In-situ Irradiation Accelerated Oxidation of Zircaloy-4 Under Proton or Electron Irradiation in PWR Primary Water

P. Wang¹, K. Kanjana², K. Gutsol², D. Bartels², G. S. Was¹

¹ University of Michigan
² University of Notre Dame

Supported by
DOE-NEUP (DE-AC07-05ID14517)
CASL (DE-AC05-00OR22725)
EnvDeg2015

August 13, 2015 – Ottawa, Ontario, Canada
Motivation and Objective

• Motivations
  – Corrosion environment in PWR primary loop
    • High temperature
    • Chemically aggressive coolant
    • Radiation field
  – Fundamental understanding of the mechanisms behind Irradiation Accelerated Corrosion (IAC) is absent

• Objective
  – Isolate the processes that contributed to IAC
  – Determine the mechanism responsible for each process
Previous Studies on IAC of Zirconium Alloys During Reactor Exposures

Asher et al., JNM, 49 (1973), pp189
Garzarolli et al., ASTM STP 1295, 1996, pp850
Previous Studies on IAC of Zirconium Alloys, Cont.

- Post-irradiation corrosion test (no significant effects on corrosion)

Electron irradiated Zry-2, exposed in 300°C D₂O. (Woo et al. 2000)

Neutron irradiated Zry-4, exposed in 316°C water (Cheng et al. 1994)

- Sustained defect damage
- Radiolysis of water

Woo et al., ASTM STP1354 (2000), pp709
Cheng et al., ASTM STP1245 (1994), pp400
Sample Design Challenges

– Sample requirements:

• Allowing protons/electrons to fully penetrate through its thickness
• Acting as a pressure barrier between 13 MPa water pressure and $10^{-8}$ torr ($1.3 \times 10^{-12}$ MPa) of vacuum at 320°C

SRIM Cal., 3.2 MeV $p^+$
$E_d(Z) = 40$ eV

Raiman et al., JNM 451(2014), p40
Sample Design at Univ. of Michigan
Experimental Setup at Univ. of Michigan

Water Inlet

1.7 MV Tandem Accelerator at Michigan Ion Beam Laboratory

3.2 MeV Proton
Experimental Setup at Univ. of Notre Dame

3 MeV Van de Graaff electron accelerator at Notre Dame Radiation Laboratory

Effect of excitons and radiolysis
Energy Transfer and Displacement Energy

3.2 MeV Protons

- Max. energy transferred to Zr and O atoms at a particle energy of ~1 MeV

1.5 MeV Electrons

- Same interfacial energy ~ 1 MeV
- Protons: \( T^{Zr} \), \( E_d^{Zr} = 40 \text{ eV} \)
- Electrons: \( T^O \), \( E_d^O = 28 \text{ eV} \)

<table>
<thead>
<tr>
<th></th>
<th>Protons</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 MeV Protons</td>
<td>43,000 eV</td>
<td>24 eV</td>
</tr>
<tr>
<td>1.5 MeV Electrons</td>
<td>221,000 eV</td>
<td>136 eV</td>
</tr>
</tbody>
</table>
## Experiments

- **Alloy:** Zircaloy-4
- **Temperature:** 320°C (608°F)
- **Water Chemistry:** simulated primary water, deionized water with 3 wt.ppm dissolved hydrogen (without B and Li addition)
- **Pressure:** ~13 MPa (1900 psi)

### Table

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample Designation</th>
<th>Damage rate in metal (dpa/s)</th>
<th>Dose rate in water (kGy/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hr Proton Irradiation</td>
<td>UM24IR</td>
<td>$4.4 \times 10^{-7}$</td>
<td>~400</td>
</tr>
<tr>
<td></td>
<td>UM24UI</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24 hr Electron Irradiation</td>
<td>ND24IR</td>
<td>0</td>
<td>~400</td>
</tr>
<tr>
<td></td>
<td>ND24UI</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>53 days Autoclave Exposure</td>
<td>UM53UI</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Zry-4 24 hr Proton Irradiation – Oxide Thickness
(3ppm H₂, 320°C, DI Water, 4.4x10⁻⁷ dpa/s)
Zry-4 24 hr Electron Irradiation – Oxide Thickness 
(3ppm H₂, 320°C, DI Water)

Irradiated
(ND24IR)

Unirradiated
(ND24UI)

~270 nm

~250 nm

~270 nm
RAMAN Spectroscopy
633 nm wavelength laser, 50 mW, 500 s

Intensity, (arbitrary unit)

Raman shift, (cm$^{-1}$)

UM proton irrad.
UM non-irrad.
ND electron irrad.
ND non-irrad.
Comparing to “in-pile” and “out-of-pile” Corrosion Rate

- No apparent effect of radiolysis on corrosion

3.2-6.5 x 10^{-8} dpa/s [1-3]
4.4 x 10^{-7} dpa/s

- Corrosion rate is proportional to damage rate

[1] Iltis et al., JNM 224 (1995), pp121
[4] MATPRO, Allison et al., EGG-2720
Effect of radiolysis products on corrosion

SS316L

Zircaloy-4
Summary

• Proton irradiation enhanced corrosion rate by a factor of 10 due to displacement damage

• Radiolysis product has no apparent effect on the corrosion rate of zirconium (provided that the non-irradiated region of the irradiated sample was in contact with radiolyzed water)

• Oxide morphology differences

<table>
<thead>
<tr>
<th></th>
<th>Irrad. region</th>
<th>Non-irrad. region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Irrad.</td>
<td>Equiaxed m-ZrO$_2$</td>
<td>Columnar m-ZrO$_2$</td>
</tr>
<tr>
<td>Electron Irrad.</td>
<td>Columnar m-ZrO$_2$</td>
<td>Columnar m-ZrO$_2$</td>
</tr>
</tbody>
</table>