KIT
Karlsruhe Institute of Technology

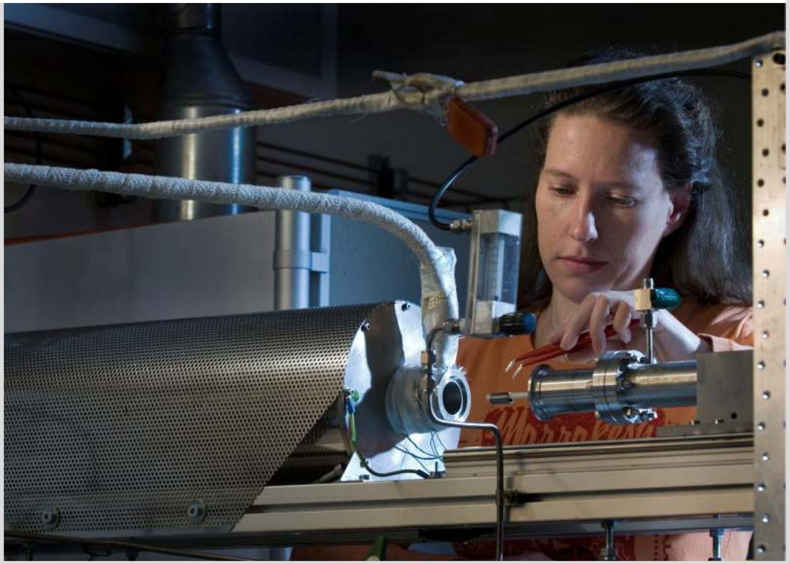
IAM
Institute for Applied Materials

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

Martin Steinbrück

EMSE Seminar, 18 December2013, St. Etienne, France

Institute for Applied Materials IAM-AWP & Program NUSAFE



Karlsruhe Institute of Technology

Founded in 2009

= FZK research center (1956) + University Karlsruhe (1825)

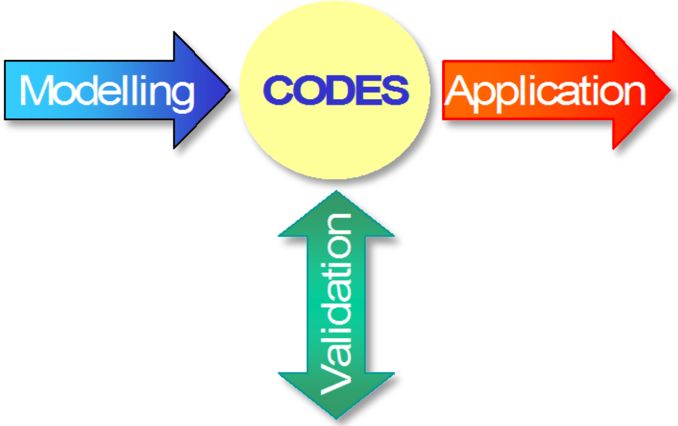
= 9000 employees

= 24 000 students

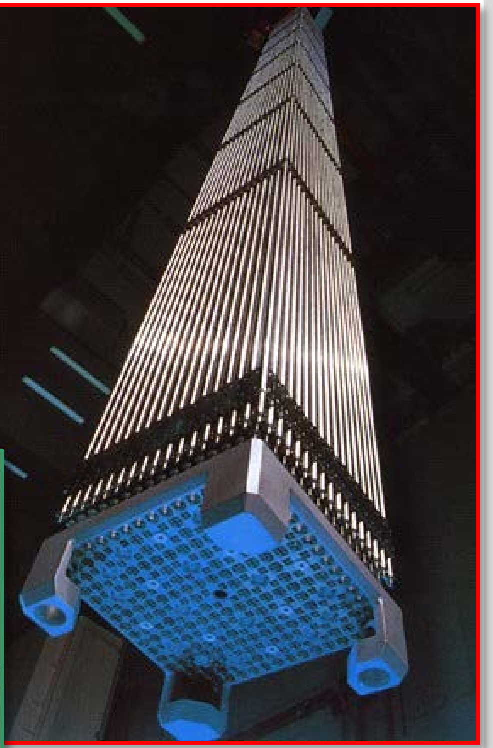
QUENCH project at KIT (program NUSAFE)

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

Separate-effects tests



Bundle experiments



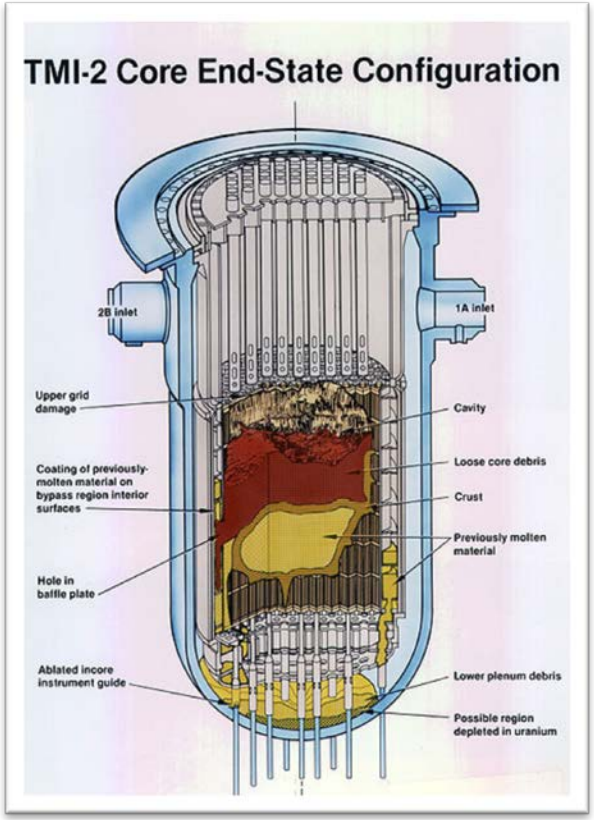
PWR fuel element

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

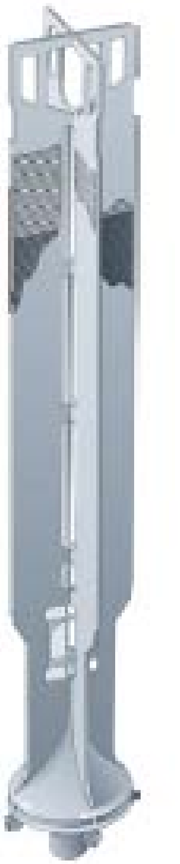
UO_2(/PuO_2) fuel:	100-200 t
Zry cladding + grid spacers:	20-40 t
Zry canister (BWR):	40 t
Various steels, Inconel:	>500 t (incl. RPV)
B_4C absorber (BWR, VVER, …):	0.3-2 t
AgInCd absorber (PWR):	3-5 t

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, …)

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

- In steam, oxygen, nitrogen, air, and various mixtures
- Temperature: 600-1600°C

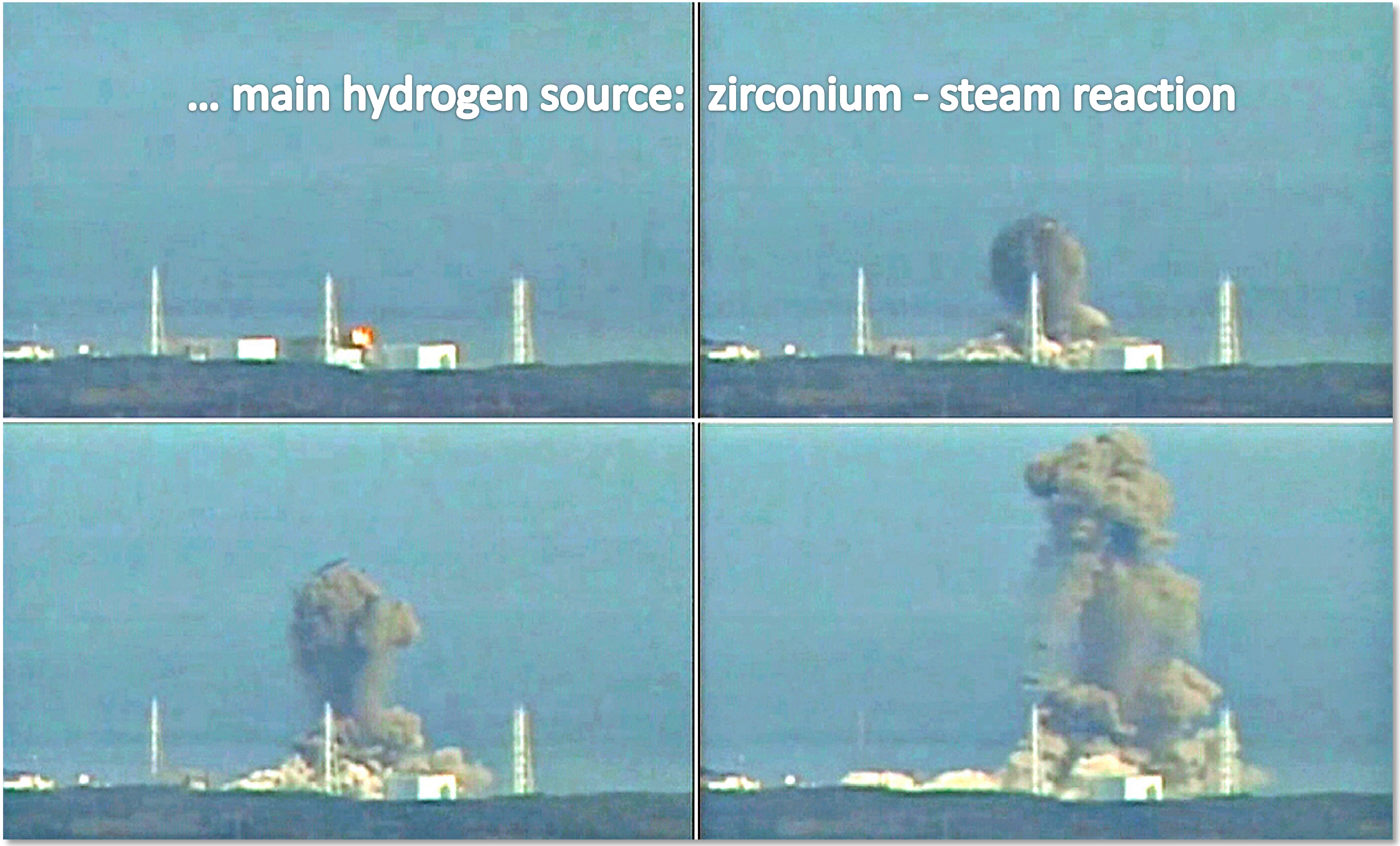
Oxidation of zirconium alloys – chemical reactions

