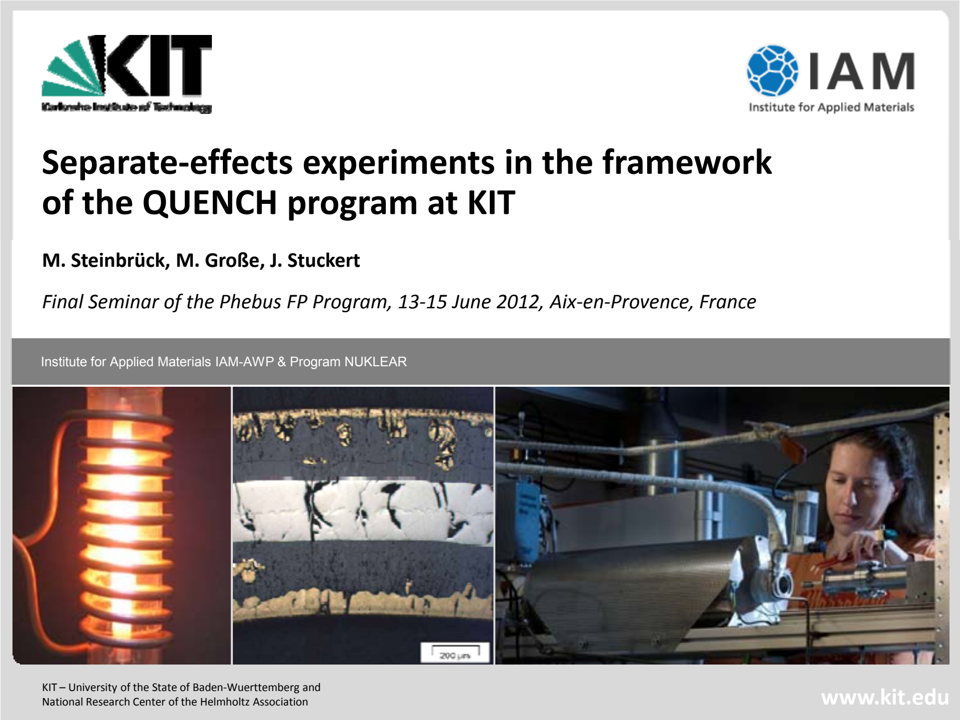

Separate-effects experiments in the framework of the QUENCH program at KIT

M. Steinbrück, M. Große, J. Stuckert

Final Seminar of the Phebus FP Program, 13-15 June 2012, Aix-en-Provence, France

Institute for Applied Materials IAM-AWP & Program NUKLEAR

KIT – University of the State of Baden-Wuerttemberg and
National Research Center of the Helmholtz Association

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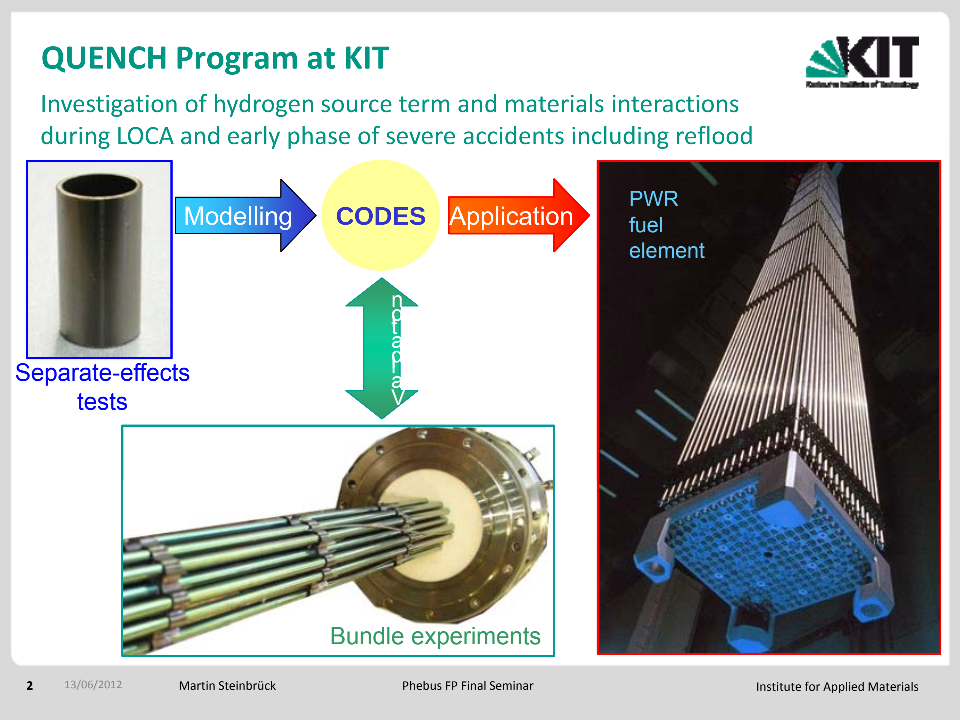
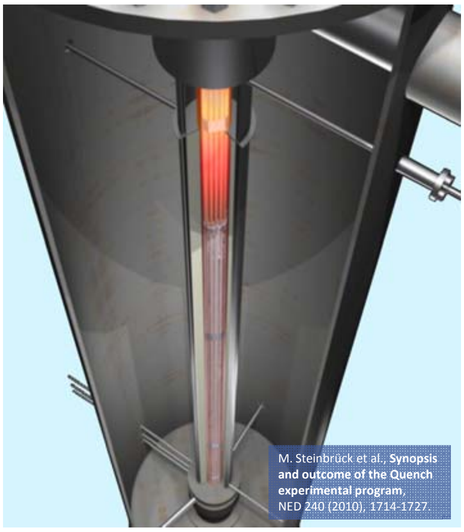


