



**HAL**  
open science

## Interlayers for Cr-coated nuclear fuel claddings

Alexandre Michau, Michael Ougier, Thomas Guilbert, Jérémy Bischoff,  
Edouard Pouillier, Hicham Maskrot

► **To cite this version:**

Alexandre Michau, Michael Ougier, Thomas Guilbert, Jérémy Bischoff, Edouard Pouillier, et al..  
Interlayers for Cr-coated nuclear fuel claddings: Preliminary study of Mo. NuMat2020 - The Nuclear  
Materials Conference, Oct 2020, Ghent, Belgium. cea-03345302

**HAL Id: cea-03345302**

**<https://cea.hal.science/cea-03345302>**

Submitted on 15 Sep 2021

**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.

The logo for CEA (Commissariat à l'énergie atomique et aux énergies alternatives) features the lowercase letters 'cea' in a white, rounded, sans-serif font. A thin green horizontal line is positioned directly beneath the letters.The logo for Framatome consists of the word 'framatome' in a blue, lowercase, sans-serif font. The letter 'o' is replaced by a stylized orange circle with a white center.The logo for EDF (Électricité de France) features a stylized orange flower-like symbol on the left, composed of five rounded petals. To its right, the letters 'edf' are written in a blue, lowercase, sans-serif font.

# Interlayers for Cr-coated nuclear fuel claddings

## *Preliminary study of Mo*

A. Michau, M. Ougier, H. Maskrot

*Université Paris-Saclay, CEA, Service d'Études Analytiques et de Réactivité des Surfaces, 91191, Gif-sur-Yvette, France*

T. Guilbert

*Université Paris-Saclay, CEA, Service de Recherches Métallurgiques Appliquées, 91191, Gif-sur-Yvette, France*

J. Bischoff

*Framatome, 10 rue Juliette Récamier, 69456, Lyon, Cedex 06, France*

E. Pouillier

*EDF R&D, MMC Department, avenue des Renardières, 77818, Moret-sur-Loing, France*

**NuMat 2020**

26-29<sup>th</sup> October 2020

## Zr-based claddings with a Cr coating

### ► Substantial improvements compared to uncoated solutions

- Corrosion kinetics reduced in primary water chemistry
- Oxidation rate decreased in steam during LOCA
- ...

### ► Beyond design basis accident

1300-1350°C

- Fast **Cr-Zr interdiffusion** → metastable  $Zr_xCr_y$
- $Zr_xCr_y + \beta\text{-Zr}$  → **liquid eutectic phase**

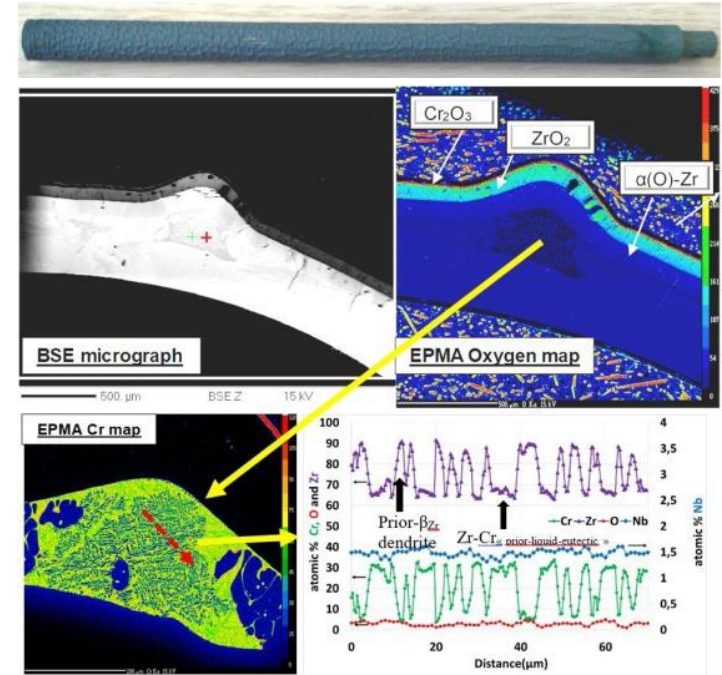
1400-1450°C

- Liquid eutectic **consumes all available Cr**

Quenching

- Precipitation of  $\beta\text{-Zr}$  dendrites, Cr-enriched inter-dendritic areas

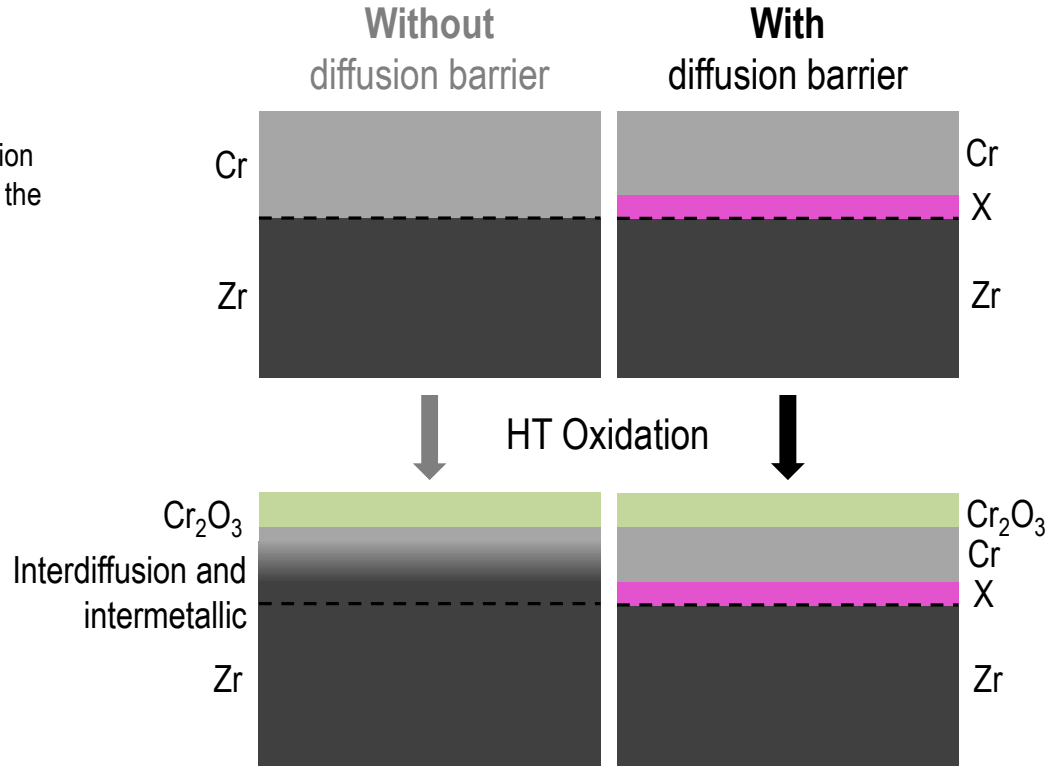
→ **Cr-Zr diffusion barrier to mitigate this effect**