ΔH_f at 1500 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

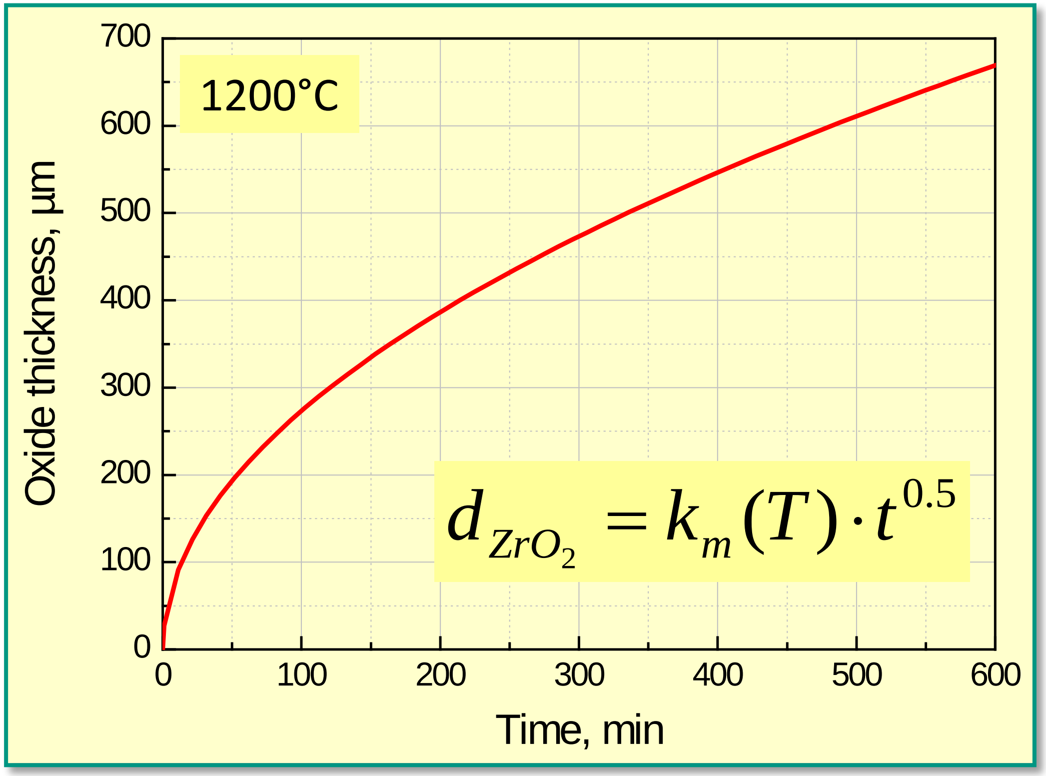
Hydrogen detonation in Fukushima Dai-ichi NPPs …



… main hydrogen source: zirconium - steam reaction

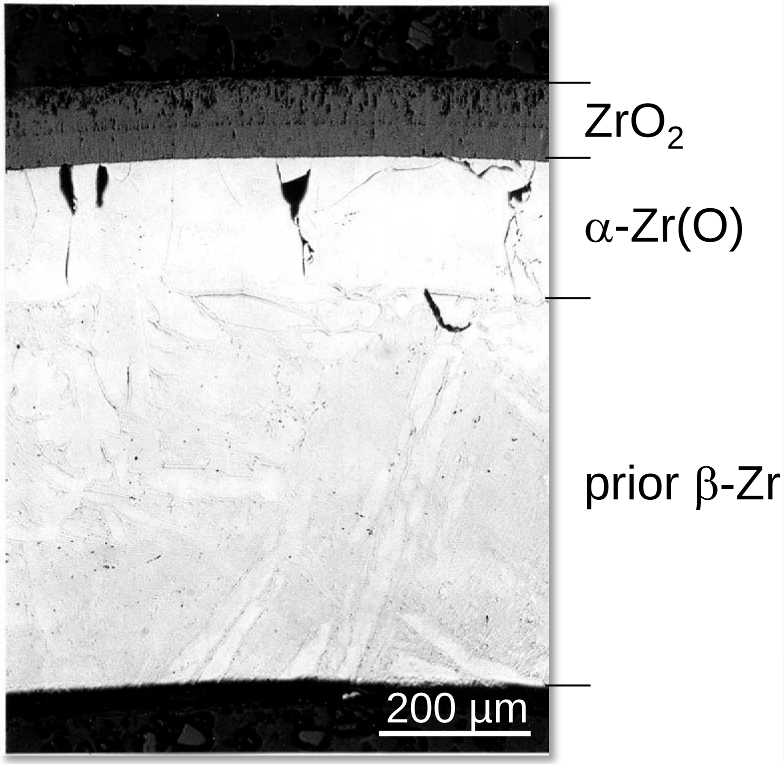
Oxidation in steam (oxygen)

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



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

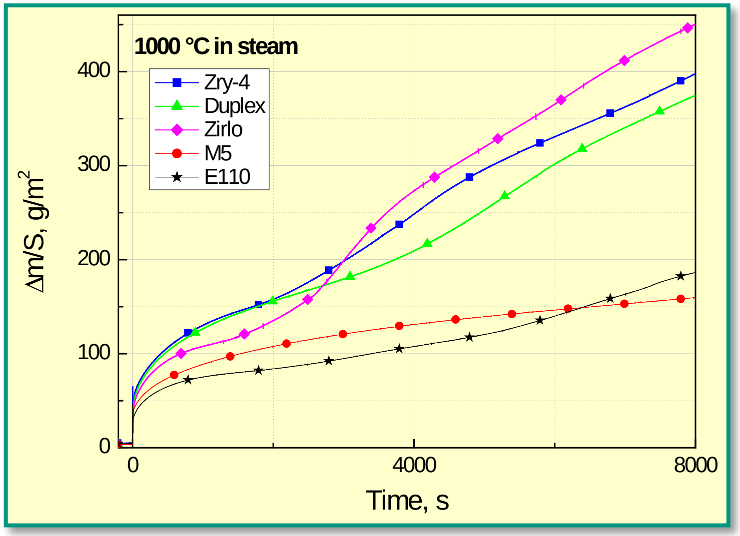
Oxide thickness during oxidation of Zry at 1200°C in steam

