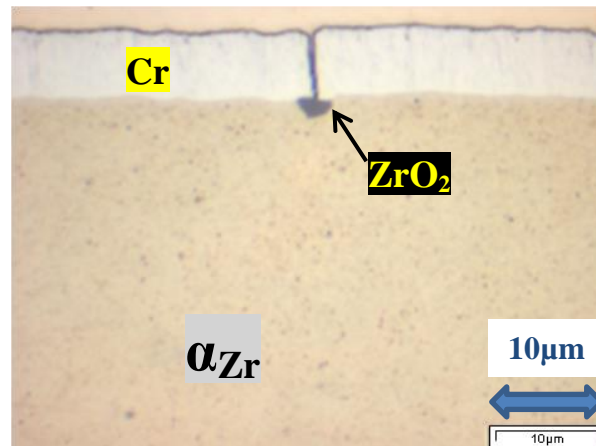
Nominal conditions



LOCA conditions



Uncoated reference Zirc-4 sheet sample



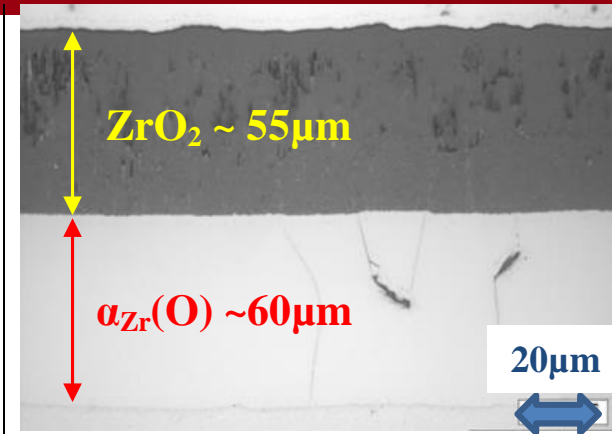
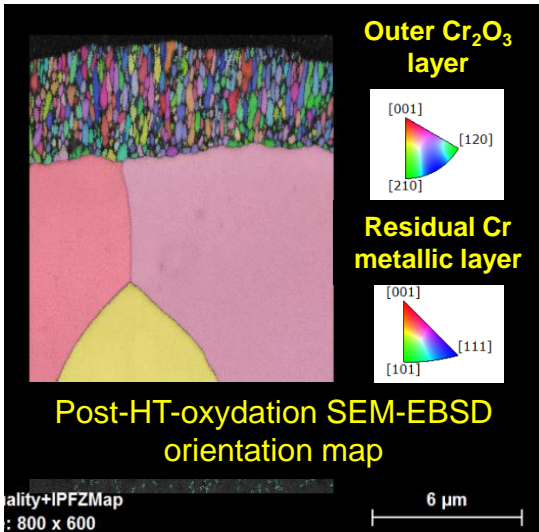
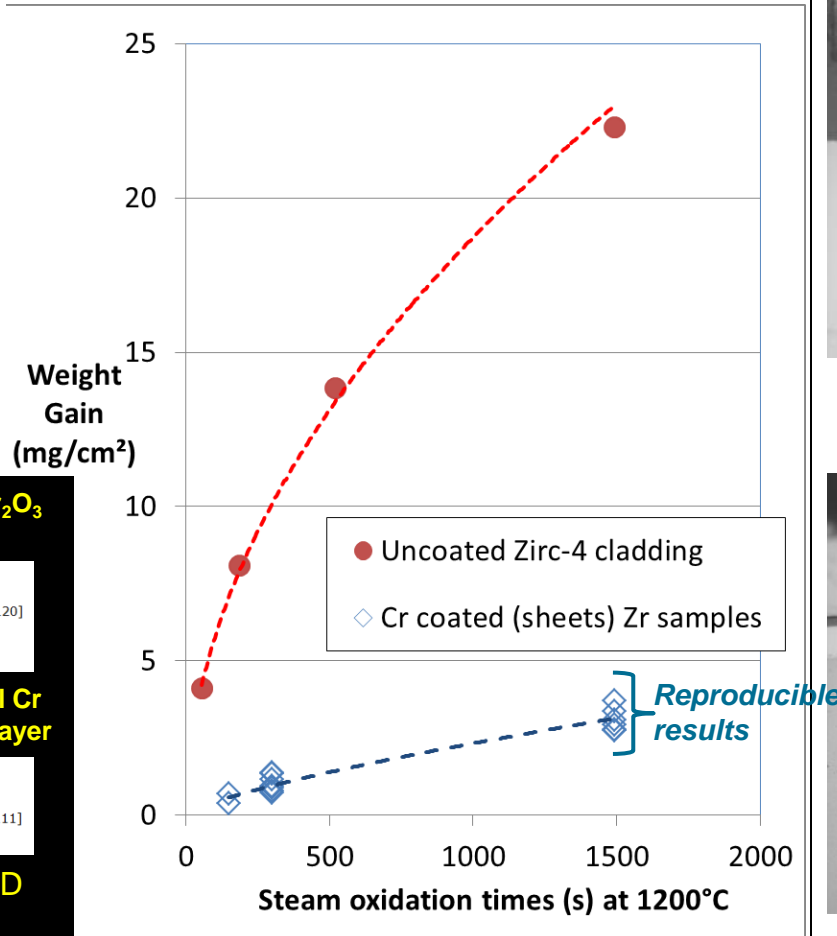
Cr Coated Zirc-4 sheet sample with a pre-existing crack throughout the coating thickness

