The Effect of Photon Irradiation on the Corrosion of Zirconium Alloys

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- The effect of \( \gamma \)-ray on corrosion of Zircaloy-4
  - Introduction
  - Experimental
  - Results: Microstructure characterization with ASTAR and TEM

- Conclusion
INTRODUCTION

SOURCES OF PHOTONS

- Various photon sources in nuclear power plants:
  
  - **Gamma rays** induced by prompt fission and nuclear decays
  - **UV light** induced by the decelerating electrons in water (Cerenkov effect)

Previous Results of UV Effect

- Effect of UV on Zr-alloy corrosion:
  - Open circuit potential of Zr alloy vary by a few tens of mV by the UV irradiation on the sample.
  - Corrosion characteristic of Zr alloy is changed by UV irradiation and it can be confirmed by In-situ electrochemical impedance spectroscopy.

Fig. Example of electrochemistry experiment results with UV irradiation [1]

**INTRODUCTION**

**PREVIOUS RESULTS OF GAMMA-RAY EFFECT**

- Effect of γ-ray on Zr-alloy corrosion:

  ![Graphs](image)

  **Fig.** Summary of the measured oxide thickness and ATR corrosion rate correlates with γ/n flux.

- Recent results show that the **weight gains from experimental data are significantly larger** than the predicted weight gains when the gamma/neutron ratio is larger.

- Potential effect of γ-rays on corrosion rate.

Part I: The effect of UV on corrosion of Zircaloy-4
**Part I: The effect of UV on corrosion of Zircaloy-4**

**MOTIVATION**

- Photo-electrochemical behavior from UV irradiation
  - When light of a suitable energy $h\nu$, is absorbed by the oxide film, electrons can be excited from occupied electric states into unoccupied ones:
    $$h\nu \rightarrow e^- + h^+$$
  - The other $\frac{1}{2}$ reaction can be with water to produce oxygen
    $$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

Our goals of this project:
- Study the effect
- Propose a mechanism to explain photon irradiation effect on corrosion rate of zirconium alloy in high temperature water condition

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**Diagram:**

- Anodic current
- Conduction band
- Electron-hole pair generation
- Electron-hole pair recombination
- Valence band
- Metal Zr
- ZrO$_2$
- Water
- Potential (eV)
Part I: The effect of UV on corrosion of Zircaloy-4

EXPERIMENTAL

- Experiment
  1) **Static autoclave** corrosion for 7 d
  2) **Flowing loop** corrosion for 7 d
- Temperature: **260 °C**

Table. Chemical composition of Zircaloy-4

<table>
<thead>
<tr>
<th>Element</th>
<th>Zr</th>
<th>Sn</th>
<th>Fe</th>
<th>Cr</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt.%)</td>
<td>Bal.</td>
<td>1.27</td>
<td>0.22</td>
<td>0.11</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Fig. Schematic of the circulation loop connected with the autoclave

Fig. Schematic of the autoclave with sapphire window for in-situ UV irradiation
**EXPERIMENTAL**

- **UV source with energy:** 1.9 – 5.0 eV. (250 – 650 nm)

![Graph showing UV source output with power density 8.62W/cm²](image)

Fig. UV source output with power density 8.62W/cm²
Part I: The effect of UV on corrosion of Zircaloy-4

SEM Analysis of Oxidized Surface

- Corrosion and exposure to the UV source for 7 days in **flowing autoclave**
SEM Analysis of Oxidized Surface

- Corrosion and exposure to the UV source for 7 days in **flowing autoclave**
- Deposits are present in the UV exposed central region of the sample.
- Deposits are distributed on the surface, their **distribution is homogeneous**.

![SEM images showing oxygen, iron, and zirconium distribution](image)

- Deposits are Fe-rich oxides particles
- No Fe oxide deposits were observed on the **back of the irradiated sample** or on the **sister sample** facing another sapphire window without UV source.
Part I: The effect of UV on corrosion of Zircaloy-4

**SEM Analysis of Oxidized Surface**

- Corrosion and exposure to the UV source for 7 days in static autoclave
Part I: The effect of UV on corrosion of Zircaloy-4

SEM Analysis of Oxidized Surface

- Corrosion and exposure to the UV source for 7 days in static autoclave

- Particles deposits are oxides rich in Fe and some Al is observed.
Part I: The effect of UV on corrosion of Zircaloy-4

TEM Analysis of Oxidized Zircaloy-4

- Cross-sectional analysis of oxidized Zircaloy-4 with UV irradiation:

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>38</td>
<td>45</td>
<td>4</td>
<td>5.8</td>
</tr>
<tr>
<td>Flowing</td>
<td>39.2</td>
<td>53.9</td>
<td>0.4</td>
<td>3.6</td>
</tr>
</tbody>
</table>

- After corrosion test in static autoclave, the dissolved Fe concentration is below 100 ppb (below ICP detection limit)

Table. Average elemental composition (at.%) for particle deposits formed after UV exposure
MECHANISM OF UV ON ZrO$_2$

- Photo-induced electrochemical process at ZrO$_2$ surface:
  - Photo-reduction of soluble cations (mostly Fe$^{2+}$)
  - Other $\frac{1}{2}$ cell reaction is still under investigation

1. UV irradiation
   - $E_g = 2 - 5$ eV
2. Electron-hole pair generation
3. Redox reactions
   - $Fe^{2+} + 2e^- \rightarrow Fe$
   - $3Fe + 2H_2O \rightarrow Fe_3O_4 + 3H_2$
   (Oxidation of Fe on the ZrO$_2$ surface)
4. Hypothesis: Oxide dissolution by holes
   - $ZrO_2 + 4h^+ \rightarrow Zr^{4+} + O_2$

Origin of CRUD?
Part II: The effect of γ-ray on corrosion of Zircaloy-4
Part II: The effect of γ-ray on corrosion of Zircaloy-4

EXPERIMENTAL

- Rapid Turnaround Experiments in collaboration with ORNL
- Zirconium oxide formation on Zircaloy-4 under three conditions:
  1) no irradiation
  2) γ irradiation (Average in-core gamma flux: $2.8 \times 10^{14} \text{ g/cm}^2/\text{s}$)
  3) γ + neutron (0.2 dpa; Neutron fluence of 127 days: $8.34 \times 10^{20} \text{n/cm}^2 (> 0.1 \text{ MeV})$
  \hspace{1cm} $9.64 \times 10^{21} \text{n/cm}^2$ (all energy))

→ 20 weeks in 290 °C water at 7 MPa with very low dissolved oxygen

This experiment: 3.5
Part II: The effect of γ-ray on corrosion of Zircaloy-4

**ASTAR RESULTS OF γ+N IRRADIATION**

- Zircaloy-4 coupons after 20 weeks of corrosion at 290 °C, γ + neutron irradiation

Fig. ASTAR measured phases and grains

Blue: Monoclinic ZrO₂, Green: Tetragonal ZrO₂, Orange: ZrO, Yellow: Zr matrix

**7.5 nm step size**

**3 nm step size**
Part II: The effect of γ-ray on corrosion of Zircaloy-4

**ASTAR RESULTS OF Γ IRRADIATION**

- Zircaloy-4 coupons after 20 weeks of corrosion at 290 °C, γ irradiation

Fig. ASTAR measured phases and grains
Blue: Monoclinic ZrO$_2$, Green: Tetragonal ZrO$_2$, Orange: ZrO, Yellow: Zr matrix
Part II: The effect of γ-ray on corrosion of Zircaloy-4

ASTAR RESULTS OF NO-IRRADIATION

- Zircaloy-4 coupons after 20 weeks of corrosion at 290 °C, No irradiation

Fig. ASTAR measured phases and grains
Blue: Monoclinic ZrO$_2$, Green: Tetragonal ZrO$_2$, Orange: ZrO, Yellow: Zr matrix

7.5 nm step size

3 nm step size
Part II: The effect of γ-ray on corrosion of Zircaloy-4

ASTAR ANALYSIS OF ZIRCALOY-4

The effect of γ-ray on corrosion of Zircaloy-4

Table. ASTAR results after corrosion with different irradiation conditions

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>Step size (nm)</th>
<th>Area (μm²)</th>
<th>Identified (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ + neutron</td>
<td>3</td>
<td>7.1</td>
<td>73.0</td>
</tr>
<tr>
<td>γ</td>
<td>3</td>
<td>2.3</td>
<td>63.7</td>
</tr>
<tr>
<td>None</td>
<td>3</td>
<td>4.8</td>
<td>76.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>Monoclinic ZrO₂ (%)</th>
<th>Tetragonal ZrO₂ (%)</th>
<th>m-ZrO₂ grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ + neutron</td>
<td>85.3</td>
<td>13.4</td>
<td>16.0</td>
</tr>
<tr>
<td>γ</td>
<td>87.5</td>
<td>12.2</td>
<td>15.2</td>
</tr>
<tr>
<td>None</td>
<td>91.9</td>
<td>8.0</td>
<td>14.6</td>
</tr>
</tbody>
</table>