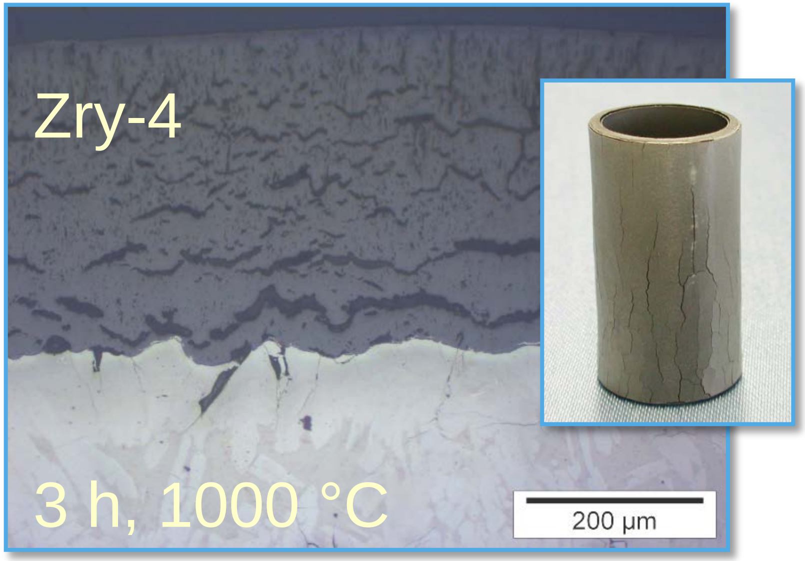


20 min at 1200°C in steam

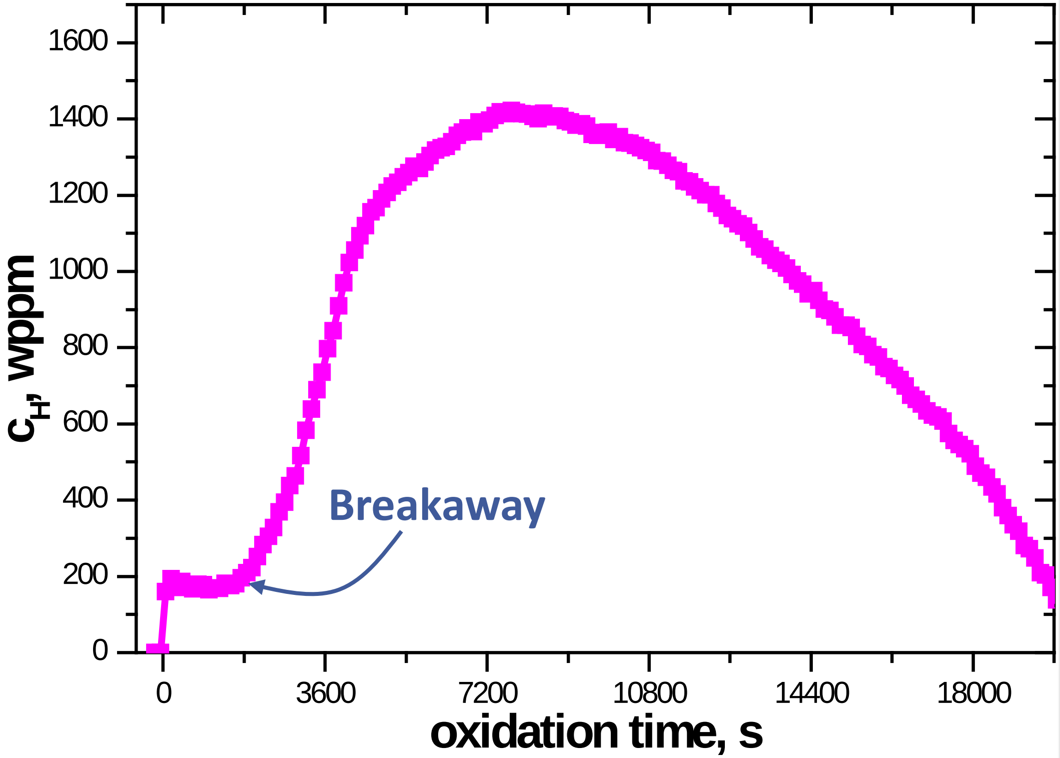
Breakaway oxidation

- 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 H_2 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

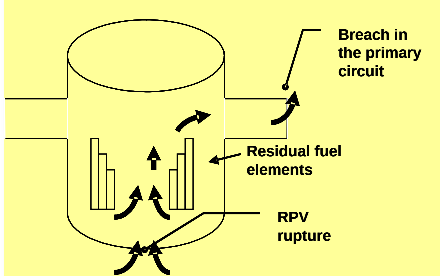
- Rapid initial hydrogen uptake
- Further strong hydrogen absorption after transition to breakaway

Oxidation in atmospheres containing nitrogen

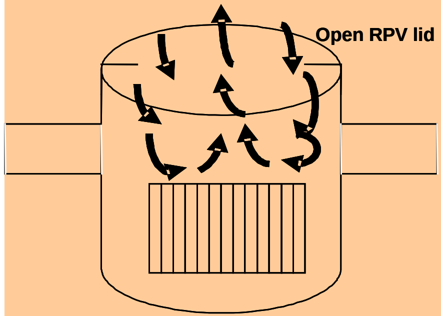
- Air ingress into reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

