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Interlayers for Cr-coated nuclear fuel claddings

Preliminary study of Mo

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NuMat 2020
26-29th 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 + β-Zr → **liquid eutectic phase**

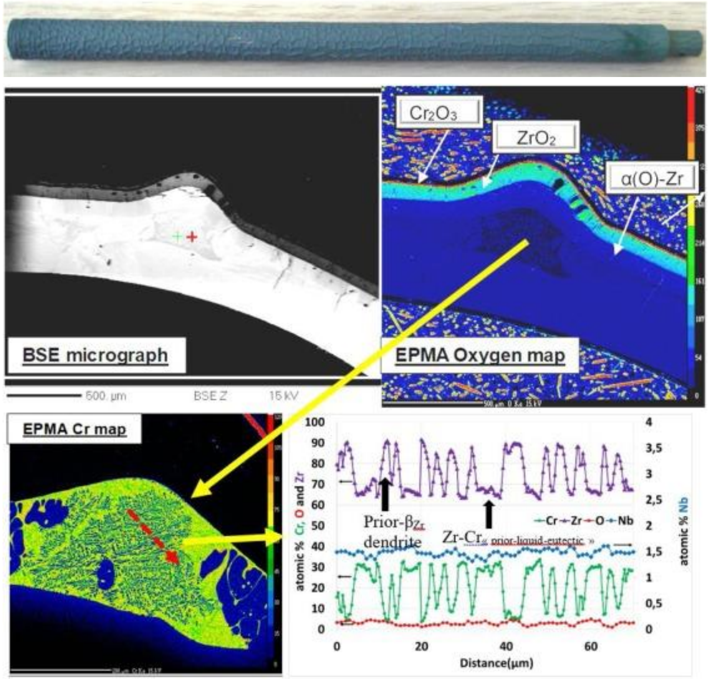
↓

1400-1450°C
- Liquid eutectic **consumes all available Cr**

↓

Quenching
- Precipitation of β-Zr dendrites, Cr-enriched inter-dendritic areas

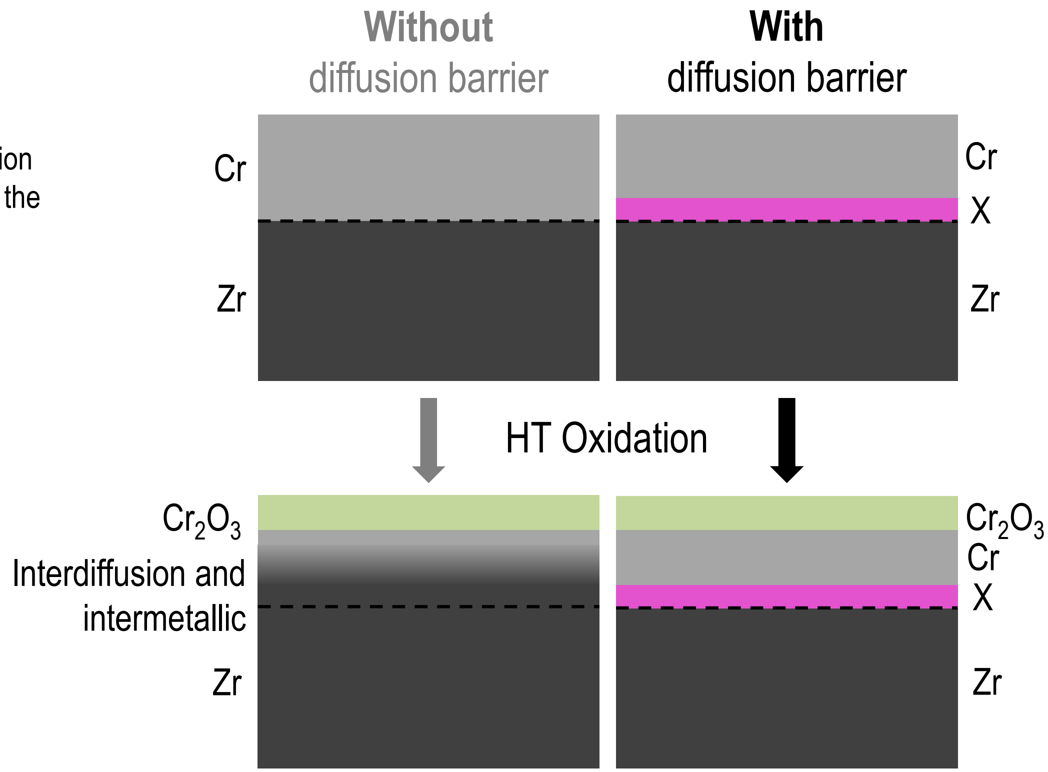
→ Cr-Zr diffusion barrier to mitigate this effect



