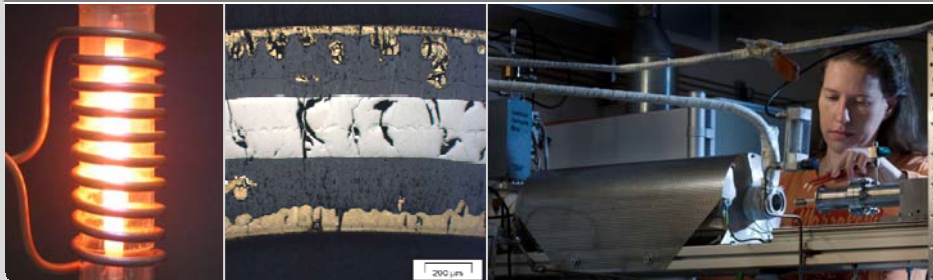


Materials behavior during the early phase of a severe nuclear accident

Martin Steinbrück

*4th Scientific & Technical Conference on Diagnostics of Materials and Industrial Components
31 May – 02 June 2012, Gdansk University of Technology, Poland*

Institute for Applied Materials, IAM-AWP / Program NUKLEAR



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

www.kit.edu

Karlsruhe Institute of Technology

Founded in 2009

= FZK + University Karlsruhe

= 8000 employees

= \$900 millions budget

Outline



- Phenomenology of severe accidents in light water reactors (LWR)
- Experimental facility and setups
- High-temperature oxidation of zirconium alloys in various atmospheres
 - Steam
 - Air
 - Mixtures
- Behavior of boron oxide control rods during severe accidents
- Behavior of silver-indium-cadmium control rods during severe accidents
- Application of neutron radiography and tomography

LWR severe accident scenario - I



- Loss of coolant causes steady heatup of the core due to
 - Residual decay heat
 - Reduced heat transfer to the remaining steam
- From ca. 1000°C oxidation of zirconium alloy cladding becomes significant leading to
 - Mechanical degradation of claddings and loss of barrier effect
 - Production of hydrogen
 - Release of heat
- 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
 - Low-temperature melts attack adjacent fuel rods and may cause early release of fission products
 - Materials and heat are relocated within the core
 - Further enhanced hydrogen production due to rapid oxidation of melts
 - Recriticality problem, if absorber materials are involved

Hydrogen detonation in Fukushima Dai-ichi NPPs

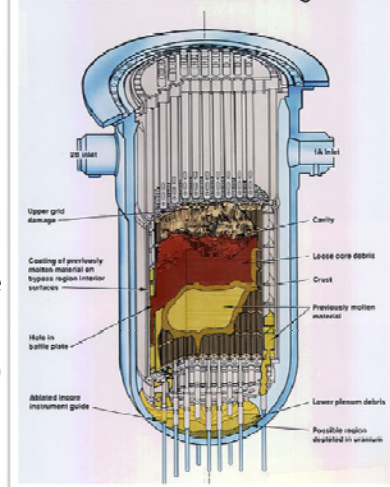


LWR severe accident scenario - II

How to stop the accident early in the reactor pressure vessel (RPV):

- Reflood and cooling as early as possible.
- If successful:
Significant gain of safety and prevention of high loads to RPV.
- If not successful:
Formation of melt pool in the core and relocation of melt/debris to the lower plenum (in-vessel, see TMI-2).
- Furthermore, failure of the RPV and release of corium melt into the containment (ex-vessel, see Chernobyl, Fukushima)
 - Molten core – concrete interactions (MCCI)
 - Fuel – coolant interactions (FCI)
 - Direct containment heating (DCH)
 - ...