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

Late phase after RPV failure

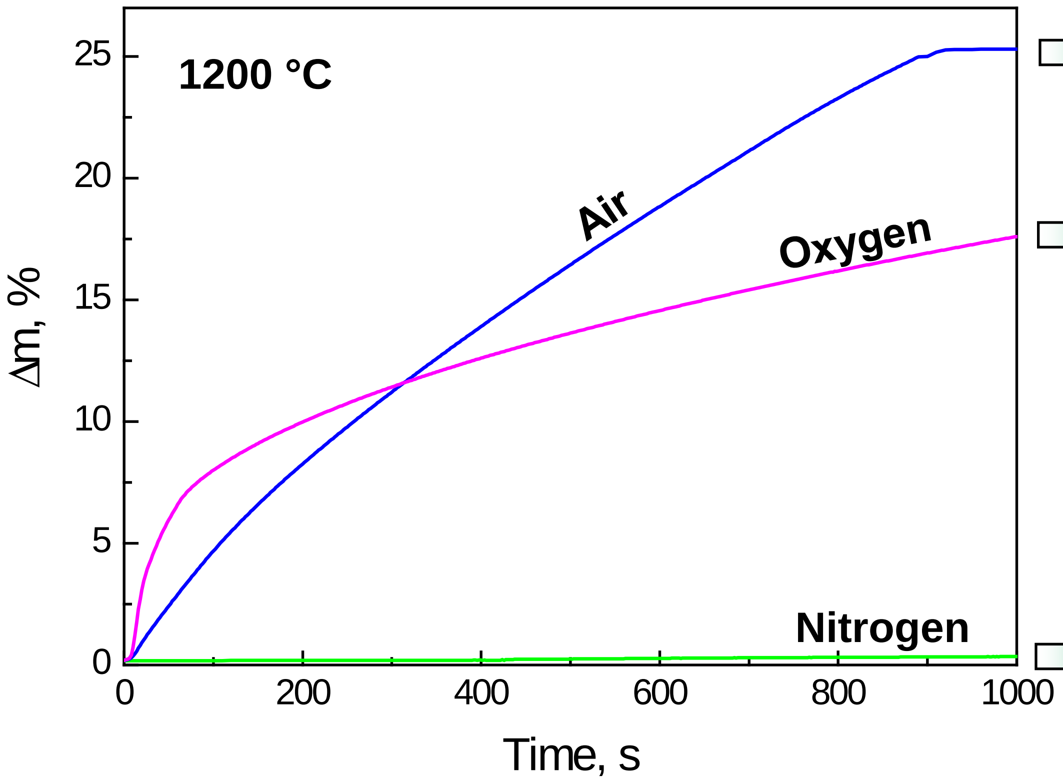


Mid loop operation



Spent fuel storage pool accident

Oxidation of Zr alloys in N_2, O_2 and air



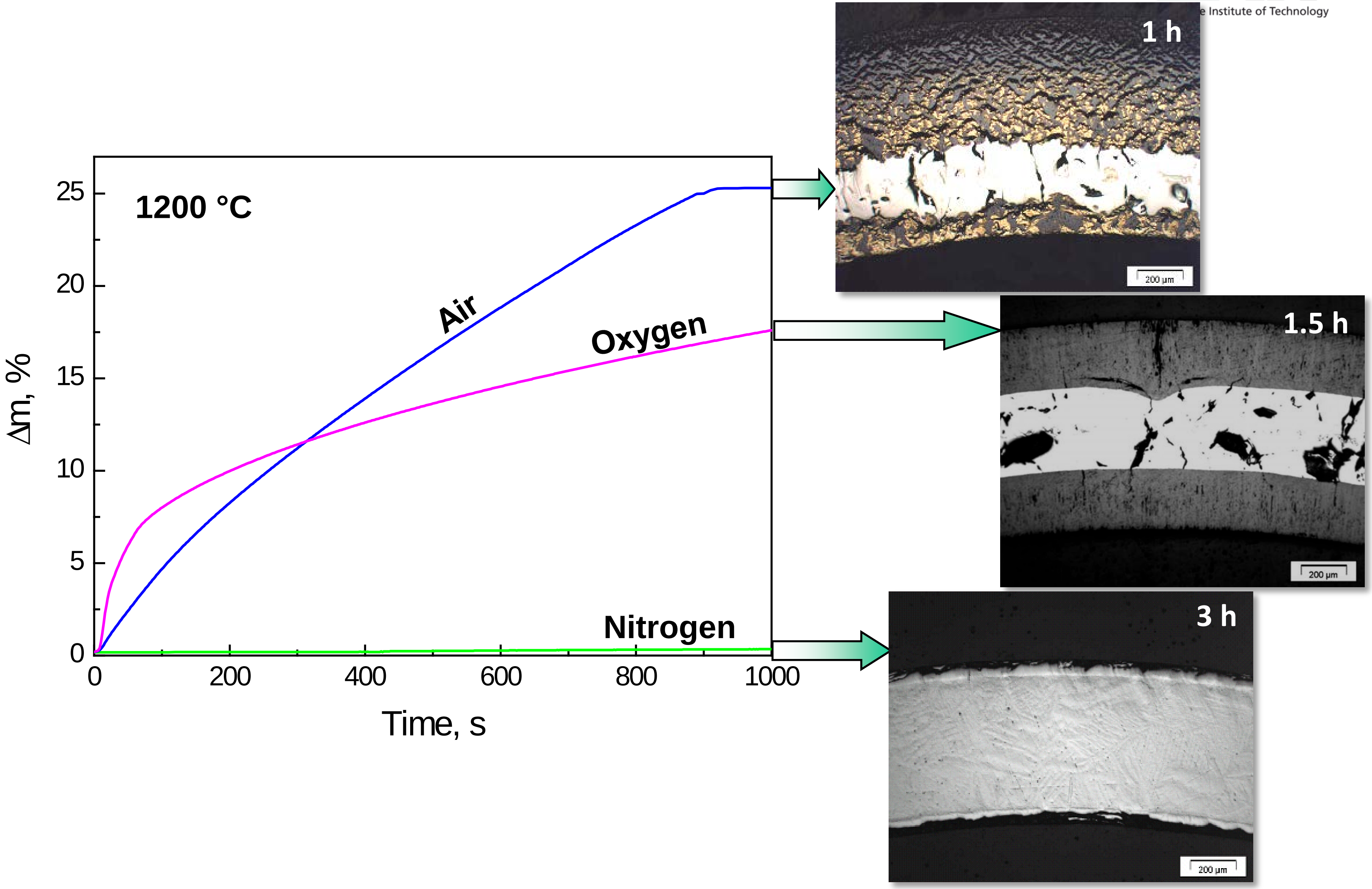
~ Linear oxidation kinetics

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

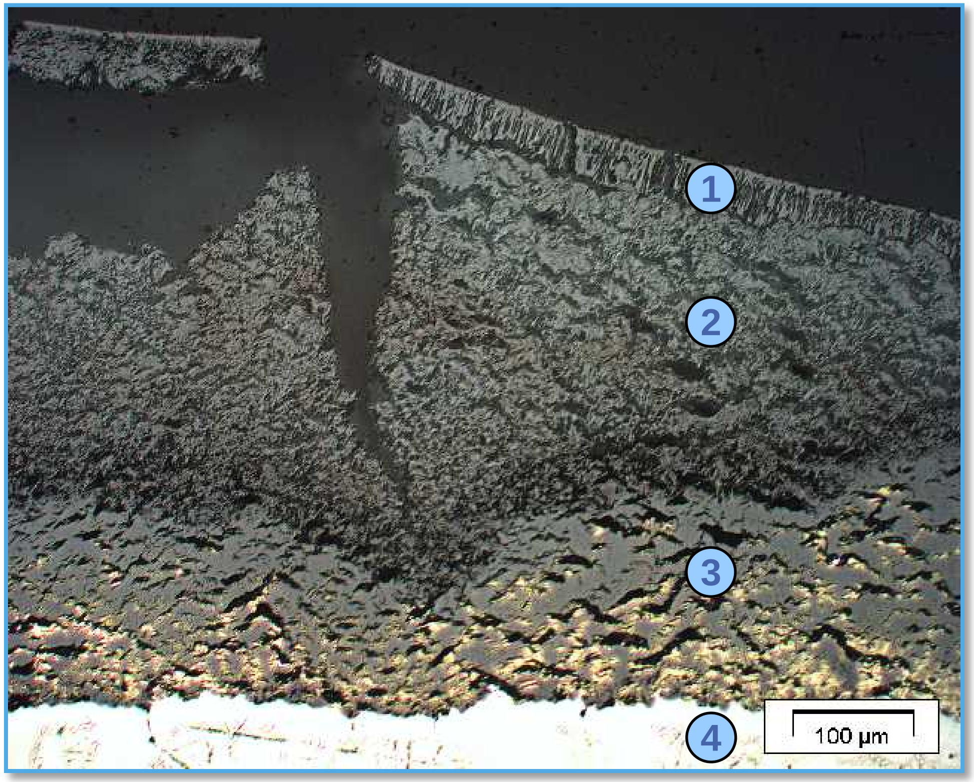
1 hour at 1200°C in air

Loss of barrier effect of cladding

Mechanism of air oxidation

- Diffusion of air through imperfections in the oxide scale to the metal/oxide 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



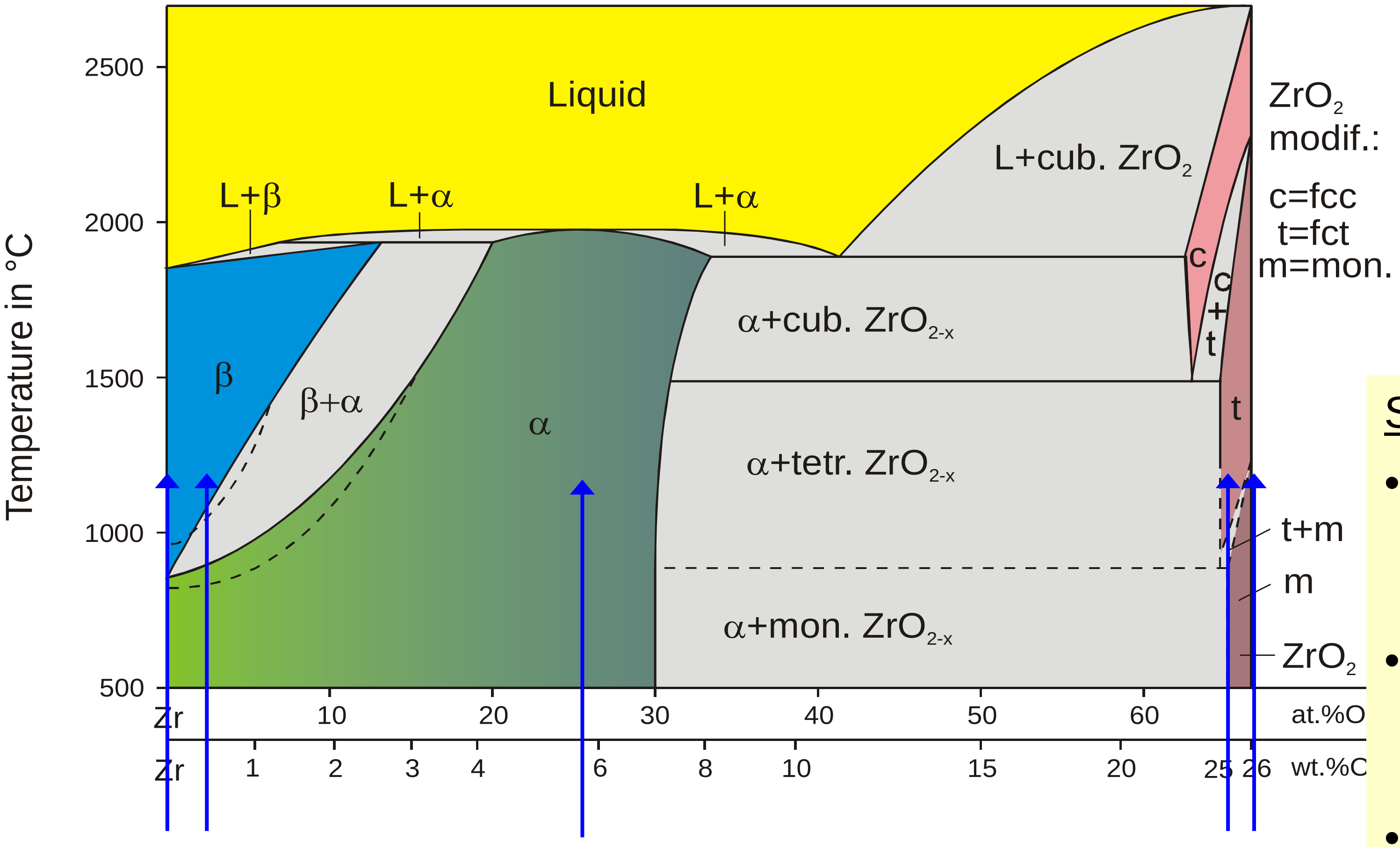
1 – initially formed dense oxide ZrO_2

2 – porous oxide after oxidation of ZrN

3 – ZrO_2 / ZrN mixture

4 – α-Zr(O)

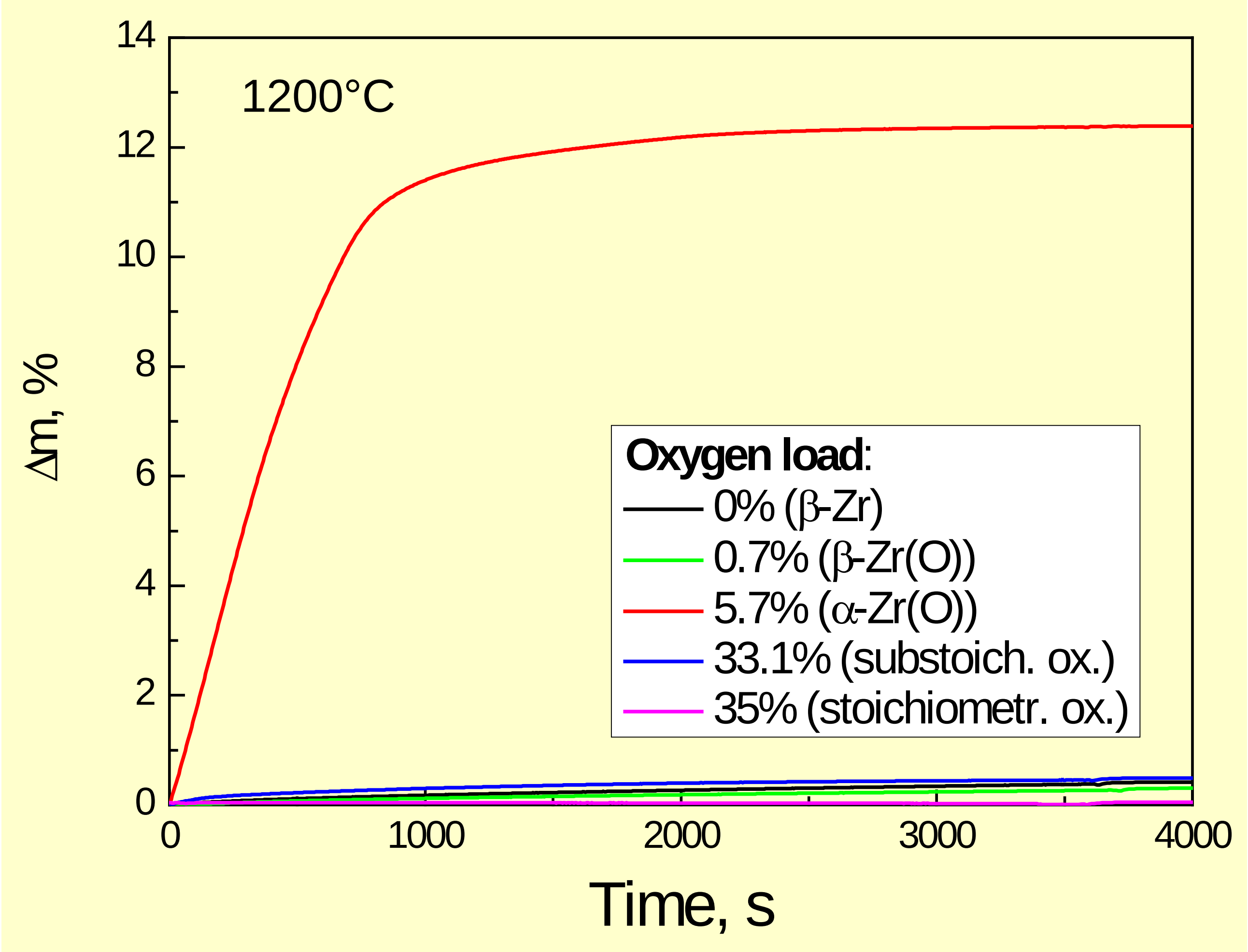
Experiments on mechanism of nitrogen attack