12-15 µm thick Cr-coated M5[Framatome] 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 β-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

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→ **in a first approach Mo fills most of these criteria**

✓ **Mo candidate for this case study**

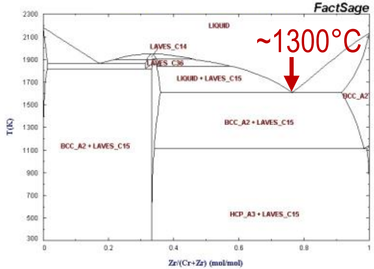
Easy access to numerous tables

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

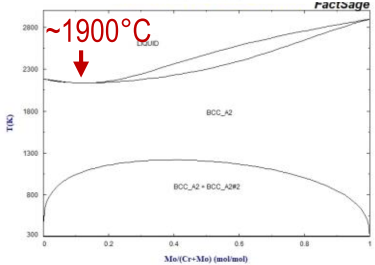
More complex data to collect

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

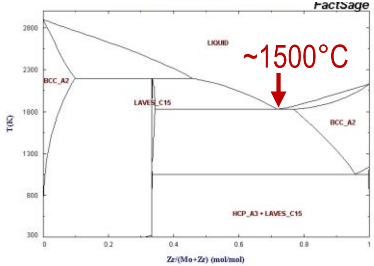
Cr-Zr



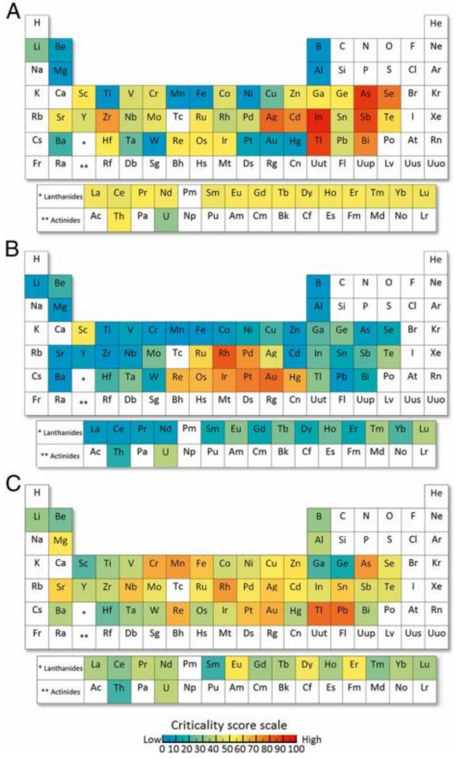
Cr-Mo



Mo-Zr



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

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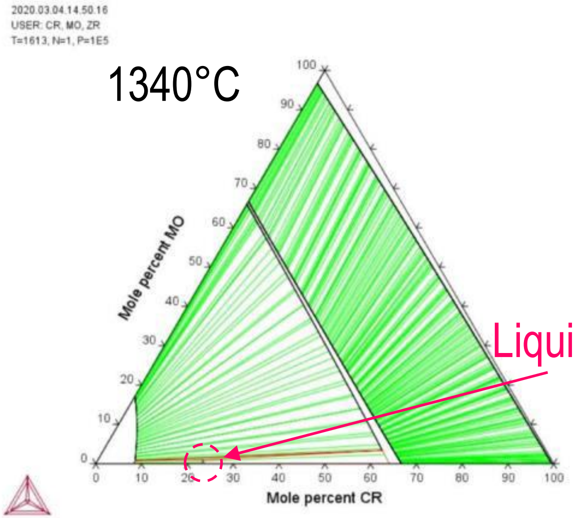
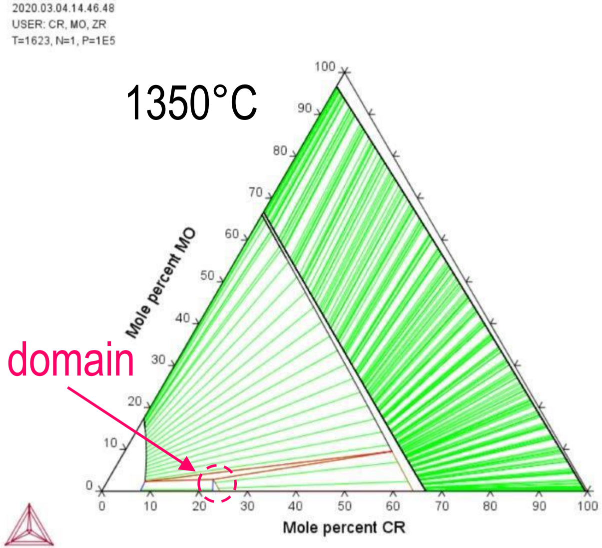
1340°C



