



HAL
open science

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

► **To cite this version:**

H. Palancher, J.C. Brachet, C. Lorrette, A. Michau, T. Forgeron, et al.. Advances in the RetD at CEA on ATF claddings. 7th EPRI/INL/DOE Joint Workshop on Accident Tolerant Fuel, Feb 2018, Fort-Worth, United States. cea-02339254

HAL Id: cea-02339254

<https://cea.hal.science/cea-02339254>

Submitted on 14 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

FROM RESEARCH TO INDUSTRY
cea den

framatome



ADVANCES IN THE R&D AT CEA ON ATF CLADDINGS

J.C. Brachet, Ch. Lorrette, L. Rancoeur

CEA, DEN, DMN (Department of Nuclear Materials) Saclay

A. Michau

CEA, DEN, DPC (Department of Physico-Chemistry) Saclay

F. Schuster

CEA, DFP, DPG, Saclay

T. Forgeron

CEA, DEN, DISN, Saclay

H. Palancher

CEA, DEN, DEC (Department of Fuel Studies) Cadarache

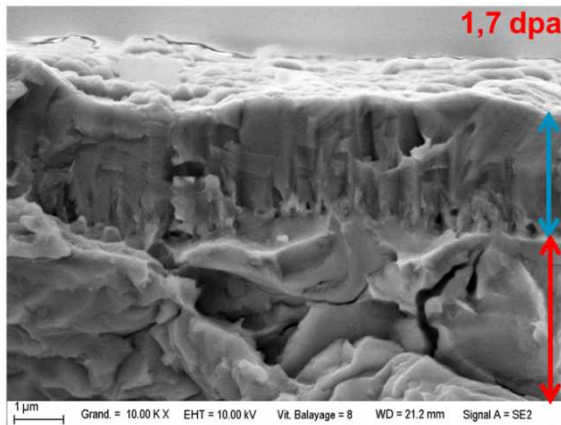
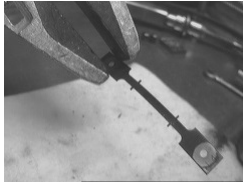
J. Bischoff, C. Delafoy

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

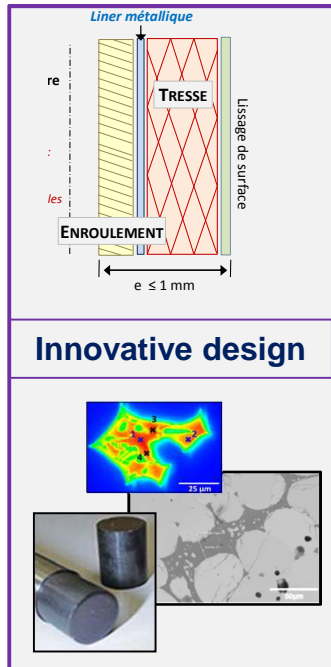
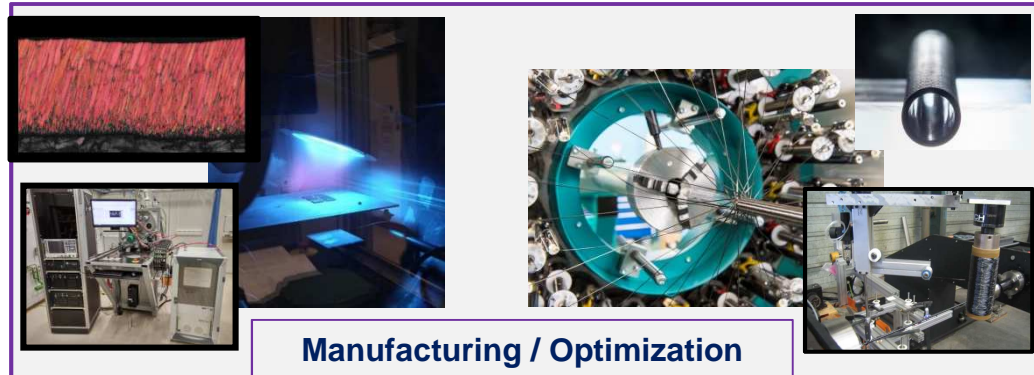
3. Behavior under irradiation:

1. Ion irradiation

2. In-pile irradiation

4. Conclusions

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

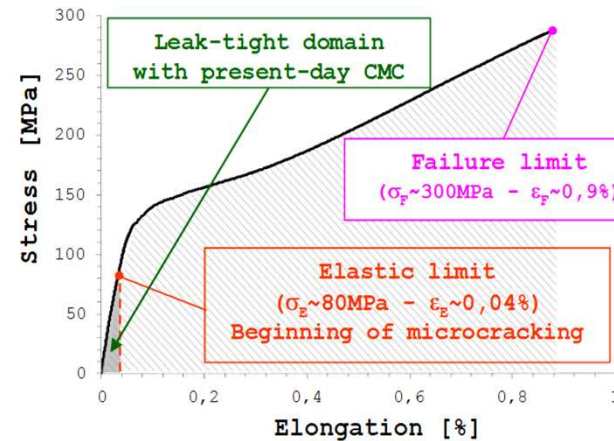
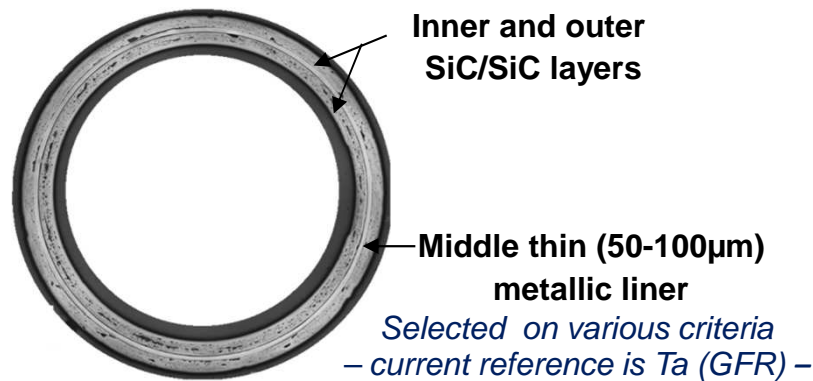