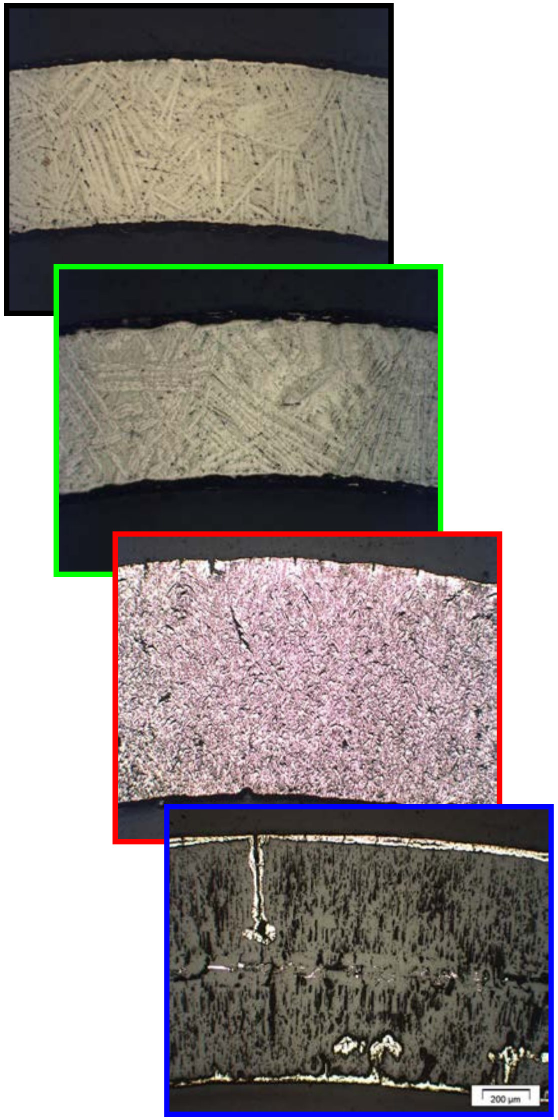


Specimens:

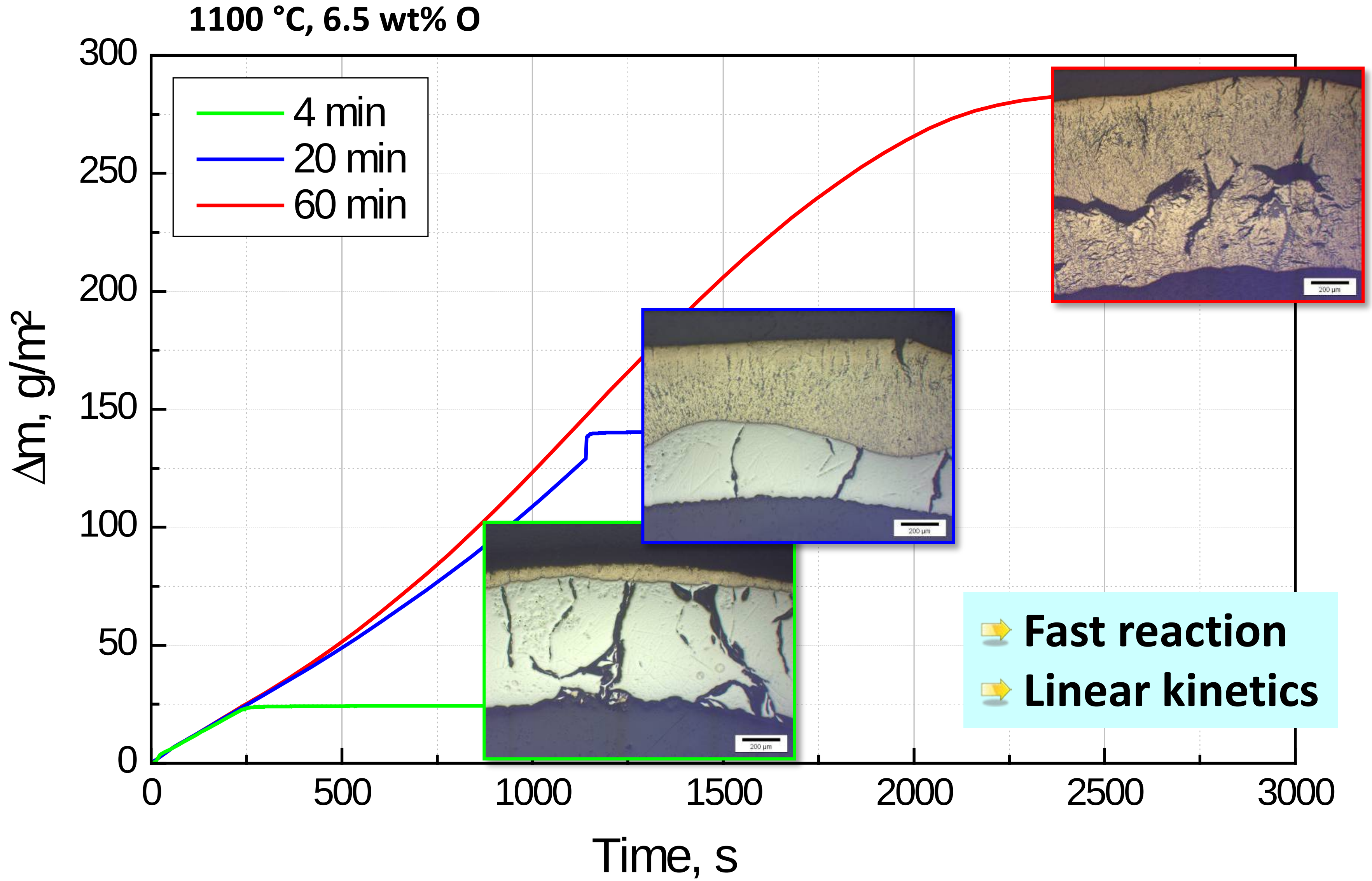
- Pre-oxidized in O_2 at 1200 °C (↑)
- Homogenized 3h at 1400 °C in Ar
- Reaction in N_2 1h at 1200 °C

Reaction of ZrO_x with nitrogen





α-Zr(O) – nitrogen reaction kinetics



- Fast reaction
- Linear kinetics

Oxidation in mixed steam-air atmospheres

Zry-4, 1 hour at 1200°C

H_2O

0.7 H_2O
0.3 air

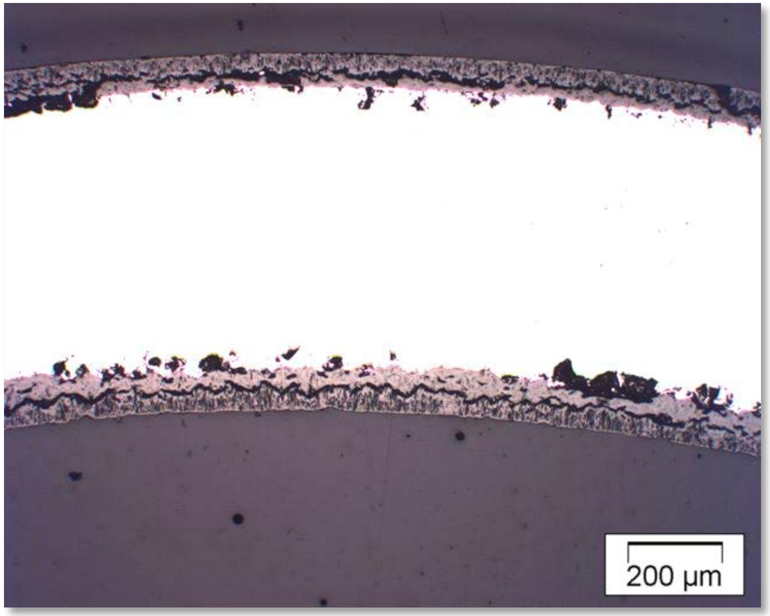
0.3 H_2O
0.7 air

0.1 H_2O
0.9 air

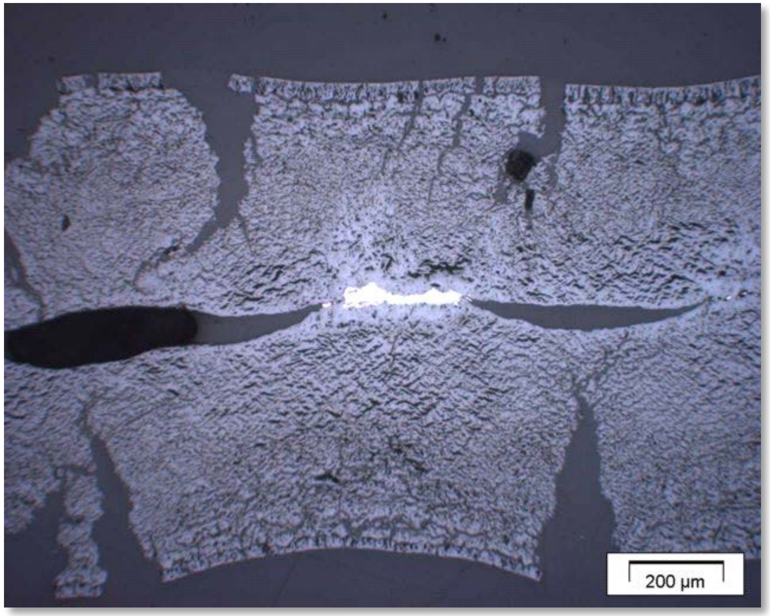
- Increasing degradation with raising content of air in the mixture

