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## Advances in the RetD at CEA on ATF claddings

H. Palancher, J.C. Brachet, C. Lorrette, A. Michau, T. Forgeron, C. Delafoy,  
J. Bischoff, E. Pouillier, L. Rancoeur

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FROM RESEARCH TO INDUSTRY  
**cea den**

**framatome**

 **edf**

# ADVANCES IN THE R&D AT CEA ON ATF CLADDINGS

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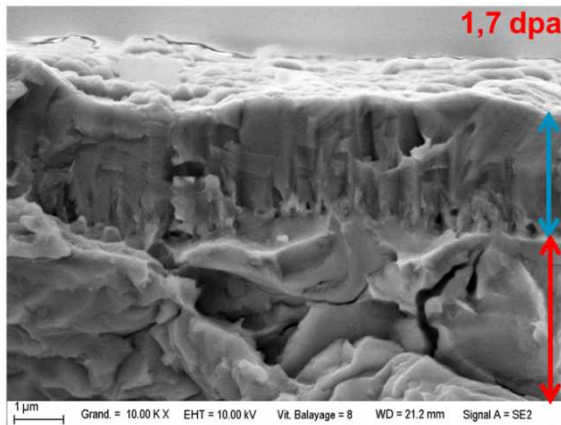
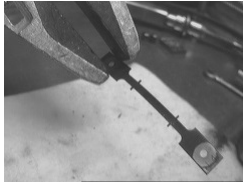
**J. Bischoff, C. Delafoy**

*FRAMATOME*

**E. Pouillier**

*EDF R&D, MMC Department*

# Outline



## 1. Introduction

## 2. SiC/SiC cladding

## 3. Cr coated Zr based claddings

### 1. Why Cr ?

### 2. Out-of-pile behavior:

#### 1. Under AOO

#### 2. Under LOCA

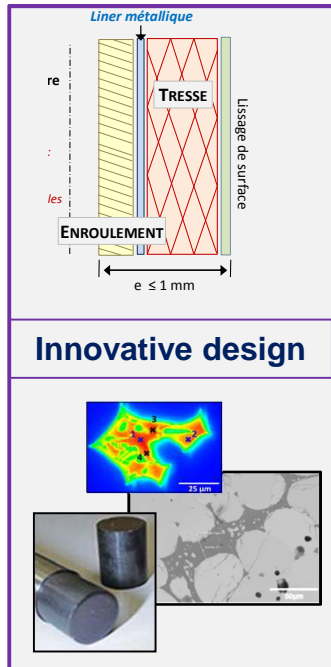
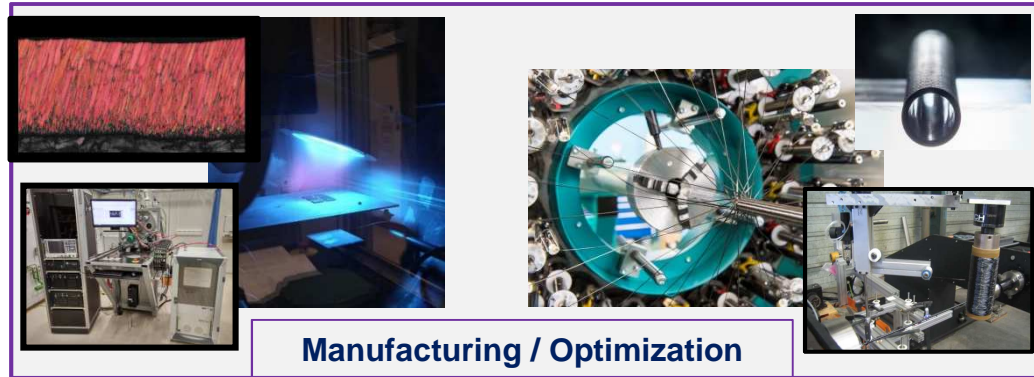
### 3. Behavior under irradiation:

#### 1. Ion irradiation

#### 2. In-pile irradiation

## 4. Conclusions

# BASES OF CEA-FRAMATOME- EDF R&D ACTIVITIES ON EATF

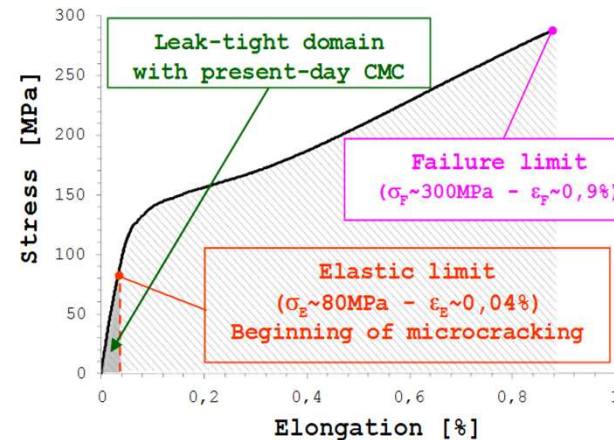
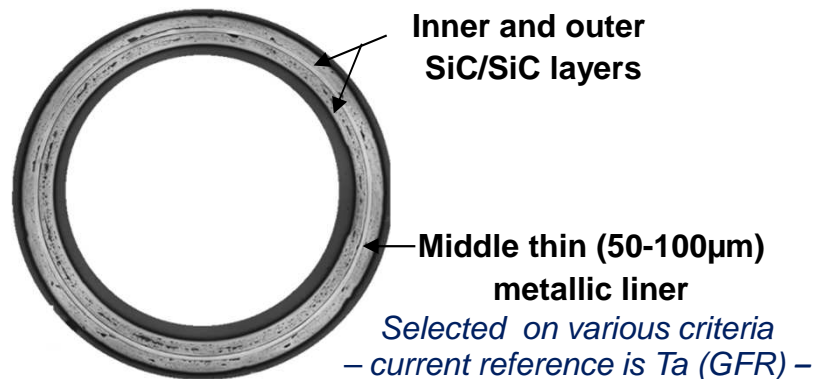


**A decade of R&D activity at CEA has been dedicated to the development of SiC/SiC composites for GFR fuel cladding application: 2005-2015**