A decade of R&D activity at CEA has been dedicated to the development of SiC/SiC composites for GFR fuel cladding application: 2005-2015

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

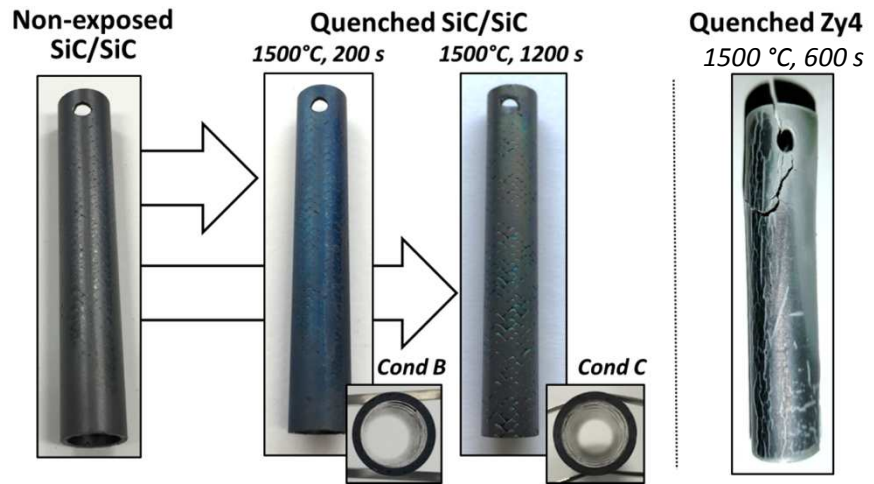
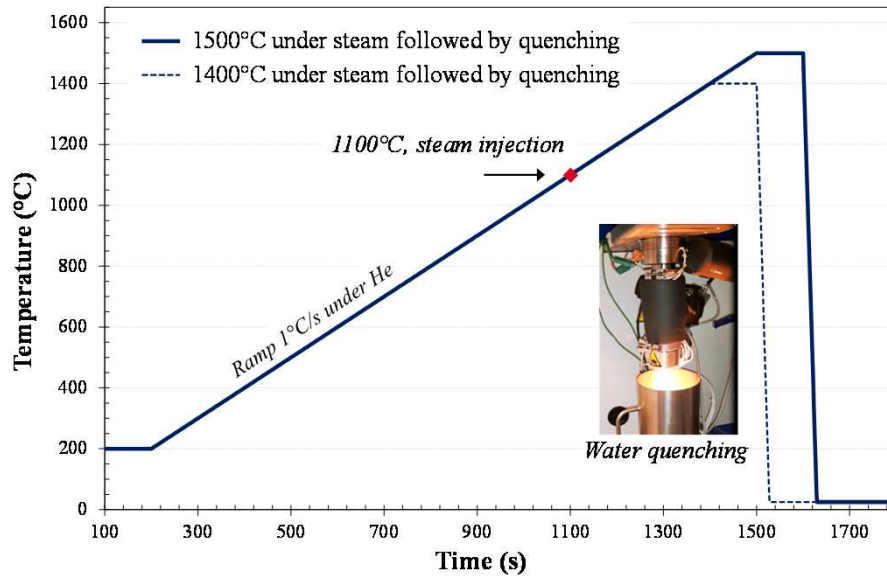
The benefits in terms of dimensional stability at high temperature make this concept very promising for ATFs

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)

