Oxidation Mechanisms in Zircaloy-2 - The Effect of SPP Size Distribution

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Outline

• Introduction
  • Materials
  • Oxidation behavior
  • Questions
• Microstructure
  • Oxide
  • Metal
• Oxygen ingress
• Transition mechanism
• Conclusions
Materials

- Zircaloy-2

- SPPs: $\text{Zr(Fe,Cr)}_2$ and $\text{Zr}_2(\text{Fe,Ni})$

- Two commercial Zircaloy-2 alloys with different heat treatments:
  - Material A has more but smaller (22 nm) SPPs
  - Material B has fewer but larger (84 nm) SPPs

- Oxidized in static steam autoclave to obtain different oxide thicknesses.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Material A</th>
<th>Material B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn (%)</td>
<td>1.46</td>
<td>1.32</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>0.12</td>
<td>0.17</td>
</tr>
<tr>
<td>Cr (%)</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Ni (%)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Si (ppm)</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>O (ppm)</td>
<td>1240</td>
<td>1300</td>
</tr>
<tr>
<td>N (ppm)</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>SPP size</th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>Average SPP diameter (nm)</td>
<td>22</td>
<td>84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Material A</th>
<th>Material B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield stress (MPa)</td>
<td>215</td>
<td>180</td>
</tr>
<tr>
<td>Fracture stress (MPa)</td>
<td>351</td>
<td>320</td>
</tr>
</tbody>
</table>
The results from autoclave corrosion testing show that Material B has a better corrosion resistance than Material A.
Material B shows better corrosion resistance also in reactor.
Questions

• How can the oxidation process in Zircaloy-2 be understood in terms of microstructure and oxygen ingress in the metal/oxide interface region?

• Can any mechanisms be found explaining the relation between SPP size distribution and corrosion rate?

• Method: The metal/oxide interface region has been investigated using transmission electron microscopy (TEM) and atom probe tomography (APT).
Metal/oxide interface morphology (1)  
(BF TEM image)

Initial observations:
1. The interface is undulating/wavy.
2. There are lateral cracks in the oxide scale.
Columnar grains, \(\sim 20–30 \times 200\) nm.

Inward diffusion of oxygen faster in oxide grain boundaries than in bulk.
The undulating interface

- The metal/oxide interface is undulating on a micrometer scale.
- No obvious difference in period or amplitude was found between materials A and B.
  [Tejland et al. J. ASTM Int. 8 (2011)]
- A cyclic dependence on oxide thickness was found.
  [Tejland et al. J. Nucl. Mat. 430 (2012)]
- Parise et al. have shown by modeling that variations in diffusion rate in different oxide grain boundaries will give rise to the characteristic wavy interface.
  [Parise et al. J. Phys. IV France 9 (1999)]
Volume expansion upon oxidation

- The transformation from Zr to ZrO$_2$ has a volume expansion of 55% (Pilling-Bedworth ratio = 1.55), with 54% expansion in radial, 0.5% in axial and 0.5% in tangential direction. [Parise et al. 1998]

- This volume expansion causes stresses to be built up in the material as oxidation proceeds.
- Volume A-B is oxidized and expands 54% until C. At D no oxidation has occurred.
- For a stress free material, voids would have to form under wave crests.

However, no voids are created, the interface does not break.

- Instead, large tensile stresses are created at wave crests.
- At wave valleys, compressive stresses are created.
- Parallel to the interface, compressive stresses exist in the oxide and tensile stresses in the metal.

The stresses in the oxide lead to crack formation in the metal lead to creep deformation.
Oxide: Crack formation

The tensile stress in the oxide is a driving force for crack formation, but also an initiation site is needed. The following crack initiation is proposed:

Intermetallic second phase particles (SPPs) oxidize slower than the surrounding matrix => absent volume increase adjacent to SPPs.

The tensile stress above the particle can be relieved in two ways:

i) By forming a void above the particle.
ii) By forming a crack further up in the oxide.

[Tejland et al. J. ASTM Int. 8 (2011)]
Oxide: Voids and cracks

There are more lateral cracks in Material A (with more SPPs) than in Material B (with fewer SPPs).