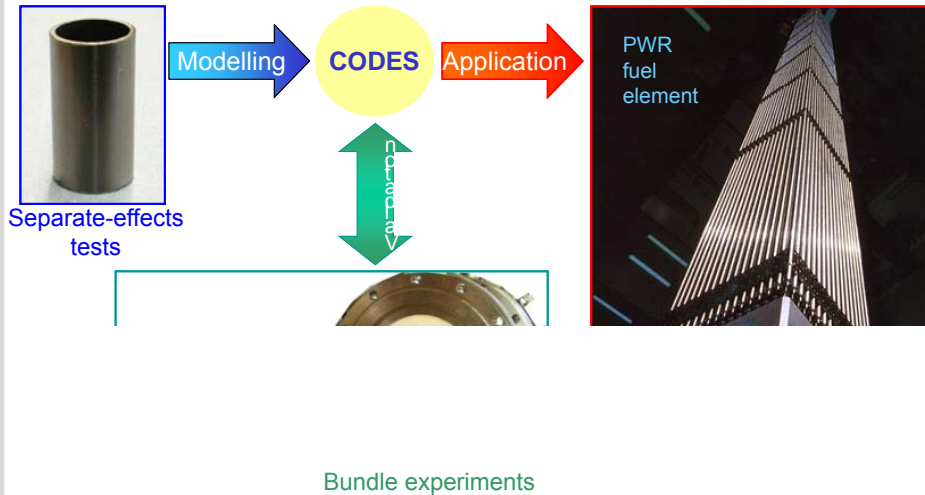
TMI-2 Core End-State Configuration



QUENCH Program at KIT



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



7

31.05.2012

Martin Steinbrück

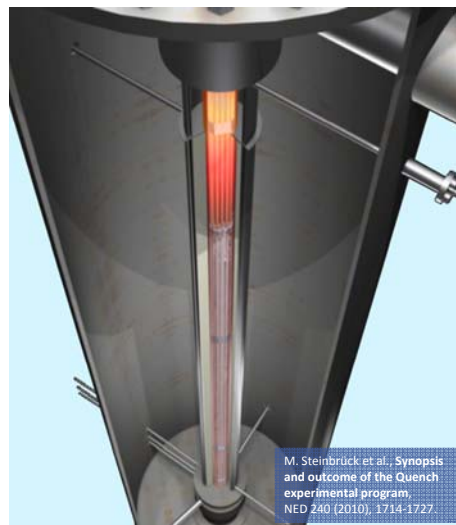
DMIUT 2012



QUENCH Facility



- Unique out-of-pile bundle facility to investigate reflood of an overheated reactor core
- 21-31 electrically heated fuel rod simulators
- Extensive instrumentation for T, p, flow rates, level, etc.
- So far, 16 experiments on SA performed (1996-today)
 - Influence of pre-oxidation, initial temperature, flooding rate
 - B₄C, Ag-In-Cd control rods
 - Air ingress
 - Advanced cladding alloys



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

8

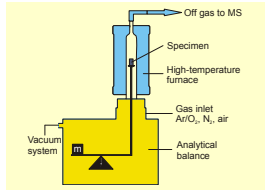
31.05.2012

Martin Steinbrück

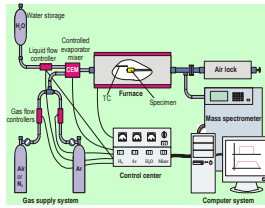
DMIUT 2012



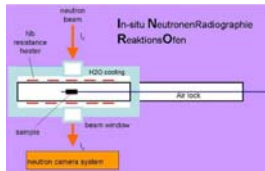
QUENCH Separate-effects tests: Main setups



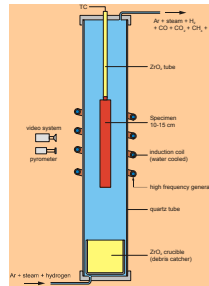
Thermobalance
 1600 °C
 1250 °C (steam)
 Specimens: 0-2 cm
 MS coupling



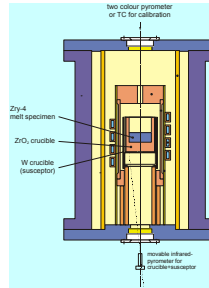
BOX Facility
 1700 °C
 Oxidising, reducing atmosphere (incl. steam)
 Specimens: 1-2 cm
 MS coupling



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

Specimens



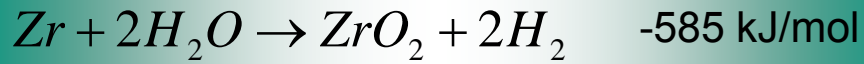
- Zirconium alloys with 98-99% Zr
- 2-cm cladding segments
- Both-side oxidation allowed



- **Composition (approx., main alloying elements)**

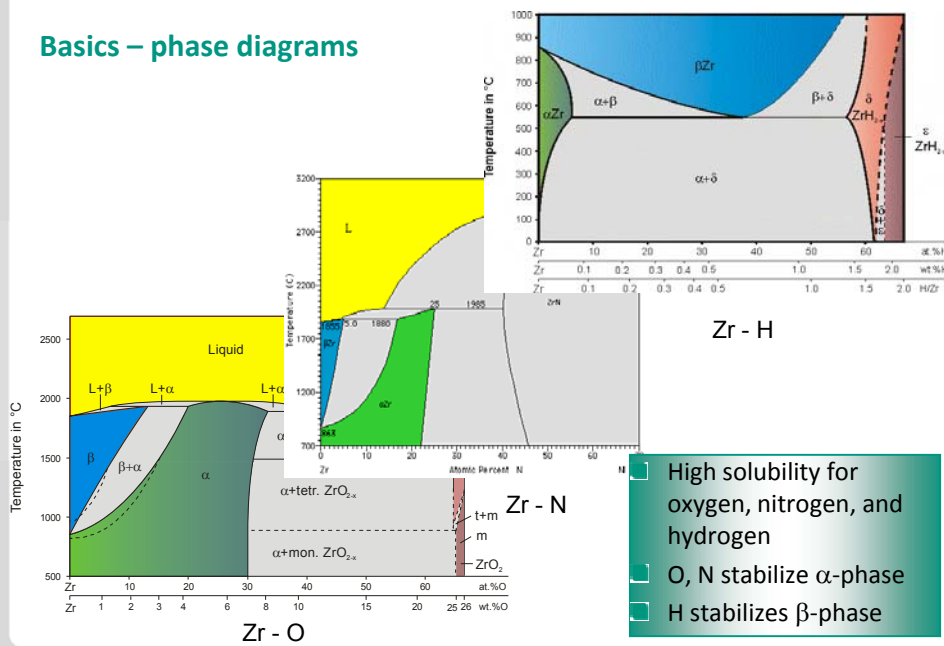
Element	Zircaloy-4	D4	M5	E110	ZIRLO
Nb	-	-	1	1	1
Sn	1.5	0.5	0.01	-	1
Fe	0.2	0.5	0.05	0.008	0.11
Cr	0.1	0.2	0.015	0.002	< 0.01