1350°C



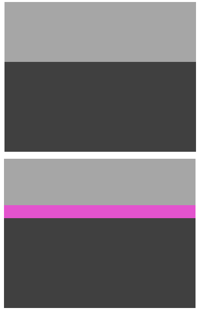
Liquid domain

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

Thermocalc calculations with Zircobase database

Method

1. Elaboration



- Ionized PVD
- 12-15 µm Cr reference coating
- 2-5 µm Mo interlayer + 10-12 µm Cr
- Flat coupons (1.2 mm thick)
- Single face vs 3d

2. Characterization

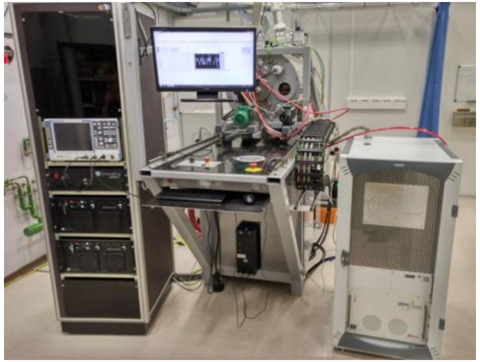
- Crystal structure, XRD
- Microstructure and composition, SEM and EPMA
- Composition profile, GDOES
- …

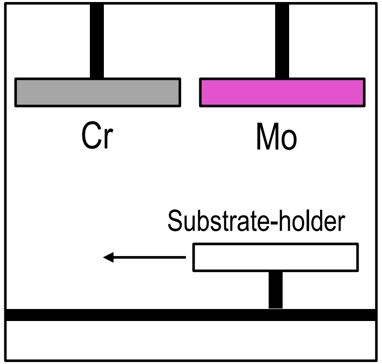
3. Tests

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

4. Characterization

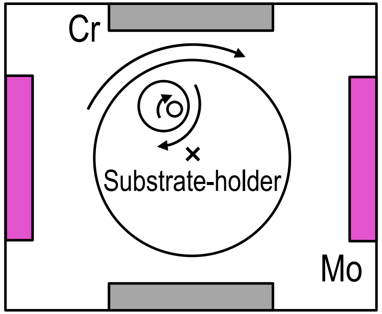
- Crystal structure, XRD
- Microstructure and composition, SEM and EPMA
- Composition profile, GDOES
- …





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)

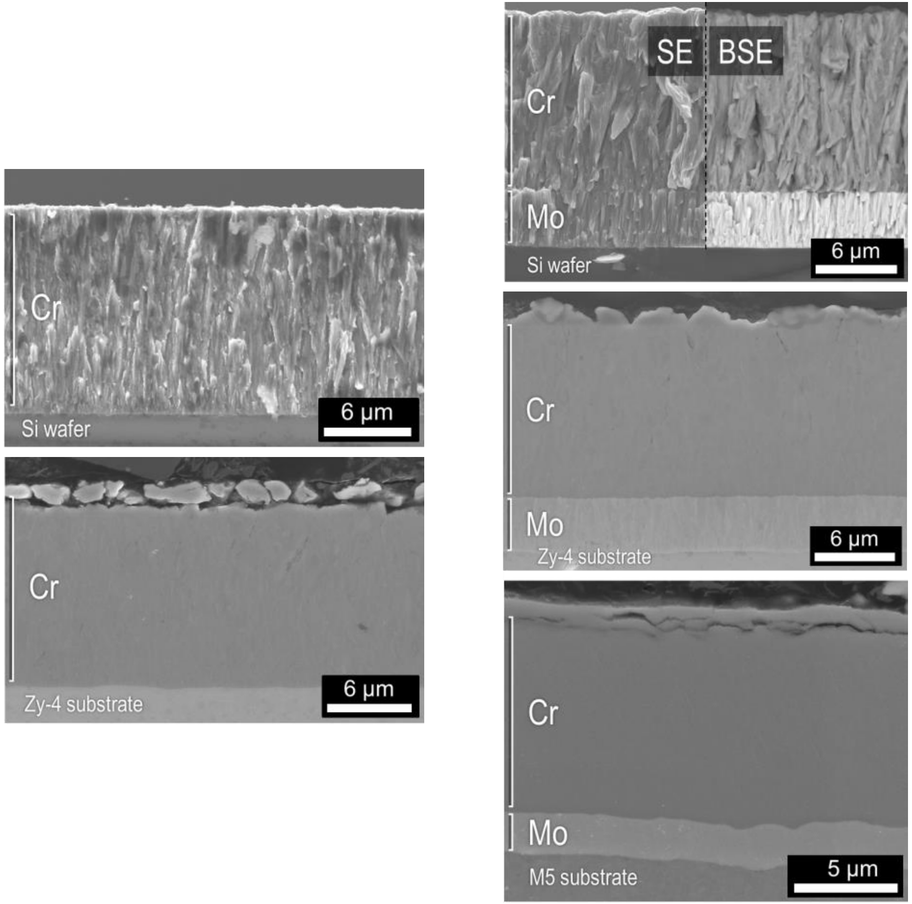
→ Duration: 10 to 20 min
Promote Cr ionization
Accelerate enough to etch