QUENCH Program at KIT

Investigation of hydrogen source term and materials interactions during LOCA and early phase of severe accidents including reflood

Quench facility

- Unique out-of-pile bundle facility to investigate reflood of an overheated reactor core
- Similar bundle geometry like Phebus FP bundle
- So far, 16 experiments on SA performed (1996-today)
  - Influence of pre-oxidation, initial temperature, flooding rate
  - B_4C, Ag-In-Cd control rods
  - Air ingress
  - Advanced cladding alloys
- **Complementary to Phebus FP in-pile experiments**



M. Steinbrück et al., **Synopsis and outcome of the Quench experimental program**, NED 240 (2010), 1714-1727.

Separate-effects tests

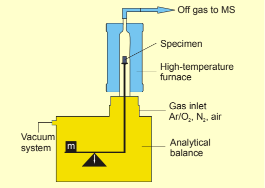
- Complementary to bundle experiments
- Extensive test series for study of selected test parameters
- Generation of data sets for implementation in SA codes (e.g. thermodynamic and kinetic parameters)
- Valuable contribution to phenomenological understanding of processes at high temperatures, e.g. by direct observation

QUENCH-SR rig

SET topics within the framework of QUENCH

- Single-rod quench experiments
- **High-temperature oxidation of various cladding alloys, including advanced ones, in various atmospheres (steam, oxygen, nitrogen, air, mixtures)**
- Effect of steam starvation
- ZrO_2 failure criteria
- Hydrogen absorption by zirconium alloys
- **Boron carbide absorber behaviour during severe accidents**
- **Single-rod tests on AgInCd control rods**
- Interaction of metal melt with zirconia (and urania)

QUENCH Separate-effects tests: Main setups

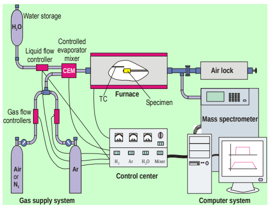


Thermobalance

1600 °C
1250 °C (steam)

Specimens: 0-2 cm

MS coupling



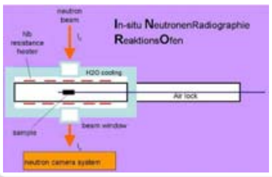
BOX Facility

1700 °C

Oxidising, reducing atmosphere (incl. steam)

Specimens: 1-2 cm

MS coupling

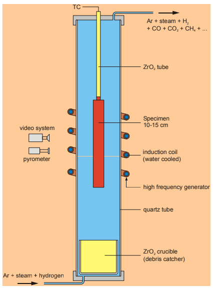


INRRO Facility

1500°C

Specimens: 1-2 cm

Transparent for neutrons



QUENCH-SR Rig

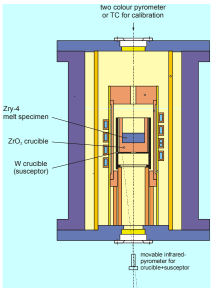
2000 °C

Induction heating

Oxidising, reducing atmosphere (incl. steam)

Specimens: 15 cm

MS coupling



LAVA Furnace

2300 °C

Induction heating

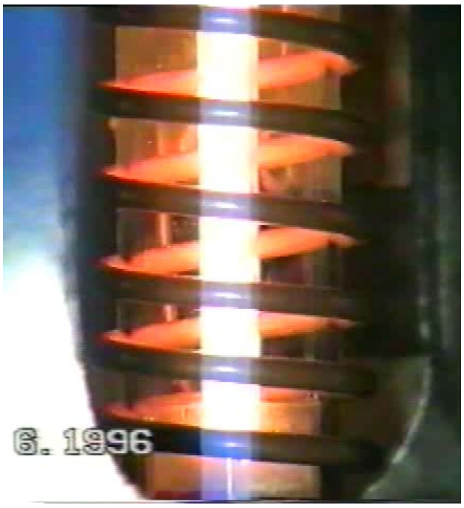
Inert, reducing atmosphere

Specimens: 1-2 cm

MS coupling

Single-rod QUENCH tests

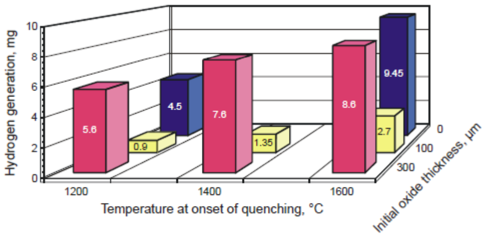
- 15-cm rods filled with ZrO_2 pellets
- Direct inductive heating
- Video recording
- Mass spectrometer for analysis of hydrogen release
- Parameters:
    - Pre-oxidation 0-350 µm
    - 1000-1600°C at onset of quenching
    - Quenching with hot/cold water or steam
    - Flooding rate 1.5 cm/s