ΔH_f at 1500 K



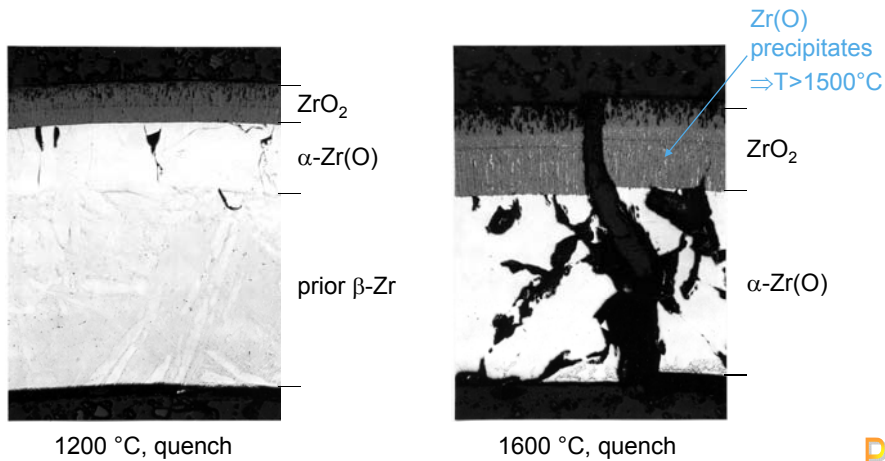
➡ Release of hydrogen and heat

Basics – phase diagrams



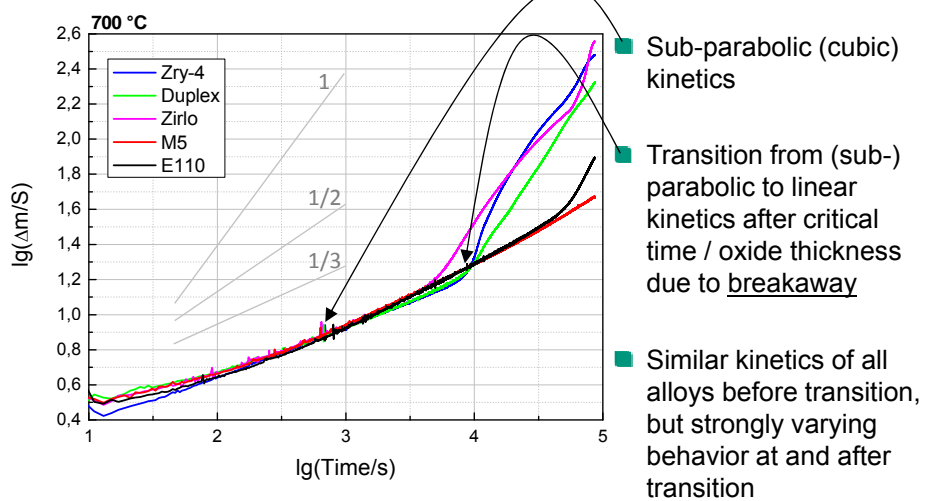
Oxidation in steam (oxygen)

- Most LOCA and SFD codes use parabolic oxidation correlations



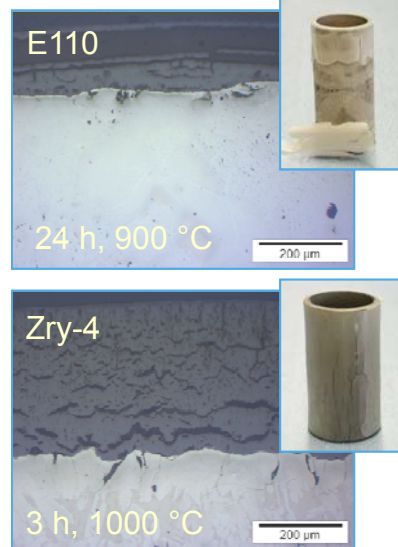
Oxidation in steam (oxygen)