C. Lorrette et al.,  
TOPFUEL (2015)

■ **Focus on metal/ceramic hybrid cladding: a solution to leak-tightness**

**CEA « SANDWICH » CLADDING DESIGN**



Patent WO 2013/017621 A1

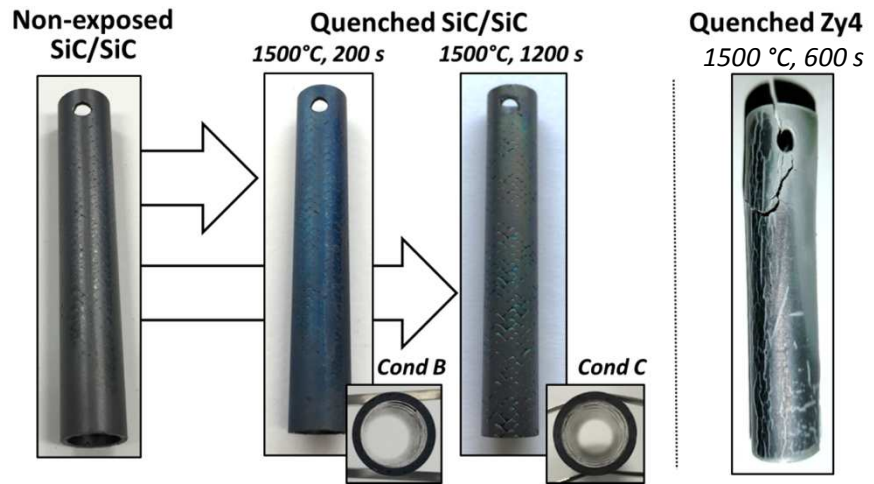
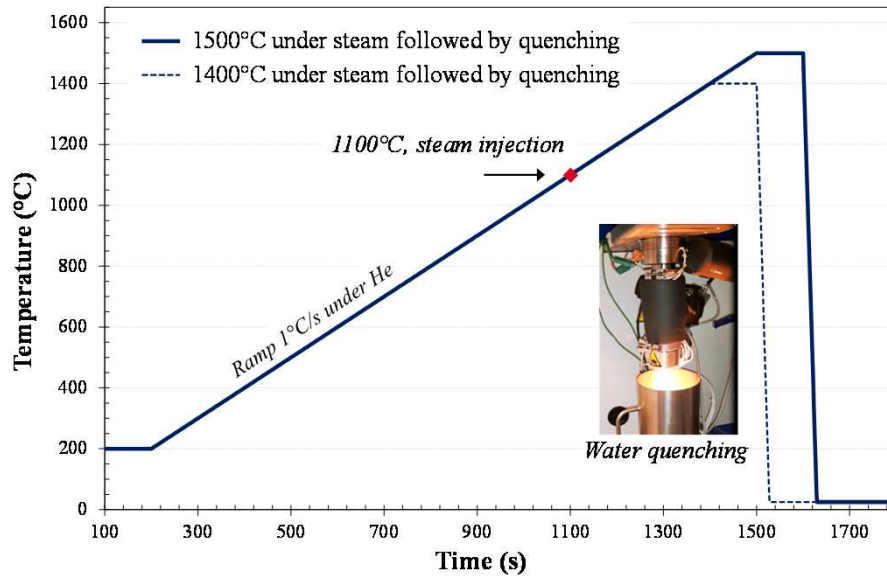
**The benefits in terms of dimensional stability at high temperature make this concept very promising for ATFs**

**Adaptation of this concept to LWR conditions is under investigation with 3 main axes:**

- **Recession in water under normal irradiation conditions,**
- **Fission gas tightness,**
- **Thermal conductivity.**

## Experimental approach

C. Lorrette et al.,  
TOPFUEL (2017)



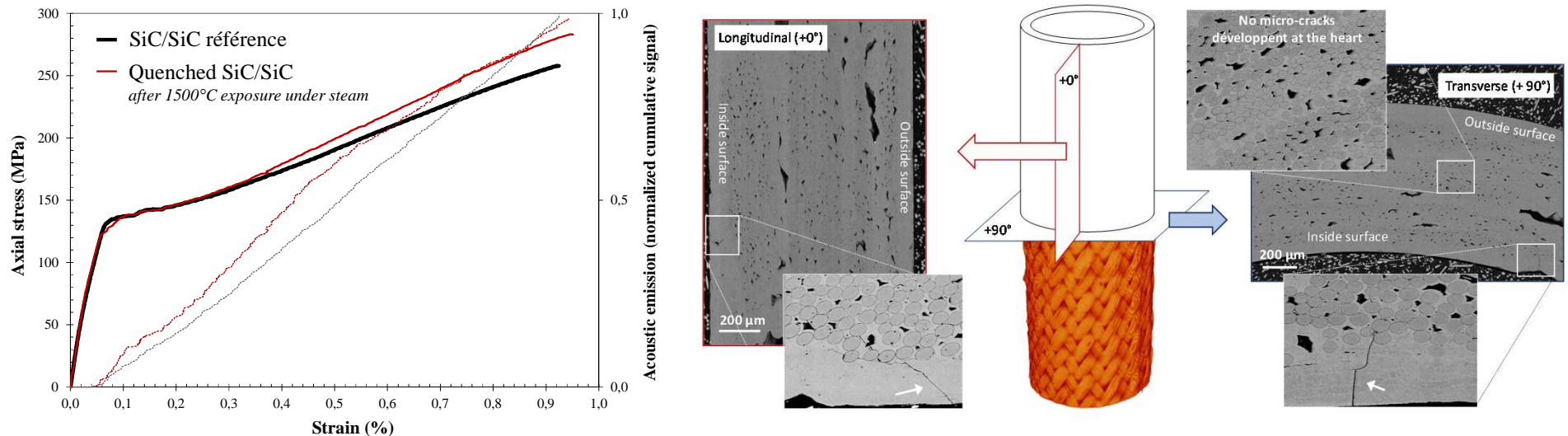
## Macroscopic results

- Integrity and geometry fully preserved for all specimen (see Zy4 for a comparison)
- Negligible material reaction:
  - ⇒ No weight change can be accurately measured
  - ⇒ Consistent results with parabolic oxidation kinetics



## Microstructural and mechanical characterization of quenched clad

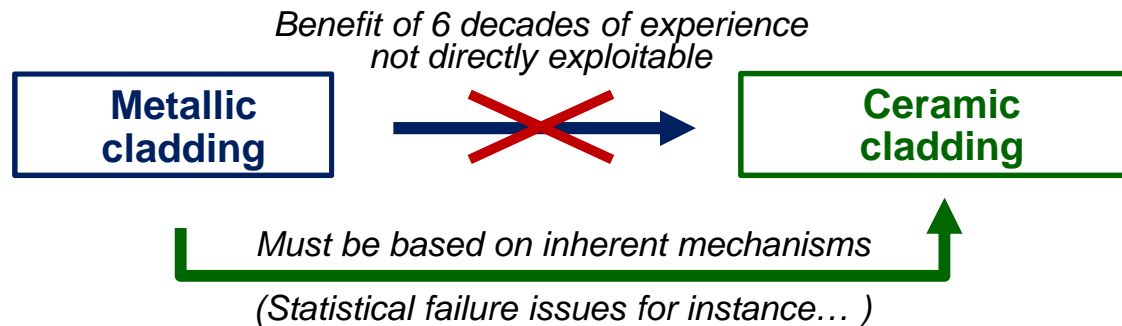
C. Lorrette et al.,  
TOPFUEL (2017)



- **Mechanical properties remain at least unchanged** ( $EP$ ,  $\sigma_y$ ,  $\epsilon_m$ ) and may be even improved (higher tensile strength) which could result from an increase of the matrix strength.
- **SEM evidences micro-crack density increase** (but no dependence on exposure time)  
 ⇒ No influence of pre-existing pores on micro-crack propagation

- The implementation of thin-walled and elongated tubular SiC/SiC structures appear challenging and...