Oxidation in mixed atmospheres

1 hour at 1000 °C in steam

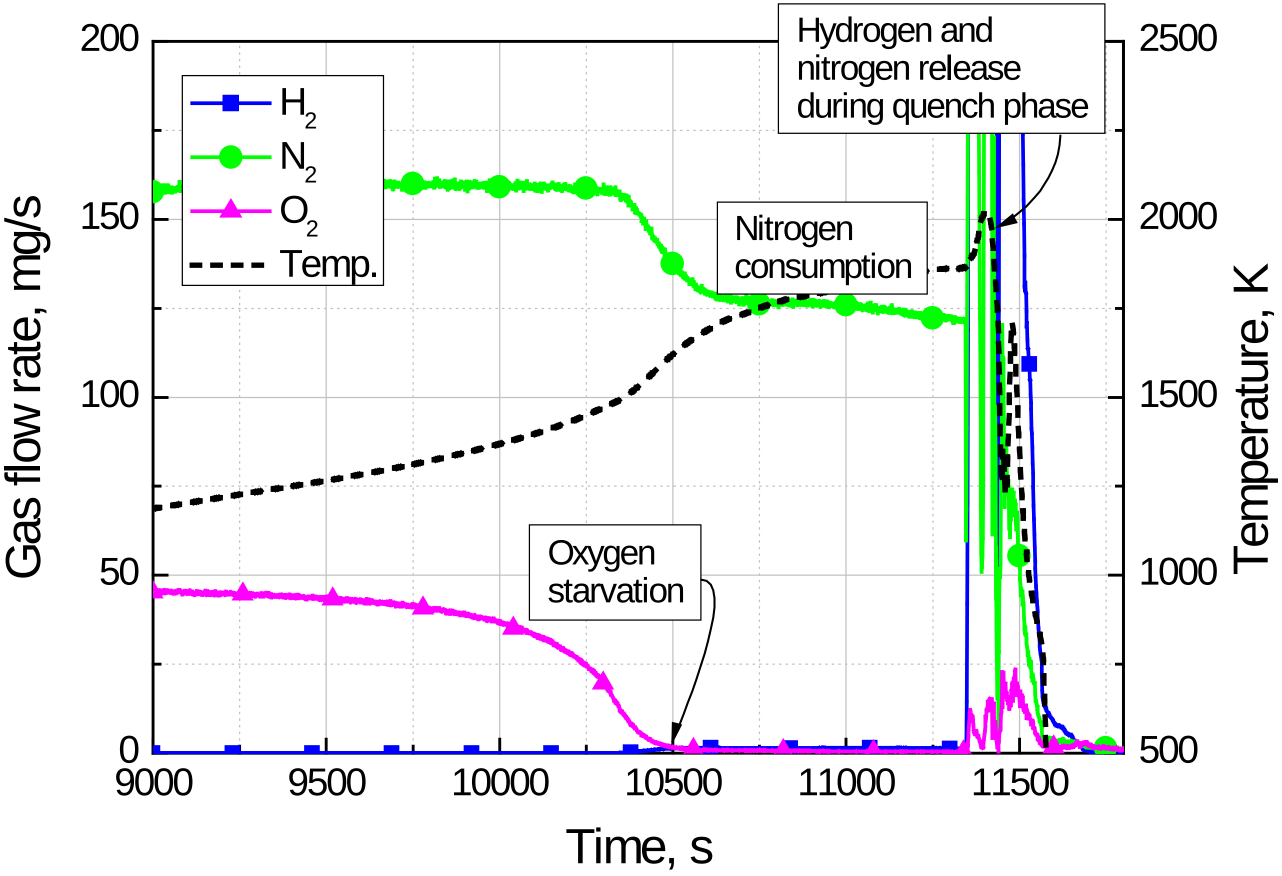


1 hour at 1000 °C in 50/50 steam/N_2



- 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

QUENCH-16 bundle test with air ingress

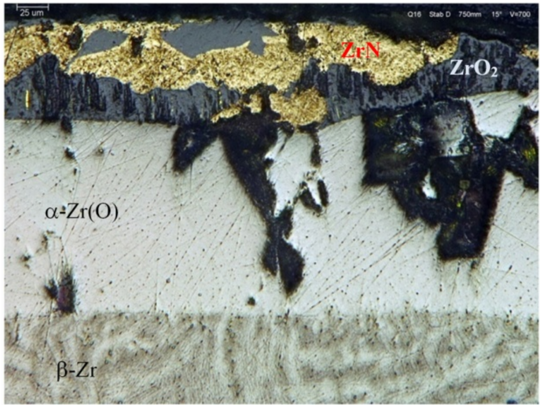


Hydrogen and nitrogen release during quench phase

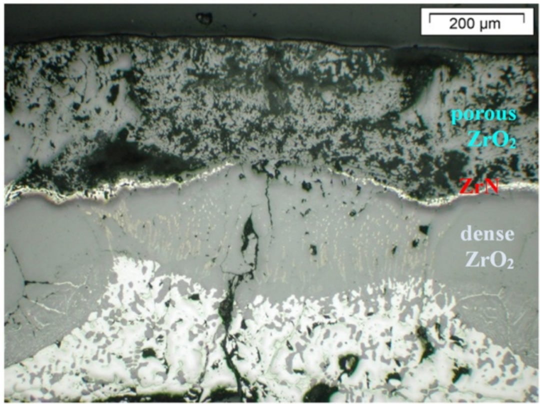
Nitrogen consumption

Oxygen starvation

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



ZrN formation at the end of air ingress phase

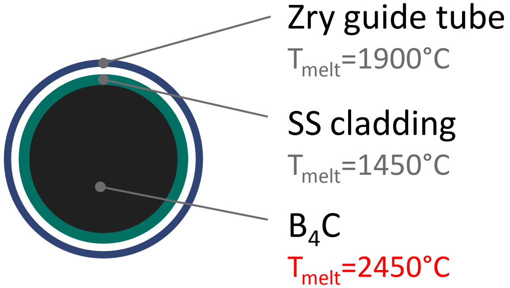


ZrN re-oxidation during quench phase

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)



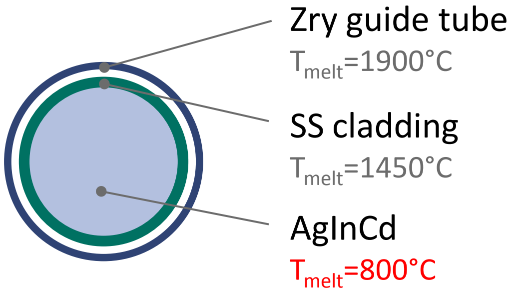
BWR control rod

BWR control blade

AgInCd alloy

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

PWR control rod assembly



PWR control rod

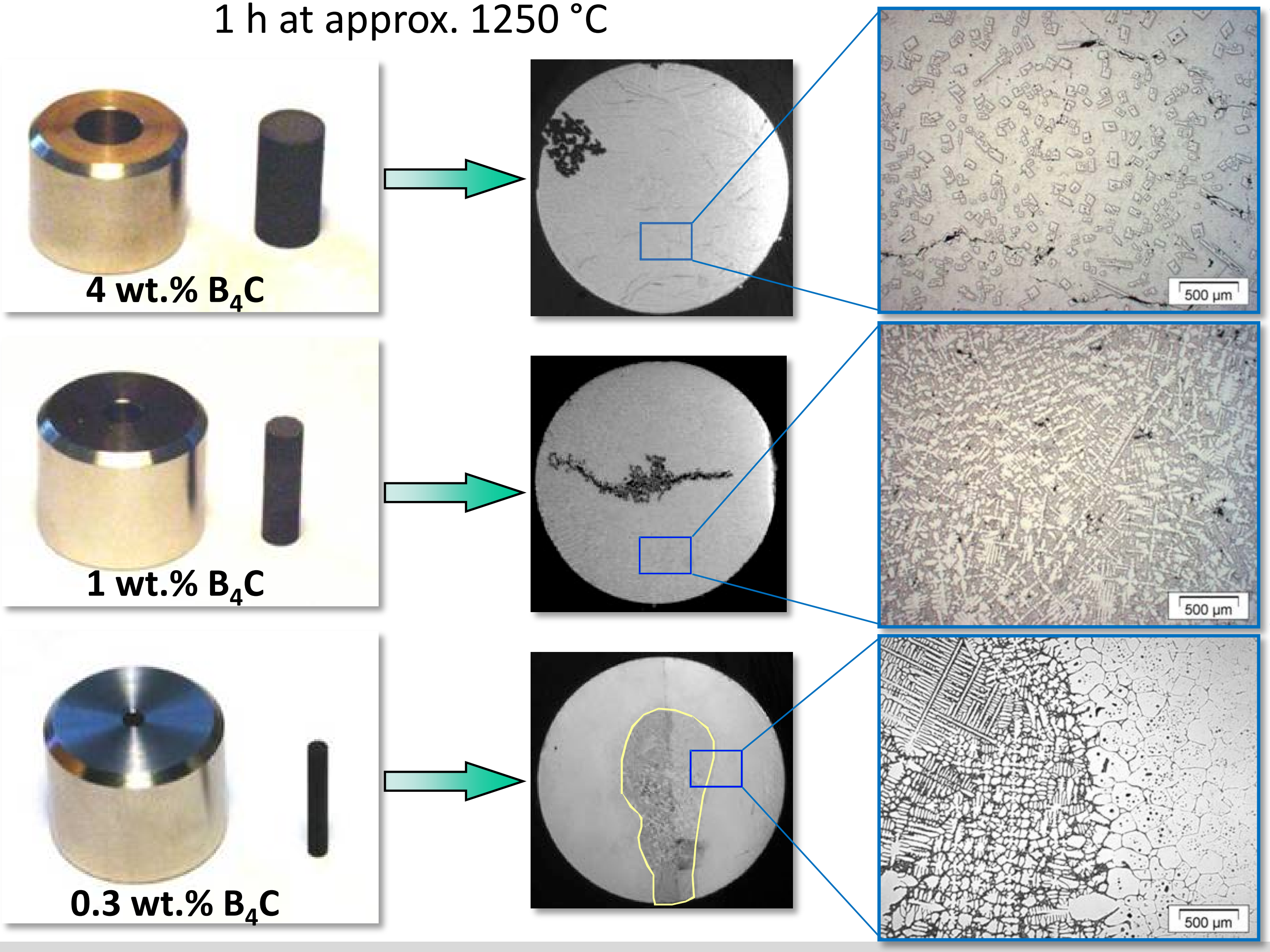
Degradation of B_4C control rods (1-pellet)