(a) After autoclave tests for 60 days at 360°C

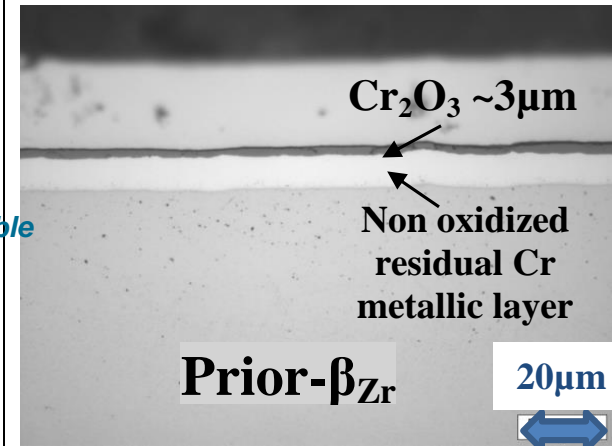
(b) After re-oxidation for 850 s at 1100°C

# HT BEHAVIOR IN STEAM - DBA-LOCA TEMPERATURE RANGE – 1-SIDED OXIDATION KINETICS

1200°C



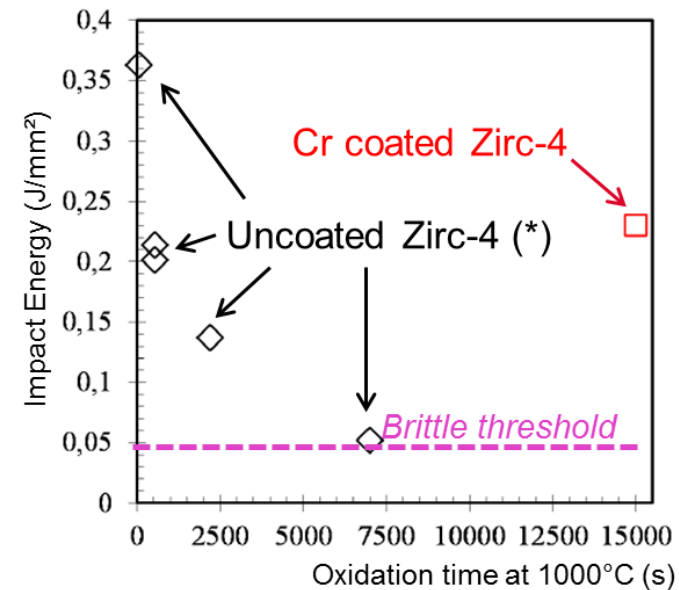
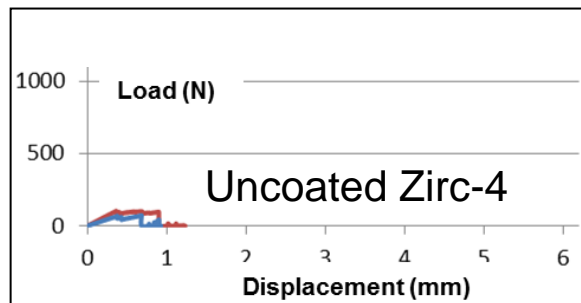
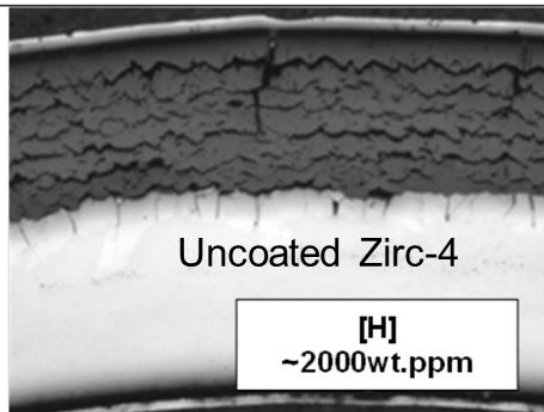
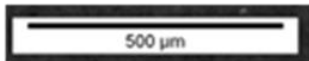
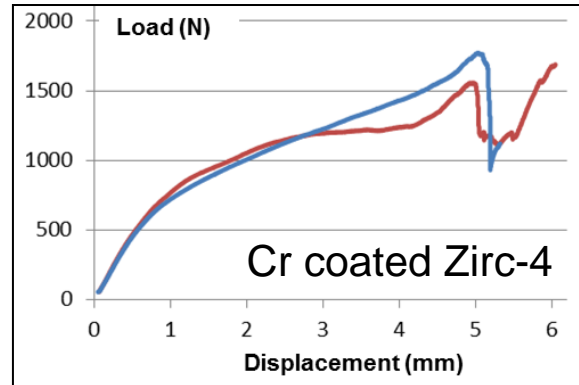
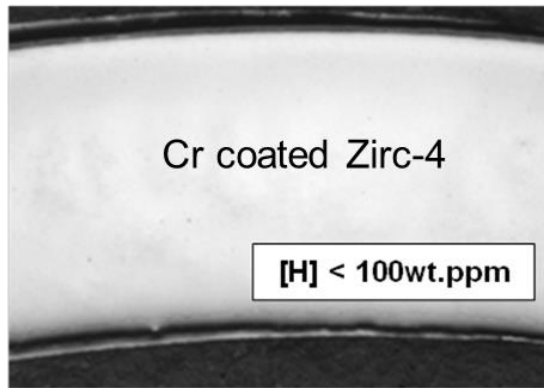
(a) Uncoated Zirc-4 after steam oxidation for 300s at 1200°C



