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BEHAVIOUR OF ION IRRADIATED CHROMIUM COATINGS ON ZIRCALOY-4 SUBSTRATE

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1 CEA Saclay DEN/ DMN/SRMA/LA2M
2 CEA Saclay DEN/ DMN/SRMP

NuMat 2016
Montpellier, FRANCE
7-10 November, 2016
Worldwide, several « Enhanced Accidental Tolerant Fuels » (EATF) concepts for LWRs are considered:

- CEA: Composite SiC/SiC « sandwich » concept with internal metallic liner
- CEA: Chromium coatings
- Mid-Term Technologies
  - High Performance UO2
  - Ceramic Claddings
  - High Density Fuels (U2Si3, UN, etc.)
  - Molybdenum Claddings
  - Near-Term Technologies
  - High Fission Product Retention

Scheme from DOE
Nominal conditions:

- **Very good corrosion resistance** at 360°C in pressurized water with PWR chemistry and at 415°C in steam (100 bars) > 200 days => formation of less than 0.1µm thick Cr$_2$O$_3$
- As previously shown by J. Bischoff et al previous talk, **negligible impact of the Cr coating on the as-received mechanical behavior** of Cr coated Zirc-4 and M5® claddings
PURPOSE OF THE PRESENT STUDY

A. Wu, NuMat 2016 (7-10 November) – Montpellier

- Behaviour of Cr coated Zr base claddings under irradiation?

  **Irradiated chromium:**
  - Hardening / Embrittlement?

  **Zr/Cr irradiated interface:**
  - Chemical stability?
  - Coherency? Crystallinity?
  - Intermetallics (ZrCr$_2$) formation at the Zr-Cr interface? & their stability upon irradiation?

  **Irradiated zirconium substrate:**
  - Is there any coating consumption due to accelerated diffusion of chromium within Zr substrate?
Purpose of the present study

- Behaviour of Cr coated Zr base claddings **under irradiation**?

**Irradiated chromium:**
- Hardening / Embrittlement?

**Zr/Cr irradiated interface:**
- Chemical stability?
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**Irradiated zirconium substrate:**
- Is there any coating consumption due to accelerated diffusion of chromium within Zr substrate?
Ion irradiations performed to get some fundamental insights on irradiation effects (and thus to anticipate neutron irradiation behavior).

Ex-situ irradiation (Jannus Saclay)

- **Bulk material**
- **Ions Kr\(^{8+}\)**
- **Energy** 20 MeV
- **Irradiation temperature** 400°C
- Average flux \(2,8 \times 10^{11} \text{ ion.cm}^{-2}.\text{s}^{-1}\)
- ~6 hours irradiation
- Dose \(5,97 \times 10^{15} \text{ ions.cm}^{-2}\)
- Damage at the interface: ~10 dpa
For the purpose of this comprehensive study, different as-received coating microstructures produced/studied (different thicknesses, grain sizes...)

Typical chromium grains morphologies studied:

- No microcracks, no voids at the interface
- Fully dense coatings, very good chromium / zirconium bonding

Transmission Electron Microscopy characterisations:
TEM observation of a FIB thin foil sample

Plasmons energy showing intermediate values at the interface?
High Resolution TEM (HRTEM) observation of a FIB thin foil sample

- Two intermetallic Laves phases Zr(Cr,(Fe))$_2$:
  - C14 (hcp) & C15 (bcc) evidenced at Zr-Cr interface
  - polytype structure of the Laves phases (interface) layers
HRTEM observation of a FIB thin foil sample

- Ledged interface between C14 - Zr(Fe,Cr)₂ and Cr
  => crystallographic continuity
- Coherency along [110]ₘ / [01\bar{1}1]₁₄
Semi-quantitative chemical profiles (EDSX) at the interface

Some Fe enrichment at the interface prior to irradiation
Evolution after irradiation?
Semi-quantitative chemical profiles (EDSX) at the interface

Ion irradiation up to ~10 dpa at the interface

Fe enrichment still present at the interface after irradiation
Semi-quantitative chemical profiles (EDSX) at the interface => Comparison before/after irradiation

Ion irradiation up to ~10 dpa at the interface

- No significant additional interdiffusion between Cr and Zr after irradiation: => Overall chemical stability of the interface
- No significant additional Fe enrichment at the interface but apparent %Fe increase in neighbouring Zr and Cr after irradiation
HRTEM observation of a FIB thin foil sample after irradiation

Ion irradiation up to ~10 dpa at the interface

Only C14 Laves phase observed (disappearance of the C15?)
Ternary phase diagram Zr, Cr, Fe
(400°C)

Possible explanation: Transformation of C15 Laves phase to C14 due to thermodynamic stabilizing effect of Fe

P. Lafaye, C. Toffolon (CEA)
HRTEM observation of a FIB thin foil sample after irradiation

Ion irradiation up to \( \sim 10 \text{ dpa} \) at the interface

- Only C14 Laves phase observed (disappearance of the C15?)
- Crystalline interfaces maintained after irradiation
- Coherency along some crystallographic directions \([10\bar{1}0]_\text{Zr} // [1\bar{2}10]_{\text{C14}}\)
Up to 10 dpa at the interface:
- Chemical stability of the overall Zr/Cr profil
- Crystalline interfaces maintained after irradiation
- Some Fe enrichment at the Zr-Cr interface before and after irradiation
- Potential stabilisation of the intermetallic phases C14 at the interface?