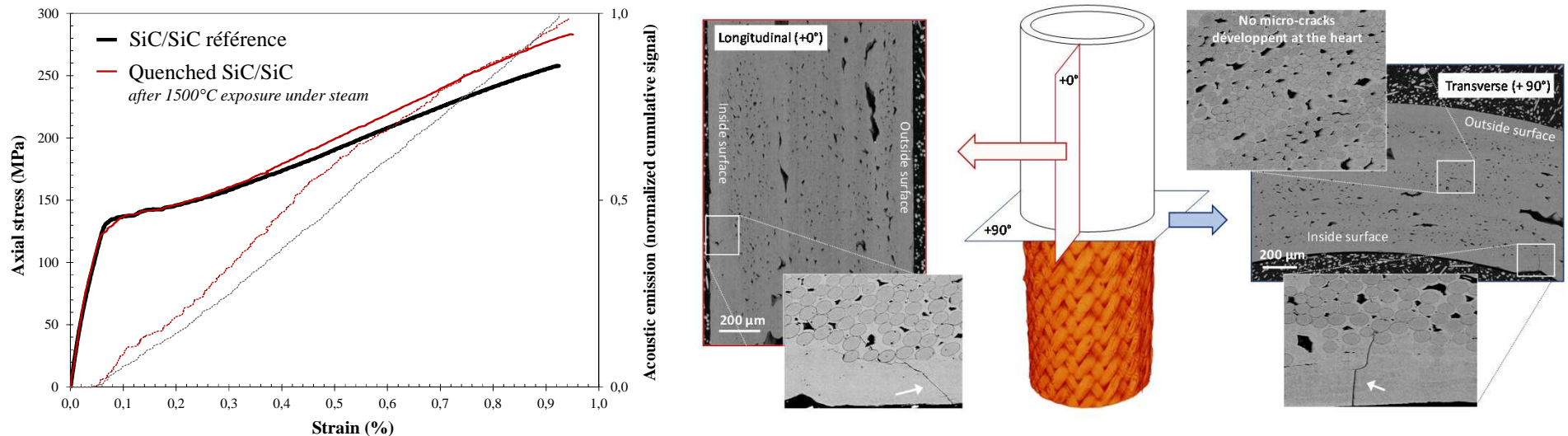


Macroscopic results

- 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

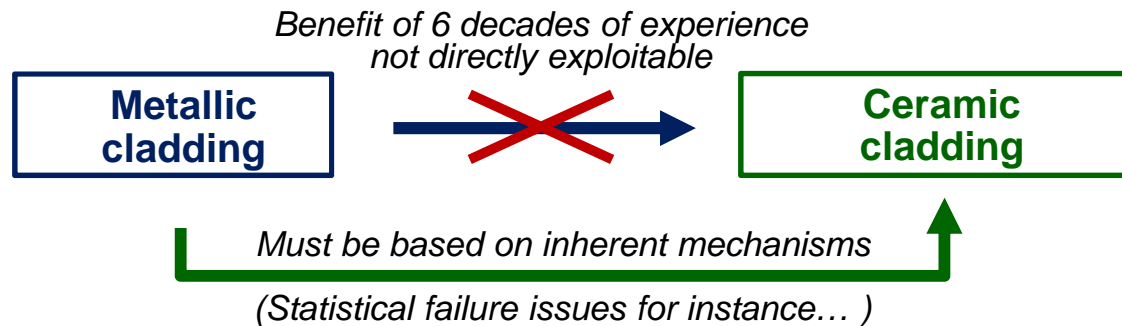
C. Lorrette et al.,
TOPFUEL (2017)



- **Mechanical properties remain at least unchanged** (EP , σ_y , ϵ_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)
 \Rightarrow No influence of pre-existing pores on micro-crack propagation

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

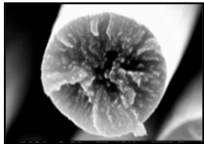
⇒ *it is an absolute necessity to define the adapted rules for design*



[Kato 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

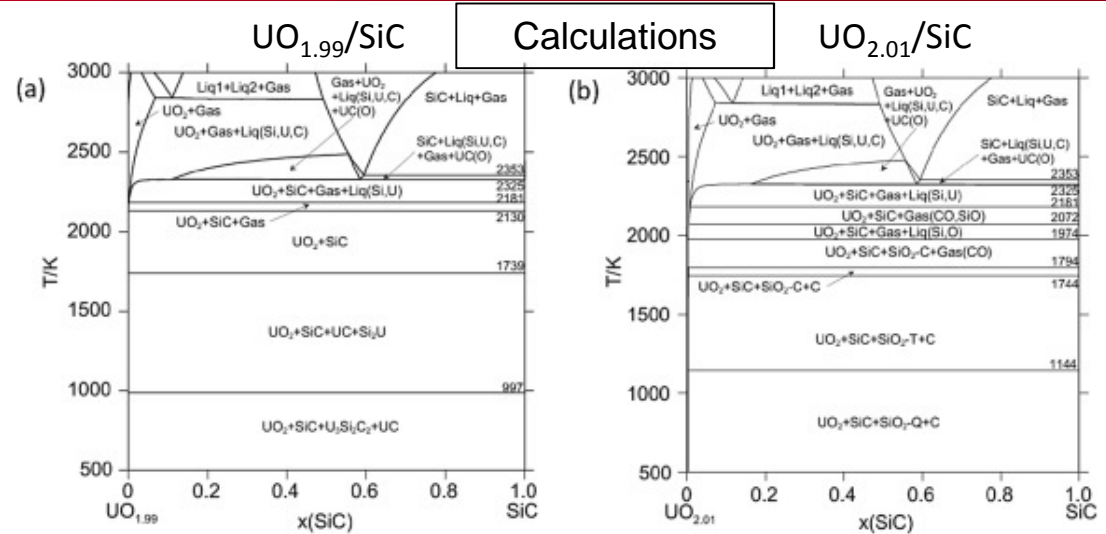
Methods

- 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)

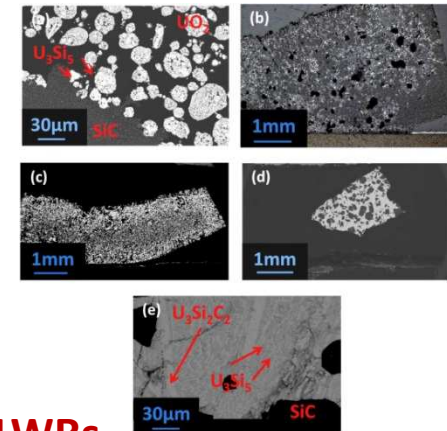
Conclusions

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

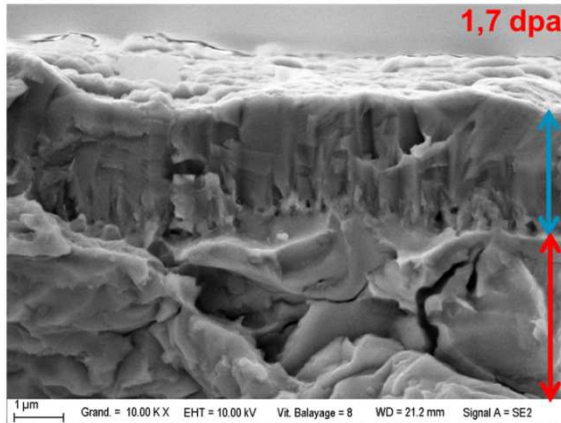
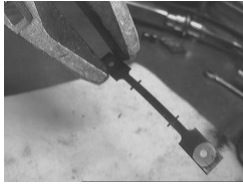
Results are encouraging for the use of SiC/SiC cladding as EATF in LWRs



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



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:

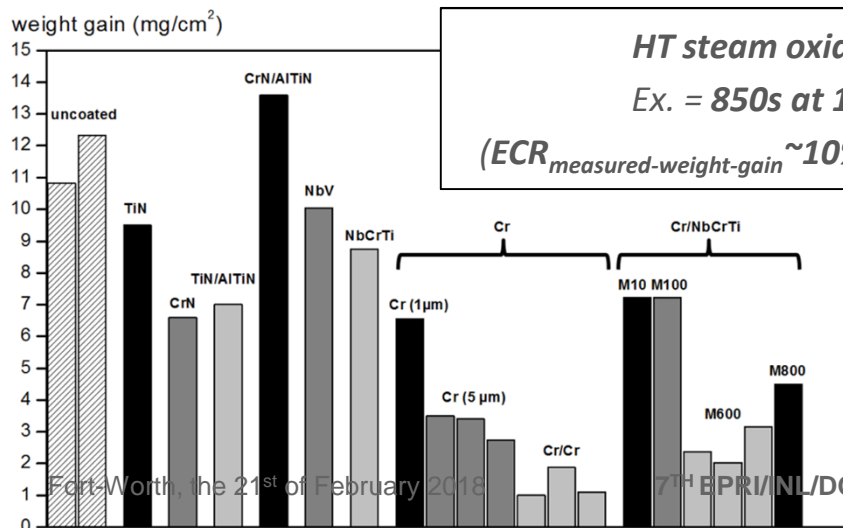
1. Ion irradiation

2. In-pile irradiation

4. Conclusions

First screening tests started at CEA about 10 years ago:

Coating	Architecture / period (λ^*)	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 _{82%} V _{18%}	Singlelayered	5
Nb _{67%} Cr _{10%} Ti _{23%}	Singlelayered	4
Cr	Singlelayered	1 and 5
	Multipass, $\lambda = 500 \text{ nm}$	7
Cr and Nb _{67%} Cr _{10%} Ti _{23%}	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

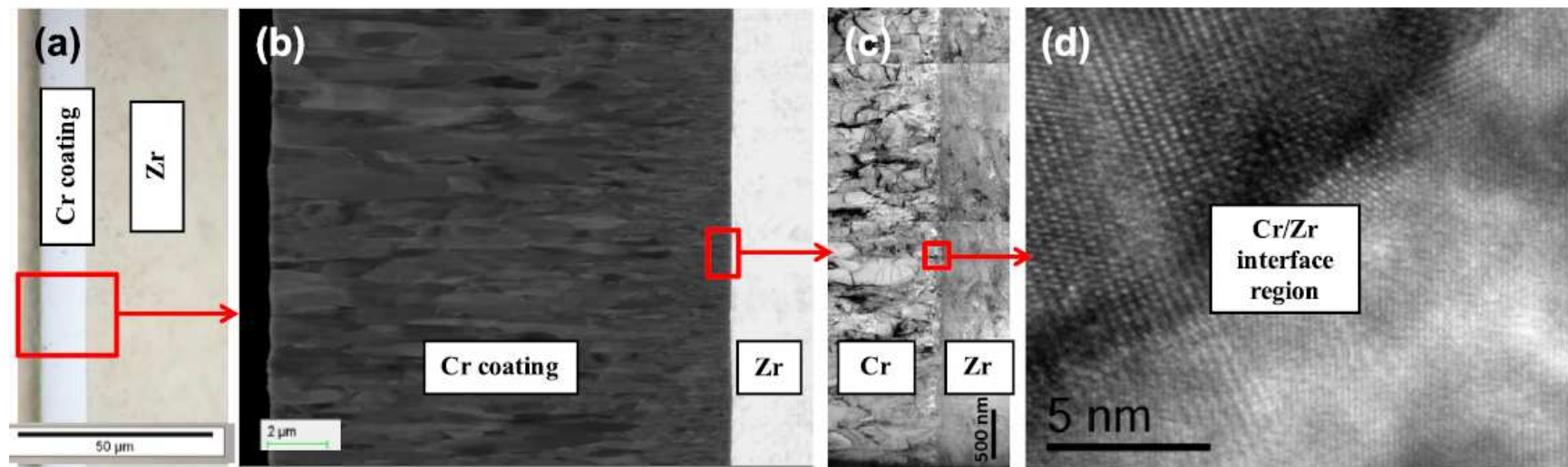


*HT steam oxidation in DBA-LOCA conditions –
Ex. = 850s at 1100°C + direct water quenching
($ECR_{measured-weight-gain} \sim 10\%$ for uncoated Zry-4 - one sided oxidation)*

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

AS-RECEIVED 10-15 μm 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)...

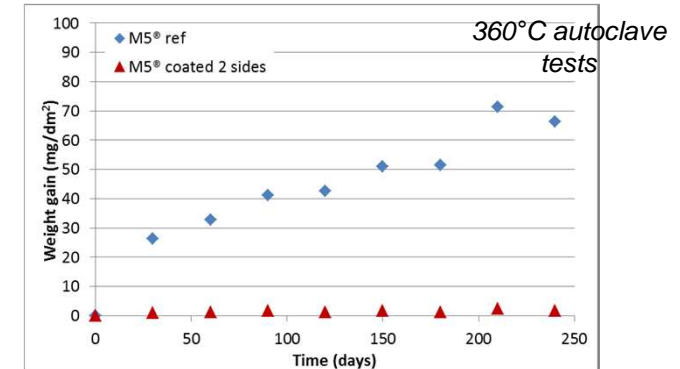


A mature coating process

Improved corrosion performances

1. Cr-coated samples exhibit significantly reduced weight gain in autoclave (1-3 mg/dm²) with very low variation with time
2. No delamination of Cr-coating observed
3. No dissolution of Cr in water

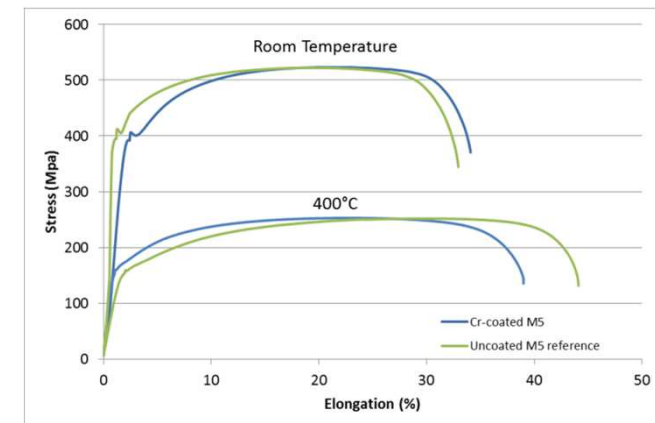
J. Bischoff et al.,
Nuclear Engineering and Technology (2018)



framatome

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):