- Deposition
  - Pure HiPIMS mode (Cr, Mo and Ar ions)
  - Low growth rates ~ 0.3 $\mu m.h^{-1}$ 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 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



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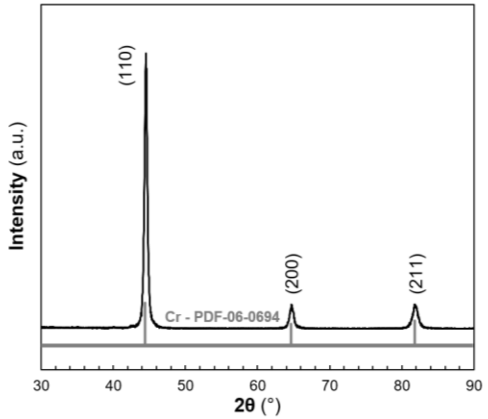

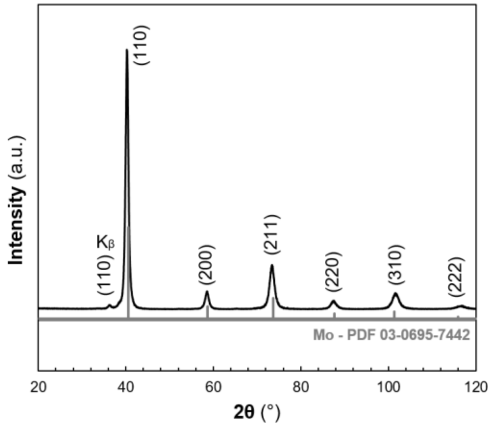

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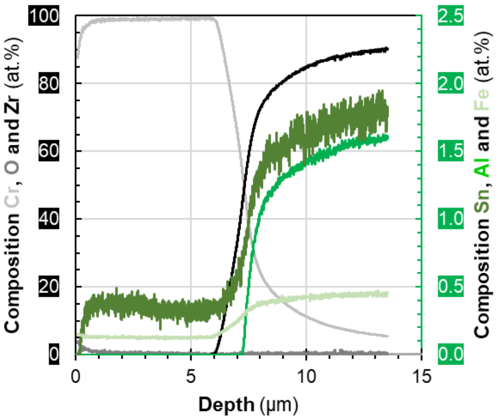
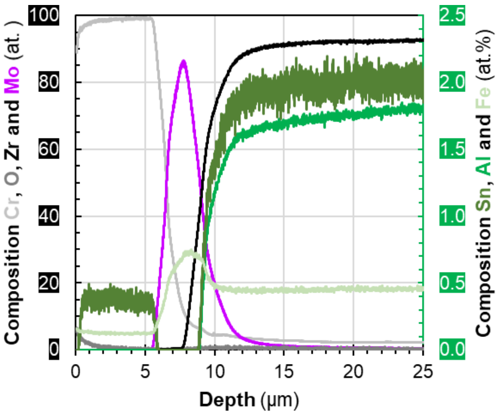
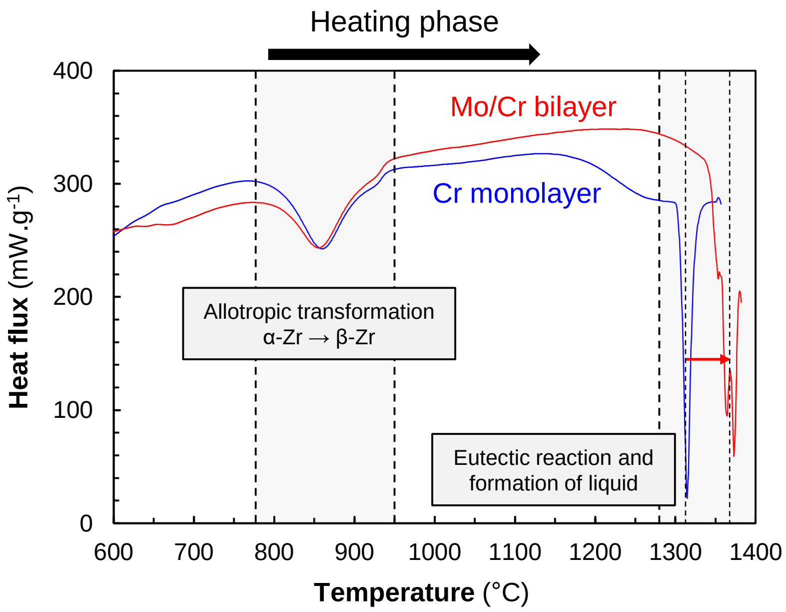