Reflood from 1400°C

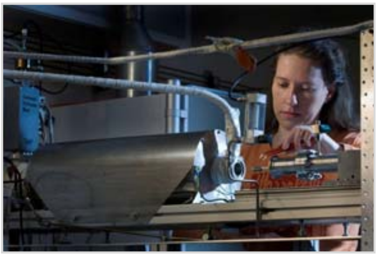
Single-rod QUENCH tests – Main results

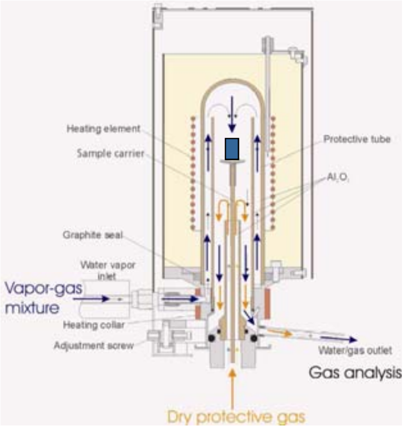
- Through-wall crack for pre-oxidation >200 µm with a density of 0.5 mm/mm^2
- Oxidation of crack surfaces connected with hydrogen absorption by the metal
- Localized spalling of oxide scales



High-temperature oxidation of zirconium alloys

- In Steam, oxygen, nitrogen, air, and various mixtures
- Zircaloy-2, Zircaloy-4, Duplex, M5®, Zirlo™, E110 and others
- 2-cm rod segments
- Temperature: 600-1600°C
- Starvation conditions
- Hydrogen behavior

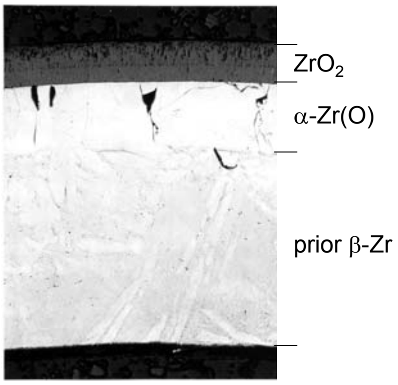

BOX rig



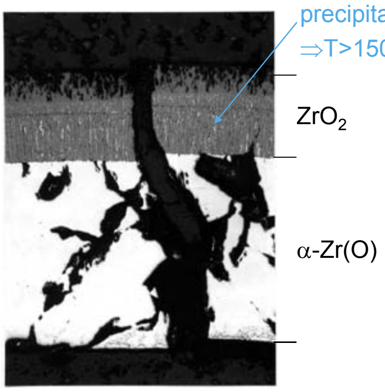
NETZSCH® steam furnace for TG

Oxidation of Zr alloys in steam (oxygen)

- Most LOCA and SFD codes use parabolic oxidation correlations



1200 °C, quench

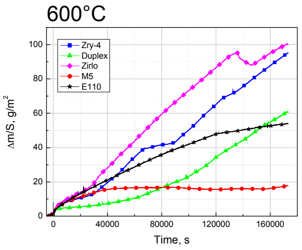


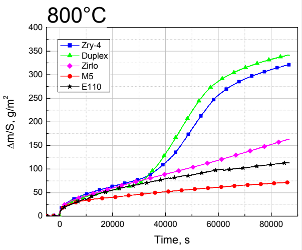
Zr(O) precipitates
⇒T>1500°C

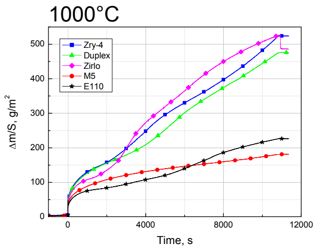
1600 °C, quench

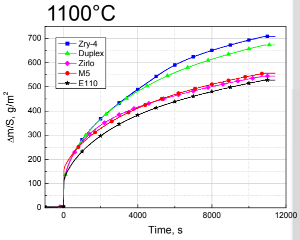
Isothermal oxidation of Zr alloys in steam

- Significant differences (up to 500%) between various alloys at temperatures below 1100°C
- From 1100°C max. differences between alloys of 30% are found
- The oxidation kinetics are mainly determined by the oxide scale (breakaway, crystallographic phase, degree of sub-stoichiometry).