12-15 μm thick Cr-coated M5<sup>Framatome</sup> cladding sample after 100 s at 1400 °C followed by direct water quenching (one-sided steam oxidation)  
 [J.-C. Brachet et al., Corrosion Science 167 (2020) 108537]

## Functional criteria

- ▶ Diffusion barrier
  - Slow the coating consumption by diffusion
  - Extend the coating available for protection against oxidation
  - Prevent embrittlement during and after quenching due to the diffusion and the formation of brittle phases
- ▶ Improve everything else ! At least do not degrade anything else...
  - Nuclear physics
  - Mechanical behaviour
  - Corrosion/oxidation
  - ...



## Technical criteria – diffusion barrier

- ▶ Diffusion barrier
  - Lower **interdiffusion coefficients** Cr-X and Zr-X with T and/or lower solubility in  $\beta$ -Zr (and reciprocally)
  - No eutectic reaction or **eutectic reaction at higher T**
- ▶ ATF application
  - Material resisting to **HT, HT oxidation, corrosion, irradiation**
  - Compatible **CTE**, ductile
  - Low impact on **neutron cross-section, thermal conductivity**
  - Toxicity, costs, criticality
  - **Decommissioning** compatible
- ▶ Deposition process
  - Possible to deposit a thin layer
  - No contamination
  - No degradation of existing solution

## Technical criteria – diffusion barrier

- ▶ Diffusion barrier
  - Lower **interdiffusion coefficients** Cr-X and Zr-X with T and/or lower solubility in  $\beta$ -Zr (and reciprocally)
  - No eutectic reaction or **eutectic reaction at higher T**
- ▶ ATF application
  - Material resisting to **HT, HT oxidation, corrosion, irradiation**
  - Compatible **CTE**, ductile
  - Low impact on **neutron cross-section, thermal conductivity**
  - Toxicity, costs, criticality
  - **Decommissioning** compatible
- ▶ Deposition process
  - Possible to deposit a thin layer
  - No contamination
  - No degradation of existing solution

→ in a first approach Mo fills most of these criteria

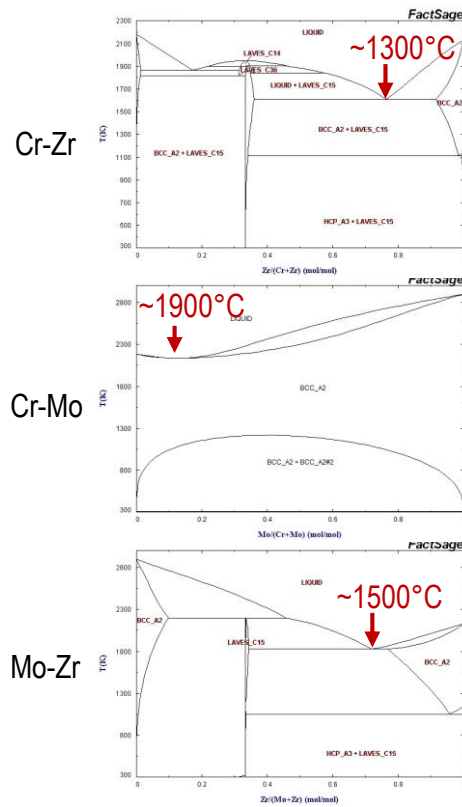
✓ **Mo candidate for this case study**

## Easy access to numerous tables

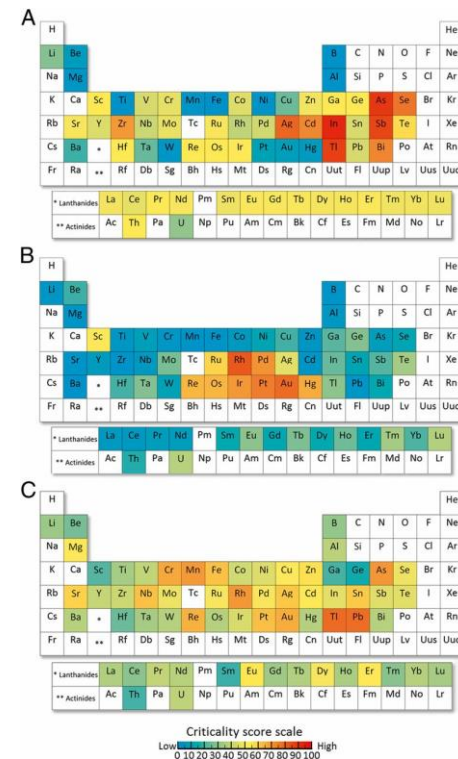
- ▶ Melting temperature
  - Cr 1907°C
  - Mo 2623°C
- ▶ Coefficient of thermal expansion (@RT)
  - Cr  $\sim 6.5 \cdot 10^{-6} \text{ K}^{-1}$
  - Mo  $\sim 5.5 \cdot 10^{-6} \text{ K}^{-1}$
- ▶ Thermal conductivity
  - Cr  $94 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
  - Mo  $139 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
- ▶ Neutron cross-section
  - Cr 3.1 barn
  - Mo 2.6 barn

## More complex data to collect

- ▶ Behaviour under and after irradiation
- ▶ Compatibility with primary water and steam
- ▶ Corrosion rate in concentrated nitric acid
- ▶ Coupled effects
- ▶ ...