- The monoclinic oxide grain size, tetragonal oxide fraction rank as follows:

\[
\text{neutron + γ} > \gamma\text{-only} > \text{non-irradiated.}
\]
Part II: The effect of γ-ray on corrosion of Zircaloy-4

**Pole Figures and Angle Distribution**

- Pole figures and the angle distribution of (10\(\overline{3}\)) m-ZrO\(_2\) and (0001) Zr measured with ASTAR

  - (10\(\overline{3}\)) m-ZrO\(_2\) oxide texture strength and m-ZrO\(_2\) twin boundaries density rank as follows:
    
    neutron + γ > γ-only > non-irradiated
Part II: The effect of γ-ray on corrosion of Zircaloy-4

**MISORIENTATION OF m-ZrO$_2$ GRAINS**

Fig. Misorientation of m-ZrO$_2$ grains measured by ASTAR

- Higher twin boundary fraction may result in a lower corrosion rate due to reduced oxygen diffusion at triple point grain boundaries [1].

CONCLUSIONS

UV effect on corrosion:
1. In-situ UV irradiation at 260°C for 7 days under reducing conditions reveals that **UV irradiation induce the nucleation of Fe-rich oxide deposits** on the top of the zirconium oxide.
2. A **UV induced photocatalytic Fe deposition mechanism** is proposed to explain the above observations and **the potential effect of UV irradiation on in-reactor CRUD nucleation is discussed**.

Gamma-ray effect on corrosion:
1. The oxide grain size, tetragonal oxide fraction, $(10\bar{3})$ m-ZrO$_2$ oxide texture strength and m-ZrO$_2$ twin boundaries density rank as follows: neutron + $\gamma$ > $\gamma$-only > non-irradiated.
2. The above results tend to indicate that, **at low dpa (0.2 dpa) neutron + $\gamma$ irradiation sample has a more protective oxide** than $\gamma$-only sample, which has a more protective oxide than non-irradiated.
THANK YOU
ACKNOWLEDGEMENT

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## Table. Oxide thickness after UV exposure in static and flowing conditions with the standard deviation.

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Static</th>
<th>Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Exposure</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>355±35</td>
<td>259±23</td>
</tr>
</tbody>
</table>
Supplementary Information

- FIB sample liftout
  - liquid nitrogen cryostage on FEI Quanta.
- ASTAR (Nanobeam electron diffraction)
  - TEM: FEI TF30, 300 kV
  - ASTAR: NanoMEGAS
  - Step size: 3 nm
  - Precession: 0.4°
  - Spot size: 7
  - Camera length: 170 mm
  - Exposure time: 10 ms
  - Template excitation error: 0.8
  - Phase reliability threshold: 10
  - Grain orientation threshold: 5°
Table. Number average of oxide grain diameter and aspect ratio measured with ASTAR

<table>
<thead>
<tr>
<th>Irradiation</th>
<th>Step size (nm)</th>
<th>Monoclinic ZrO₂</th>
<th>Tetragonal ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diameter (nm)</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>γ + neutron</td>
<td>3</td>
<td>16.0 ± 0.3</td>
<td>0.514 ± 0.002</td>
</tr>
<tr>
<td>γ</td>
<td>3</td>
<td>15.2 ± 0.3</td>
<td>0.509 ± 0.003</td>
</tr>
<tr>
<td>None</td>
<td>3</td>
<td>14.6 ± 0.2</td>
<td>0.499 ± 0.002</td>
</tr>
</tbody>
</table>
### Supplementary Information

Table. Report of neutron/γ irradiation effect to ZrO$_2$ phase formed during corrosion

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Irradiation</th>
<th>Fluence (n/cm$^2$ or g/cm$^2$, or dpa)</th>
<th>t-ZrO$_2$ fraction (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Neutron: 8.34×10$^{20}$ (&gt; 0.1 MeV), γ: 3.1×10$^{21}$</td>
<td>8.0</td>
<td>This work</td>
</tr>
<tr>
<td>296</td>
<td>Neutron + γ</td>
<td>Neutron: 8.34×10$^{20}$ (&gt; 0.1 MeV), γ: 3.1×10$^{21}$</td>
<td>8.0</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Neutron</td>
<td>4.35×10$^{21}$ (&gt; 1 MeV)</td>
<td>less</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Neutron</td>
<td>1-2 dpa</td>
<td>more</td>
<td>[2]</td>
</tr>
<tr>
<td>310</td>
<td>Neutron</td>
<td>4.35×10$^{21}$ (&gt; 1 MeV)</td>
<td>less</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>Neutron</td>
<td>1-2 dpa</td>
<td>more</td>
<td>[2]</td>
</tr>
</tbody>
</table>