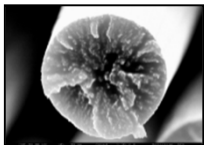
⇒ *it is an absolute necessity to define the adapted rules for design*



[Katoh et al. 2014]

- Normalization procedure in progress at CEA

### SiC fibers testing at HT



800 to 1600°C  
various atm.

### SiC/SiC tubes testing at RT



25°C, air

C. Lorrette (2018) ISO 20323

### SiC/SiC tubes testing at HT



800 to 1600°C  
various atm.

**Innovative cLading maTeRials fOr adVAnced accideNT-tolerant eneRgy systEMs**



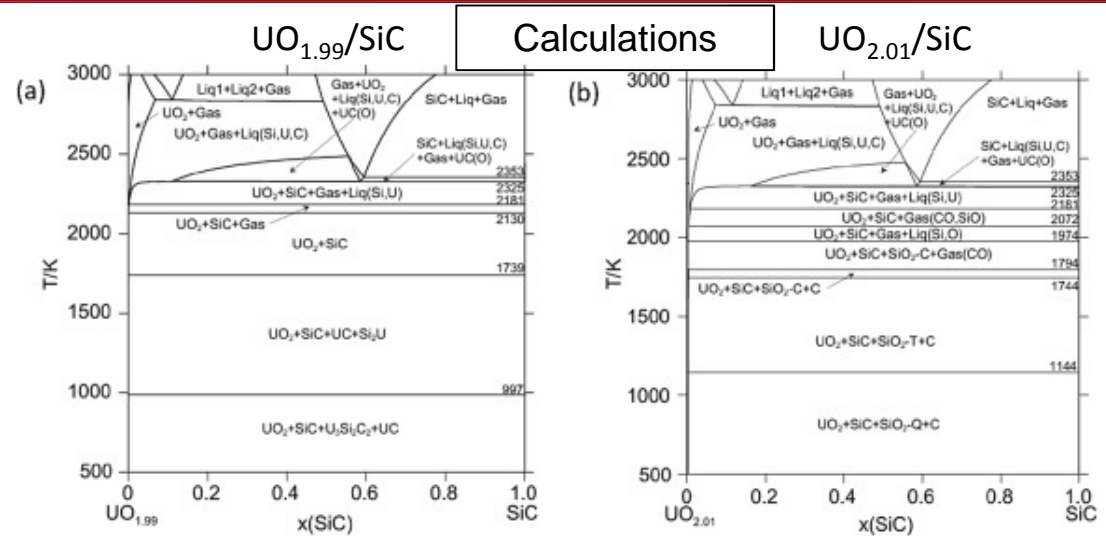
## Methods

- Knudsen cell mass spectrometry to characterize reaction gases (i.e. open system ~clad failure)
- Diffusion couples (i.e. closed system ~accidental increase of the temperature)

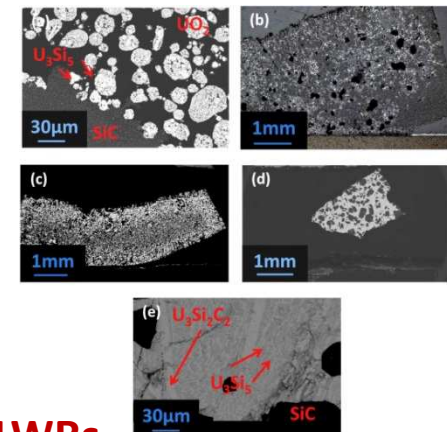
## Conclusions

- The chemical reaction between SiC and UO<sub>2+x</sub> is limited up to 1514 K.
- CO gas along with the generation of USi<sub>x</sub> are detected for temperatures higher than 1514 K in open system.
- A liquid phase forms between 1850 and 1950 K in the UO<sub>2+x</sub>/SiC system.

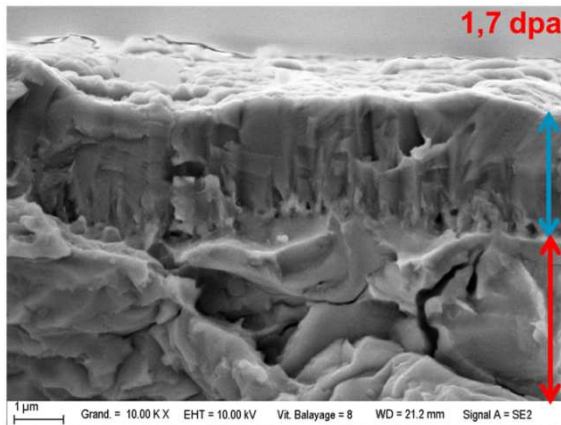
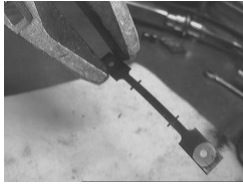
**Results are encouraging for the use of SiC/SiC cladding as EATF in LWRs**



J. Braun et al.,  
J. Nucl. Mater. 487 (2017) 380-395



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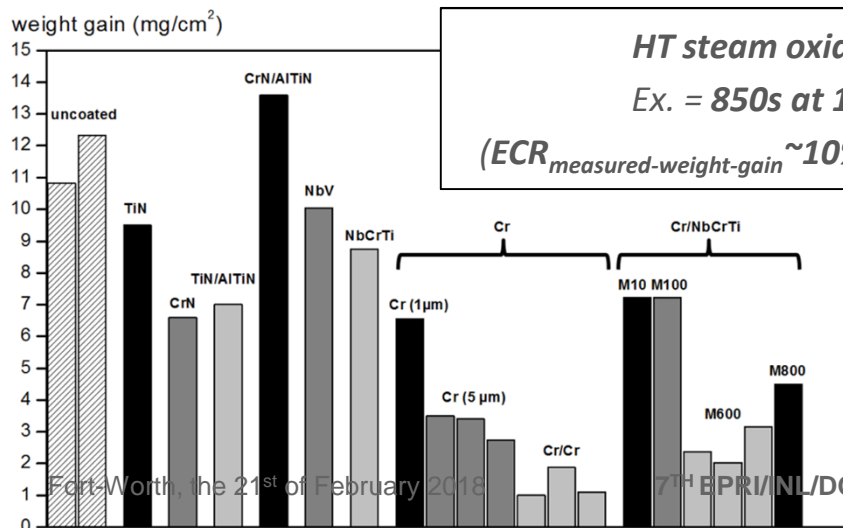
#### 1. Ion irradiation