Binary phase diagrams.  
SGTE 2014 alloy and FSsteel steel alloy databases



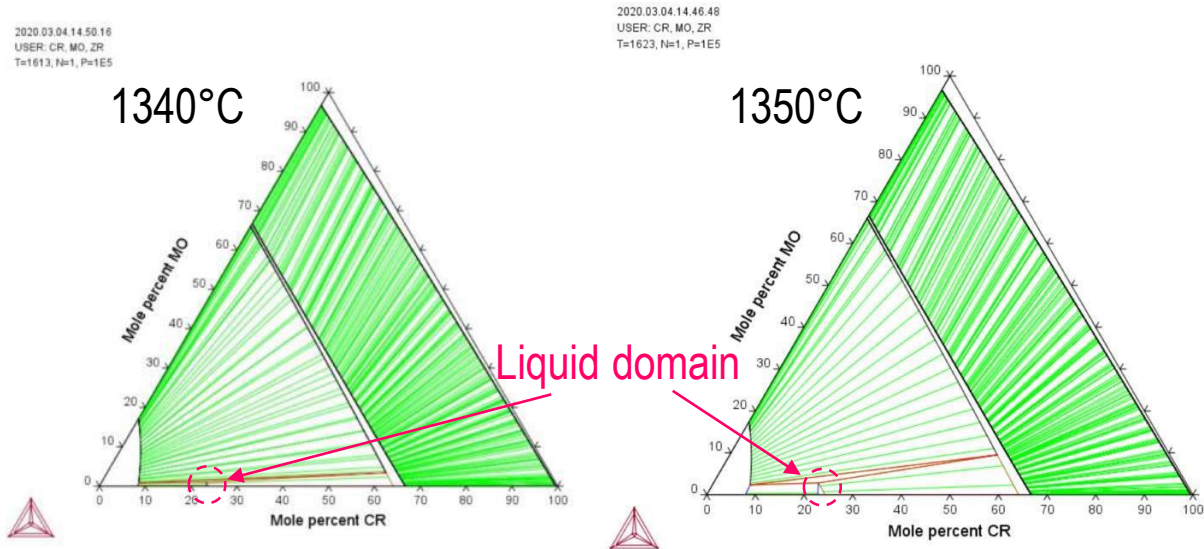
Criticality maps for (A) supply risk, (B) environmental implications, and (C) vulnerability to supply restriction.  
T.E. Graedel et al., PNAS April 7, 2015 112 (14) 4257-4262

## Easy access to numerous tables

- ▶ Melting temperature
  - Cr 1907°C
  - Mo 2623°C
- ▶ Coefficient of thermal expansion (@RT)
  - Cr  $\sim 6.5 \cdot 10^{-6} \text{ K}^{-1}$
  - Mo  $\sim 5.5 \cdot 10^{-6} \text{ K}^{-1}$
- ▶ Thermal conductivity
  - Cr  $94 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
  - Mo  $139 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
- ▶ Neutron cross-section
  - Cr 3.1 barn
  - Mo 2.6 barn

## More complex data to collect

- ▶ Behaviour under and after irradiation
- ▶ Compatibility with primary water and steam
- ▶ Corrosion rate in concentrated nitric acid
- ▶ Coupled effects
- ▶ ...



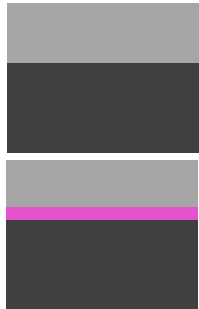
Isothermal cross-sections of Cr-Mo-Zr ternary diagrams

*Thermocalc calculations with Zircobase database*



## Method

### 1. Elaboration

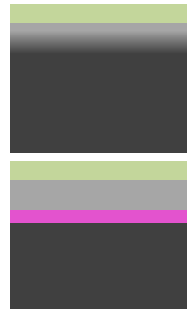


- Ionized PVD
- 12-15  $\mu\text{m}$  Cr reference coating
- 2-5  $\mu\text{m}$  Mo interlayer + 10-12  $\mu\text{m}$  Cr
- Flat coupons (1.2 mm thick)
- Single face vs 3d

### 2. Characterization

- Crystal structure, XRD
- Microstructure and composition, SEM and EPMA
- Composition profile, GDOES
- ...

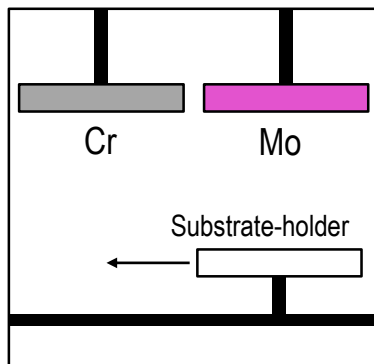
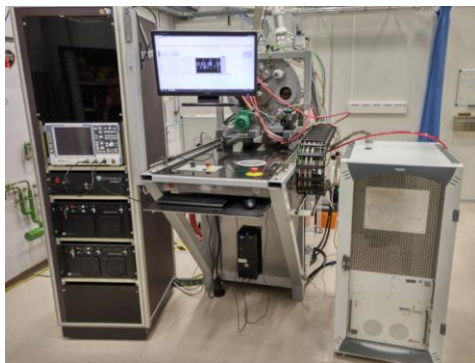
### 3. Tests



- Heat treatment in argon, air and steam
- 1100 and 1400°C
- 1.2 to 60 minutes

### 4. Characterization

- Crystal structure, XRD
- Microstructure and composition, SEM and EPMA
- Composition profile, GDOES
- ...