Post-test appearance and axial cross section of B_4C/SS/Zry specimens after 1 hour isothermal tests at temperatures between 1000 and 1600 °C

1000°C 1200°C 1300°C 1400°C 1500°C 1600°C

Eutectic interaction of stainless steel with B_4C

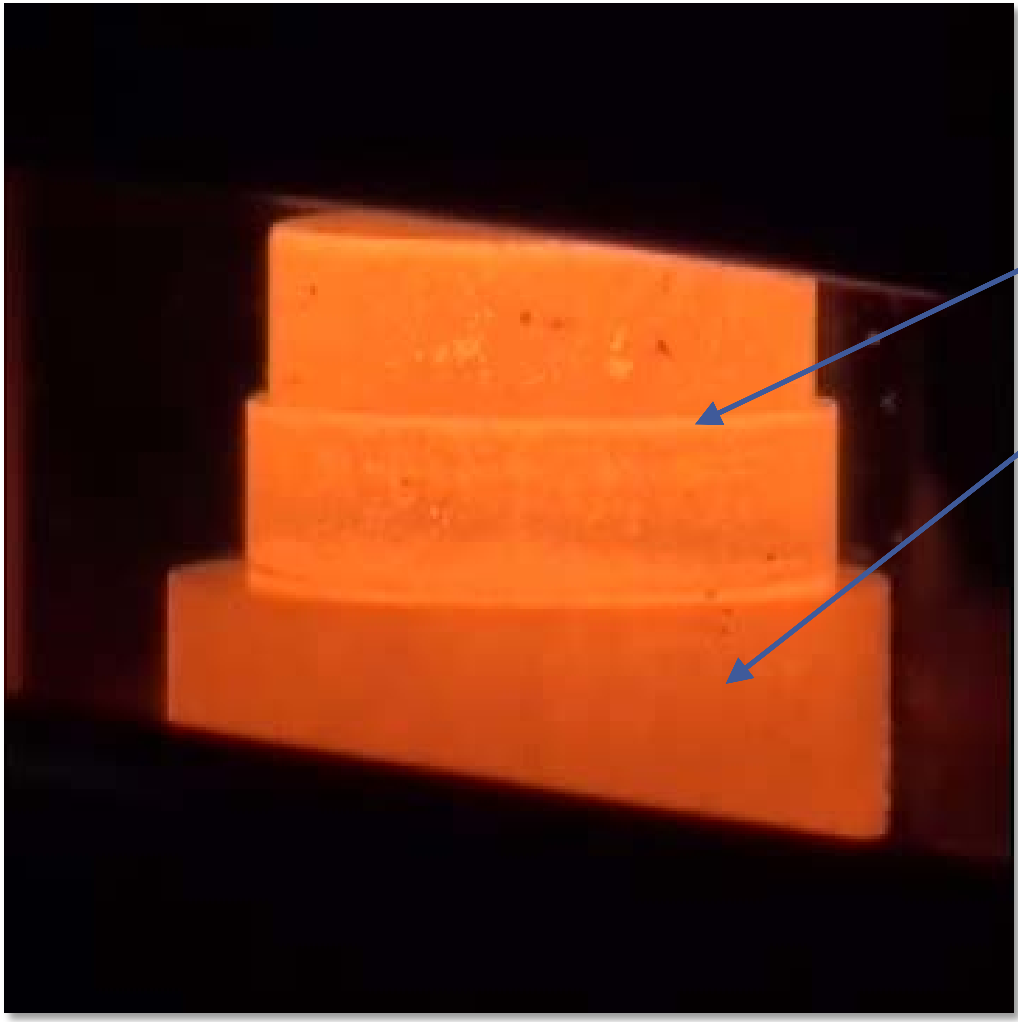
1 h at approx. 1250 °C

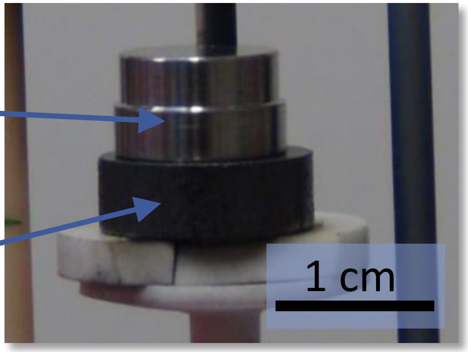


Complete liquefaction of stainless steel

1/3 of SS liquefied

Eutectic interaction of stainless steel with B_4C





- Rapid and complete melting of SS at 1250°C starting at B_4C/SS boundary

Oxidation of boron carbide; main chemical reactions

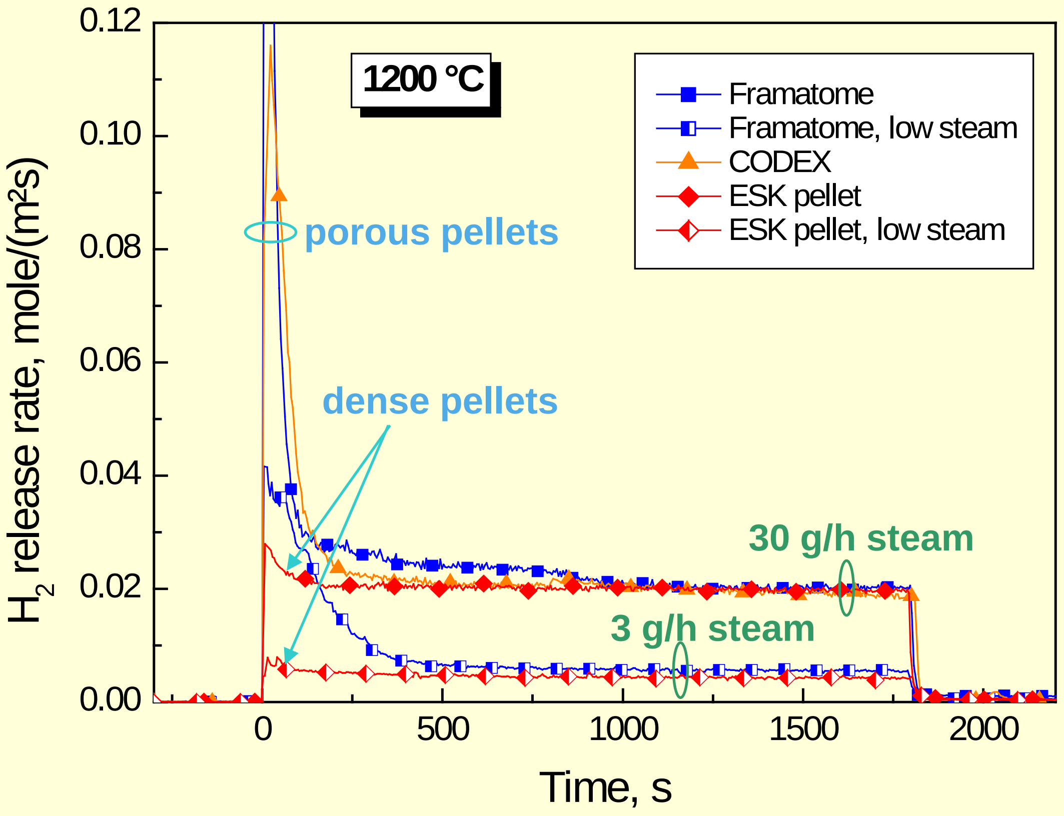
$$B_4C + 8H_2O(g) \rightarrow 2B_2O_3(l) + CO_2(g) + 8H_2(g)$$ -760 kJ/mol