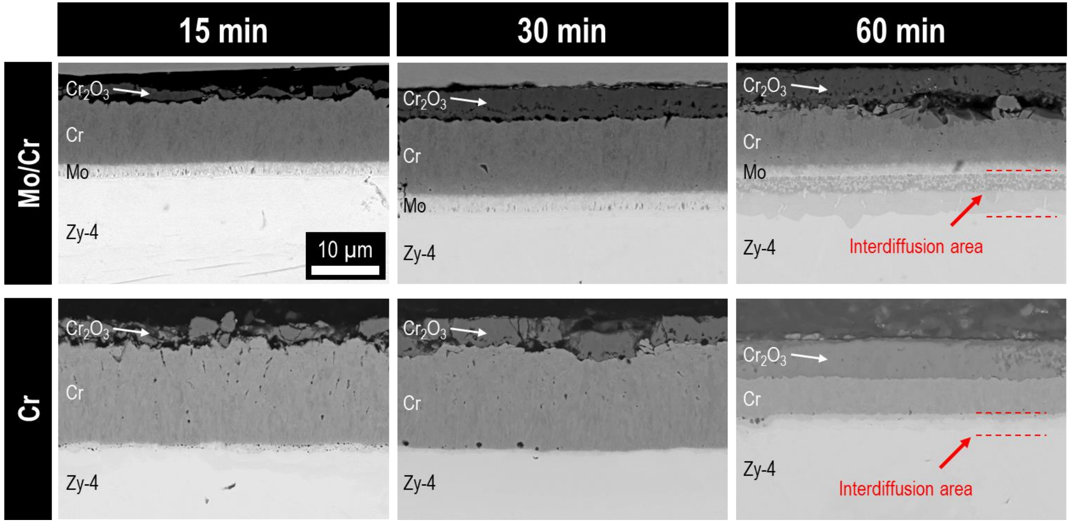
Calorimetry in argon @10°C.min^{-1}

- **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 Cr_2O_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



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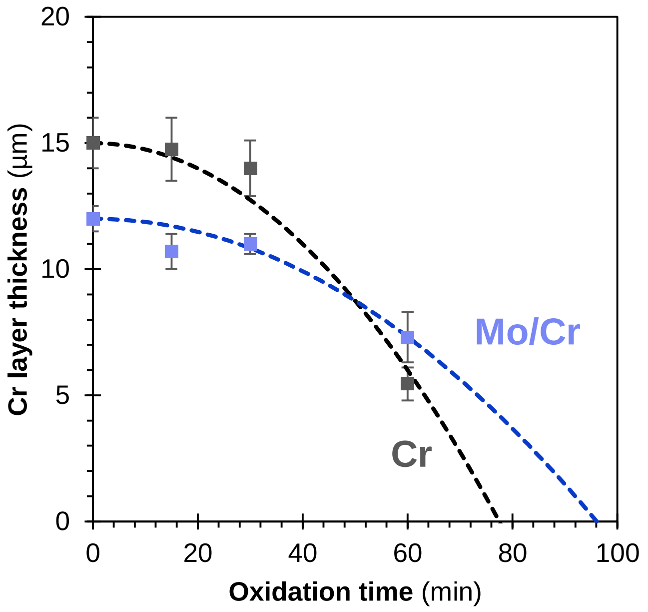