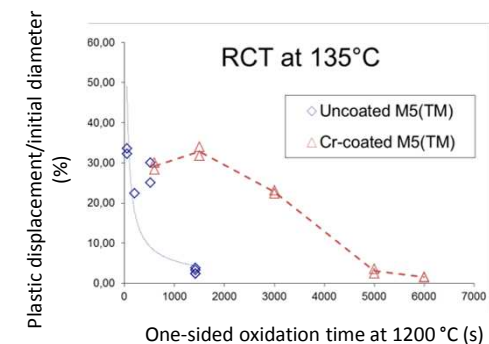
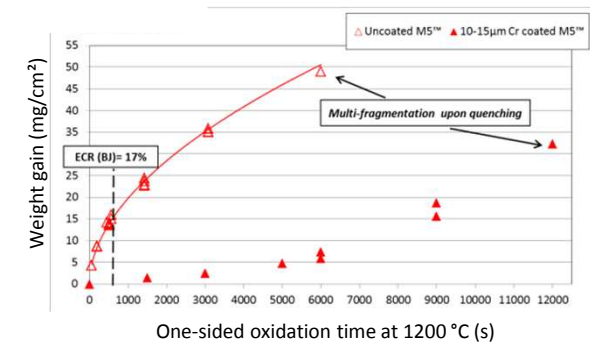
1. Cr-coating HT strengthening effect, especially within the α_{Zr} temperature range
2. For any internal pressure investigated, creep time to rupture of Cr-coated M5™ increased by a factor of ~2,5 vs. the uncoated cladding
3. Significant decrease of the balloon size and/or rupture opening of Cr-coated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

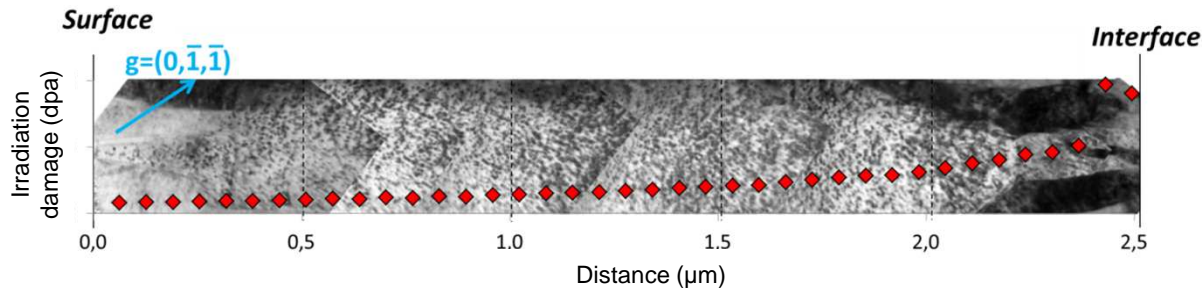


Cr COATING MICROSTRUCTURAL EVOLUTION AND HARDENING UNDER IRRADIATION (Zy4 SUBSTRATE)



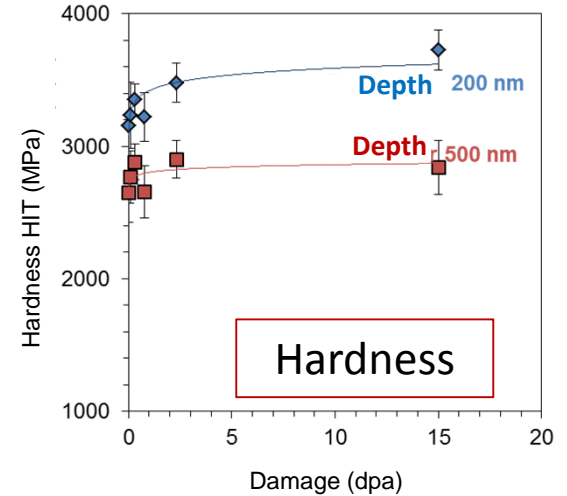
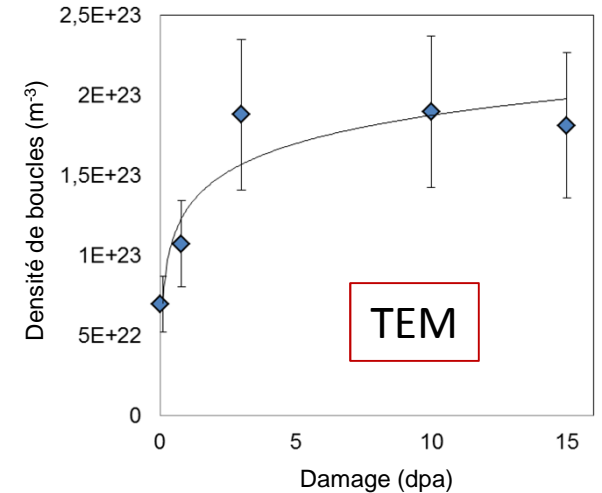
- ☐ Ex-situ ion irradiation
- ☐ Ions: 6 MeV Au³⁺
- ☐ Temperature: 400°C
- ☐ 5 doses in Cr: 0.1, 0.3, 0.8, 2.3, 15 dpa

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

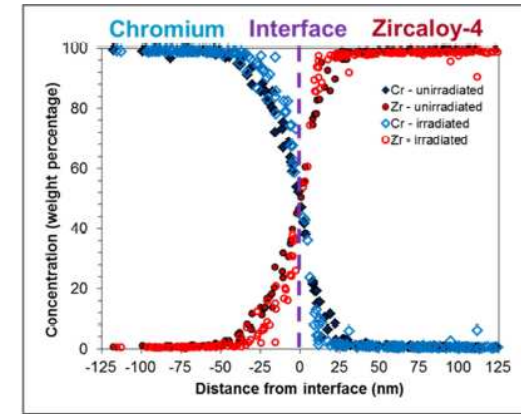
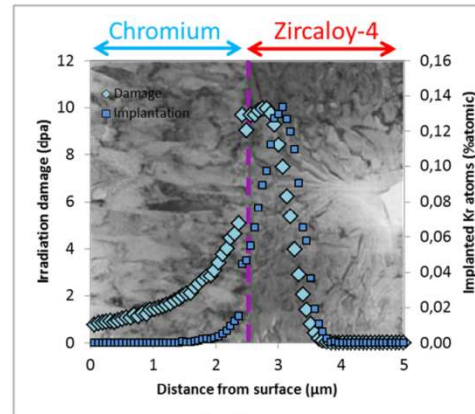
⇒ Hardness saturation for damages higher than 2 dpa
 ⇒ Hardness increase by 7 to 18% at saturation (as compared to the as-recieved conditions)