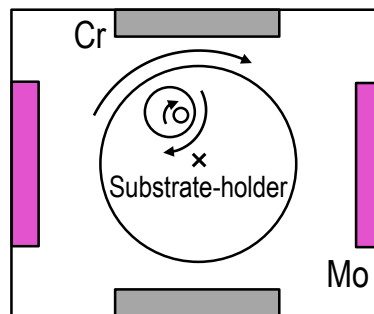
## Laboratory scale (pre-study)

### ► Configuration

- 2 circular cathodes (12.5 cm), 1 Cr and 1 Mo
- Co-planar configuration
- Translatable substrate-holder
- Fixed source-substrate distance
- Single face deposition on flat samples ~ 5 cm

### ► Processes

- Magnetron sputtering, DC, pulsed, HiPIMS



## Pilot scale

### ► Configuration

- 4 rectangular cathodes (15 x 65 cm), 2 Cr and 2 Mo
- Triple rotation substrate-holder
- Variable source-substrate distance
- Deposition on 3d samples ~ 50 cm

### ► Processes

- Magnetron sputtering, DC, pulsed, HiPIMS
- Cathodic arc
- PECVD

## Elaboration sequence

### ► Cleaning (sonication)

- Degreasing
- Drying

### ► *In situ* etching

- Remove surface pollutants
- Remove the native oxide layer
- HiPIMS mode (Cr and Ar ions) instead of standard diode (Ar)



Duration: 10 to 20 min

**Promote Cr ionization**

**Accelerate enough to etch**

### ► Deposition

- Pure HiPIMS mode (Cr, Mo and Ar ions)
- Low growth rates  $\sim 0.3 \mu\text{m}\cdot\text{h}^{-1}$  due to the deposition configuration



Duration: 50 to 70 h

**Promote Cr ionization**

**Accelerate enough to densify**

## Characteristics

### ► Microstructure

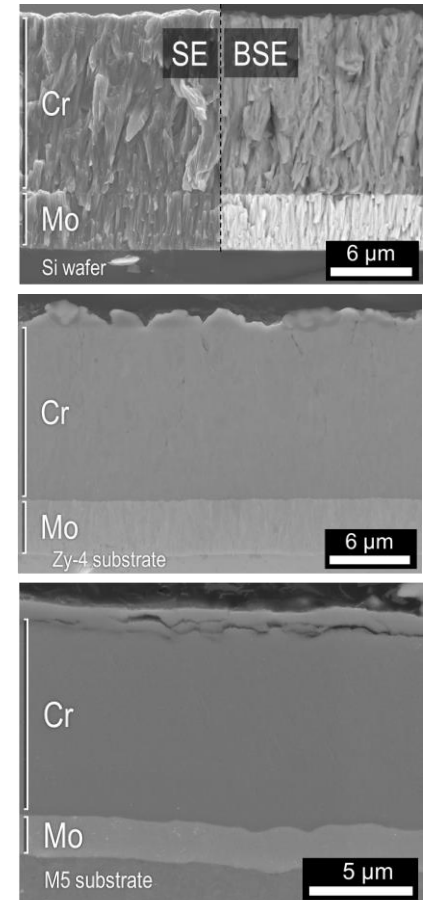
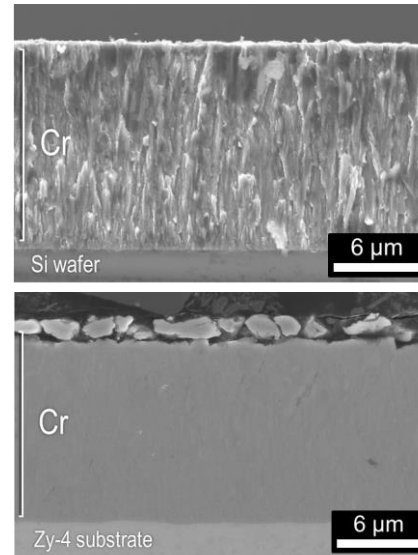
- Dense columnar on cleaved Si and polished Zr alloy
- Sharp interfaces

### ► Crystallinity

- Polycrystalline coatings
- Single phase cubic centered Cr ( $2.89 \text{ \AA}$ ), (110) texture
- Single phase cubic centered Mo ( $3.15 \text{ \AA}$ )

### ► Composition

- Interfaces with GDOES not so sharp compared to EPMA
- Cr enrichment at the interface due to implantation during etching



## Characteristics

### ► Microstructure

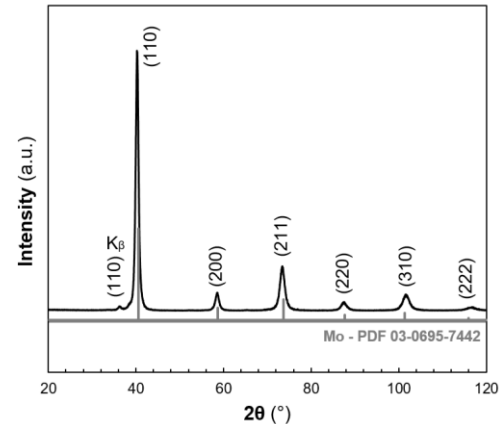
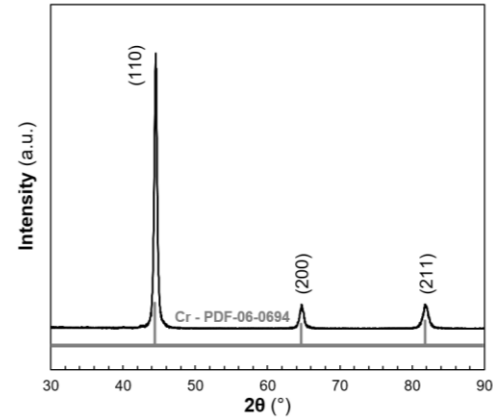
- Dense columnar on cleaved Si and polished Zr alloy
- Sharp interfaces

### ► Crystallinity

- Polycrystalline coatings
- Single phase cubic centered Cr (2.89 Å), (110) texture
- Single phase cubic centered Mo (3.15 Å)