600°C

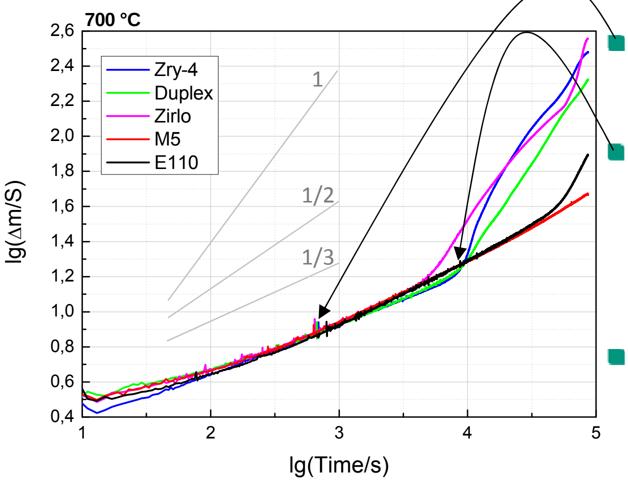

800°C


1000°C


1100°C

Oxidation of Zr alloys in steam (oxygen)

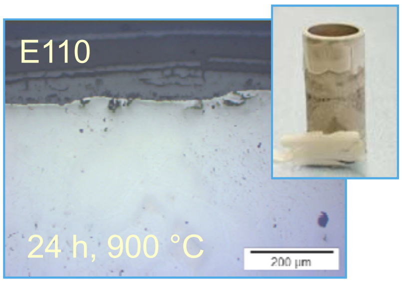
- Deviations from parabolic kinetics at temperatures <1100°C

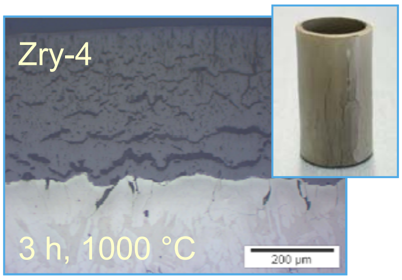


- Sub-parabolic (cubic) kinetics
- Transition from (sub-) parabolic to linear kinetics after critical time / oxide thickness due to breakaway
- Similar kinetics of all alloys before transition, but strongly varying behavior at and after transition

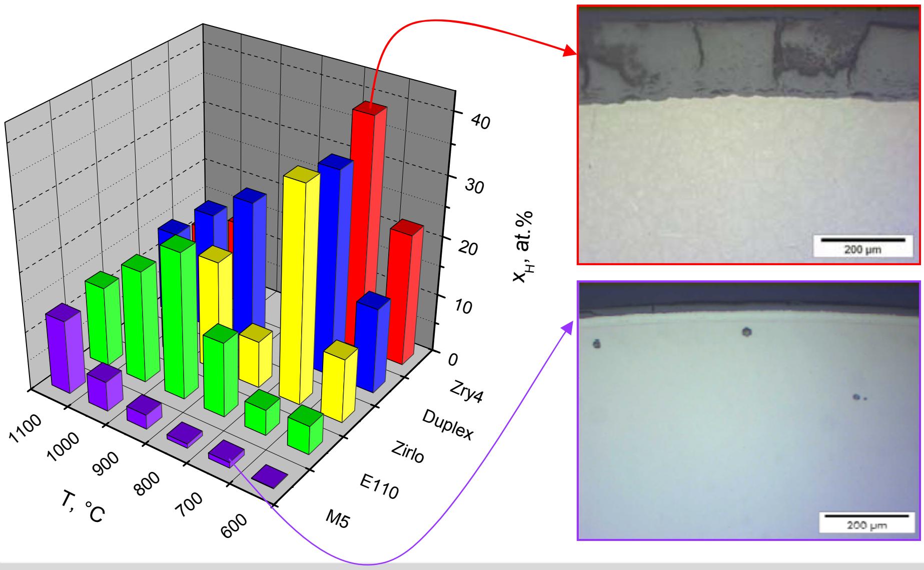
Breakaway oxidation

- Loss of protective properties of oxide scale due to its mechanical failure.
- Breakaway is caused by phase transformation from 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 H_2 in pores and cracks near the metal/oxide boundary ("hydrogen pump").

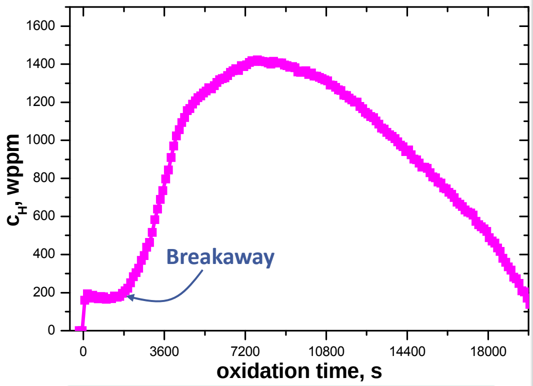




Correlation of H absorption and oxide morphology



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

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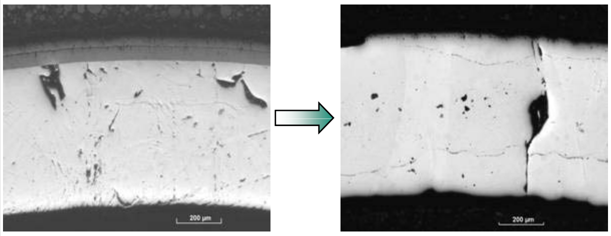
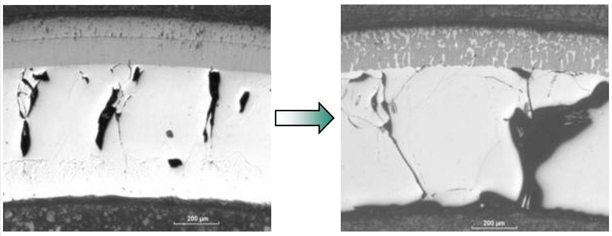
Effect of steam/oxygen starvation on oxide scale