#### 2. In-pile irradiation

## 4. Conclusions

First screening tests started at CEA about 10 years ago:

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

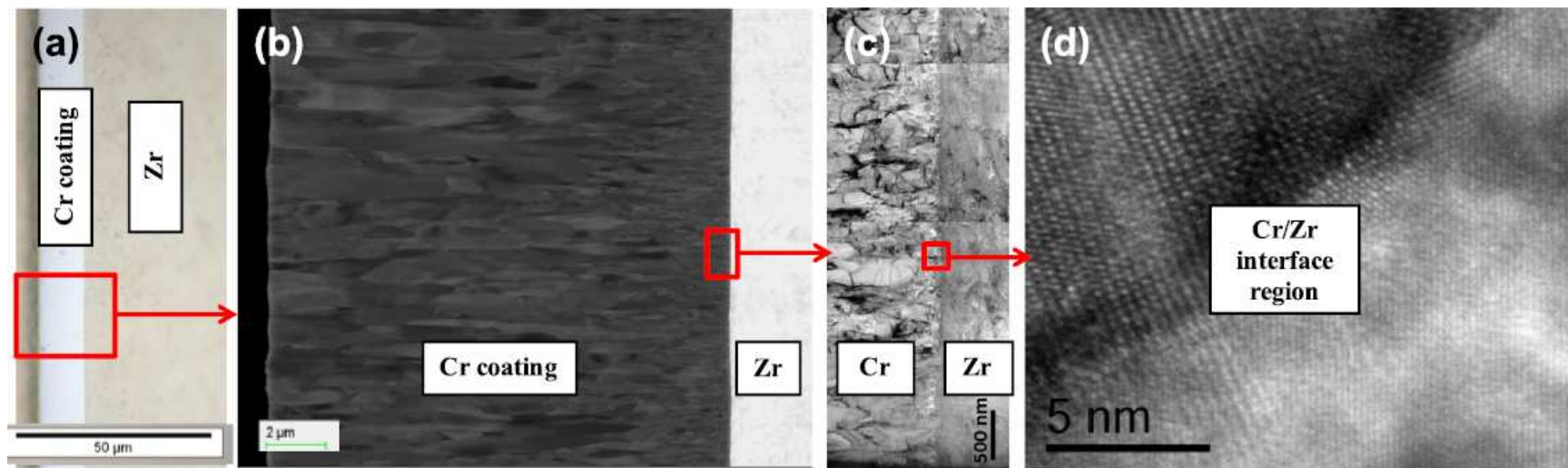


*HT steam oxidation in DBA-LOCA conditions –  
Ex. = 850s at 1100°C + direct water quenching  
( $ECR_{measured-weight-gain} \sim 10\%$  for uncoated Zry-4 - one sided oxidation)*

**Metallic Cr coatings show the best steam oxidation resistance at HT**  
⇒ **selected for further optimization**

# AS-RECEIVED 10-15 $\mu\text{m}$ Cr COATED Zr-BASED CLAD

- Special PVD deposition process (*CEA patent*) on **50 cm long Zr-based clad segments**
  - => **Dense and very homogenous coating** obtained (no cracks)
  - => **Very good bonding** on the M5™ substrate (no interfacial defects)
- => **No modification of the as-received metallurgical conditions/properties** of the M5™
- Multi-scale characterization: Optical microscopy, XRD, SEM-EBSD, EPMA, TEM (High resolution mode) on thin foils (FIB)...

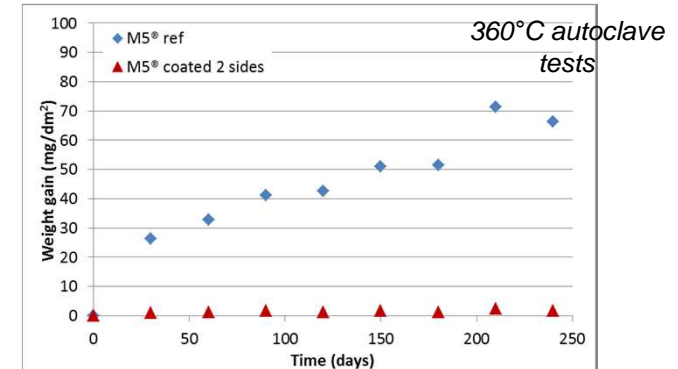


**A mature coating process**

### Improved corrosion performances

1. Cr-coated samples exhibit significantly reduced weight gain in autoclave (1-3 mg/dm<sup>2</sup>) with very low variation with time
2. No delamination of Cr-coating observed
3. No dissolution of Cr in water

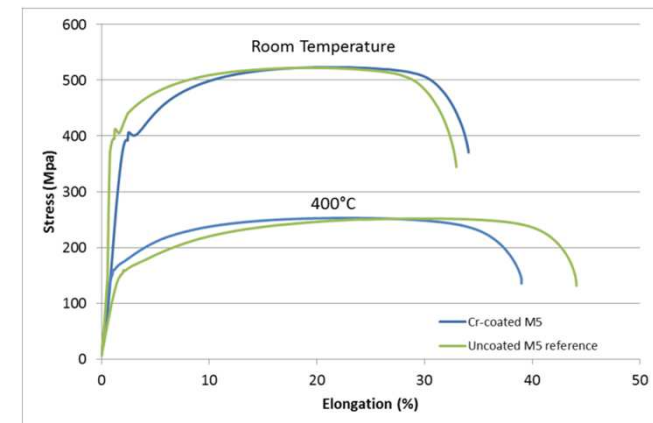
J. Bischoff et al.,  
Nuclear Engineering and Technology (2018)



framatomé

### Mechanical properties

1. Mechanical properties of coated samples fall within the range of uncoated samples
2. Similar mechanical behavior: ease of licensing



### Isothermal creep (“EDGAR”) test (internal pressure, steam, 600-1000°C):

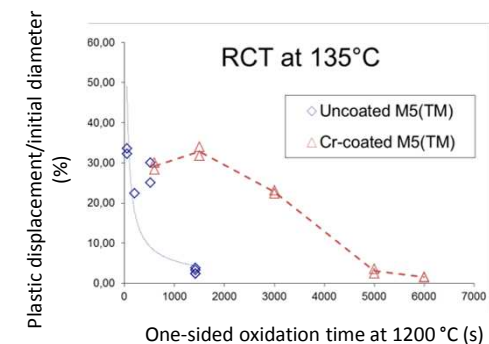
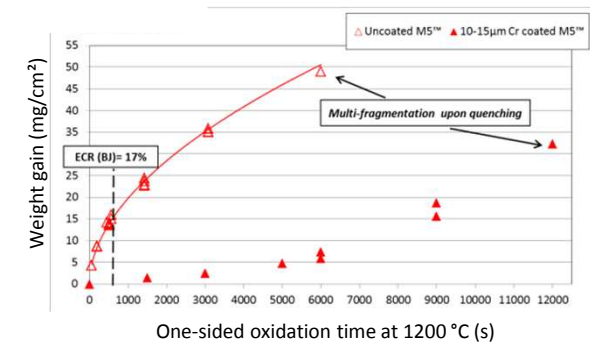
1. Cr-coating HT strengthening effect, especially within the  $\alpha_{Zr}$  temperature range
2. For any internal pressure investigated, creep time to rupture of Cr-coated M5™ increased by a factor of ~2,5 vs. the uncoated cladding
3. Significant decrease of the balloon size and/or rupture opening of Cr-coated M5™

