Deviations from the parabolic kinetics during oxidation of zirconium alloys

Martin Steinbrück, Mirco Große
Karlsruhe Institute of Technology, Institute for Applied Materials, Germany

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Motivation

- Oxidation of zirconium alloy claddings during severe accidents causes degradation of cladding and loss of barrier effect as well as production of hydrogen and heat.

- Oxidation kinetics and corresponding hydrogen source term have to be known for appropriate accident management measures.

- At KIT extensive investigations on oxidation of zirconium alloys in various atmospheres have been performed in the framework of the QUENCH program including integral bundle tests and small-scale separate-effects experiments.
Motivation

Post-test appearance of Zry samples oxidized in various atmospheres

- 20min, 1200°C, steam
- 3min, 1600°C, steam
- 1.5h, 980°C, steam
- 1.5h, 1200°C, oxygen
- 3h, 1200°C, nitrogen
- 10min O₂, then 50min N₂, 1200°C
- α-Zr(O), 1h N₂, 1200°C
- 15min, 1200°C, air

Very complex reaction behavior depending on conditions (temperature, atmosphere)
Experimental

- Most tests were conducted in a NETZSCH STA409 coupled with steam injector and mass spectrometer; some in horizontal tube furnace with air lock.
- Typical temperature range: 600-1600°C.
- Zr alloys: Zry-4, Zry-2, Duplex DX-D4, M5®, E110, Zirlo™.
- Atmospheres: steam, oxygen, air, nitrogen, mixtures of these.
- Mostly isothermal tests, some transient experiments.
Oxidation in steam (oxygen)

Most LOCA and SFD codes use parabolic oxidation correlations, (i.e. \( n=1/2 \) in \( \Delta m / S = k_m \cdot t^n \))

1200 °C, quench

1600 °C, quench

\( \text{ZrO}_2 \)

\( \alpha\text{-Zr(O)} \)

prior \( \beta\text{-Zr} \)

\( \text{Zr(O)} \) precipitates \( \Rightarrow T>1500^\circ\text{C} \)
Oxidation in steam (oxygen)

- Deviations from parabolic kinetics at temperatures <1100°C

![Graph showing oxidation kinetics at 700°C](image)

- Sub-parabolic (cubic) kinetics

- Transition from (sub-) parabolic to linear kinetics after critical time / oxide thickness due to breakaway

- Similar kinetics of all alloys before transition, but strongly varying behavior at and after transition
Breakaway oxidation

- Loss of protective properties of oxide scale due to its mechanical failure.

- Breakaway is caused by phase transformation from meta-stable tetragonal to monoclinic oxide and corresponding change in density up to ca. 1050°C.

- Critical times and oxide thicknesses for breakaway strongly depend on type of alloy and boundary conditions (ca. 30 min at 1000°C and 8 h at 600°C).

- During breakaway significant amounts of hydrogen can be absorbed (>40 at.%, 7000 wppm) due to local enrichment of H₂ in pores and cracks near the metal/oxide interface ("hydrogen pump").
Transition times (h) and corresponding critical oxide scale thickness (µm) during oxidation in steam

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Zircaloy-4</th>
<th>Duplex-D4</th>
<th>Zirlo&lt;sup&gt;TM&lt;/sup&gt;</th>
<th>M5&lt;sup&gt;®&lt;/sup&gt;</th>
<th>E110</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>8.2 (7)</td>
<td>7.7 (3)</td>
<td>6.3 (8)</td>
<td>nt</td>
<td>nt</td>
</tr>
<tr>
<td>700</td>
<td>2.2 (9)</td>
<td>2.2 (9)</td>
<td>1.4 (9)</td>
<td>nt</td>
<td>13 (21)</td>
</tr>
<tr>
<td>800</td>
<td>7.4 (41)</td>
<td>7.3 (35)</td>
<td>5.2 (32)</td>
<td>nt</td>
<td>0.9 (12)</td>
</tr>
<tr>
<td>900</td>
<td>1.3 (40)</td>
<td>1.4 (38)</td>
<td>2.1 (40)</td>
<td>nt</td>
<td>0.8 (24)</td>
</tr>
<tr>
<td>1000</td>
<td>0.6 (89)</td>
<td>0.9 (105)</td>
<td>0.6 (76)</td>
<td>nt</td>
<td>0.6 (48)</td>
</tr>
<tr>
<td>≥1100</td>
<td>nt</td>
<td>nt</td>
<td>nt</td>
<td>nt</td>
<td>nt</td>
</tr>
</tbody>
</table>
Correlation of H absorption and oxide morphology

In-situ NR of H uptake during oxidation of Zry-4 at 1000°C in steam
Oxidation in atmospheres containing nitrogen

- Air ingress reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

Consequences:
- Significant heat release causing temperature runaway from lower temperatures than in steam
- Strong degradation of cladding causing early loss of barrier effect
- High oxygen activity influencing FP chemistry and transport
Oxidation of Zr alloys in N$_2$, O$_2$ and air

1200 °C

- Linear oxidation kinetics
- Parabolic oxidation kinetics
- Parabolic reaction kinetics