Oxidation

Steam starvation at 1700 K

Dissolution of oxide scale



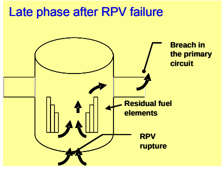
Thinning of oxide scale and precipitation of α-Zr(O) in oxide

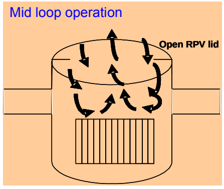
- Weakening of protective effect of ZrO_2 oxide layer

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

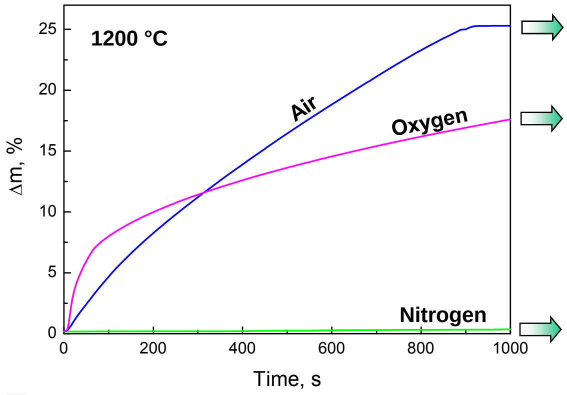
- Consequences:
  - Significant heat release causing temperature runaway from lower temperatures than in steam
  - Strong degradation of cladding causing early loss of barrier effect
  - High oxygen activity influencing FP chemistry and transport


Late phase after RPV failure


Mid loop operation


Spent fuel storage pool accident

Oxidation of Zr alloys in N_2, O_2 and air



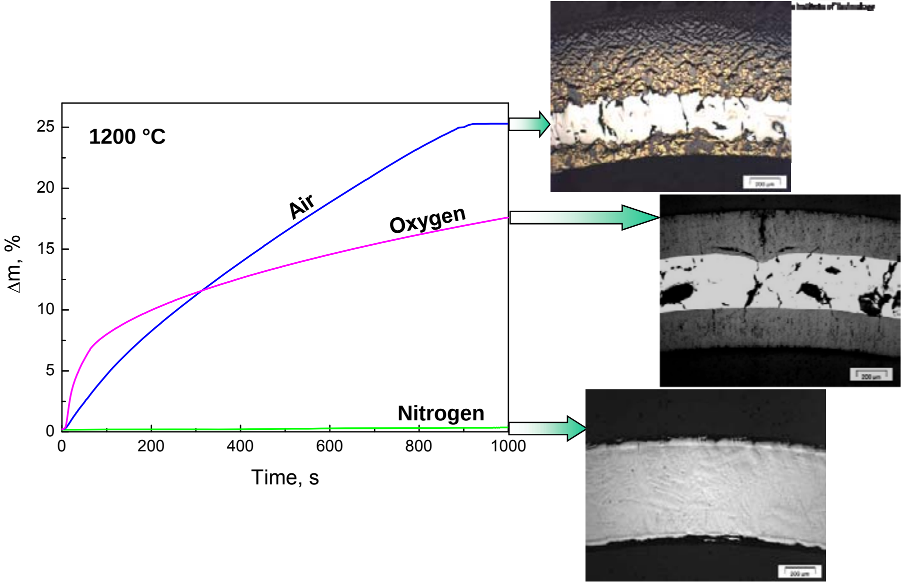
~ Linear oxidation kinetics

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



Consequences of air ingress for cladding

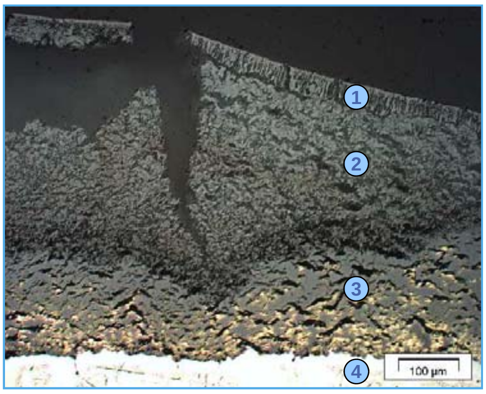
1 hour at 1200°C in steam

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 boundary
- 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



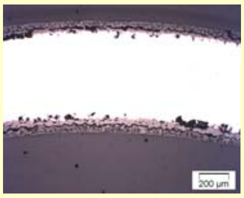
1 – initially formed dense oxide ZrO_2
2 – porous oxide after oxidation of ZrN
3 – ZrO_2 / ZrN mixture
4 – α-Zr(O)

