Towards a mechanistic understanding of corrosion mechanisms in zirconium alloys

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Outline

◆ Why do we study corrosion mechanisms
◆ How do we study corrosion mechanisms
◆ Results and Discussion
◆ Conclusion and Future Work
Why do we study corrosion mechanisms
Why do we study corrosion mechanisms

- What causes transition
  - Does tetragonal to monoclinic phase transformation cause cracking that enhances transport mechanisms through the oxide

- How does alloy chemistry, microstructure affect time to transition
How do we study corrosion mechanisms

- **In-situ electrochemical impedance spectroscopy**
  - Oxide properties
- **Synchrotron x-ray diffraction (at ESRF and BESSY)**
  - Stress, oxide phase fractions, texture, in-situ
- **Raman spectroscopy**
  - Stress, oxide phase fractions
- **Transmission electron microscopy**
  - Oxide microstructure, nano porosity, m/o interface
- **3D atom probe**
  - Nano chemical analysis
Material

- Steam tested material (600 days @ 415°C):
  - Optimised-ZIRLO™ and Zircaloy-2

- Autoclave tested material (360°C, primary water chemistry)
  - Zircaloy-4 (two different manufacturers)
  - Optimised-ZIRLO™
  - ZIRLO™
  - X2
Results: Thick oxide grown at 415°C in steam

Optimized-ZIRLO™

Residual stresses in the monoclinic phase measured by synchrotron x-ray diffraction

- In-plane stress profile is not affected by metal substrate creep alone (creep according to M. Blat-Yrieix, Zr conference 2006)
- Other possible mechanisms: creep of oxide and local delamination of oxide layers
Thick oxide grown at 415°C in steam

Characterization of tetragonal phase fraction and monoclinic oxide texture by synchrotron x-ray diffraction – note stresses are from the monoclinic phase.
Pre-transition/transition/post-transition

- Water Chemistry: 360° C, 18 bar, primary water chemistry (pure H\textsubscript{2}O with additions of 2 ppm LiOH and 1000 ppm boric acid)

- Material tested:
  - sheet – ZIRLO\textsuperscript{TM} – RX
  - tube – ZIRLO\textsuperscript{TM} – RX
  - sheet – Zircaloy-4 – RX

- Samples show relatively similar corrosion behaviour
Residual Stresses

- **Sheet - Zircaloy-4 – RX**
- Oxide stresses relax during pre-transition – particularly in tetragonal
- Slight tensile stresses in the metal substrate
- Just before transition sudden increase of stress in monoclinic
- Tetragonal phase is destabilised and form highly stresses monoclinic grains
Nano pores – pre-transition – ZIRLO™ (RX)

overview

Linked pores at 500 nm from the m/o interface

Oxide growth direction

20 nm

Linked pores at 700 nm from the m/o interface

Oxide growth direction

50 nm

100 days exposure
Nano pores – pre-transition – ZIRLO™ (RX)

Linked pores at 350 nm from the m/o interface

Network of pores at 700 nm from the m/o interface

140 days exposure
ZrO at the metal/oxide interface – ZIRLO™ (RX)

- Isosurface of a constant concentration of oxygen
  - Red for 55 at.% oxygen and blue for 45 at.% oxygen

34 days (pre-transition)

100 days (pre-transition)

140 days (post-transition)
ZrO at the metal/oxide interface – ZIRLO™ (RX)

34 days (pre-transition)
ZrO at the metal/oxide interface – ZIRLO™ (RX)

100 days (pre-transition)
ZrO at the metal/oxide interface – ZIRLO™ (RX)

114 days (pre-transition)
ZrO at the metal/oxide interface – ZIRLO™ (RX)

140 days (post-transition)
Chemical segregation at the m/o interface

ZIRLO\textsuperscript{TM} (RX) after 100 days of exposure

pre-transition

- Corroding material differs significantly in its chemistry from base material
In-situ EIS study – properties of the oxide

Tube ZIRLO™ (RX) at 360° C primary water

Resistivity of outer oxide

\[ R_{s} = \text{solution resistance} \]
\[ R_{ol} = \text{outer layer oxide resistance} \]
\[ W_{ol} = \text{Warburg resistance due to diffusion of the outer layer} \]
\[ C_{ol} = \text{capacitance of outer layer} \]
\[ R_{bl} = \text{resistance of barrier layer} \]
\[ C_{PEbl} = \text{constant phase element of barrier layer due its capacitance} \]

Resistivity of outer oxide - Porosity
In-situ EIS study – properties of the oxide

Tube ZIRLO™ (RX) at 360°C primary water

Rs = solution resistance
Rol = outer layer oxide resistance
Wol = Warburg resistance due to diffusion of the outer layer
Col = capacitance of outer layer
Rbl = resistance of barrier layer
CPEbl = constant phase element of barrier layer due its capacitance

Resistivity of barrier oxide - Thickness

Diagram showing the graph with data points and the circuit diagram with labels.
Conclusions

- Stress profile cannot be explained by creep of the substrate only but indicates other stress relaxation mechanisms such delamination of the oxide layers and creep of the oxide.
- Stresses in the oxide changes during pre and post-transition. Stress evolution of both oxide phases suggest significant destabilisation of the tetragonal phase just before transition.
- TEM studies show that porosity aligned perpendicular to the metal/oxide interface increases around transition. In-situ EIS confirms increased porosity of the outer oxide towards transition.
Conclusions

- ZrO sub-oxide can be observed but changes dramatically with time as transition is approached. The oxygen level builds up in the metal substrate and is retained during transition. Therefore oxygen level during early post transition is very different from early pre-transition.

- Very high levels of Fe were found in the oxide and metal of ZIRLO\textsuperscript{TM} (RX). It seems that the actual metal substrate that corrodes is significantly different from base material.
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