High-temperature oxidation and mutual interactions of materials during severe nuclear accidents

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Karlsruhe Institute of Technology

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= 9000 employees

= 23 000 students
Outline

- Phenomenology of severe accidents in light water reactors (LWR)
- High-temperature oxidation of zirconium alloys in various atmospheres
- Behavior of boron oxide control rods during severe accidents
- Silver-indium-cadmium control rod failure during severe accidents
LWR severe accident scenario

- Loss of coolant causes steady heatup of the core due to residual decay heat
- From ca. 1000°C oxidation of zirconium alloy cladding becomes significant
- From ca. 1250°C chemical interactions between the different core materials (stainless steel, Zr alloys, boron carbide ...) lead to the local formation of melts significantly below the melting temperatures of the materials
- From ca. 1800°C formation of melt pool in the core and relocation of melt/debris to the lower plenum (in-vessel, see TMI-2).
- Subsequently, failure of the RPV and release of corium melt into the containment (ex-vessel, see Fukushima)
Core materials in Light Water Reactors

- UO$_2$/(PuO$_2$) fuel: 100-200 t
- Zry cladding + grid spacers: 20-40 t
- Zry canister (BWR): 40 t
- Various steels, Inconel: >500 t (incl. RPV)
- B$_4$C absorber (BWR, VVER, ...): 0.3-2 t
- AgInCd absorber (PWR): 3-5 t

Environment

- Water, steam
- Air
- Nitrogen

After failure of RPV/primary circuit

PWR fuel assembly  BWR control blade
High-temperature oxidation of zirconium alloys

Most cladding alloys consist of 98-99 wt% zirconium plus some alloying elements (Sn, Nb, Fe, Cr, ...)

<table>
<thead>
<tr>
<th>Element</th>
<th>Zircaloy-4</th>
<th>D4</th>
<th>M5</th>
<th>E110</th>
<th>ZIRLO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sn</td>
<td>1.5</td>
<td>0.5</td>
<td>0.01</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2</td>
<td>0.5</td>
<td>0.05</td>
<td>0.008</td>
<td>0.11</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1</td>
<td>0.2</td>
<td>0.015</td>
<td>0.002</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

In steam, oxygen, nitrogen, air, and various mixtures

Temperature: 600-1600°C
Oxidation of zirconium alloys – chemical reactions

\[ \Delta H_f \text{ at } 1500 \text{ K} \]

\[ Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \]  
-585 kJ/mol

\[ Zr + O_2 \rightarrow ZrO_2 \]  
-1083 kJ/mol

\[ Zr + 0.5N_2 \rightarrow ZrN \]  
-361 kJ/mol

- Release of hydrogen and heat
- Hydrogen either released to the environment or absorbed by Zr metal
Hydrogen detonation in Fukushima Dai-ichi NPPs ...

... main hydrogen source: zirconium - steam reaction
Oxidation in steam (oxygen)

Most LOCA and SFD codes use parabolic oxidation correlations (determined by the diffusion of oxygen through growing oxide scale).

\[ d_{ZrO_2} = k_m(T) \cdot t^{0.5} \]

Oxide thickness during oxidation of Zry at 1200°C in steam

20 min at 1200°C in steam
Breakaway oxidation

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

- Breakaway is caused by phase transformation from pseudo-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 boundary (“hydrogen pump”).
In-situ investigation of hydrogen uptake during oxidation of Zry in steam by neutron radiography

Zry-4, 1000°C
30 g/h steam, 30 l/h argon

- Rapid initial hydrogen uptake
- Further strong hydrogen absorption after transition to breakaway
Oxidation in atmospheres containing nitrogen

- Air ingress into 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 N₂, O₂ 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 N₂, O₂ and air

Time, s

Δm, %

Air

Oxygen

Nitrogen

1200 °C

1 h

1.5 h

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 proceeding 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)
Oxidation in mixed steam-air atmospheres

Zry-4, 1 hour 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
QUENCH-16 bundle test with air ingress

Off-gas composition during the air ingress phase (after pre-oxidation in steam)

- Hydrogen and nitrogen release during quench phase
- Nitrogen consumption
- Oxygen starvation

ZrN formation at the end of air ingress phase

ZrN re-oxidation during quench phase
Absorber materials in LWRs

**Boron carbide**
- Used in boiling water reactors (BWR), VVERs, some pressurized water reactors (PWR)
- Control rods (PWR) or cross-shaped blades (BWR)
- Surrounded by stainless steel (cladding, blades) and Zry (guide tubes, canisters)

- **Zry guide tube** $T_{\text{melt}} = 1900^\circ\text{C}$
- **SS cladding** $T_{\text{melt}} = 1450^\circ\text{C}$
- **$B_4C$** $T_{\text{melt}} = 2450^\circ\text{C}$

**AgInCd alloy**
- Used in PWRs
- Surrounded by stainless steel cladding and Zry guide tubes
- Rods in Zry guide tubes combined in control rod assemblies

- **Zry guide tube** $T_{\text{melt}} = 1900^\circ\text{C}$
- **SS cladding** $T_{\text{melt}} = 1450^\circ\text{C}$
- **AgInCd** $T_{\text{melt}} = 800^\circ\text{C}$
Degradation of B$_4$C control rods (1-pellet)

Post-test appearance and axial cross section of B$_4$C/SS/Zry specimens after 1 hour isothermal tests at temperatures between 1000 and 1600 °C.
Degradation of $\text{B}_4\text{C}$ control blade (BWR bundle test)  
CORA-16