Oxidation in mixed atmospheres

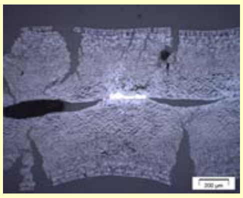
Zry-4, 1 hour at 1200°C

H_2O | 0.7 H_2O 0.3 air | 0.3 H_2O 0.7 air | 0.1 H_2O 0.9 air

1 hour at 1000 °C in



steam



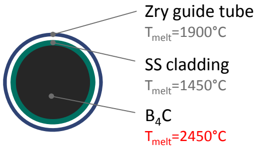
50/50 steam/N_2

- 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

Absorber materials in LWRs

Boron carbide

- Used in boiling water reactors (BWR), VVERs, some pressurized water reactors (PWR)
- Surrounded by stainless steel
- Control rods (PWR) or cross-shaped blades (BWR)
- Rods in Zry guide tubes

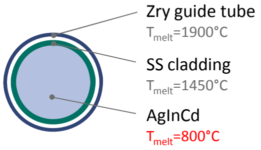


BWR control blade

AgInCd alloy

- Used in PWRs
- Surrounded by stainless steel
- Rods in Zry guide tubes combined in control rod assemblies

PWR control rod assembly



Oxidation of boron carbide; main chemical reactions

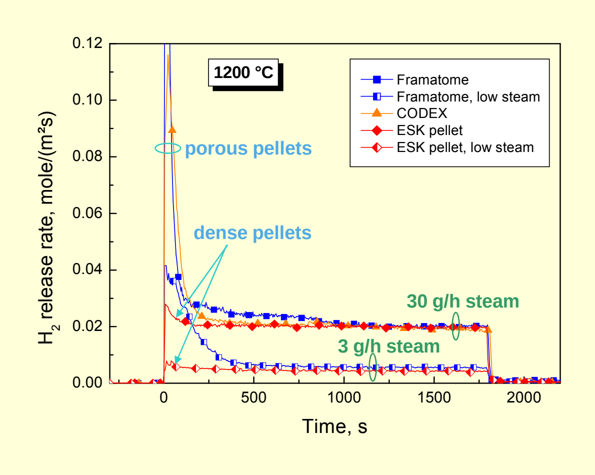
$$B_4C + 8H_2O(g) \rightarrow 2B_2O_3(l) + CO_2(g) + 8H_2(g) \qquad -760 \text{ kJ/mol}$$

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

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

- Release of hydrogen, various carbon-containing gases and heat
- Formation of a superficial boron oxide layer and its vaporization

Oxidation kinetics of B_4C in steam



- Strongly dependant on B_4C structure and thermo hydraulic boundary conditions like pressure and flow rates
- No methane!

Degradation of B_4C absorber rod

Isothermal tests (1 h) in steam/Ar atmosphere
Post-test appearance and gas release


1000°C


1200°C

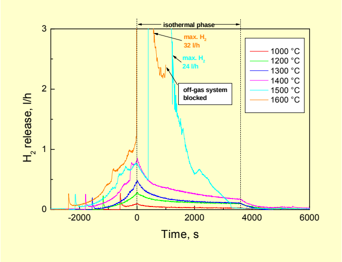

1300°C

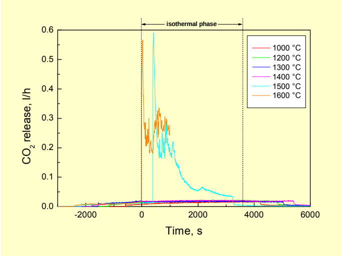

1400°C


1500°C (1)

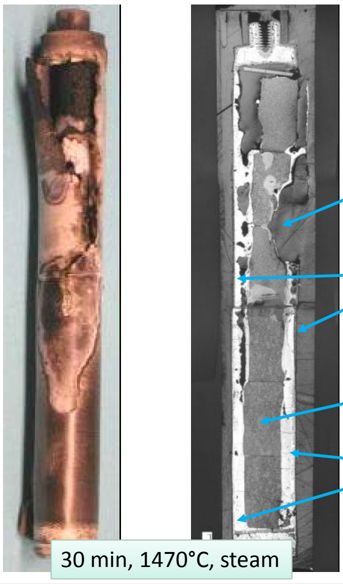

1500°C (2)


1600°C





Degradation of B_4C absorber rod (single-rod)


30 min, 1470°C, steam

Local oxide shell failure and oxidation of B_4C

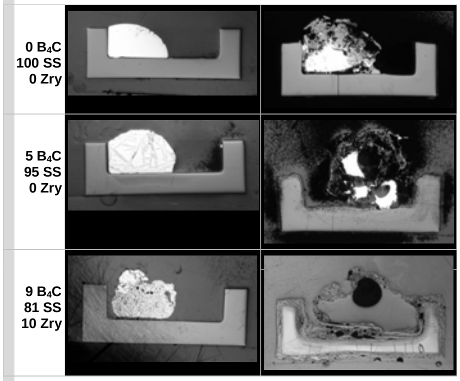
ZrO_2 scale enclosing the absorber melt

Partly dissolved B_4C pellet

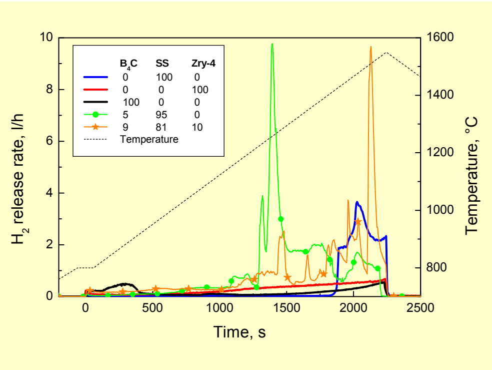
Relocated absorber melt

Oxidation of B_4C absorber melt

Transient oxidation of B_4C/SS/Zry-4 absorber melts
in steam between 800 and 1550 °C