J.C. Brachet *et al.*,  
TOPFUEL (2017)  
TOPFUEL (2016)



### One-sided steam oxidation at 1200°C and quenching behavior

1. For the Cr-coated M5™ significant delay of the oxidation time (inducing fragmentation upon final (direct) water quenching) due to much slower HT steam oxidation kinetics
2. For the Cr-coated M5™, significant increase of critical oxidation time to achieve macroscopic post quench brittle behavior (RCT at 135°C)



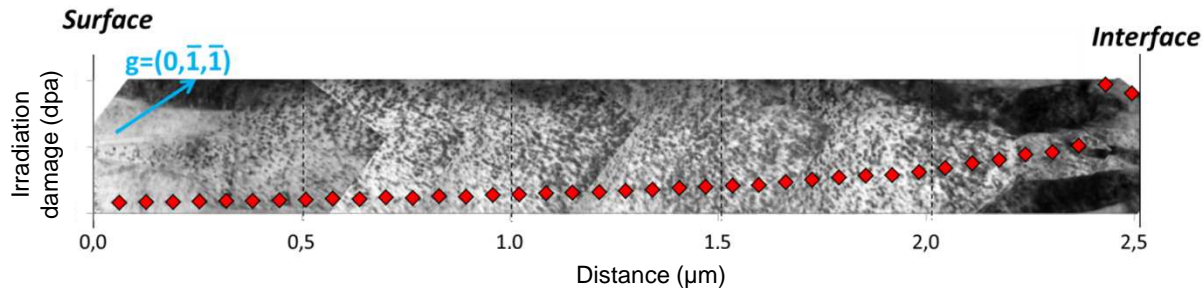


# Cr COATING MICROSTRUCTURAL EVOLUTION AND HARDENING UNDER IRRADIATION (Zy4 SUBSTRATE)



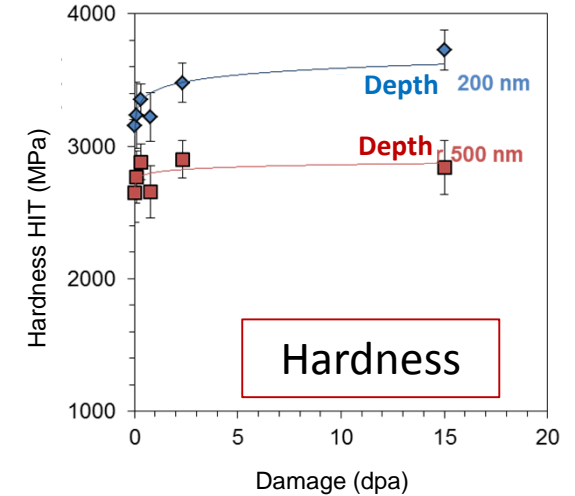
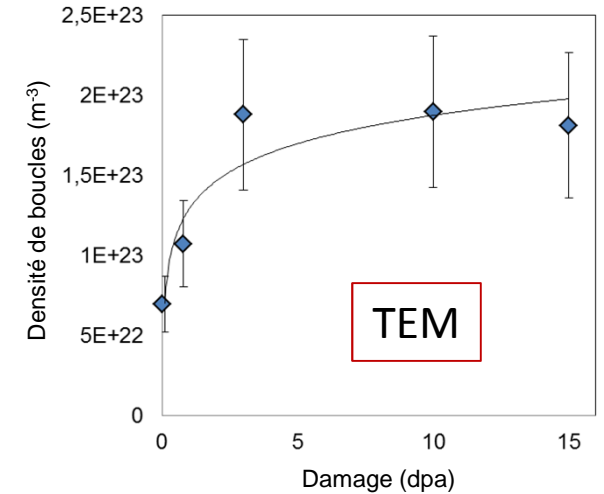
- ☐ Ex-situ ion irradiation
- ☐ Ions: 6 MeV Au<sup>3+</sup>
- ☐ Temperature: 400°C
- ☐ 5 doses in Cr: 0.1, 0.3, 0.8, 2.3, 15 dpa

A. Wu *et al.*,  
Ph.D thesis



⇒ Dislocation loop density saturation for damage ranging from 1 to 3 dpa  
 ⇒ Dislocation loop size below 10 nm

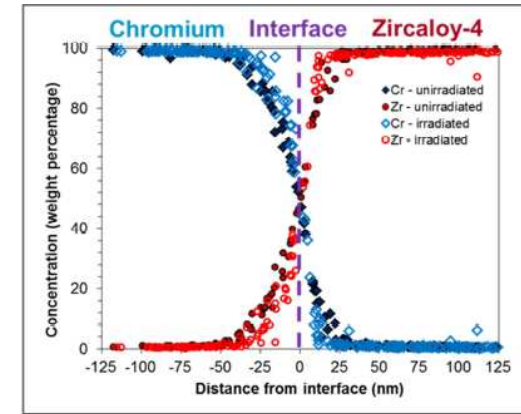
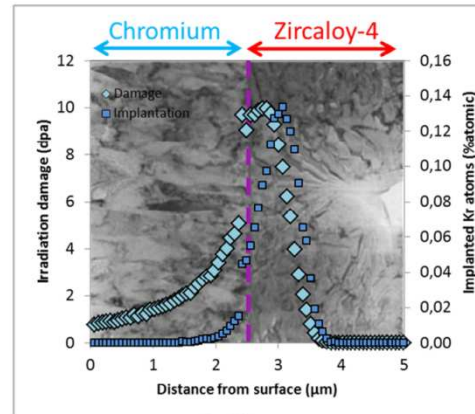
⇒ Hardness saturation for damages higher than 2 dpa  
 ⇒ Hardness increase by 7 to 18% at saturation (as compared to the as-recieved conditions)





- Ex-situ ion irradiation
- Ions: 20 MeV Kr<sup>8+</sup>
- Temperature: 400°C
- Up to 15 dpa

J. Ribis *et al.*,  
J. Nucl. Mater. (2018) accepted



**As –received samples**  
(1<sup>st</sup> generation)

- Limited Fe segregation at the interface
- Nanometer sized Zr(Fe,Cr)C<sub>2</sub> Lave phases: both C14 and C15