### ► Composition

- Interfaces with GDOES not so sharp compared to EPMA
- Cr enrichment at the interface due to implantation during etching



## Characteristics

### ▶ Microstructure

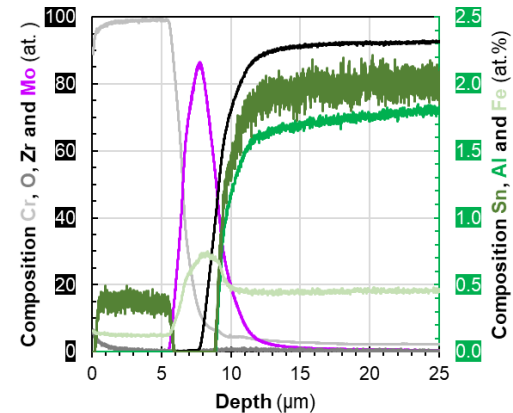
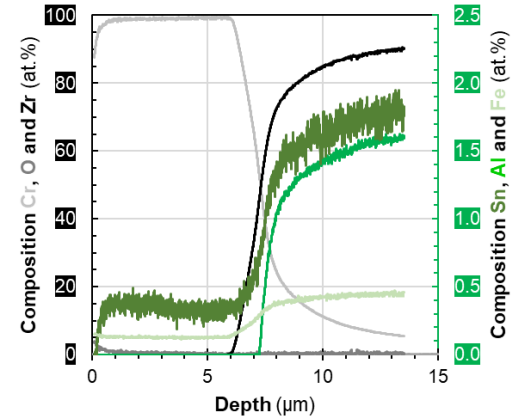
- Dense columnar on cleaved Si and polished Zr alloy
- Sharp interfaces

### ▶ Crystallinity

- Polycrystalline coatings
- Single phase cubic centered Cr (2.89 Å), (110) texture
- Single phase cubic centered Mo (3.15 Å)

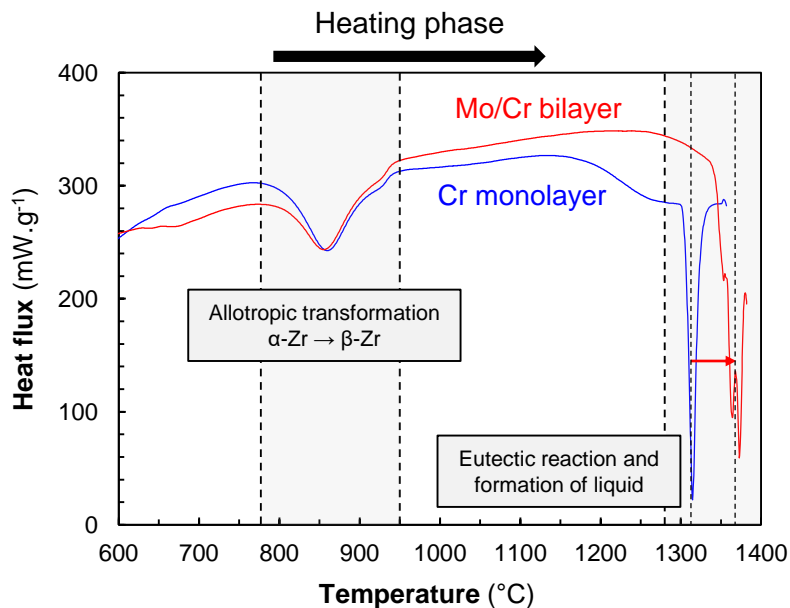
### ▶ Composition

- Interfaces with GDOES not so sharp compared to EPMA
- Cr enrichment at the interface due to implantation during etching



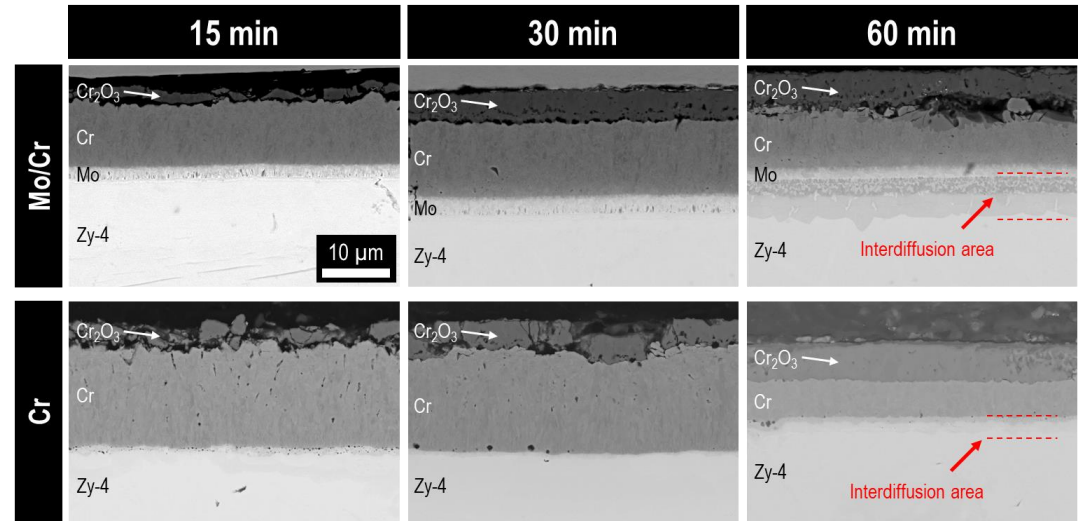
## Calorimetry in argon @10°C.min<sup>-1</sup>

- **Shift of the liquid formation** for Mo/Cr towards **higher temperatures** (~40°C) → should be **greater in dynamic conditions**



