OUT-OF-PILE R&D ON COATED NUCLEAR FUEL ZIRCONIUM BASED CLADDINGs FOR ENHANCED ACCIDENT TOLERANCE IN LWRS

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(**) now belonging to EDF R&D

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Objective of R&D on coatings in the framework of the French CEA-EDF-AREVA Collaborative Program: to protect the cladding against corrosion and reduce hydrogen uptake during normal operating and accidental conditions and then to provide additional margins on the nuclear fuel clad behavior in LWRs accidental conditions such as LOCA by decreasing the HT oxidation rate with steam at HT (and the associated heat production):

1. Increase resistance to HT oxidation:
   - Delay formation of brittle ZrO\textsubscript{2} & \(\alpha_{\text{Zr}}(\text{O})\)
   - Limit/delay gaseous H\textsubscript{2} production
   - Decrease Peak Cladding Temperature

2. Increase the quenching resistance

3. Increase PQ ductility/toughness (long term cooling)

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OUTLINE

(1) Early studies – scoping tests on different types of coatings including ceramic and metallic, mono or multilayered ones => chromium coatings have been selected as the most promising for next R&D steps

(2) Improvement of the HT oxidation resistance of Cr coatings (DBA-LOCA)

(3) Cr-coated Zr nuclear fuel clad behavior upon nominal conditions:
⇒ as-received microstructure/properties
⇒ corrosion resistance in PWR environment at 360°C & steam (100 bar) at 415°C

(4) Cr-coated Zr nuclear fuel clad behavior upon steam oxidation at 1200°C:
⇒ numerous tests performed so far
⇒ determination of the Cr-coating oxidation/consumption mechanism
⇒ quantification/modelisation of the overall coating consumption kinetics

(*) Remark: Additional studies/results for beyond LOCA conditions already published, including:
- "post-breakaway" conditions, i.e., oxidation at 1000°C up to > 4 hours;
- HT oxidation testing up to 1300°C, > 1 hour;
⇒ Assessment of the final quenching resistance and Post-Quenching (PQ) ductility...

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(1.1) EARLY STUDIES / SCOPING TESTS OF DIFFERENT TYPES OF COATINGS ON ZIRCALOY-4 SHEET SUBSTRATE

The different coatings studied (PVD - DC Magnetron sputtering):

<table>
<thead>
<tr>
<th>Coating type</th>
<th>notation</th>
<th>Architecture / period ((\lambda^*))</th>
<th>Period number</th>
<th>Total thickness ±0,2 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>TiN</td>
<td>Singlelayered</td>
<td></td>
<td>2,6</td>
</tr>
<tr>
<td>CrN</td>
<td>CrN</td>
<td>Singlelayered</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>TiN and AlTiN</td>
<td>TiN/AlTiN</td>
<td>Multilayered, (\lambda = 2 \times 8) nm</td>
<td>&gt;200</td>
<td>3,4</td>
</tr>
<tr>
<td>CrN and AlTiN</td>
<td>CrN/AlTiN</td>
<td>Multilayered, (\lambda = 2 \times 8) nm</td>
<td>&gt;200</td>
<td>3,2</td>
</tr>
<tr>
<td>Nb(<em>{82}%)V(</em>{18}%) (at%)</td>
<td>NbV</td>
<td>Singlelayered</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Nb(<em>{67}%)Cr(</em>{10}%)Ti(_{23}%) (at%)</td>
<td>NbCrTi</td>
<td>Singlelayered</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr</td>
<td>Singlelayered</td>
<td></td>
<td>1 and 5</td>
</tr>
<tr>
<td></td>
<td>Cr/Cr</td>
<td>Multipass, (\lambda = 500) nm</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>Cr and</td>
<td>Cr/NbCrTi</td>
<td>Multilayered, (\lambda = 2 \times 5) nm</td>
<td>&gt;500</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Cr/NbCrTi</td>
<td>Multilayered, (\lambda = 2 \times (50) to 80) nm</td>
<td>40</td>
<td>5,5</td>
</tr>
<tr>
<td></td>
<td>Cr/NbCrTi</td>
<td>Multilayered, (\lambda = 2 \times 300) nm</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Cr/NbCrTi</td>
<td>Multilayered, (\lambda = 2 \times 400) nm</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