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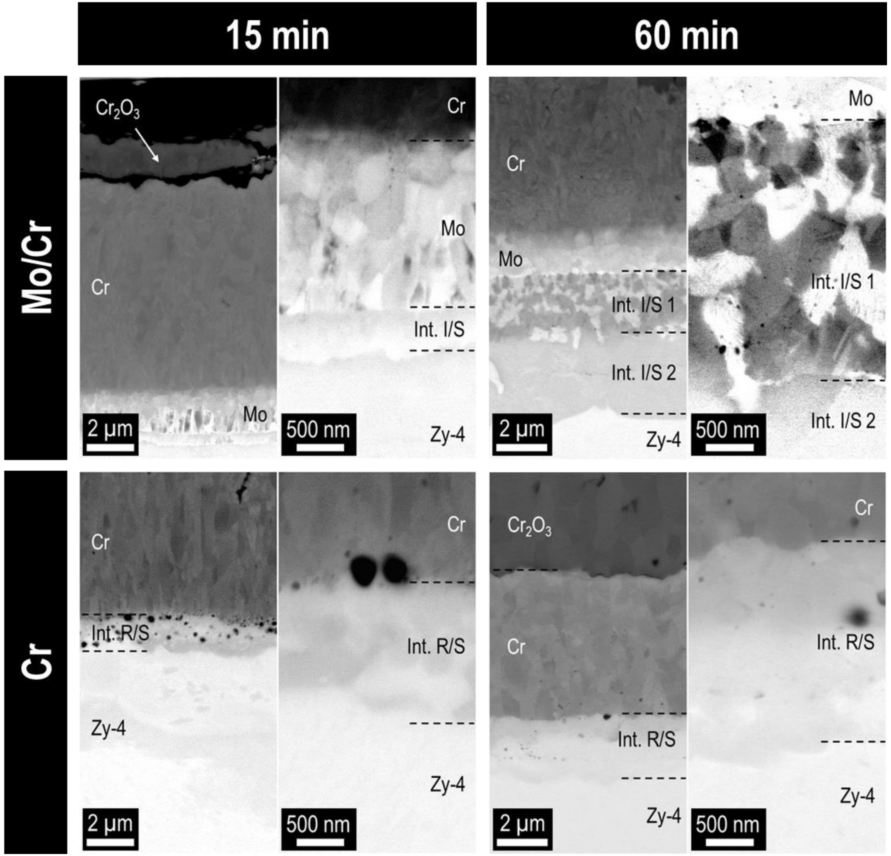