BF TEM images of voids adjacent to SPPs.
Metal: Microstructure underneath the oxide scale

Evidence of plastic deformation:
Areas with high dislocation density

Oxide
Metal
Small hydrides

1 μm
Metal: Small hydrides

- Needle shaped streaks, most clearly visible using HAADF contrast but also using BF STEM.

- Shown by EELS to be hydrides (shift in the plasmon peak of about 2 eV).

However, it is important to notice that these hydrides are formed during cooling from autoclave temperature, and therefore not present during the oxidation process!
Metal: Creep deformation

- Evidence of heavy plastic deformation:
  - Areas of high dislocation density
  - Twinning
  - Sub-grain boundary formation

- A result of the high stress levels caused by oxidation.

- No apparent difference between Material A and B.
Sub-grain boundaries

- Decorated with Fe and Ni
- Inherited by the oxide
- APT reconstruction
These decorated sub-grain boundaries are important for hydrogen transport, but might also play a role in oxygen diffusion.

[Sundell, G. et al., Corr. Sci. 65 (2012)]
Microstructure – Summary
Correlation to SPP size distribution

• SPPs are initiation sites for crack formation
  => more SPPs lead to more cracking
• SPPs increase the strength of the material through particle hardening
  => less stress relaxation by plastic deformation
  => more stresses remaining in the material
  => more cracking
• The transition in corrosion kinetics is connected to this cracking of the oxide scale

Conclusion: Material B, with fewer (and larger) SPPs should exhibit the superior corrosion resistance.
Oxygen ingress

• Not a sharp step from the 67 at. % oxygen of ZrO₂ to 1 at. % in the metal.

• Using EDX in TEM, a suboxide with ~50 at. % (ZrO) was found, and in some cases also a step to ~30 at. %. The oxide is "pre-transition", 1 µm thick.
Oxygen ingress

- APT heat maps, red is max concentration and blue is min.
- All profiles from 1 µm thick oxide scales
- Varying thickness and morphology of the ~50 at.% oxygen suboxide layer
- Always a step to ~31 at.% oxygen. Higher than the oxygen solubility limit (28.6 at.%), an effect of deformation?
- Crystallographic dependence of oxygen diffusion in metal.
Oxygen ingress

Presence of grain boundary demonstrated by Fe segregation.
Oxygen ingress

- Uneven interface also on this scale
- Oxygen ingress appears to be crystallographic

Enhanced O ingress below the grain boundary

Blue areas contain >45% O
Oxygen ingress

The ZrO suboxide layer sometimes consists of a mixture of regions with different oxygen content. "Fingers" of high oxygen content (~60 at. %) with a diameter of approximately 5 nm penetrate ~50 nm into regions of lower oxygen content (~50 at. %).
Oxygen ingress

Red color: Metal with over 50 at. % zirconium.
Blue color: Oxide with over 56 at. % oxygen.
Investigation of 1 µm ”pre-transition” oxide scales shows a large variation in oxygen ingress into the metal.

A suboxide layer containing ~50 at. % oxygen exists in some cases, with varying thickness and morphology.

This finding suggests that the kinetic transition in this material might be a localized phenomenon.

Always a step to ~31 at. % oxygen followed by a diffusion profile of varying width.

31 > 28.6 at. %, which is the solubility limit for oxygen in zirconium. Due to the heavy plastic deformation?

No obvious difference in oxygen ingress between Material A and Material B.
Transition mechanism

- Zircaloy-2 does not exhibit the same cyclic oxidation behavior as other zirconium alloys.
- The material might still go through a transition but it seems to be more of a local phenomenon rather than an overall sudden change along the metal/oxide interface.
- APT investigations show varying oxygen gradients into the metal in samples with the same oxide thickness, “pre-transition”
- Transition is assisted by a weaker oxide scale and a harder metal matrix, as that kind of material will have an oxide that is easier to crack.
- This explains why a material with more but smaller SPPs will have a poorer corrosion resistance than one with fewer but larger SPPs.
Conclusions

• The transition in oxidation rate in Zircaloy-2 is a local phenomenon.

• A material with many small SPPs will have a weaker oxide scale and a harder metal matrix, both properties leading to a poorer corrosion resistance.

➤ Thank you!