**After ion irradiation**

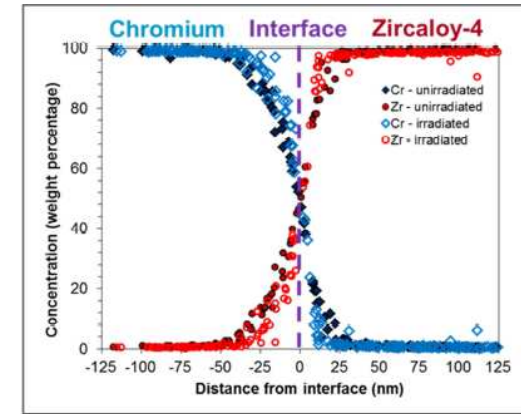
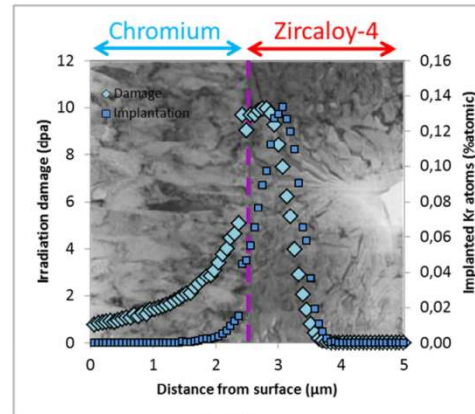
- Slight increase of Fe segregation at the interface
- Stabilization of C14 phase/ destabilization of C15 in agreement with thermodynamic calculations \*

(\* ) “Thermocalc®” + CEA “Zircobase”, i.e., CEA thermodynamic database for multicomponent Zr based alloy



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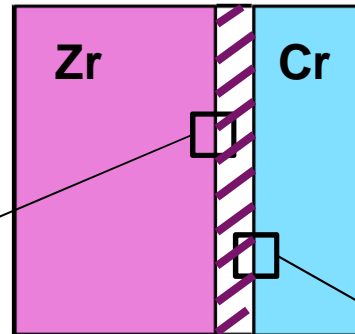
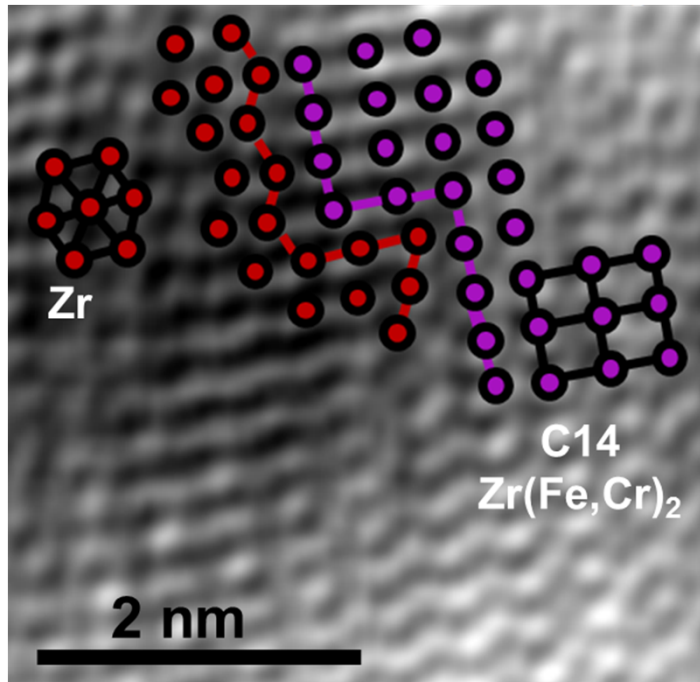
**After ion irradiation**

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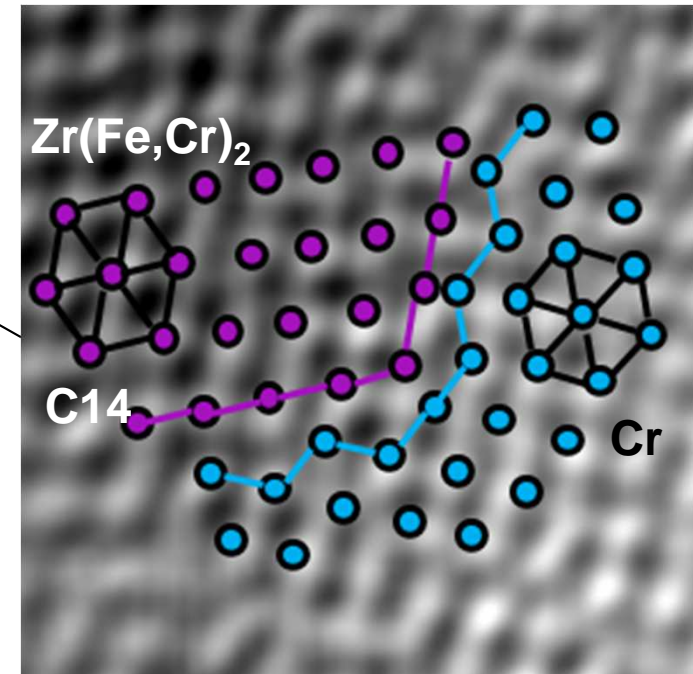
- No evolution of the C15 phase*
- No obvious evolution of the Zr/Cr profiles after irradiation (the interface remains about 100 nm thick) – as observed on samples irradiated in OSIRIS (~2 dpa, EPMA)*
- The interface remains crystalline (TEM)*
- Atomic planes are found in coherence (HRTEM) → excellent bounding (adherence)*

## HRTEM analysis of ion irradiated interfaces

### Interface Zr/C14



### Interface C14/Cr

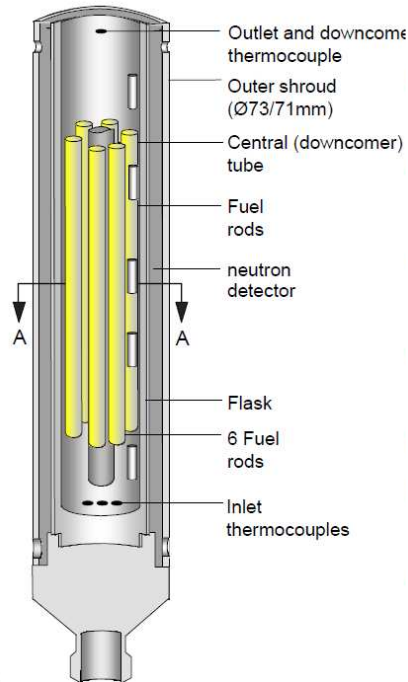


A. Wu *et al.*,  
Ph.D thesis



## START of the irradiation test in July 2017

CEA-AREVA-EDF provided Cr coated cladding specimens for 4 rodlets:  
3 M5 and 1 Zry-4 with ~7 or ~15 μm thick Cr coating (special PVD process)