* The period corresponds to the number of “layers”, i.e. 1 layer of Cr in the case of Cr/Cr coating and 2 successive layers of different materials for TiN/AlTiN, CrN/AlCrN and Cr/NbCrTi coatings

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(1.2) EARLY STUDIES / SCOPING TESTS OF DIFFERENT TYPES OF COATINGS ON ZIRCALOY-4 SHEET SUBSTRATE

Autoclave tests, 360°C, pressurized water, PWR chemistry (M. Tupin, P. Billaud et al., CEA):

- Poor behavior of TiN and NbV coatings
- Loss of weight gain observed for Al containing multilayered coatings, probably due to outward migration of aluminum and potential release in the pressurized water as observed by some other authors (Alat et al. – 2015, R. Van Nieuwenhove – this conference, etc...)
- Best behavior observed for CrN, Cr, Cr/Cr and multilayered Cr/NbCrTi coatings

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Coatings resistance to HT steam oxidation in DBA-LOCA conditions - Ex. = Steam oxidation for 850s at 1100°C (ECR measured - weight-gain ~10% for uncoated Zry-4 - one sided oxidation) + direct water quenching

Cr/Cr coatings show the best steam oxidation resistance at HT (for the conditions tested here) => has thus been selected for further evaluation (next slides)

Non protective:

Partially protective:

Protective:

Cr/Cr coatings show the best steam oxidation resistance at HT (for the conditions tested here) => has thus been selected for further evaluation (next slides)
(2.1) IMPROVEMENT OF THE HT OXIDATION RESISTANCE OF CR BASED COATINGS (DBA-LOCA):

1\textsuperscript{st} R&D step: improvement of the HT steam oxidation resistance of Cr-coated materials conducted on Zircaloy-4 sheet samples and focusing on DBA-LOCA conditions at first (i.e., max. PCT = 1200°C, max. ECR (BJ) = 17% => oxidation time <600s for one-sided oxidation)

One-sided steam oxidation at 1200°C for 300s (ECR (BJ) ~ 10%):

Reference uncoated Zircaloy-4
Weight Gain = 10.5 – 11.0 mg/cm\textsuperscript{2}

1\textsuperscript{st} generation of Cr-coated Zirc-4
Weight Gain = 1.5 – 2.0 mg/cm\textsuperscript{2}

Last generation of Cr-coated Zirc-4
Weight Gain = 0.4 – 0.9 mg/cm\textsuperscript{2}
(2.2) IMPROVEMENT OF THE HT OXIDATION RESISTANCE (DBA-LOCA)

2nd R&D step: Cr-coatings on tubular geometry
(One-sided steam oxidation at 1200°C for 300s - ECR (BJ) ~ 10%):

Uncoated-reference Zircaloy-4:

Weight-Gain ~ 11 mg/cm²

30 mm

ZrO₂

Zr-α(O)

Zy-4

100 μm

Cladding oxidation of coating due to peeling

Blistering of coating

Ni coating

Blistering

Peeling

Weight-Gain ~ 11 mg/cm²

45 mm

ZrO₂

Zr-α(O)

Zy-4

100 μm

Weight-Gain ~ 1-2 mg/cm²

45 mm

Ni coating

Blistering

Internal coating oxidation

Cr₂O₃

Cr

Zr-α(O)

Zy-4

50 μm

Last generation Cr-coated Zircaloy-4:

Weight-Gain < 1 mg/cm²

30 mm

Zy-4

50 μm

Cr₂O₃

Cr

ZrCr₂ layer

2 μm

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As-received μstructure:

- Thicknesses studied: 1–20μm

- Multi-scale characterization: Optical microscopy, XRD, SEM-EBSD, EPMA, TEM (High resolution mode) on thin foils (FIB)...