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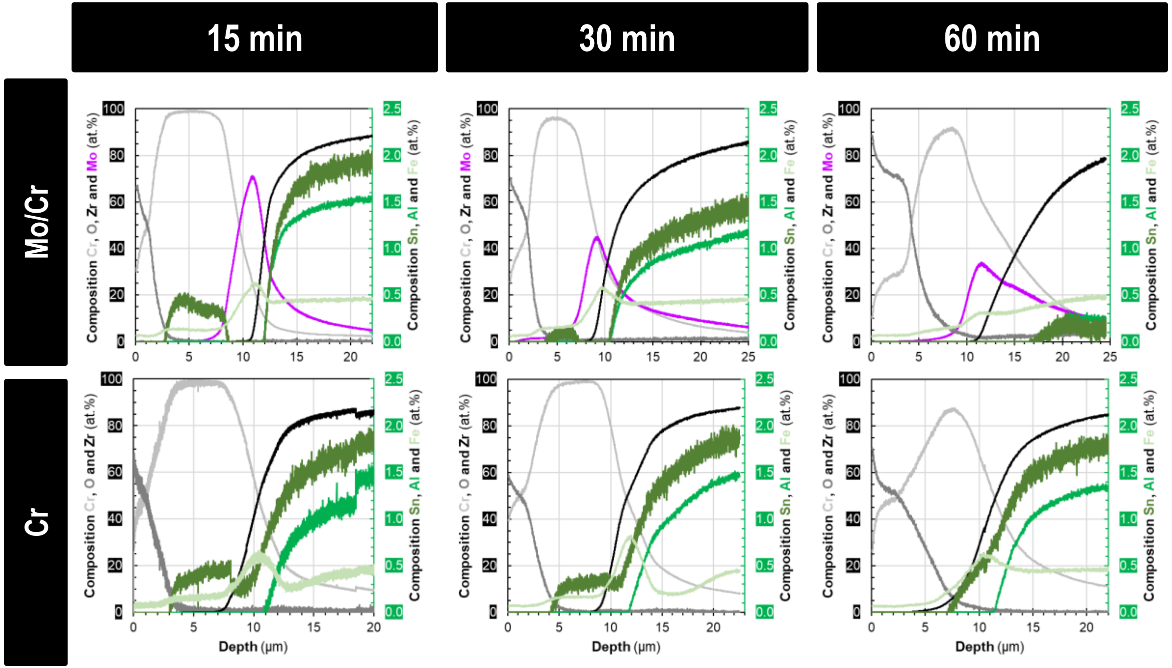
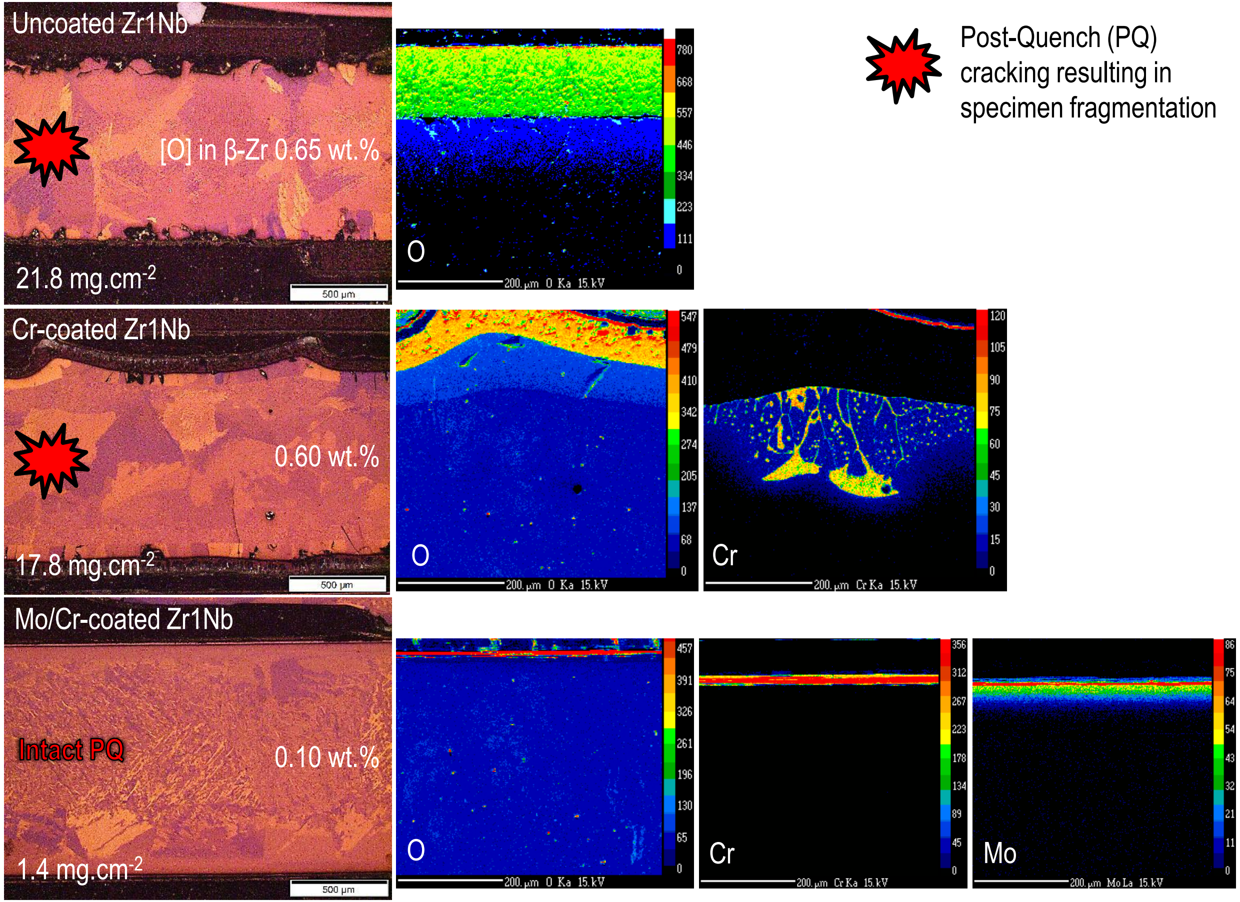
→ Longer lifetime of Mo/Cr