Oxidation rate in air is much higher than in oxygen or steam
Oxidation of Zr alloys in N$_2$, O$_2$ and air

[Graph showing weight change ($\Delta m, \%$) over time (s) for Nitrogen, Oxygen, and Air at 1200 °C, with images corresponding to 1 h, 1.5 h, and 3 h.]
Consequences of air ingress for cladding

1 hour at 1200°C in steam

1 hour at 1200°C in air

Loss of barrier effect of cladding
Mechanism of air oxidation

- Diffusion of air through imperfections in the oxide scale to the metal/oxide interface
- Consumption of oxygen
- Remaining nitrogen reacts with zirconium and forms ZrN
- ZrN is re-oxidized by fresh air with progressing reaction associated with a volume increase by 48%
- Formation of porous and non-protective oxide scales

1 – initially formed dense oxide ZrO₂
2 – porous oxide after oxidation of ZrN
3 – ZrO₂ / ZrN mixture
4 – α-Zr(O)
Reaction of ZrO$_x$ with nitrogen

1200°C

Oxygen load:
- 0% (β-Zr)
- 0.7% (β-Zr(O))
- 5.7% (α-Zr(O))
- 33.1% (substoich. ox.)
- 35% (stoichiometr. ox.)
Influence of pre-oxidation (PO) in steam on subsequent reaction in air and nitrogen

Example: Zry-4, 1200°C

Protective effect of PO on subsequent oxidation in air as long as oxide scale is intact

Accelerating effect of PO on subsequent reaction in nitrogen
Oxidation of Zr alloys in various atmospheres

1200°C

- Air
- H₂O
- O₂
- PO + Air
- α-Zr + N₂
- PO + N₂
- N₂

Δm, %

Time, s

1200°C
### Oxidation of Zr alloys in various atmospheres

<table>
<thead>
<tr>
<th>Reaction of Zry-4 in</th>
<th>Kinetic rate law</th>
<th>Relative reaction rate, a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>parabolic</td>
<td>1</td>
</tr>
<tr>
<td>( \text{N}_2 ) after pre-oxidation in ( \text{O}_2 )</td>
<td>linear</td>
<td>10</td>
</tr>
<tr>
<td>( \text{N}_2 ) with oxygen-stabilized ( \alpha)-Zr(O)</td>
<td>linear</td>
<td>70</td>
</tr>
<tr>
<td>( \text{O}_2, \text{H}_2\text{O} )</td>
<td>parabolic</td>
<td>100</td>
</tr>
<tr>
<td>Air after pre-oxidation in ( \text{O}_2 )</td>
<td>parabolic</td>
<td>100</td>
</tr>
<tr>
<td>Air</td>
<td>linear</td>
<td>150</td>
</tr>
</tbody>
</table>

* at 1200°C
Increasing degradation with raising content of air in the mixture
Oxidation in mixed atmospheres

1 hour at 1000 °C in steam

1 hour at 1000 °C in 50/50 steam/N₂

- Strong effect of nitrogen on oxidation and degradation
- Nitrogen acts like a catalyst (NOT like an inert gas)
- Enhanced hydrogen source term by oxidation in mixtures containing nitrogen
Conclusions

The usually applied parabolic oxidation kinetics are, strictly speaking, only valid at temperatures above 1000°C and for fast transients (with fast passing of the breakaway region).

Sub-parabolic kinetics is observed at temperatures below 1000°C.

Breakaway has to be taken into account for slow transients and long duration scenarios at medium temperatures (600-1000°C).

Nitrogen is not an inert gas under the conditions of a nuclear accident. It accelerates oxidation and causes rather linear kinetics.

Computer codes simulating severe accident scenarios should take into account non-parabolic oxidation kinetics. Various activities are ongoing worldwide.
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Phase diagram Zr - O

- Liquid
- L+β
- L+α
- L+cub. ZrO₂
- c=fcc
- t=fct
- m=mon.
- α+cub. ZrO₂-x
- α+tetr. ZrO₂-x
- α+mon. ZrO₂-x
- ZrO₂

Temperature in °C

ZrO₂

at.%O

wt.%O

L+cub. ZrO₂
Phase diagram Zr - O

- Liquid
- L+α
- L+β
- β+α
- α
- α+mon. ZrO$_2$$_{2-x}$
- α+tetr. ZrO$_2$$_{2-x}$
- α+cub. ZrO$_2$$_{2-x}$
- L+cub. ZrO$_2$
- ZrO$_2$ modif.:
  - c=fcc
  - t=fct
  - m=mon.

Temperature in °C

Zr and at.%O on the x-axis
Zr and wt.%O on the y-axis
Phase diagram Zr - H

Sievert's law:

$$\frac{H}{Zr} = k_S \cdot \sqrt{p_{H_2}}$$

with

$$k_S = A \cdot e^{\frac{-B}{RT}}$$
Reaction of $\alpha$-Zr(O) with nitrogen

$1200 \, ^\circ\text{C}, \, 6.5 \, \text{wt}\% \, \text{O}$