## Oxidation in air at 1100°C followed by a water quench

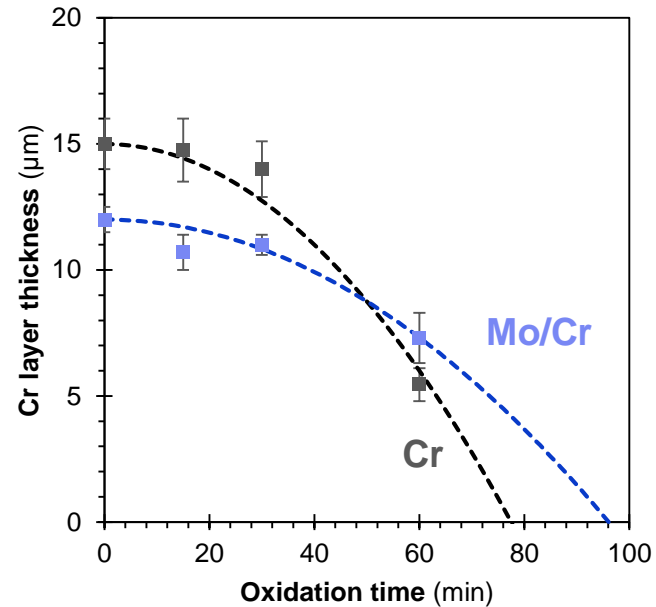
- ▶ Similar between Cr and Mo/Cr
  - Growth of  $\text{Cr}_2\text{O}_3$  layer at the same rate
  - Formation of an interdiffusion layer
- ▶ Advantageous for Mo/Cr
  - Thickness of the Cr layer decreases, slower for Mo/Cr
  - Formation and growth of porosities, slower for Mo/Cr





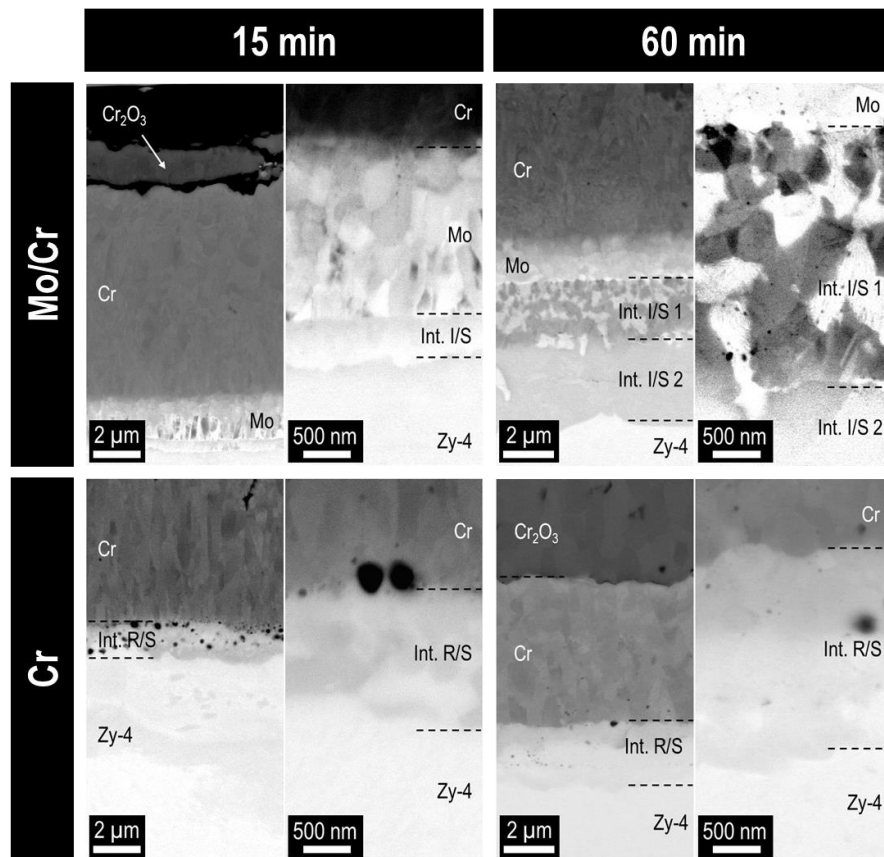
## Oxidation in air at 1100°C followed by a water quench

- ▶ Similar between Cr and Mo/Cr
  - Growth of  $\text{Cr}_2\text{O}_3$  layer at the same rate
  - Formation of an interdiffusion layer
- ▶ Advantageous for Mo/Cr
  - Thickness of the Cr layer decreases, slower for Mo/Cr
  - Formation and growth of porosities, slower for Mo/Cr



## Oxidation in air at 1100°C followed by a water quench

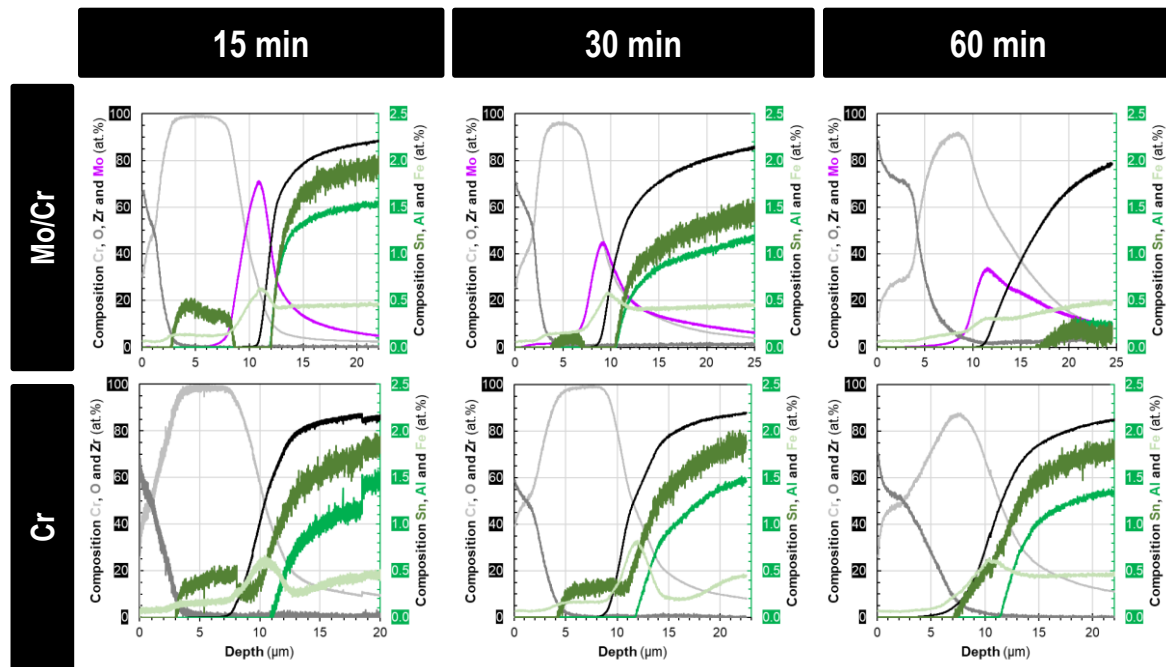
- ▶ Similar between Cr and Mo/Cr
  - Growth of  $\text{Cr}_2\text{O}_3$  layer at the same rate
  - Formation of an interdiffusion layer
- ▶ Advantageous for Mo/Cr
  - Thickness of the Cr layer decreases, slower for Mo/Cr
  - Formation and growth of porosities, slower for Mo/Cr