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

- ZrO_2 formation
  - 160 µm for uncoated
  - 90 µm for Cr-coated
  - None for Mo/Cr-coated
- Cr_2O_3 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

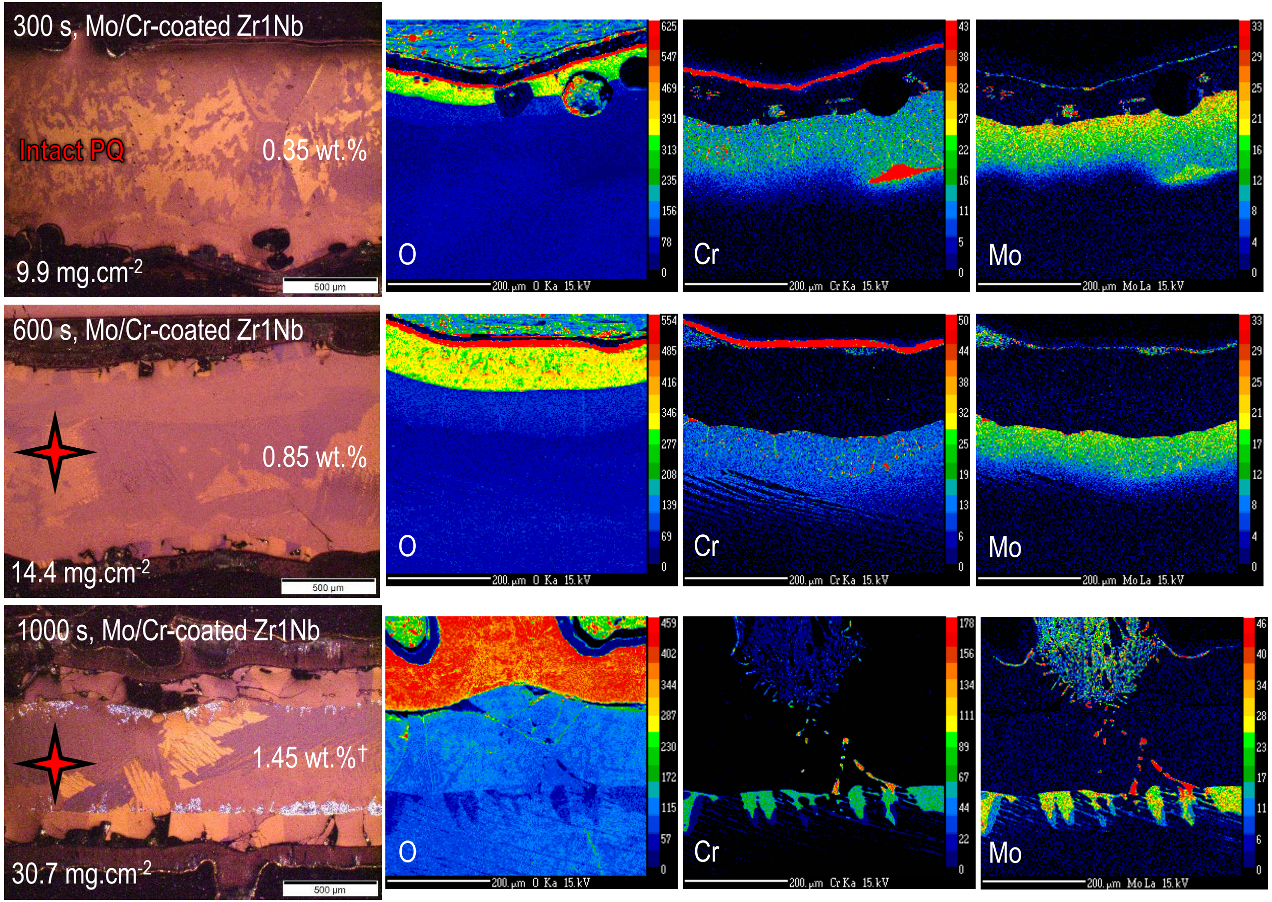
→ Better resistance of Mo/Cr at higher temperatures which delays the Cr-Zr eutectic reaction
→ Decreases the O ingress in β-Zr and may induce a better PQ residual strength,ductility and toughness



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 α-Zr(O)
  - Only Cr_2O_3 left, no residual metallic layers
- 600 and 1000 s
  - Partial loss of integrity
  - Larger ZrO_2 and α-Zr(O) areas

✦ Quench cracking initiated at pre-existing stress concentrations



† [O] in β_{Zr} (+potential α_{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…)

Thank you for your attention !

Do you have any questions?

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