- Deviations from parabolic kinetics at temperatures <1100°C

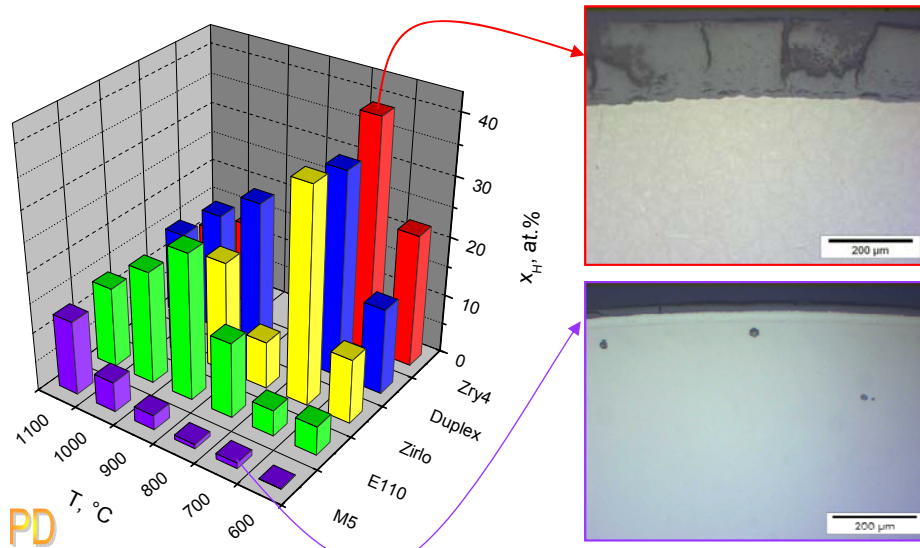


Breakaway oxidation

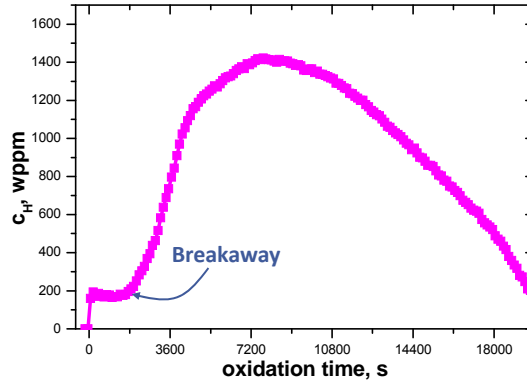
- Loss of protective properties of oxide scale due to its mechanical failure.
- Breakaway is caused by phase transformation from pseudo-stable tetragonal to monoclinic oxide and corresponding change in density up to ca. 1050°C.
- Critical times and oxide thicknesses for breakaway strongly depend on type 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”).



Correlation of H absorption and oxide morphology



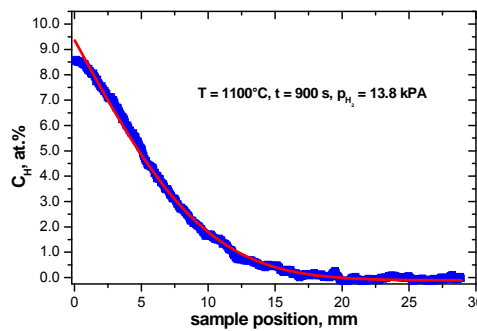
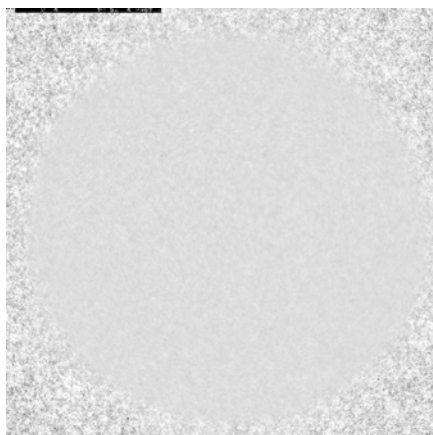
In-situ investigation of hydrogen uptake during oxidation of Zry in steam by neutron radiography



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

- Rapid initial hydrogen uptake
- Further strong hydrogen absorption after transition to breakaway

In-situ investigation of hydrogen diffusion in Zry



T = 1100°C, t = 900 s, p_{H₂} = 13.8 kPa

$$D_H(T = 1373 \text{ K}) = 3.39 \cdot 10^{-4} \frac{\text{cm}^2}{\text{s}}$$

Hydrogen diffusion into a Zry-4 cylinder (Ø = 12mm, l = 20 mm) at 1100°C (time ratio: 1 : 100)

M. Grosse, 16th Intern. Symposium on Zirconium in the Nuclear Industry (ASTM)

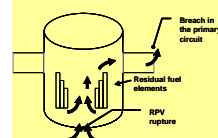
Oxidation in atmospheres containing nitrogen

- 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

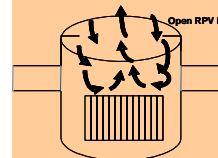
- Consequences:
 - Significant heat release causing temperature runaway from lower temperatures than in steam
 - Strong degradation of cladding causing early loss of barrier effect
 - High oxygen activity influencing FP chemistry and transport