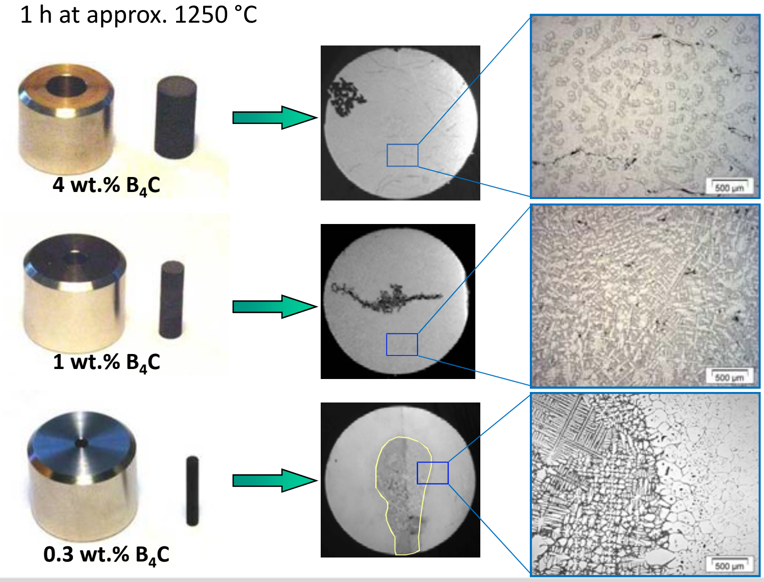
before oxidation after oxidation



Hydrogen release during oxidation of absorber melts and pure CR components

Eutectic interaction of stainless steel with B_4C

1 h at approx. 1250 °C

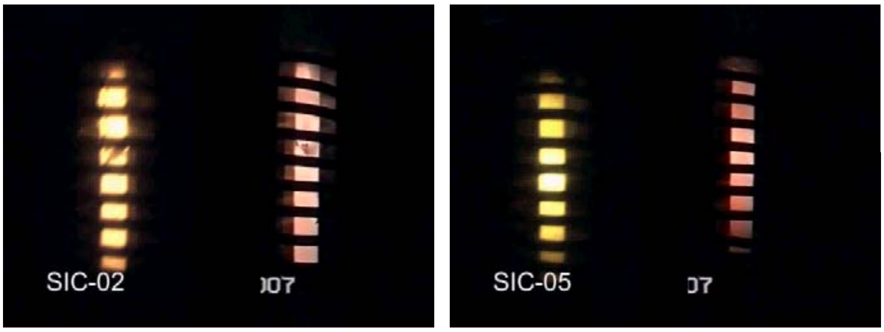


Complete liquefaction of stainless steel

1/3 of SS liquefied

Failure of AgInCd absorber rod

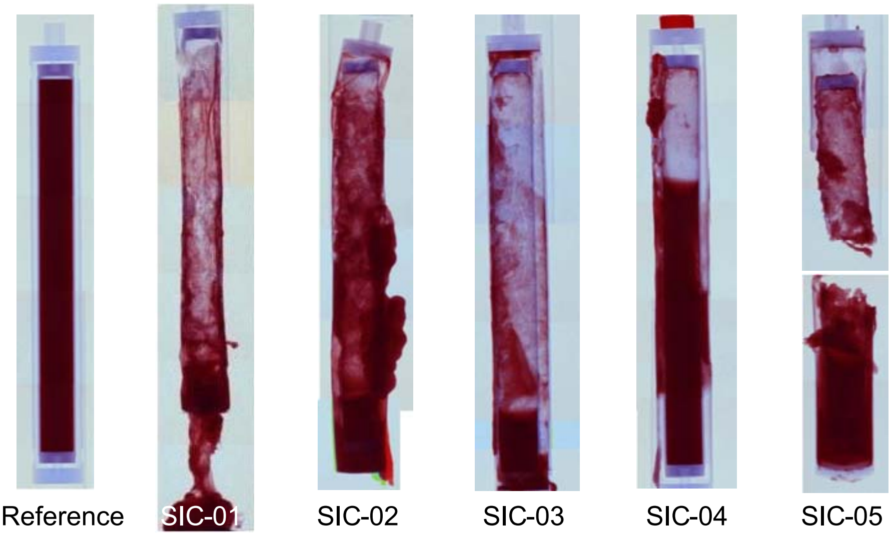
- Different failure mechanisms: from local failure with melt release to global detonation depending sample geometry
- Failure temperatures always above 1200°C due to interaction of SS with Zry-4 and high vapor pressure of Cd
- Release of Cd vapor and absorber melt