Last generation of Cr-coatings:

=> Dense coatings, with no cracks, good Zr-Cr bonding with no interfacial defects

Additionally, nano-hardness, scratch and preliminary fretting/wear tests have been done

=> Good adhesion properties and good resistance to fretting for as-received conditions
(3.2) (OUT-OF-PILE) NOMINAL BEHAVIOR OF (LAST GENERATION) CR-COATED ZR:

Corrosion properties

360°C PWR pressurized water

- Cr-coated samples exhibit significantly reduced weight gain in autoclave (1-3 mg/dm²) with very little variation with time
- No dissolution or delamination of Cr-coating observed
- No ZrO₂ «pockets» formed under the Cr-coating = coating is very protective

415°C pressurized steam (100 days)

Ni deposit (Sample prep)
ZrO₂
Cr₂O₃ layer ~100 nm
ZrO₂ layer ~10 µm
Uncoated Zy4
Cr-coated Zy4

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(3.3) HT STEAM OXIDATION BEHAVIOR CR-COATED ZR => CHROMIUM COATING EVOLUTION/CONSUMPTION KINETICS UNDER STEAM ENVIRONMENT AT HT:

**SEM-EBSD map in phase contrast imaging mode of Cr-coated Zircaloy-4 after steam oxidation for 300s at 1200°C (E. Rouesne, CEA):**

**Cr diffusion profiles into the prior-β substrate from Zr/Cr interface after oxidation at 1200°C:**

- D : thermal (volumic) diffusion coefficient in prior-β\(_{\text{Zr}}\), (from the litterature) = \(6.29 \times 10^{-4} \, \text{m}^2/\text{s} \) at 1200°C,
- \( C(x, t) \) is the Cr concentration diffusing into prior-β\(_{\text{Zr}}\) at distance x from Zr-Cr interface, and for diffusion time t,
- \( C_0 \) is the initial Cr concentration in the Zircaloy-4 substrate (~0.1 wt%)
- \( C_s \) the concentration at the Cr/Zr interface assuming local thermodynamic equilibrium

=> calculated thanks to CEA-"Zircobase" thermodynamic database => ~3 wt% at 1200°C (solubility limit of Cr in β\(_{\text{Zr}}\))

**1D diffusion calculation** performed (semi-infinite volume assumption):

\[
C(x, t) - C_s = (C_s - C_0)(1 - \text{erf}(x/(2\sqrt{Dt})))
\]
- D : thermal (volumic) diffusion coefficient in prior-β\(_{\text{Zr}}\), (from the litterature) = \(6.29 \times 10^{-4} \, \text{m}^2/\text{s} \) at 1200°C,
- \( C(x, t) \) is the Cr concentration diffusing into prior-β\(_{\text{Zr}}\) at distance x from Zr-Cr interface, and for diffusion time t,
- \( C_0 \) is the initial Cr concentration in the Zircaloy-4 substrate (~0.1 wt%)
- \( C_s \) the concentration at the Cr/Zr interface assuming local thermodynamic equilibrium

Dots: EPMA (D. Hamon, CEA);
Full lines: Cr diffusion profiles calculations

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Cr coating consumption mechanism during steam oxidation at HT

Two main contributions:

1. Growth/thickening of outer Cr$_2$O$_3$ scale;
2. Diffusion of Cr from the Zr/Cr interface into the prior-β substrate.

For coating thicknesses of at least a few micrometers and as far as DBA-LOCA oxidation times are considered, the two basic kinetics are parabolic:

\[ X_1(\mu m) = 0.094 \times t_{(s)}^{1/2} \]

\[ X_2(\mu m) = 0.091 \times t_{(s)}^{1/2} \]

Cr coating thickness consumption kinetics due to oxidation (outer Cr$_2$O$_3$ thickening) only:

Cr coating thickness consumption kinetics due to Cr diffusion into the prior-β only:

1200°C
(3.5) HT STEAM OXIDATION BEHAVIOR OF CR-COATED ZR:

Consistent with previously published results (J.C, Brachet et al., Fontevraud 8, 2014):