(b) Cr coated Zirc-4 after steam oxidation for 300s at 1200°C



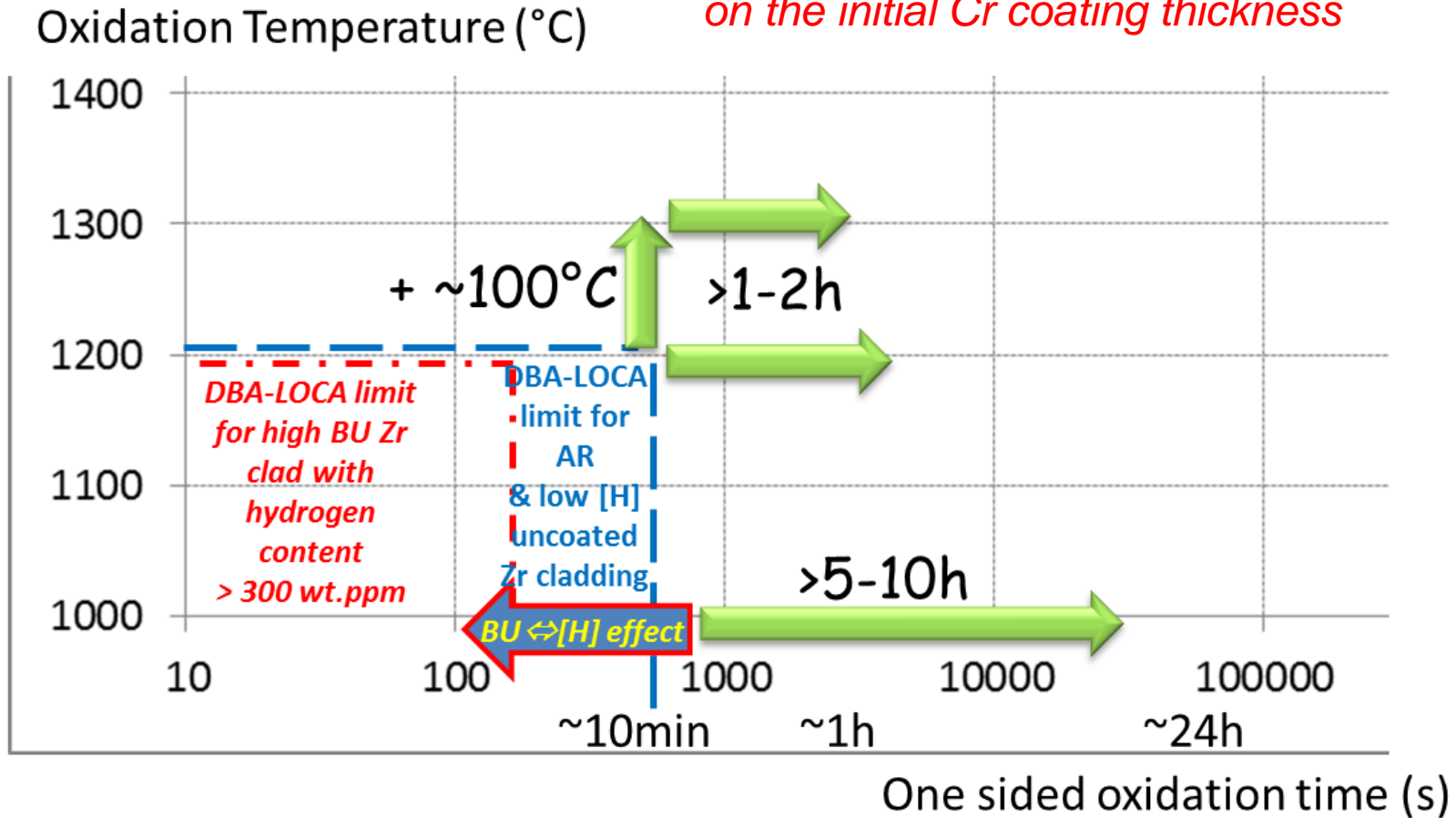
#### Ring Compression Test at 135°C:



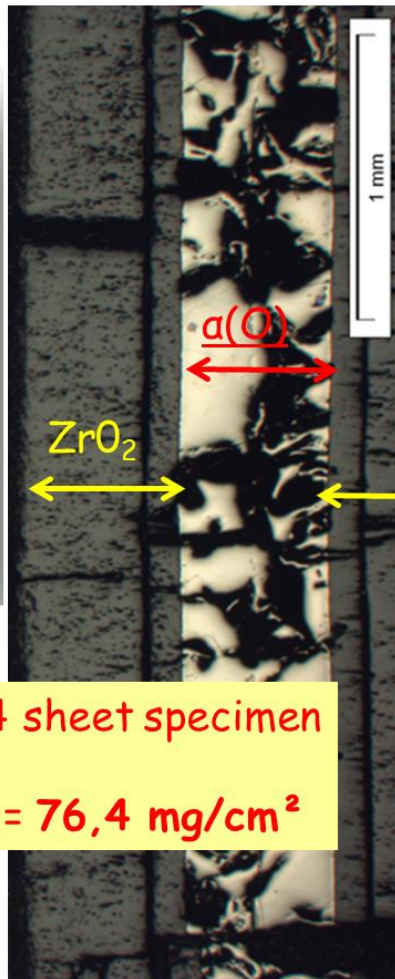
(\*) reference:  
L. Portier et al., Journal of ASTM International, Feb. 2005, Vol. 2, No. 2, Paper ID JAI12468

# Expected additional HT steam oxidation time/temperature margins for ~5-20 $\mu$ m thick optimized Cr coated Zirc-4 claddings vs. current DBA-LOCA limits

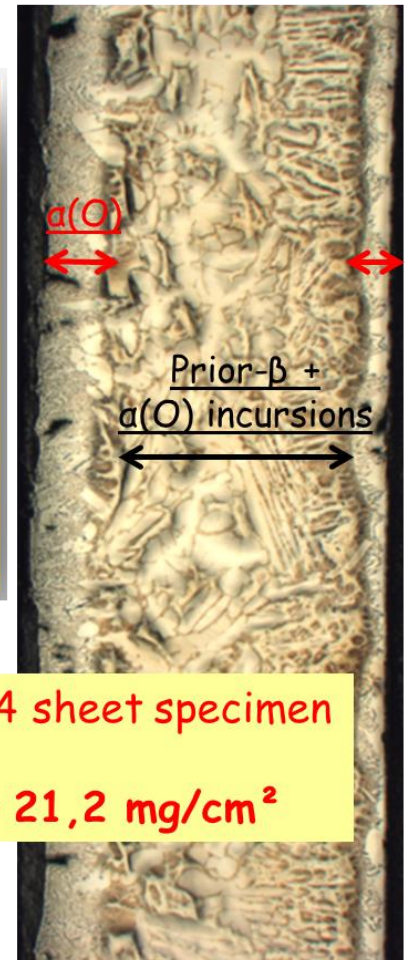
*Remark: of course, additional « grace time-temperature » which can be achieved depends on the initial Cr coating thickness*



1300°C, oxidation time = 5400s



Uncoated Zirc-4 sheet specimen  
=> Weight Gain = 76,4 mg/cm<sup>2</sup>



Cr coated Zirc-4 sheet specimen  
Weight Gain = 21,2 mg/cm<sup>2</sup>