## Oxidation in air at 1100°C followed by a water quench

- ▶ Similar between Cr and Mo/Cr
  - Growth of  $\text{Cr}_2\text{O}_3$  layer at the same rate
  - Formation of an interdiffusion layer
- ▶ Advantageous for Mo/Cr
  - Thickness of the Cr layer decreases, slower for Mo/Cr
  - Formation and growth of porosities, slower for Mo/Cr

→ Longer lifetime of Mo/Cr

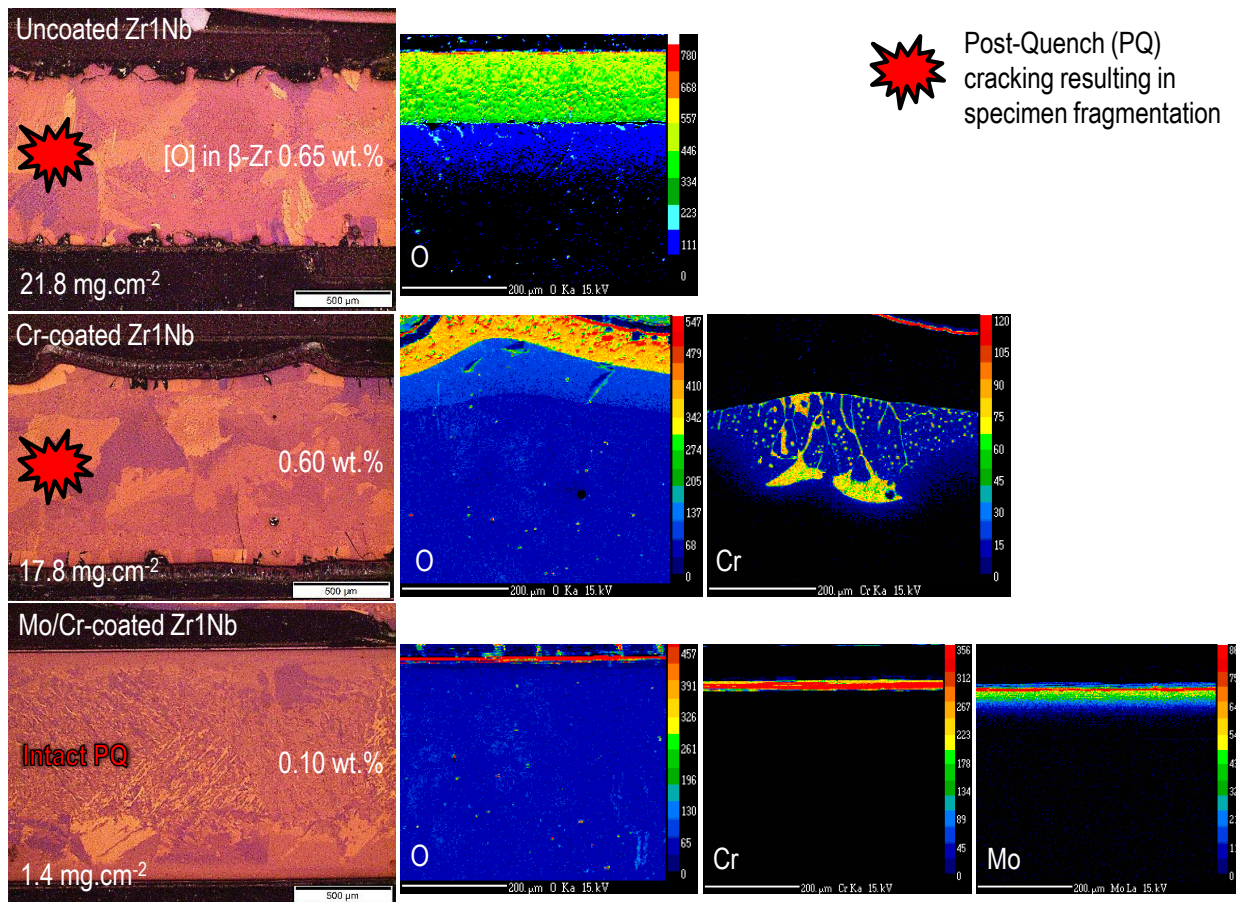


## Oxidation in steam, 100 s @1400°C followed by a water quench

- ▶ ZrO<sub>2</sub> formation
  - 160 μm for uncoated
  - 90 μm for Cr-coated
  - None for Mo/Cr-coated
- ▶ Cr<sub>2</sub>O<sub>3</sub> formation
  - Partially consumed the Cr for Cr-coated
  - Residual Cr and Mo layers on Mo/Cr-coated
- ▶ Cr diffusion
  - Cr-Zr eutectic structure at the specimen surface after quenching
  - None for Mo/Cr-coated

