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Contributions of thermodynamic calculations to the understanding of microstructural evolutions of E-ATF Cr coated Zr-based nuclear fuel claddings upon high temperature transients

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Context

«Enhanced Accident Tolerant Fuel» (E-ATF) claddings must be able to:

- delay the High Temperature (HT) steam oxidation kinetics
- decrease the hydrogen production (explosion risk)
- improve the resultant Post-Quenching (PQ) cladding strength and ductility upon and following hypothetical accident conditions such as Loss-of-Coolant-Accident (LOCA) (Fig.1).

Among them, Cr-coated Zr based alloys are very promising (Fig.2) [1,2].

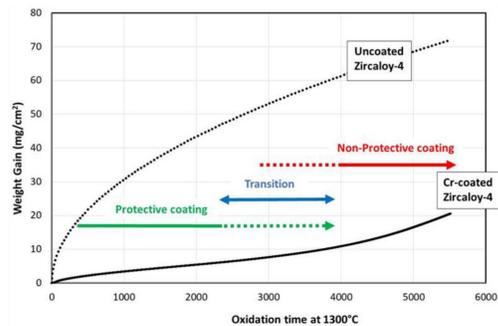


Fig 2. Comparison between the measured weight gain evolutions of uncoated and Cr-coated Zircaloy-4 upon steam oxidation at 1300°C [2].

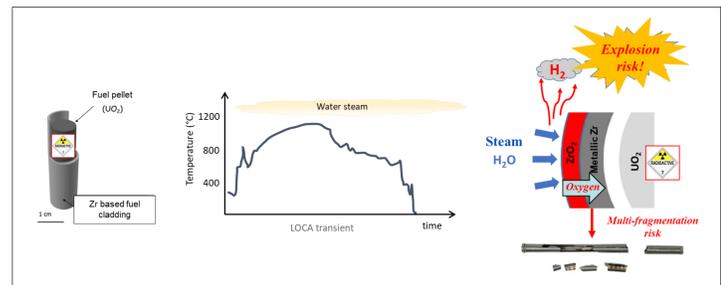


Fig 1. Uncoated cladding behavior during LOCA transient.

Furthermore, a new thermodynamic database for Zr alloys, containing Nb, Sn, Fe, Cr, O and H, has been developed by the CALPHAD method including a systematic use of DFT calculations and experiments [3]. The final database contains 19 binary systems and 18 ternary systems (see T.-M. VU presentation– O72 at this conference).

Interface structure of as-received Cr-coated Zy-4 material

On a first generation-coated Zircaloy-4 sample with a few micrometers thick Cr outer layer [4], the interface exhibits nanometer-thick Zr(Fe,Cr)₂ Laves phases, with both C14 and C15 structures.

The calculated pseudo-binary Zy-4–Cr phase diagram, (Fig.3) shows the successive presence of C14 and C15 Laves phases with the increase of Cr.

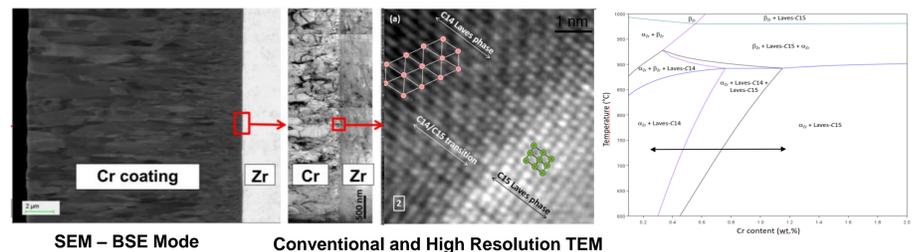


Fig 3. Images obtained along the Zy-4/Cr interfacial region at different scales and Pseudo-binary Zy-4–Cr phase diagram calculated with fixed Sn(1.4 wt.%), Fe (0.2 wt.%) and oxygen (0.13 wt.%) respective contents.

Microstructural evolutions during steam oxidation at 1200°C

Beginning of oxidation : Protective coating (Fig.4)

Three outer layers can be distinguished:

- ① A dense outer Cr₂O₃ layer
- ② A sub-oxide residual metallic chromium layer
- ③ A continuous Zr(Fe,Cr)₂ micrometer thick layer at Cr/prior-β_{Zr} interface due to the interdiffusion between Zr substrate and Cr

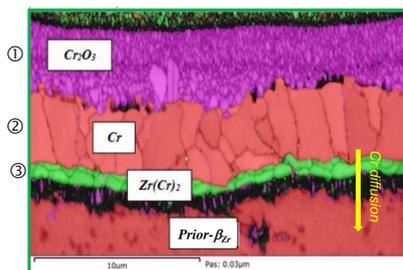


Fig 4. Post-Quench typical microstructure of Cr coated Zr1Nb(O) alloy after steam oxidation for 1500s at 1200°C