Failure of AgInCd absorber rod

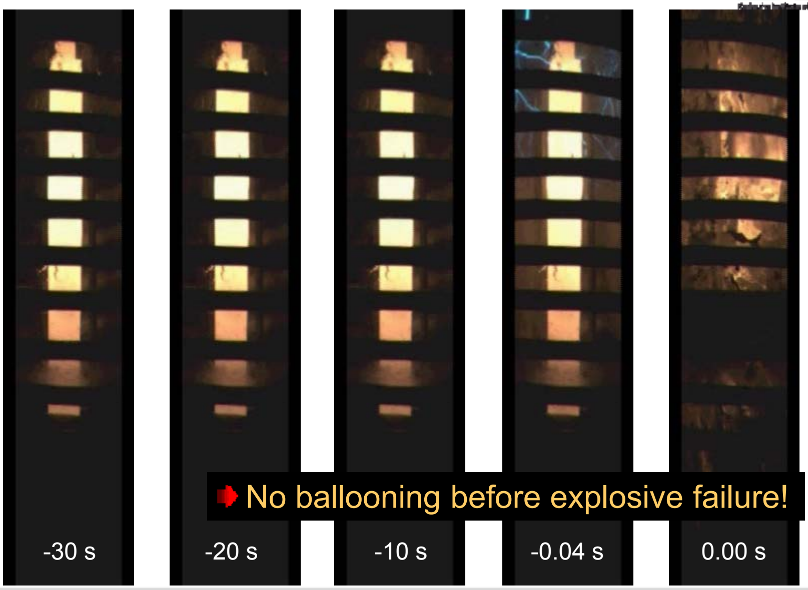
SIC-01 SIC-02 SIC-03 SIC-04 SIC-05

Neutron radiographs



Reference SIC-01 SIC-02 SIC-03 SIC-04 SIC-05

Explosive failure of SIC-11 w/o Zry guide tube



➧ No ballooning before explosive failure!

Comparison between the behaviour of B_4C and AIC absorber rods

B_4C

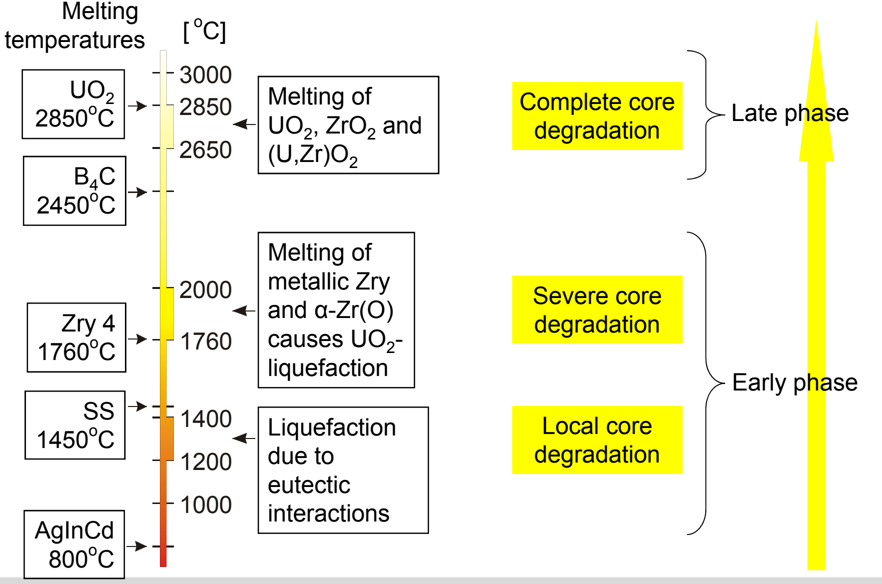
- T_m = 2450 °C
- rapid eutectic melt formation with SS cladding at T >1200 °C
- preferably axial melt relocation after failure of the Zry guide tube (oxide scale) at T > 1250 °C
- oxidation of B_4C and absorber melt causing strong heat release and gas and aerosol production (H_2, CO, CO_2, CH_4, boric acids)

AIC (80% Ag, 15% In, 5% Cd)

- T_m = 800 °C
- thermodynamically stable against the SS cladding
- radial and axial relocation after failure of the SS control rod as a result of its eutectic interaction with the Zry guide tube or after mechanical failure due to pressure build-up at T >1250 °C
- generation of Ag, In, Cd aerosols

Both absorber materials initiate early melt formation and melt relocation connected with local core damage and transport of material and heat to the lower part of the bundle at comparable temperatures (>1250 °C). Additionally, AIC and B_4C have a strong impact on FP chemistry.

Core degradation - summary



Melting temperatures

[°C]

UO_2 2850°C

B_4C 2450°C

Zry 4 1760°C

SS 1450°C

AgInCd 800°C

3000

2850

2650

2000

1760

1400

1200

1000

Melting of UO_2, ZrO_2 and $(U,Zr)O_2$

Melting of metallic Zry and α-Zr(O) causes UO_2-liquefaction

Liquefaction due to eutectic interactions

Complete core degradation

Severe core degradation

Local core degradation

Late phase

Early phase

Finally…

You are invited to the

18th International QUENCH Workshop

Karlsruhe Institute of Technology

20-22 November 2012

http://quench.forschung.kit.edu/

Thank you for your attention!