- Ex-situ ion irradiation
- Ions: 20 MeV Kr⁸⁺
- Temperature: 400°C
- Up to 15 dpa

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



**As –received samples
(1st generation)**

- Limited Fe segregation at the interface
- Nanometer sized Zr(Fe,Cr)C₂ Lave phases: both C14 and C15

After ion irradiation

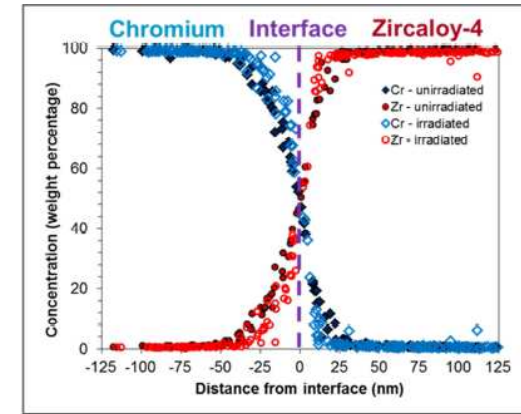
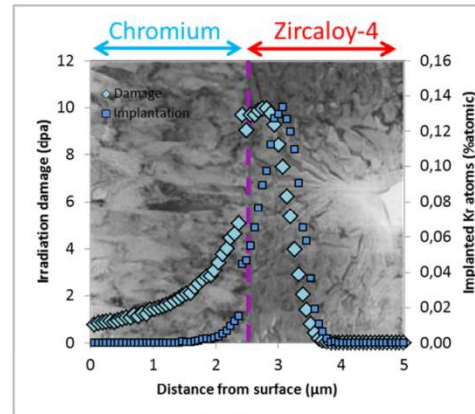
- Slight increase of Fe segregation at the interface
- Stabilization of C14 phase/ destabilization of C15 in agreement with thermodynamic calculations *

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



- Ex-situ ion irradiation
- Ions: 20 MeV Kr⁸⁺
- Temperature: 400°C
- Up to 15 dpa

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



As –received samples
(1st generation)

- Limited Fe segregation at the interface
- Nanometer sized Zr(Fe,Cr)C₂ Lave phases: both C14 and C15

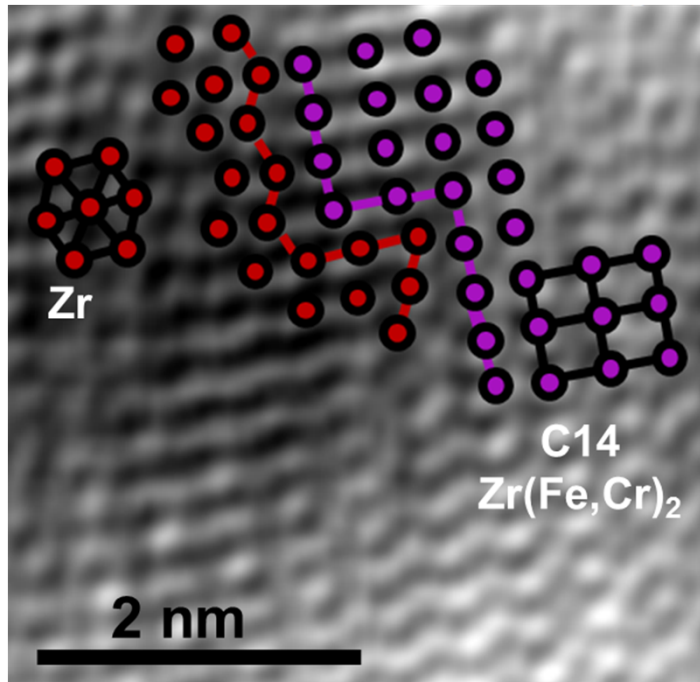
After ion irradiation

- Slight increase of Fe segregation at the interface
- Stabilization of C14 phase/ destabilization of C15

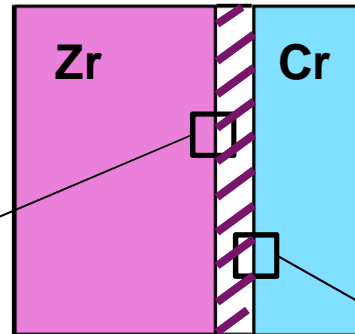
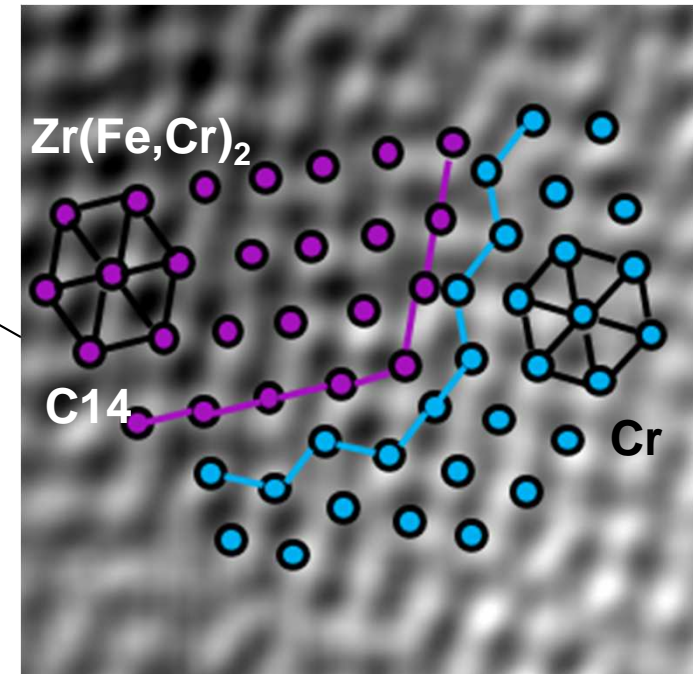
- No evolution of the C15 phase*
- No obvious evolution of the Zr/Cr profiles after irradiation (the interface remains about 100 nm thick) – as observed on samples irradiated in OSIRIS (~2 dpa, EPMA)*
- The interface remains crystalline (TEM)*
- Atomic planes are found in coherence (HRTEM) → excellent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