→ Better resistance of Mo/Cr at higher temperatures which delays the Cr-Zr eutectic reaction

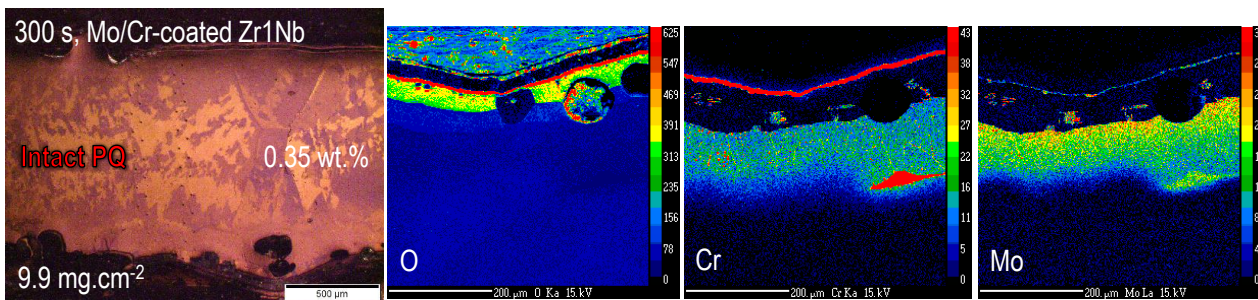
→ Decreases the O ingress in β-Zr and may induce a better PQ residual strength, ductility and toughness



## Oxidation in steam @1400°C followed by a water quench

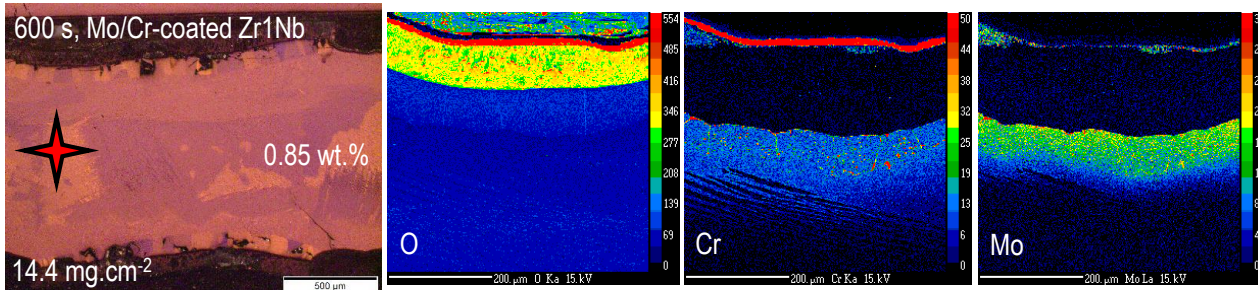
### ▶ 300 s

- Formation of wrinkles due to the eutectic reaction
- Growth of  $ZrO_2$  and formation  $\alpha$ -Zr(O)
- Only  $Cr_2O_3$  left, no residual metallic layers

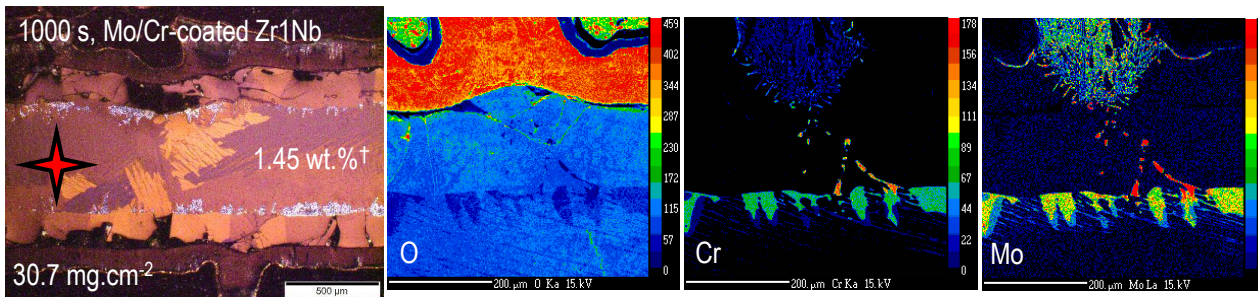


### ▶ 600 and 1000 s

- Partial loss of integrity
- Larger  $ZrO_2$  and  $\alpha$ -Zr(O) areas



Quench cracking initiated at pre-existing stress concentrations



† [O] in  $\beta_{Zr}$  (+potential  $\alpha_{Zr}$ (O) incursions) ~ 1.45 wt. %

## Conclusions

- ▶ Choosing an interlayer material is a complex compromise
  - Quick selection based on tables
  - Longer identification due to complex data and coupled effects
  - Safety gains to quantify compared to the complexity and cost
  
- ▶ Mo diffusion barrier has a beneficial effect in both slow and dynamic conditions on a Cr-coated Zr alloy
  - Compatibility in the PVD elaboration process that provides dense microstructures
  - The eutectic reaction is shifted towards higher temperatures
  - Metallic Cr is available for longer times

→ **Mo interlayer shows promising results for longer coping times at higher temperatures but further characterization is needed to fully quantify benefits**

## Perspectives

- ▶ Keep characterizing the Mo interlayer for further evaluation
- ▶ Extend selection criteria to more complex materials (alloys and multi-elements phases, doping...)

The logo for CEA (Commissariat à l'énergie atomique et aux énergies alternatives) features the lowercase letters 'cea' in a white, sans-serif font, positioned above a thin green horizontal line.The logo for Framatome consists of the word 'framatome' in a blue, lowercase, sans-serif font, with a small orange circle placed above the letter 'o'.The logo for EDF (Électricité de France) features an orange stylized flower-like symbol to the left of the lowercase letters 'edf' in a blue, sans-serif font.

Thank you for your attention !

Do you have any questions?

**Acknowledgements** : Michel Tabarant for GDOES, Caroline Toffolon-Masclat for thermodynamic calculations