- Complete loss of absorber blade
- Dissolution of cladding and fuel
- Massive melt relocation ($\text{B}_4\text{C}$, SS, Zry, $\text{UO}_2$)
Eutectic interaction of stainless steel with $\text{B}_4\text{C}$

1 h at approx. 1250 °C

- 4 wt.% $\text{B}_4\text{C}$: Complete liquefaction of stainless steel
- 1 wt.% $\text{B}_4\text{C}$: 1/3 of SS liquefied
- 0.3 wt.% $\text{B}_4\text{C}$:
Eutectic interaction of stainless steel with $\text{B}_4\text{C}$

- Rapid and complete melting of SS at 1250°C starting at $\text{B}_4\text{C}/\text{SS}$ boundary
Oxidation of boron carbide; main chemical reactions

\[ B_4C + 8H_2O(g) \rightarrow 2B_2O_3(l) + CO_2(g) + 8H_2(g) \]  \(-760 \text{ kJ/mol}\)

\[ B_4C + 6H_2O(g) \rightarrow 2B_2O_3(l) + CH_4(g) + 4H_2(g) \]  \(-987 \text{ kJ/mol}\)

\[ B_2O_3 + H_2O(g) \rightarrow 2HBO_2(g) \]  \(+341 \text{ kJ/mol}\)

- Release of hydrogen, various carbon-containing gases and heat
- Formation of a superficial boron oxide layer and its vaporization
Oxidation kinetics of $\text{B}_4\text{C}$ in steam

Strongly dependant on $\text{B}_4\text{C}$ structure and thermo hydraulic boundary conditions like pressure and flow rate.
Oxidation of $\text{B}_4\text{C}$ absorber melts

Transient oxidation of $\text{B}_4\text{C}/\text{SS}/\text{Zry-4}$ absorber melts in steam between 800 and 1550 °C

<table>
<thead>
<tr>
<th>B$_4$C</th>
<th>SS</th>
<th>Zry-4</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.5</td>
<td>95</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>81</td>
<td>10</td>
</tr>
</tbody>
</table>

Oxidation rate during reaction of absorber melts and pure CR components in steam
Gas release due to oxidation of B\(_4\)C (melts)

- **Hydrogen**
  - Up to 290 g H\(_2\) per kg B\(_4\)C
  - Up to 500 kg additional H\(_2\) production for BWRs

- **Carbon monoxide/dioxide**
  - Ratio depending on temperature and oxygen activity
  - Non-condensable gases affecting THs and pressure
  - CO combustible and poisonous

- **Methane**
  - Would have strong effect on fission product chemistry (iodine!)
  - Bundle experiments and SETs reveal only insignificant release of CH\(_4\)

- **Boric acids**
  - Volatile and soluble in water
  - Deposition at colder locations in the circuit
Energetic effects of $\text{B}_4\text{C}$ oxidation

- Oxidation of $\text{B}_4\text{C}$ in steam: 13 MJ/kg$_{\text{B}_4\text{C}}$
- Oxidation of $\text{B}_4\text{C}$ in oxygen: 50 MJ/kg$_{\text{B}_4\text{C}}$
- Significant contribution to energy release in the core

For comparison:

- Oxidation Zr in steam: 6 MJ/kg$_{\text{Zr}}$
- Fuel value of mineral oil: 12 MJ/kg$_{\text{oil}}$
- Fuel value of black coal: 30 MJ/kg$_{\text{coal}}$
Possible consequences for Fukushima accidents

- Boiling water reactors with cruciform-shaped blades
- 1 control blade = 7 kg $B_4C + 93$ kg SS
- Complete liquefaction of the blade at $T>1200^\circ$C

Fukushima Daiichi NPPs:
- Unit 1: 97 control blades
- Unit 2-4: 137 control blades

- Complete oxidation of $B_4C$ inventory by steam:
  - $195/275$ kg $H_2$
  - $2700/3800$ kWh ($10/14$ GJ)
Failure of AgInCd absorber rod

- Ag-In-Cd control rods fail at temperatures above 1200°C due to the eutectic interaction between SS and Zry-4

- Failure is very stochastic (from local to explosive) with the tendency to higher temperatures for symmetric samples and specimens with inner oxidation

- No ballooning of the SS cladding tube was observed before rupture

- Burst release of cadmium vapour is followed by continuous release of indium and silver aerosols and absorber melt
Different failure types of AgInCd absorber rod

SIC-02 (asym. rod)
Local failure at 1230°C

SIC-05 (symmetric rod)
Global failure at 1350°C
Explosive failure of SIC-11 w/o Zry guide tube

-30 s
-20 s
-10 s
-0.04 s
0.00 s

No balloning before explosive failure!
No direct interaction between AIC and steel

Increasing interactions between relocated AIC and Zry in gap with temp.

Increasing interaction between melt and steel with increasing Zr content
QUENCH-13 bundle test: aerosol release

- First burst release of cadmium vapor, then aerosols mainly consisting of silver and indium
Summary

- Chemical interactions may strongly affect the early phase of a severe nuclear accident.
- The main hydrogen source term is produced by metal-steam reactions.
- Exothermal chemical reactions can cause heat release larger than the decay heat and hence strongly contribute to the power generation in the core.
- Nitrogen does not behave like an inert gas during the conditions of a severe accident.
- Eutectic interactions between the various materials in the core (i.e. B₄C-SS, SS-Zry) cause liquefaction of materials significantly below their melting temperatures.
- Boron carbide may (at least locally) significantly contribute to release of heat, hydrogen and other gases.
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Phase diagram Zr - H

Sieverts’ law:

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

with

\[ k_S = A \cdot e^{-\frac{B}{RT}} \]
Decrease of melting temperatures due to eutectic interactions