Ex.: One-sided steam oxidation for 6000s at 1200°C (beyond DBA-LOCA conditions):

\[ X_{\text{tot}}^{(\mu m)} = 0.185 \times t_s^{1/2} \]

Overall Cr coating consumption due to steam oxidation at 1200°C

(a) Uncoated Zircaloy-4 clad segment, weight gain = 40.4 mg/cm²

(b) Coated Zircaloy-4 clad segment, weight gain = 11.4 mg/cm²

PQ Zircaloy-4 clad segments appearance after steam oxidation for 6000 s at 1200°C

Sample preparation => outer Ni layer deposition

Prior β + α(O)

α(O)

ZrO₂
CONCLUSION, ON-GOING AND FURTHER WORK:

- In the framework of the French CEA-EDF-AREVA Collaborative Program, zirconium based coated claddings are developed as potential Enhanced Accident Tolerant Fuels (EATF) materials for LWRs applications:

  => **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**

- From the early scoping tests performed on different types of coatings (including metallic, ceramics, multi-layered...), chromium coatings have been selected and further improvement of its HT oxidation resistance has been conducted;

- Last generation of chromium coated zirconium based nuclear fuel clad behavior shows:
  1. **very good nominal corrosion resistance** *(PWR environment at 360°C & steam at 415°C)*
  2. **attractive HT steam oxidation resistance** for DBA-LOCA and beyond (up to 1300°C);

  => for prototypical DBA-LOCA oxidation times, Cr-coating coating consumption mechanism and kinetics established at 1200°C *(can be extended at other oxidation temperatures)*;

- **Ballooning & burst tests under internal pressure at HT (LOCA) are on-going showing encouraging behavior** *(protective effect maintained, no peeling ... cf. Topfuel 2016)*

- **Ions and neutron irradiation experiments are on-going/planned** *(cf. poster A. Wu - this conference, Halden-IFA-796 project...)*
THANK YOU
FOR YOUR ATTENTION

Some CEA references:


Additional/back slides
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...

(a) After autoclave tests for 60 days at 360°C  
(b) After re-oxidation for 850 s at 1100°C
HT BEHAVIOR IN STEAM - DBA-LOCA TEMPERATURE RANGE — 1-SIDED OXIDATION KINETICS

1200°C

(a) Uncoated Zirc-4 after steam oxidation for 300s at 1200°C

(b) Cr coated Zirc-4 after steam oxidation for 300s at 1200°C

\[ \alpha_{Zr}(O) \sim 60 \mu m \]

\[ ZrO_2 \sim 55 \mu m \]

\[ \text{Cr}_2\text{O}_3 \sim 3 \mu m \]

Non oxidized residual Cr metallic layer

20µm

Prior-\( \beta \)\textsubscript{Zr}

20µm

Reproducible results

Uncoated Zirc-4 cladding

Cr coated (sheets) Zr samples

Weight Gain (mg/cm\textsuperscript{2})

Steam oxidation times (s) at 1200°C

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HT BEHAVIOR IN STEAM - DBA-LOCA TEMPERATURE RANGE
- POST-QUENCHING (PQ) MECHANICAL PROPERTIES
- 1000°C FOR « POST-BREAKAWAY » 1-SIDED OXIDATION TIME = 15000s

Ring Compression Test at 135°C:

Cr coated Zirc-4

Cr coated Zirc-4

Uncoated Zirc-4

Uncoated Zirc-4

(4-a) Cr coated clad (*)
(4-b) Uncoated clad (*)
(4-c) As-received uncoated materials

[H] < 100wt.ppm
[H] ~2000wt.ppm

(*) reference:
Expected additional HT steam oxidation time/temperature margins for ~5-20µm thick optimized Cr coated Zirc-4 claddings vs. current DBA-LOCA limits

**Remark:** of course, additional « grace time-temperature » which can be achieved depends on the initial Cr coating thickness.
Uncoated Zirc-4 sheet specimen

=> Weight Gain = 76.4 mg/cm²

Cr coated Zirc-4 sheet specimen

Weight Gain = 21.2 mg/cm²

1300°C, oxidation time = 5400s