IFA-796 for LWR conditions

Seg.	CEA Rod 1	KAERI Rod 2	WEC/OR NL Rod 3	ORNL Rod 4	EPRI Rod 5	REF Rod 6
Top	~7 μm Cr	~50 μm CrAl	Cr coat	FeCrAl	Mo/Nb/Zr-Nb	Zry-4
Top-mid	~15 μm Cr	ODS + ~50 μm CrAl	FeCrAl		Mo/Zr-Nb	Zry-4
Bot-mid	~15 μm Cr	~100 μm Cr/FeCrAl	Cr coat		Mo/Nb/Zr-Nb	Zry-4
Bottom	~7 μm Cr	ODS + ~100 μm Cr/FeCrAl	FeCrAl		Mo/Zr-Nb	Zry-4

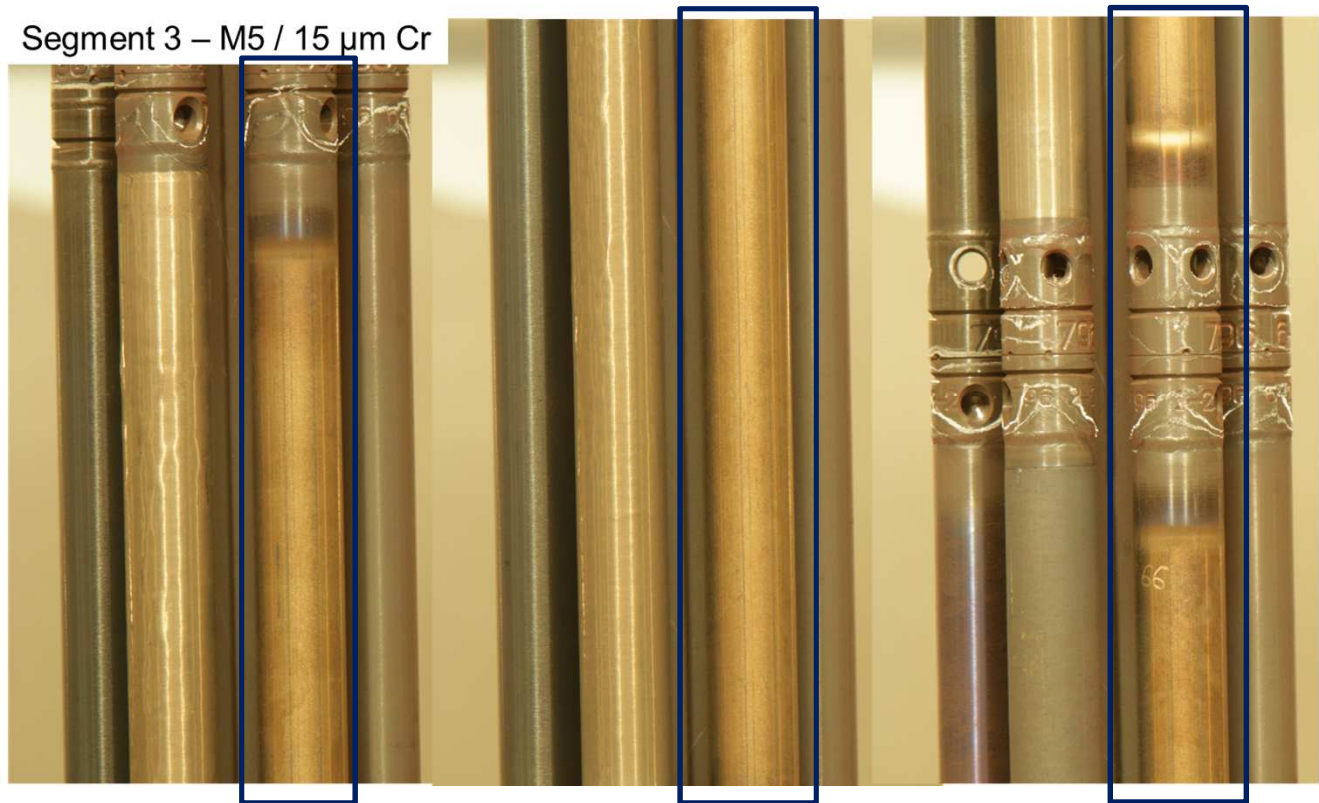
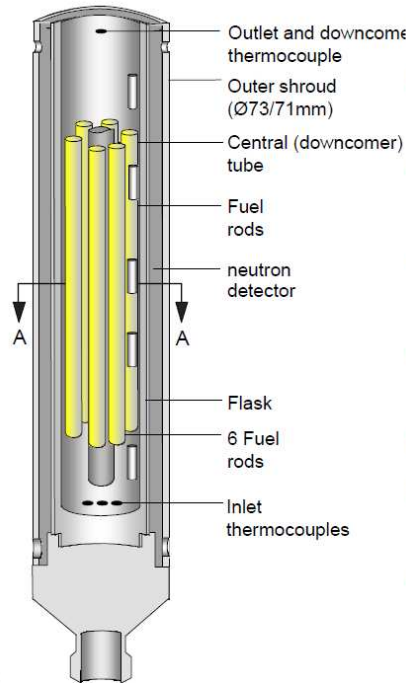
ALCYONE calculations used for irradiation design







## Interim visual inspection after about 50 irradiation days



Good behavior of the coating at this point:  
No evidence for any macroscopic delamination

IFA-796 for LWR conditions





## Analytical irradiation test performed in 2015 up to 2 dpa

### Many irradiated samples with:

1. Different coating thicknesses (from 2 to 15  $\mu\text{m}$ ),
2. Different coating processes,
3. Different Zr-based substrates: M5, Zy4, Q12,
4. Different sample geometries (flat and tubular).