HRTEM analysis of ion irradiated interfaces

Interface Zr/C14



Interface C14/Cr

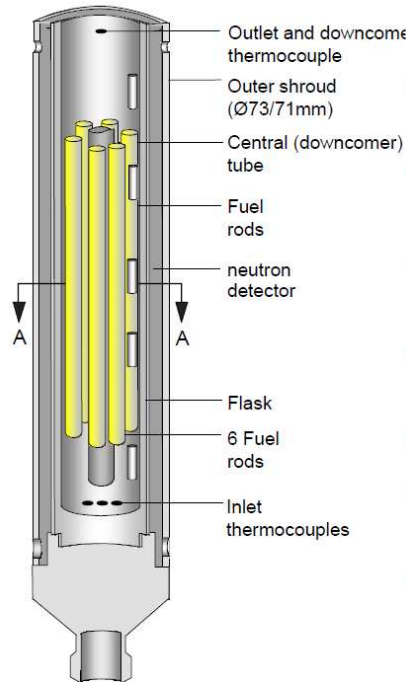


A. Wu *et al.*,
Ph.D thesis



START of the irradiation test in July 2017

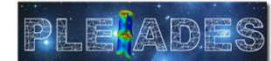
CEA-AREVA-EDF provided Cr coated cladding specimens for 4 rodlets:
3 M5 and 1 Zry-4 with ~7 or ~15 μm thick Cr coating (special PVD process)



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

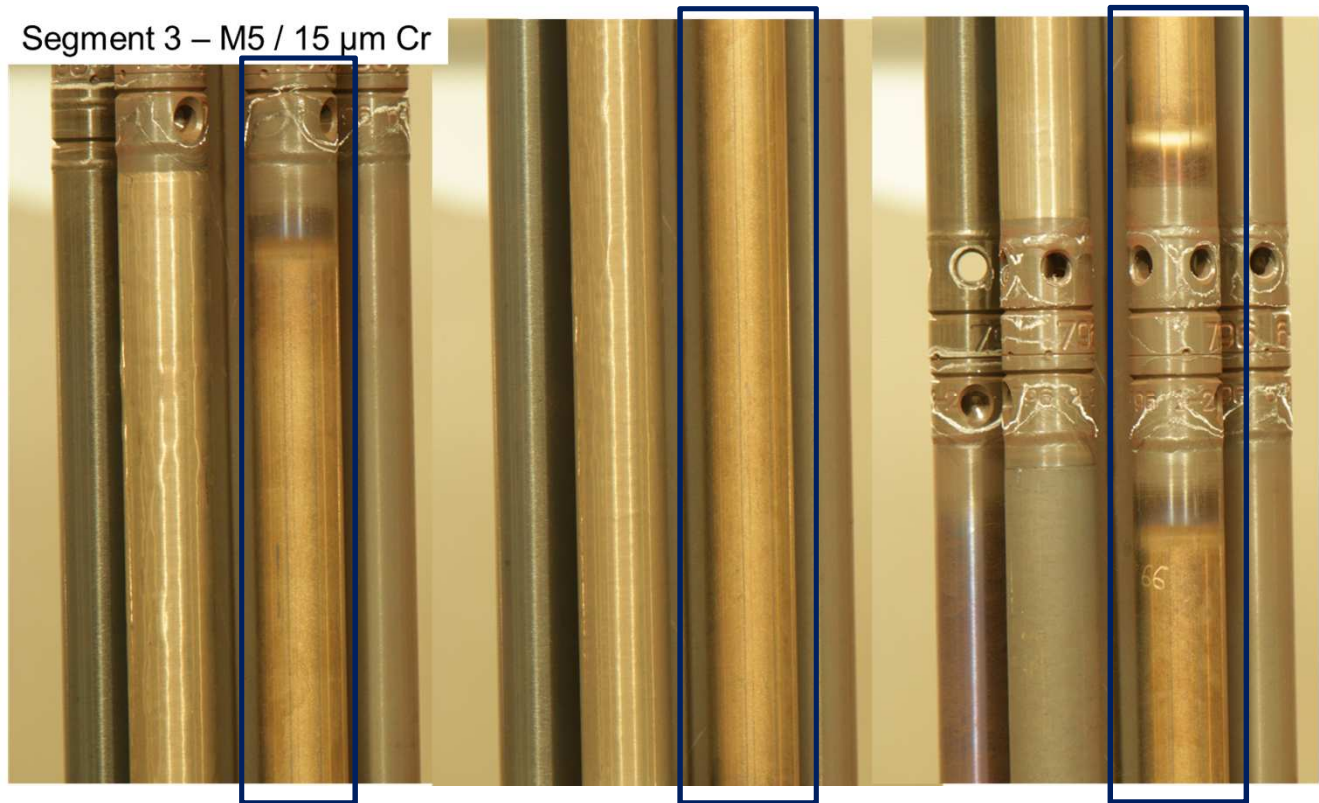
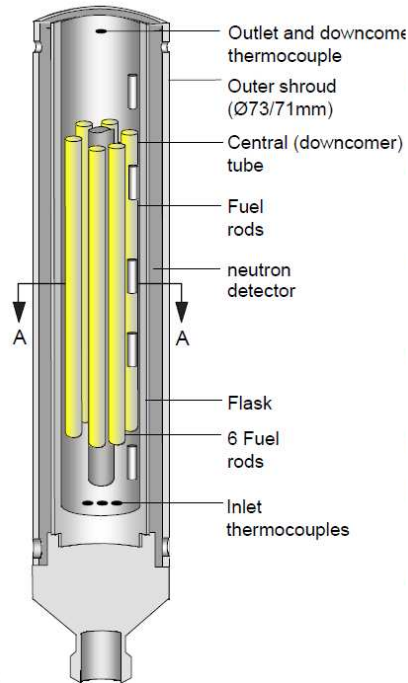
IFA-796 for LWR conditions