Late phase after RPV failure



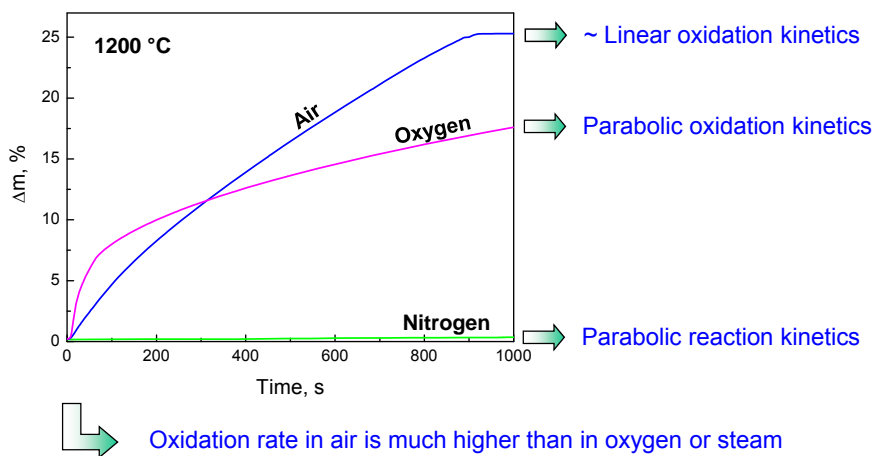
Mid loop operation



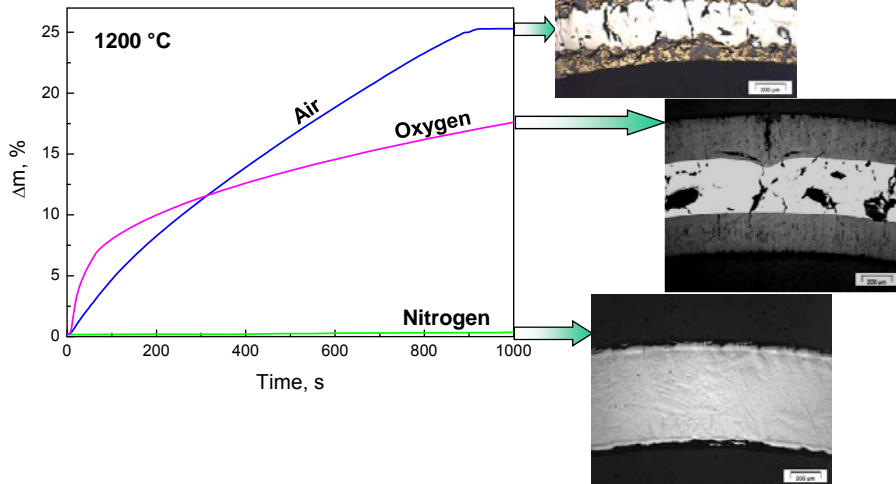
Spent fuel storage pool accident



Oxidation of Zr alloys in N₂, O₂ and air



Oxidation of Zr alloys in N₂, O₂ and air



Consequences of air ingress for cladding



1 hour at 1200 °C in steam

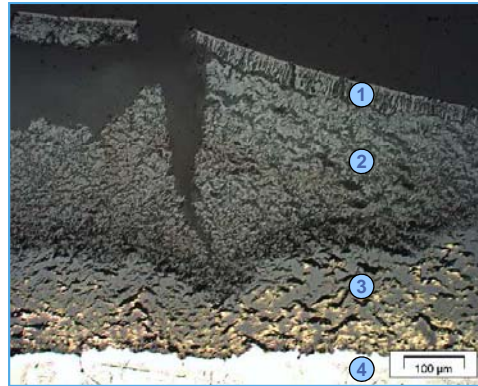


1 hour at 1200 °C in air

➔ Loss of barrier effect of cladding

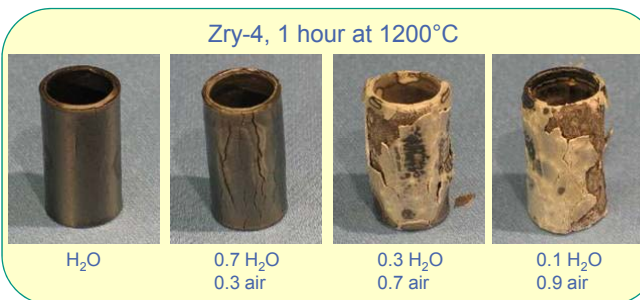
Mechanism of air oxidation

- 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

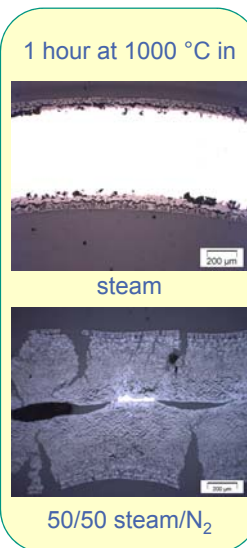


- 1 – initially formed dense oxide ZrO_2
- 2 – porous oxide after oxidation of ZrN
- 3 – ZrO_2 / ZrN mixture
- 4 – α -Zr(O)