Uncoated references

### Irradiation conditions:

1. Fast neutron fluence ( $E > 1 \text{ MeV}$ ) at MFP:  $1.2 \times 10^{21} \text{ n.cm}^{-2}$
2. Temperatures:  $308 < T < 350^\circ\text{C}$
3. NaK environment

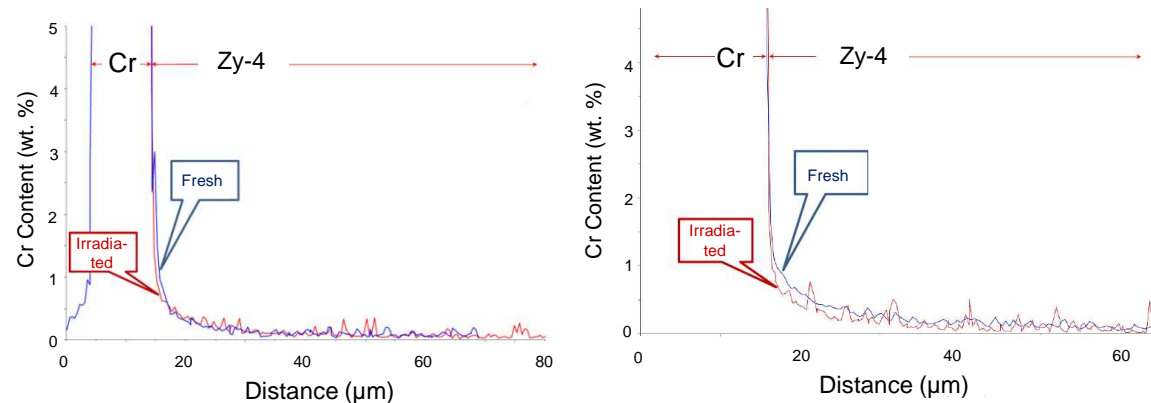
**Irradiation completed with the OSIRIS definitive shutdown  
(mid-december 2015)**



**PIEs are in progress at the LECI hot-laboratory (2016-)**  
**Examinations of related fresh archives also on-going**

First analyses (preliminary results) show that:

1. The Cr thickness is **stable under these irradiation conditions: no Cr diffusion** towards the Zr substrate (EPMA)



2. **Excellent adherence** of the Cr coating i.e. no local delamination: defects are very difficult to find (SEM)

Further studies should focus on high resolution measurements FIB/TEM and APT (currently under commissioning at LECI)



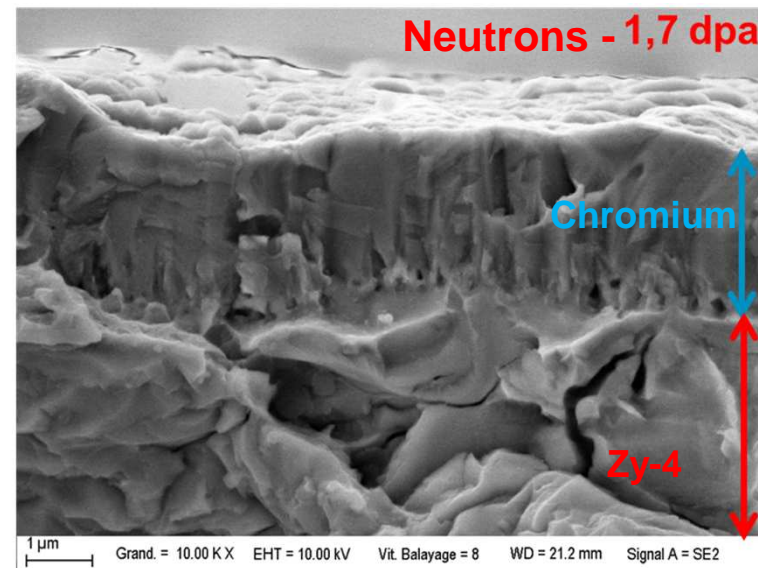
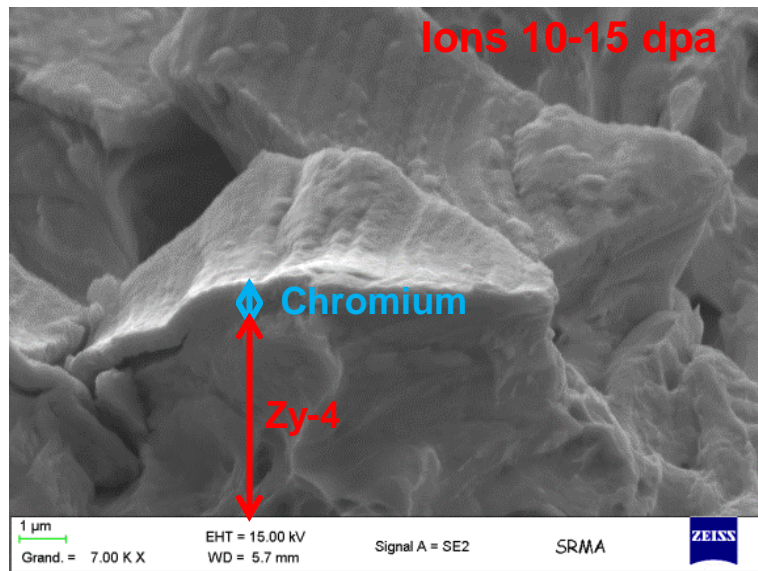
## Ions

- ❑ Hardening after irradiation at 400 °C – 15 dpa
  - 10 % - 20%
- ❑ Excellent adherence of the coating after ion irradiation

## Neutrons (in-pile)

- ❑ Hardening after irradiation at 340 °C - 2 dpa
  - 25%
- ❑ Excellent adherence of the coating after in-pile irradiation

*Fractograph after tensile tests at 350°C on similar Cr coatings*



The use of NaK environment could impact Zy mechanical properties

## CEA-FRAMATOME-EDF collaborative program on eATF: two cladding developments

### - SiC/SiC cladding:

⇒ Longer term (>10 years) R&D with many challenges to overcome

⇒ Promising materials

### - Zr based Cr coated claddings

⇒ 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

⇒ Last generation of Cr-coated M5 nuclear fuel clad behavior shows enhanced performances under out-of-pile tests in both:

⇒ *Normal conditions*

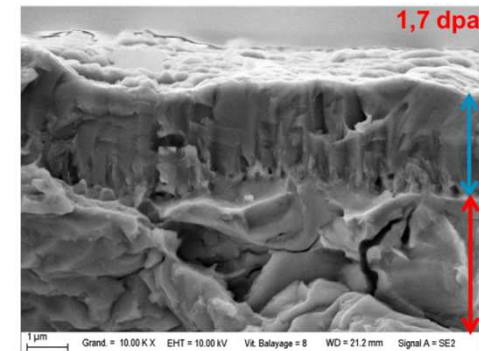
⇒ *LOCA conditions*

⇒ Behavior under irradiation is actively investigated:

⇒ *OSIRIS test: completed*

⇒ *HALDEN test: in progress – preliminary results already available*

⇒ *In-pile tests are supported by well spotted ion irradiation experiments (fruitful approach)*



**M. Dumerval, V. Lezaud-Chaillieux, M. Le Saux, J. Ribis, A. Wu,  
E. Rouesne, S. Urvoy, P. Bossis, T. Guilbert, M. Le Flem,  
Y. Robert, J. Braun, C. Sauder**  
*CEA, DEN, DMN (Department of Nuclear Materials) Saclay*



**F. Lomello, H. Maskrot, C. Guéneau, F. Balbaud**  
*CEA, DEN, DPC (Department of Physico-Chemistry) Saclay*

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