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 μm),
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

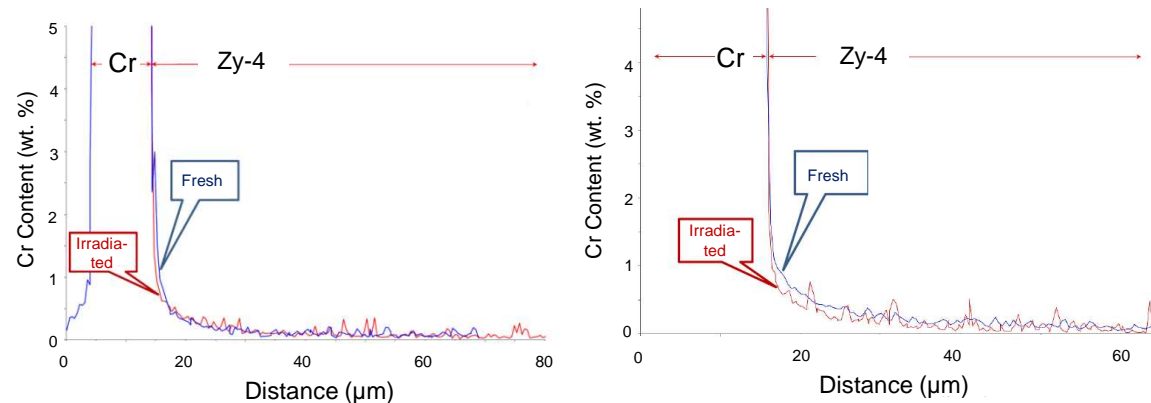
**Irradiation completed with the OSIRIS definitive shutdown
(mid-december 2015)**



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)



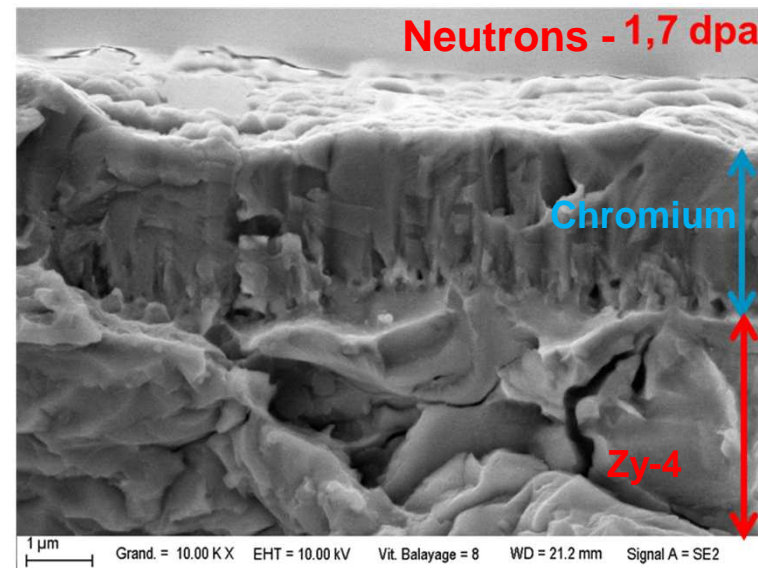
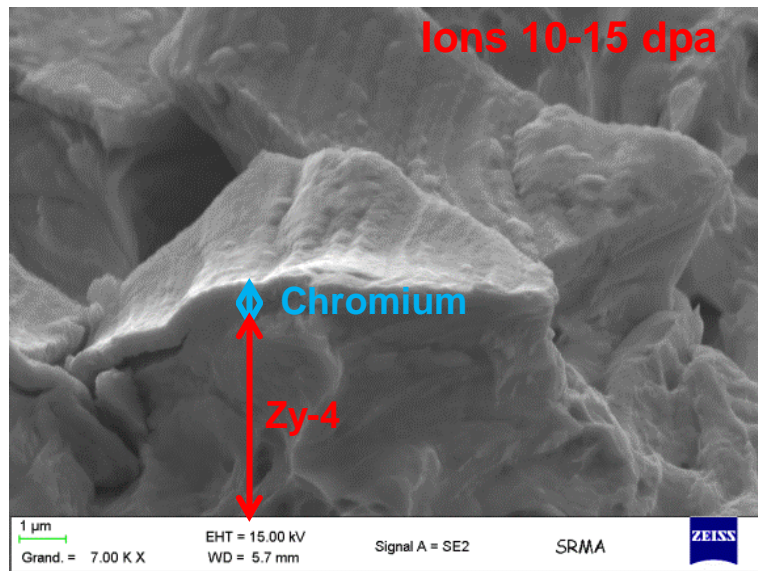
Ions

- ❑ 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*

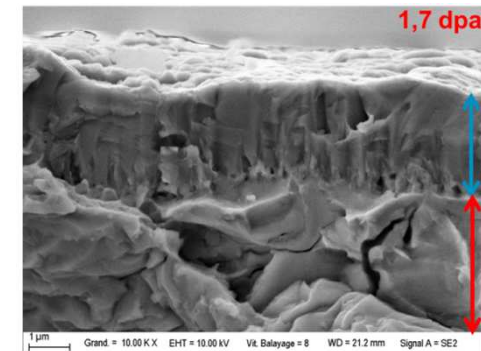
⇒ *LOCA conditions*

⇒ 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

M5 is a registered trademark of FRAMATOME or Affiliate in the USA or other countries

THANK YOU FOR YOUR ATTENTION