Oxidation in mixed atmospheres



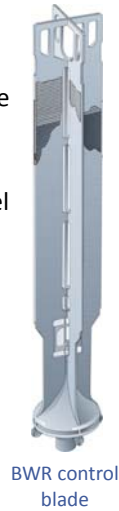
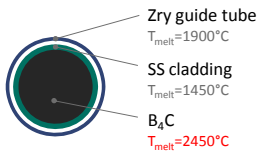
- Strong effect of nitrogen on oxidation and degradation
- Nitrogen acts like a catalyst (NOT like an inert gas)
- Enhanced hydrogen source term by oxidation in mixtures containing nitrogen



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

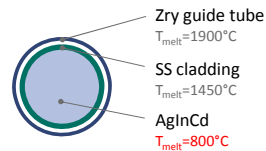


AgInCd alloy

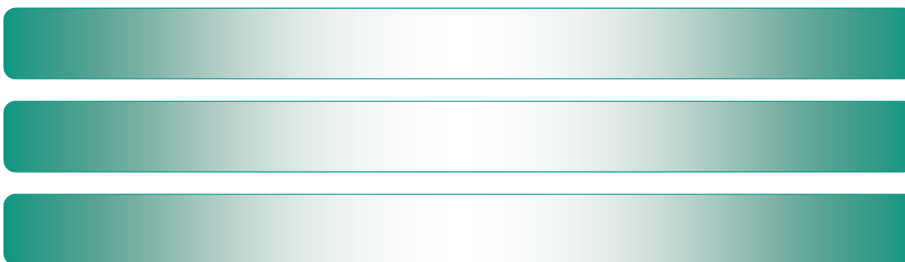
- Used in PWRs
- Surrounded by stainless steel
- Rods in Zry guide tubes combined in control rod assemblies



PWR control rod assembly

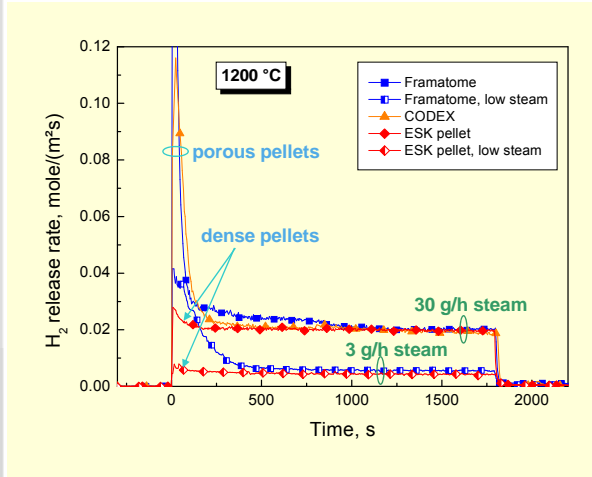


Oxidation of boron carbide; main chemical reactions



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

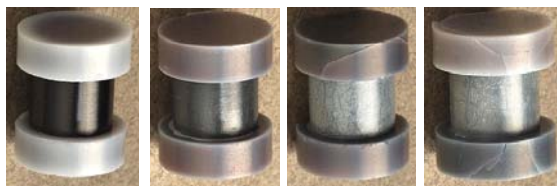
Oxidation kinetics of B₄C in steam



Strongly dependant on B₄C structure and thermo hydraulic boundary conditions like pressure and flow rates
 No methane!

Degradation of B₄C absorber rod

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



1000 °C

1200 °C

1300 °C

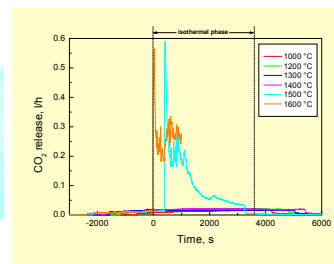
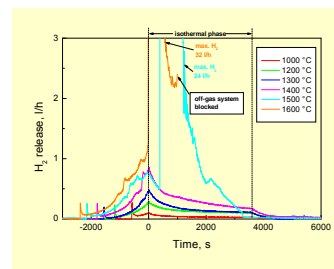
1400 °C



1500 °C (1)

1500 °C (2)

