MICROSTRUCTURE EVOLUTION IN ION-IRRADIATED OXIDIZED ZIRCALOY-4 STUDIED WITH SYNCHROTRON RADIATION MICRO-DIFFRACTION AND TRANSMISSION ELECTRON MICROSCOPY

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BACKGROUND: STUDY OF IMPACT OF IRRADIATION ON ZIRCONIUM CLADDING

Out-of-pile Zircaloy-4 corrosion kinetics under isothermal conditions

PWR environment, including neutron irradiation, significantly increases the corrosion kinetics of Zircaloy-4 cladding

[Gilbon, Monographie DEN, 2008]
FACTORS IMPACTING CORROSION UNDER IRRADIATION

Several hypotheses have been advanced to explain the in-reactor acceleration of corrosion of Zircaloy-4.

- Hydride accumulation at the oxide/metal interface
  - Bossis, ASTM, 2005
  - Tupin, Corr. Sc., 2015

- Irradiation Effects
  - Garner, ANS LWR, 2007

- Influence of Sn

- Effect of Li in water

- Oxide irradiation

- Metal irradiation

- Radiolysis

- Radiation damage
  - Zu, Phil. Mag., 2012

- Precipitate Amorphization
  - Lefebvre, JNM, 1990

- Iron dissolution
  - Lefebvre, JNM, 1989
Irradiation effects have a strong impact on Zircaloy-4 corrosion.

It is important to separate the various effects of irradiation in order to understand their impact on the corrosion mechanisms.

**Impact of metal irradiation**
- **Objective**: Study the impact of ion-irradiation induced damage of the *metal matrix* on corrosion kinetics.
  - What is the radiation damage induced by ion-irradiation of the metal matrix?
  - How are the corrosion kinetics affected by metal matrix irradiation?
  - What is the microstructure of the oxide layer formed on an irradiated matrix?

**Impact of oxide irradiation**
- **Objective**: Study the impact of ion-irradiation induced damage of the *oxide layer* on corrosion kinetics.
  - How is the oxide microstructure affected by ion-irradiation?
  - How does oxide irradiation affect the corrosion kinetics?
  - What is the microstructure of an oxide layer formed on an irradiated oxide layer?

How do metal irradiation and oxide irradiation compare in terms of oxide microstructure and corrosion kinetics?
**Corrosion experiments**
- Static 0.5 L autoclave
- 360°C, 187 bars
- PWR chemistry: 2 ppm [Li], 1000 ppm [B]

**Irradiation experiments**
- **JANNUS irradiation platform**

**Metal irradiation**
- 300 keV H⁺
- 350°C irr. T°C
- Fluence: $10^{18}$ ions/cm²
- Avg Flux: $8.10^{13}$ ions/cm²/s
- Max. damage: 4.9 dpa

**Oxide irradiation**
- 1.3 MeV He⁺
- 20°C irr. T°C
- Fluence: $10^{17}$ ions/cm²
- Avg Flux: $8.10^{12}$ ions/cm²/s
- Max. damage: 0.35 dpa
EXPERIMENTAL TECHNIQUE: SYNCHROTRON MICRO-DIFFRACTION AND FLUORESCENCE

Advanced Photon Source Synchrotron, ANL, USA - 2-ID-D Beamline

Evolution across oxide thickness of:
- **Peak intensity:** tetragonal phase fraction, texture
- **Peak position:** oxide elastic strain, stoichiometry
- **Peak FWHM:** oxide grain size

3D Map of a line scan

XRD pattern of one point

Fluorescence detector

X-ray beam

Epoxy

Oxide

Metal

CCD Camera

Diffraction rings

Integration

Fluorescence spectrum

[Yilmazbayhan, JNM, 2004]
IMPACT OF METAL IRRADIATION ON CORROSION BEHAVIOR
Zircaloy-4 Unirradiated metal

- Formation of <a>-loops. No <c>-loops observed.
- No amorphization of the intermetallic precipitates

Zircaloy-4 Irradiated metal

300 keV protons at 350°C. 4.6 dpa peak damage
Irradiation of the metal matrix leads to an early acceleration of corrosion.

Transition occurs sooner in irradiated sample but at a similar oxide thickness.

Post-transition corrosion rate slightly higher for the irradiated sample.
IMPACT OF METAL IRRADIATION ON OXIDE MICROSTRUCTURE - TEM OBSERVATIONS OF OXIDE LAYERS (1/2)

Zircaloy-4 Unirradiated sample

Corrosion: 30 days
Oxide thickness: 1.2 µm

Many cracks are observed in the oxide layer grown on an irradiated metal matrix.

Zircaloy-4 Oxide grown on irradiated metal

Corrosion: 14 days
Oxide thickness: 1.5 µm

300 keV protons at 350°C. $10^{18}$/cm² fluence. 4.6 dpa.

30 days
Oxide thickness: 1.2 µm

14 days
Oxide thickness: 1.5 µm
Zircaloy-4 Unirradiated sample
Corrosion: 30 days
Oxide thickness: 1.2 µm

Zircaloy-4 Oxide grown on irradiated metal
Corrosion: 14 days
Oxide thickness: 1.5 µm

- Observation of nano-sized pores ~100 nm below the oxide surface in the irradiated sample.