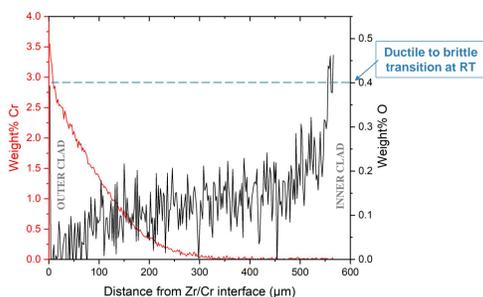


Fig 5. O and Cr diffusion profiles measured by EPMA on 12-15µm Cr-coated Zr1Nb(O) after steam oxidation 1500s at 1200°C

Cr and O contents, measured by EPMA in prior-β_{Zr} metallic substrate, show Cr diffusion profile and no significant O diffusion, except a slight increase in inner clad region (Fig.5). According to thermodynamic calculations (Fig.6), O solubility in β_{Zr} drastically decreases with an increase in Cr content : this would explain the lower oxygen content measured by EPMA in the Cr-enriched prior-β_{Zr} substrate, following HT incursion and oxidation.

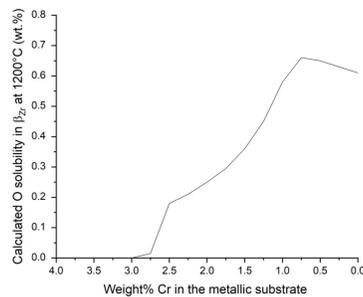


Fig 6. Calculated O solubility in β_{2x} at 1200°C in a Zr1Nb(O) alloy as a function of Cr content.

Transition between protective and non-protective coating (Fig.7)

At this stage, O reacting with the Cr-coated material diffuses deeper into the material and reaches the Zr/Cr interface, via Cr grain boundaries. This is highlighted by :

- Thinning of the Zr(Fe,Cr)₂ interlayer associated with the appearance of a Cr + ZrO₂ layer
- Growth of α_{Zr}(O) enriched in O in the substrate

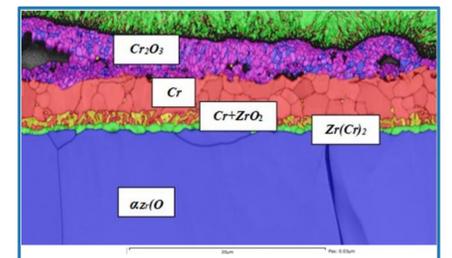


Fig 7. Post-Quench typical microstructure of Cr coated Zr1Nb(O) alloy after steam oxidation for 3000s at 1200°C

Non protective coating (Fig.8)

Cr coating is not protective anymore :

- Cr₂O₃ layer heavily damaged : not protective anymore
- Intergranular ZrO₂ network in Cr layer : O diffuses via this path
- Transformation of the Zr(Fe,Cr)₂ layer into a mixture of Cr + ZrO₂
- Growth of a thick sub-coating zirconia layer

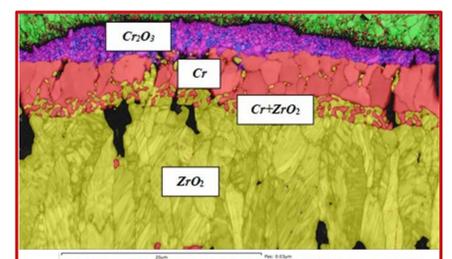


Fig 8. Post-Quench typical microstructure of Cr coated Zr1Nb(O) alloy after steam oxidation for 6000s at 1200°C

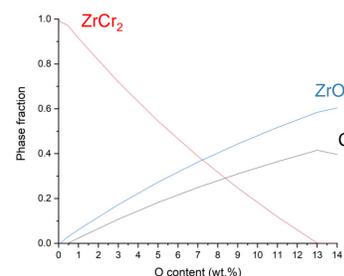
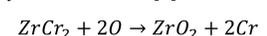


Fig 9. Simulation of ZrCr₂ transformation upon oxidation at 1200°C

Thermodynamic simulation of the oxidation of the ZrCr₂ C15_Laves phase at 1200°C, as shown in Fig.9, is in good agreement with the reaction displayed by Brachet et al. [2] :



explaining the disappearance of the ZrCr₂ layer

Conclusion

This poster aims at showing how the development of a multi-elements thermodynamic database for Zr based alloys can be helpful to anticipate and interpret the quite complex microstructural and microchemical phenomena occurring in E-ATF Cr-coated Zr based nuclear fuel claddings upon High Temperature (LOCA) transients (in steam environment).

To support the whole HT oxidation mechanisms and associated phase transformation kinetics, next step will consist in introducing thermal diffusion modelling.

[1] J.-C. Brachet et al., "Early studies on Cr-Coated Zircaloy-4 as E-ATF Nuclear Fuel Claddings for LWRs", Journal of Nuclear Materials 517 (2019) 268-285
 [2] J.-C. Brachet et al., "High temperature steam oxidation of chromium-coated zirconium-based alloys: Kinetics and process", Corrosion Science Volume 167, 1 May 2020, 108537
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 [4] J. Ribis et al., "Atomic-scale interface structure of a Cr-coated Zircaloy-4 material", Journal of Materials Science 53:9879-9895