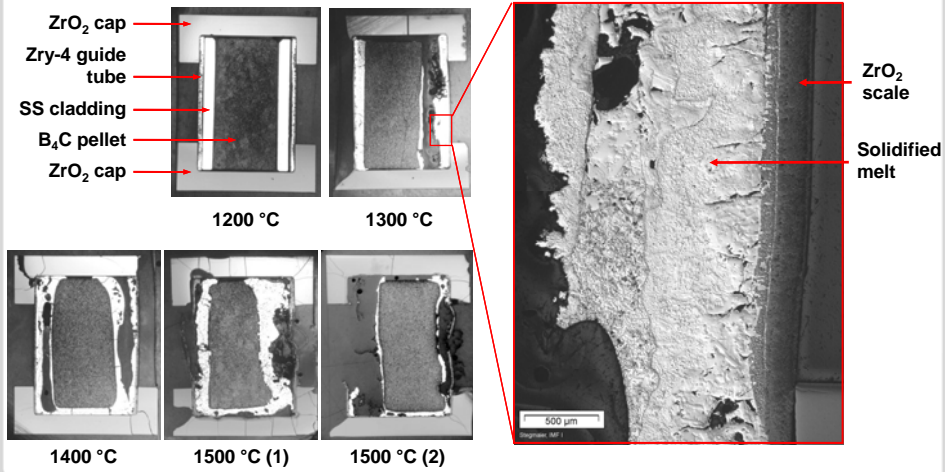
1600 °C



Degradation of B₄C absorber rod



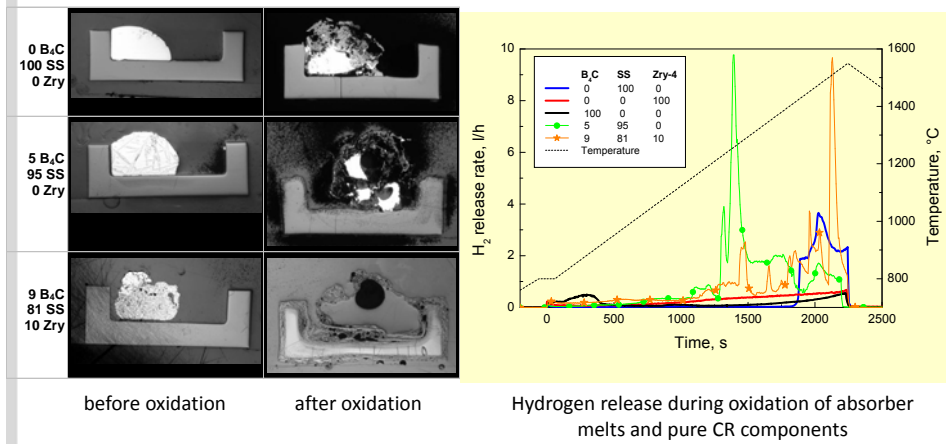
Metallographic post-test examination of control rod segments



Oxidation of B₄C absorber melt

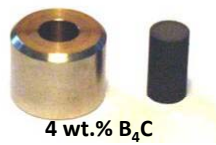


Transient oxidation of B₄C/SS/Zry-4 absorber melts in steam between 800 and 1550 °C

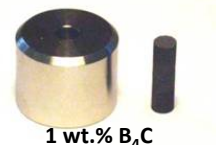
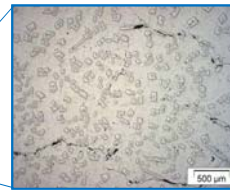
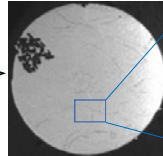


Eutectic interaction of stainless steel with B_4C

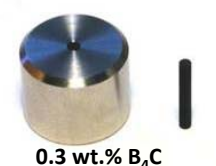
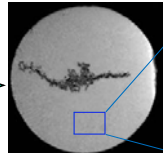
1 h at approx. 1250 °C



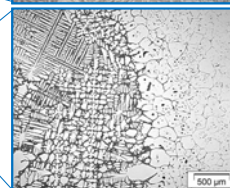
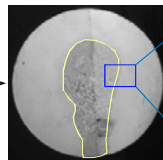
4 wt.% B_4C



1 wt.% B_4C



0.3 wt.% B_4C



Complete
liquefaction
of stainless
steel

1/3 of SS
liquefied

31

31.05.2012

Martin Steinbrück

DMIUT 2012



Consequences for Fukushima accidents

- 1 control blade = 7 kg B_4C + 93 kg SS
- ➡ Complete liquefaction of the blade at $T > 1200^\circ C$

- Unit 1: 97 control blades
- Unit 2-4: 137 control blades

- Complete oxidation of B_4C inventory:
 - ➡ 195/275 kg H_2
 - ➡ 2700/3800 kWh



BWR control rod

32

31.05.2012

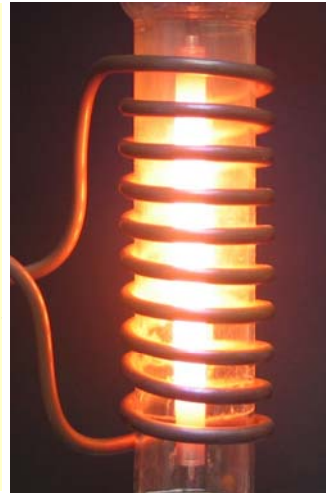
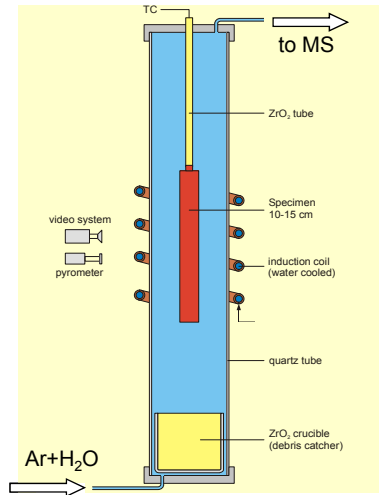
Martin Steinbrück