What happens if we increase the damage?
- In-situ irradiation (Jannus Orsay) up to 30 dpa at the interface
  - FIB thin foil sample
  - Ions Au^{2+}
  - Energy 4 MeV
  - Irradiation temperature 400°C
  - Average flux $2.8 \times 10^{11} \text{ ion.cm}^{-2}\text{s}^{-1}$
  - Total dose $6 \times 8.10^{14} \text{ ion.cm}^{-2}$
  - Dose totale
  - In Cr: ~ 21 dpa
  - In Zr: ~ 36 dpa
  - At the interface: ~ 30 dpa
In-situ characterisations: EDS before irradiation

On some very localized zone, apparent Fe enrichment into the Zircaloy-4 substrate just close to the Zr-Cr interface
In-situ characterisations: EDS during ion irradiation

Ion irradiation up to ~10 dpa at the interface
In-situ characterisations: EDS during ion irradiation

Ion irradiation up to ~15 dpa at the interface
In-situ characterisations: EDS during ion irradiation

Ion irradiation up to ~20 dpa at the interface

CHROMIUM/ZIRC-4 INTERFACE AFTER IRRADIATION
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In-situ characterisations: EDS during ion irradiation

Ion irradiation up to ~25 dpa at the interface

Stability of the Zr / Cr profiles after irradiation up to 25 dpa

Apparent additional Fe enrichment into the Zirc-4 substrate close to the interface when the irradiation dose increases (needs more statistics)
CONCLUSIONS

- Cr coated Zr-alloys are considered as potential EATF claddings for LWRs
- As received coatings show no cracking/voids at the interface
- First ion irradiation experiments performed (at 400°C)
- HRTEM and microchemical analyses focused on the Zr/Cr interface:

**Zr/Cr irradiated interface:**
- Chemical stability?
- Coherency? Crystallinity?
- Intermetallics (ZrCr₂) formation at the Zr-Cr interface? & their stability upon irradiation?

**Irradiated zirconium substrate:**
- Is there any coating consumption due to accelerated diffusion of chromium within Zr substrate?
- No evolution of the Cr/Zr profile → no accelerated interdiffusion of Cr↔Zr under ion irradiation at 400°C
- Crystallographic continuity at the interface maintained after irradiation (~10 dpa)
- C15 and C14 Zr(Fe,Cr)₂ intermetallic Laves phases and some Fe enrichment highlighted before/after irradiation

- No irradiation accelerated Cr coating consumption and Cr coating adhesion preserved after ion irradiation
In-situ (SEM) mechanical testing of unirradiated and irradiated coatings

No Cr coating delamination up to rupture

Study of the chromium hardening under irradiation  
(nanohardness measurements and scratch tests planned...)

Further (Longer Term) CEA-AREVA-EDF R&D on Cr coated Zr base claddings:

- Study of last generation Cr coated cladding tubes, including M5® substrate
- Neutron irradiation on-going or planned (Halden...)

ε=0%  ε=1%  ε=2.5%  ε=8%  ε=11%  ε=14%
THANK YOU FOR YOUR ATTENTION

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⇒ Likely from the Zircaloy-4 substrate (0.2 wt% Fe)

⇒ **Potential physical mechanisms:**

1) Fe is a fast interstitial-like diffusing elements in Zr

- IF: Local depletion of Fe in Zirc-4 close to Zr/Cr interface
- Chemical Fe gradient in Zirc-4
- Net diffusion flux of Fe atoms

2) Limited content of residual Fe in the Zirc-4 matrix solid-solution

- SPPs C14-Zr(Fe,Cr)$_2$ precipitates in the Zirc-4 partially dissolve and/or loose some Fe
- Diffusion of Fe at the interface

⇒ **Needs complementary experiments** to confirm and get a better understanding of this phenomena.
The potential negative impact of a pre-existing defect (i.e., as-received crack) within the Cr coating on the subsequent coated clad oxidation is an important issue:

⇒ Results obtained so far show only a limited and very localized impact of a pre-existing thru-wall Cr layer crack on the subsequent oxidation behavior for both nominal and accidental (LOCA) conditions (i.e., neither local accelerated corrosion, nor coating spallation)

⇒ However, further work is necessary: longer oxidation times...

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