300 keV protons at 350°C. 10^{18} /cm² fluence. 4.6 dpa.
IMPACT OF METAL IRRADIATION ON OXIDE MICROSTRUCTURE – XRD PATTERN

XRD patterns close to oxide/metal interface

- Unirradiated
- Irradiation of metal matrix

Integrated intensity (a. u.) vs. D-spacing (Å)

- α-Zr (101)
- M (020)
- α-Zr (002)
- M (200)
- T (002)
- α-Zr (100)
- M (111)
- T (101)
- M (-111)
EFFECT OF METAL IRRADIATION ON OXIDE MICROSTRUCTURE – TETRAGONAL FRACTION (1/2)

Zircaloy-4 Unirradiated – 50 days – 1.4 µm oxide layer

- Increase of the tetragonal phase fraction across the oxide layer
- Average tetragonal fraction ~ 27%
• Uneven variations of tetragonal phase fraction across the oxide layer which could be linked to local damage values

• Average tetragonal phase fraction ~18 %

Metal irradiation seems to lower the tetragonal phase fraction
IMPACT OF METAL IRRADIATION ON OXIDE MICROSTRUCTURE – OXIDE D-SPACING

Unirradiated sample

Metal matrix irradiation

Unstressed

T(101)

M(111)

M(-111)
The impact of metal irradiation on the corrosion kinetics and on the oxide microstructure have been studied in this first part. The main results are:

- **What is the irradiation damage induced by the ion-irradiation of the metal matrix**
  - With our irradiation conditions: formation of \(<a>-loops. No amorphization of the precipitates.

- **How are the corrosion kinetics affected by metal matrix irradiation?**
  - Increase of the corrosion kinetics for the irradiated sample. Transition occurs sooner but at the same oxide thickness.

- **What is the microstructure of an oxide layer formed on an irradiated matrix?**
  - Lower tetragonal phase fraction for the irradiated sample.
  - Lower d-spacing of the monoclinic phase: higher compressive stresses and/or stoichiometry variation.
  - Cracks observed in the oxide layer formed on the irradiated sample.

- **What does it mean in terms of corrosion mechanisms?**
  - If the oxide phase formed on irradiated metal is indeed more compressed: possible stabilization of O vacancies by the inner compressive stress?
  - Are we seeing stoichiometry variations in the irradiated sample (sub-oxide)?
IMPACT OF OXIDE IRRADIATION ON CORROSION BEHAVIOR
• Irradiation of the oxide layer induces an acceleration of corrosion.

• After 23 days of accelerated corrosion, the corrosion rate of the irradiated sample follows that of the unirradiated one.
IMPACT OF OXIDE IRRADIATION ON MICROSTRUCTURE – TEM RESULTS

- No major differences observed in irradiated oxide layer compared to unirradiated oxide layer
IMPACT OF OXIDE IRRADIATION ON MICROSTRUCTURE – TETRAGONAL FRACTION

Irradiated oxide

Re-oxidized irradiated oxide (1 day)

Avg. fraction ~18%

Avg. fraction ~23%
Irradiation of the oxide seems to release some of the compressive stresses in the monoclinic phase.
The impact of oxide irradiation on the corrosion kinetics and on the oxide microstructure have been studied in this second part. The main results are:

- **How is the oxide microstructure affected by oxide irradiation?**
  - No major differences observed in TEM.
  - The compressive stresses in the monoclinic phase are relaxed.
  - Lower tetragonal phase fraction.

- **How does oxide irradiation affect the corrosion kinetics?**
  - Increase of the corrosion kinetics for the irradiated sample.

- **What is the microstructure of an oxide layer formed on an irradiated oxide?**
  - Most of the studied parameters are situated in between the irradiated oxide and the unirradiated oxide even after 1 day of corrosion (tetragonal fraction, monoclinic compressive stress).

- **What does it mean in terms of corrosion mechanisms?**
  - The defects induced by irradiation of the oxide layer are likely small, point-defects.
  - These defects have a strong impact on the corrosion kinetics but not so much on the oxide microstructure.
The impact of irradiation on the corrosion kinetics and oxide microstructure have been studied using TEM and synchrotron micro-diffraction of ion-irradiated samples.

The effects of the irradiation of the metal matrix and of the oxide layer have been studied separately.

**Common observations between metal irradiation and oxide irradiation:**
- Ion-irradiation of the metal matrix and of the oxide layer both lead to an acceleration of the corrosion kinetics.
- Irradiation induces a decrease of the tetragonal phase fraction.

**Differences observed between metal irradiation and oxide irradiation**
- Oxide formed on irradiated metal is severely cracked and presents a lower d-spacing (compression and/or stoichiometry variations)
- Irradiation of the oxide releases some of the compressive stresses in the monoclinic phase. No differences are observed in TEM: defects formed are likely point-defects.

The impact of irradiation of the metal and of the oxide is different in terms of oxide microstructure but similar in terms of corrosion kinetics.
Additional investigations can be performed on the oxide layers formed on an irradiated metal matrix:

- Stress tensors can be derived from detailed refinement of μ-XRD data.
- Stoichiometry variations can be investigated (WDS, APT).

What happens when concurrent metal and oxide irradiation occur?

- Is there a synergistic effect?
- What is the impact of other parameters such as precipitate amorphization and dissolution?

What about post-transition oxide layers? How are they affected by irradiation?

Are the results observed on ion-irradiated samples transferable to neutron-irradiated samples?