DMIUT 2012



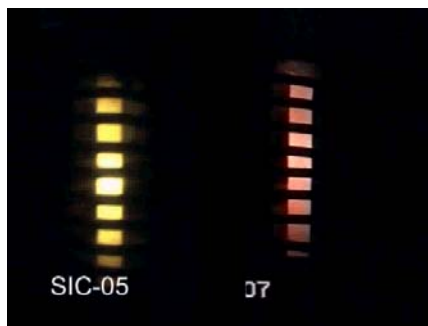
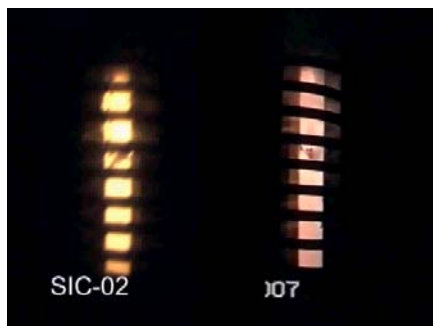
Failure of AgInCd absorber rods - QUENCH-SR rig

- Inductive heating
- Two video systems (SVHS and digital, 90°)
- Mass spectrometer for H₂ analysis
- Melt catcher (from 2nd test)



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



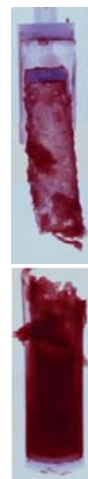
SIC-02



SIC-03



SIC-04



SIC-05

Comparison between the behaviour of B₄C and AIC absorber rods



B₄C

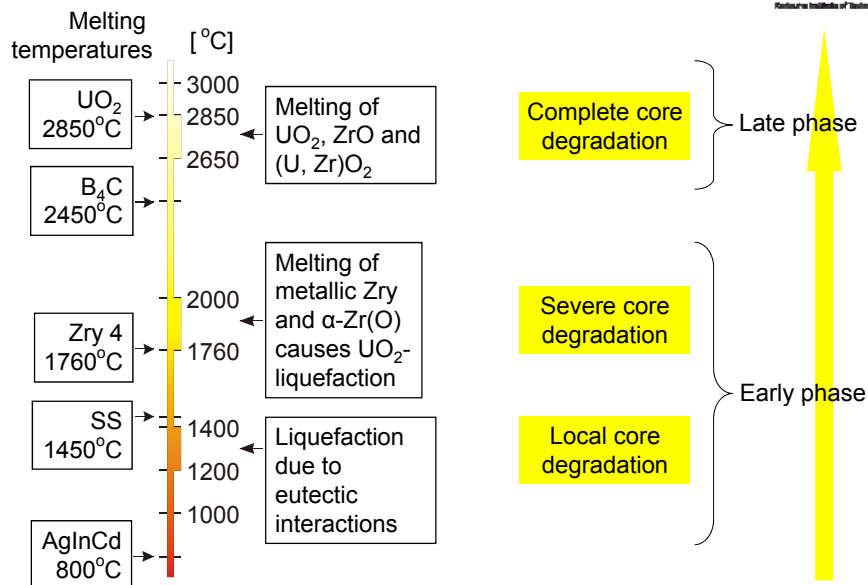
- $T_m = 2450\text{ °C}$
- rapid eutectic melt formation with SS cladding at $T > 1200\text{ °C}$
- preferably axial melt relocation after failure of the Zry guide tube (oxide scale) at $T > 1250\text{ °C}$
- oxidation of B₄C and absorber melt causing strong heat release and gas and aerosol production (H₂, CO, CO₂, CH₄, boric acids)

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

- $T_m = 800\text{ °C}$
- 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 $T > 1250\text{ °C}$
- 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 ($>1250\text{ °C}$). Additionally, AIC and B₄C have a strong impact on FP chemistry.

Core degradation - summary



Finally...



You are invited to the

17th International QUENCH Workshop

Karlsruhe Institute of Technology

20-22 November 2012

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

Thank you for your attention!

39 31.05.2012

Martin Steinbrück

DMIUT 2012

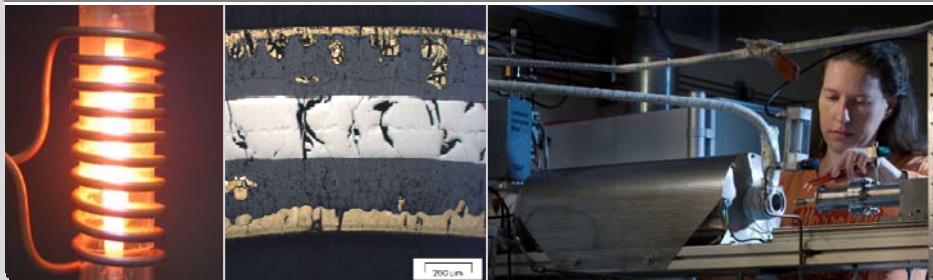


Materials behavior during the early phase of a severe nuclear accident

Martin Steinbrück

*4th Scientific & Technical Conference on Diagnostics of Materials and Industrial Components
31 May – 02 June 2012, Gdansk University of Technology, Poland*

Institute for Applied Materials, IAM-AWP / Program NUKLEAR



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

www.kit.edu