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

$$B_2O_3 + H_2O(g) \rightarrow 2HBO_2(g)$$ +341 kJ/mol

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

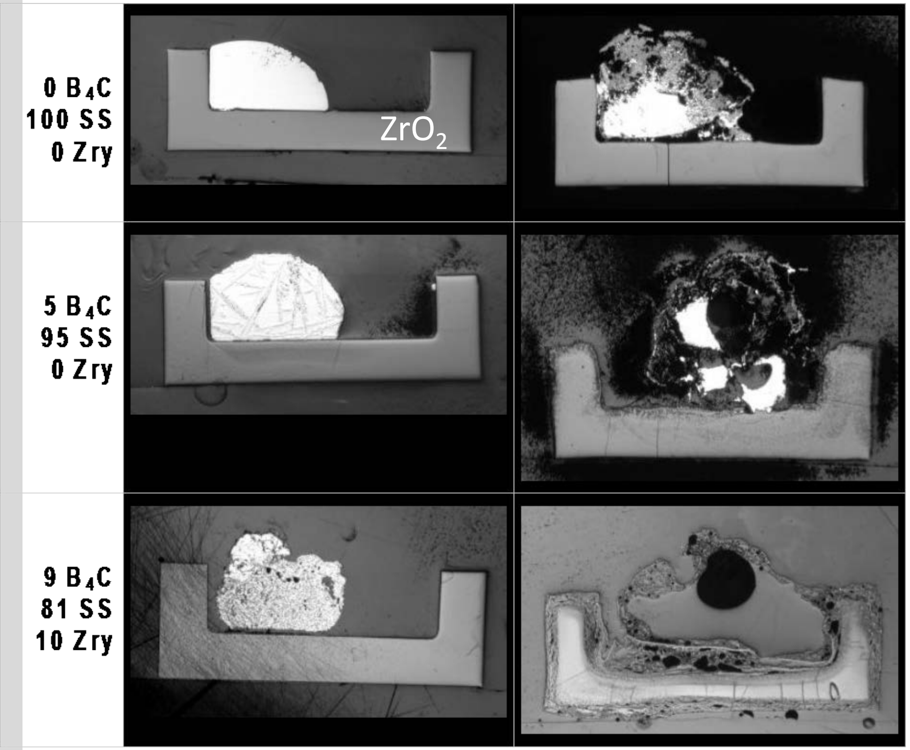
Oxidation kinetics of B_4C in steam

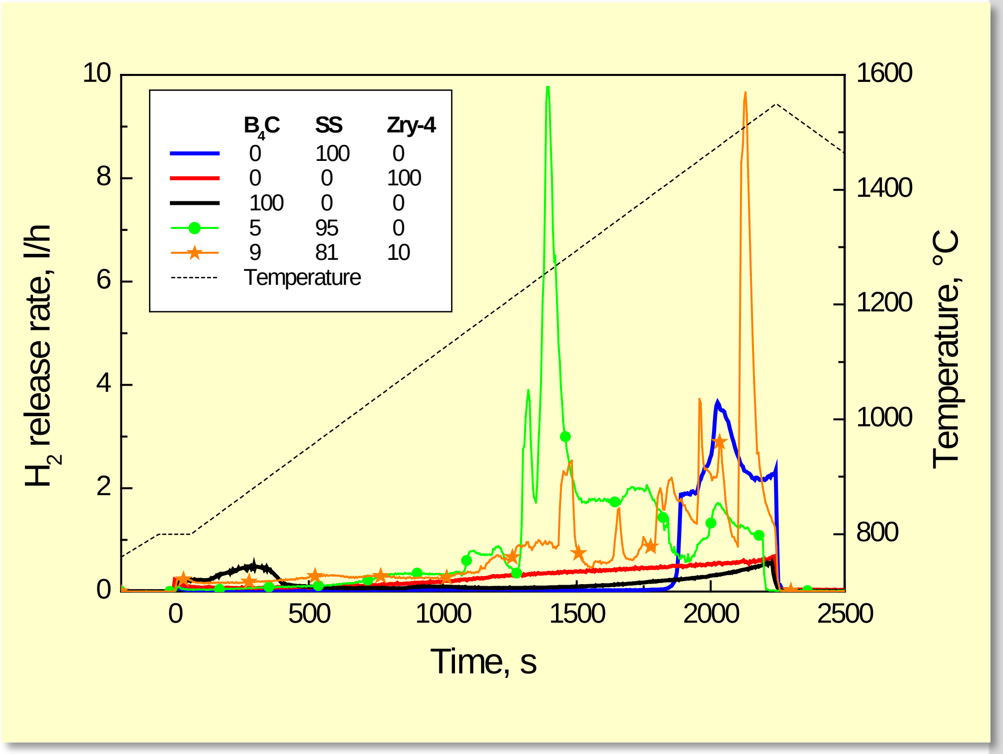


- Strongly dependant on B_4C structure and thermo hydraulic boundary conditions like pressure and flow rate

Oxidation of B_4C absorber melts

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



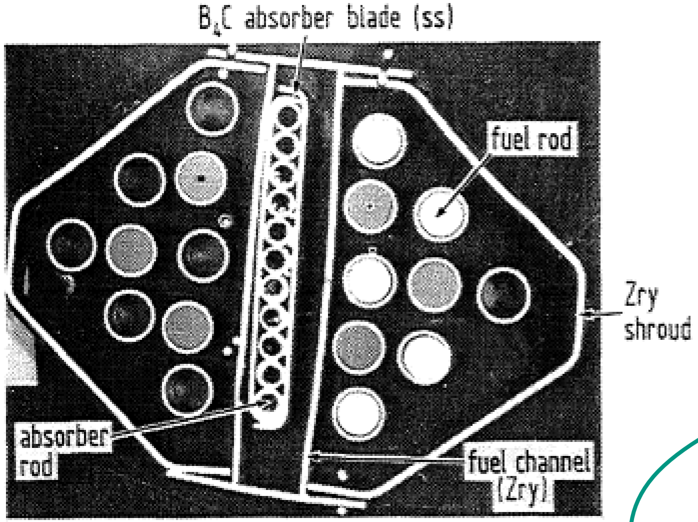


before oxidation

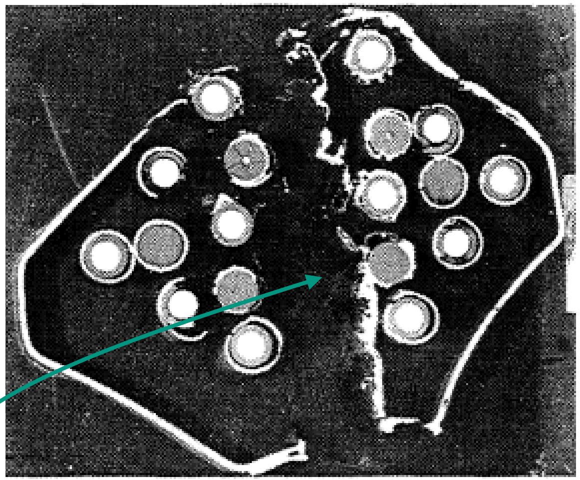
after oxidation

Oxidation rate during reaction of absorber melts and pure CR components in steam

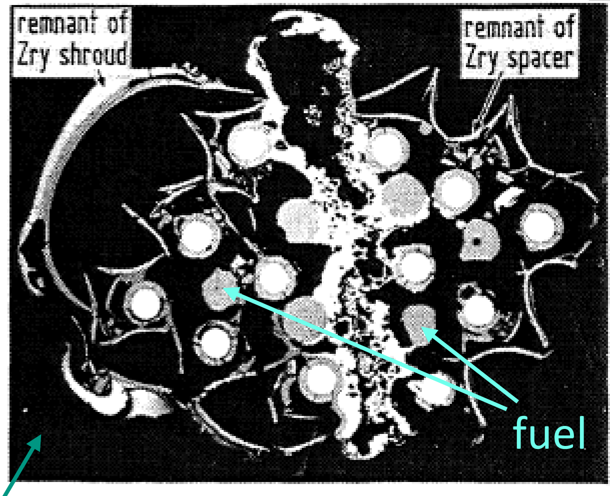
Degradation of B_4C control blade (BWR bundle test) CORA-16



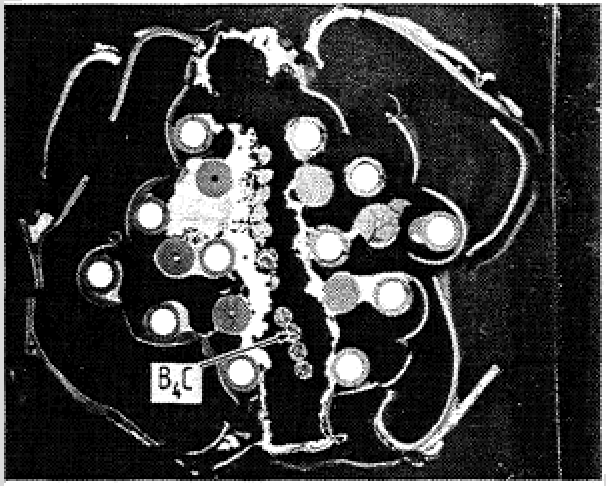
16-08 (1145mm), bottom view



-07 (963mm), top view

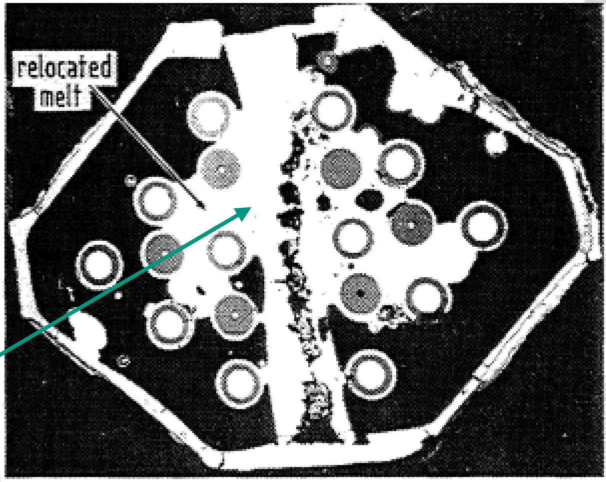


16-09 (525mm), top view
center grid spacer elevation



16-03 (310mm), top view

- Complete loss of absorber blade
- Dissolution of cladding and fuel
- Massive melt relocation (B_4C, SS, Zry, UO_2)



16-01 (110mm), top view

Gas release due to oxidation of B_4C (melts)

- Hydrogen
  - Up to 290 g H_2 per kg B_4C
  - 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 a
  - CO combustible and poisonous
- Methane
  - Would have strong effect on fission pr
  - Bundle experiments and SETs reveal o
- Boric acids
  - Volatile and soluble in water
  - Deposition at colder locations in the circuit

Energetic effects of B_4C oxidation

- Oxidation of B_4C in steam: $13\ \mathrm{MJ/kg}_{B4C}$
- Oxidation of B_4C in oxygen: $50\ \mathrm{MJ/kg}_{B4C}$

➡ Significant contribution to energy release in the core

For comparison:

- Oxidation Zr in steam: $6\ \mathrm{MJ/kg}_{Zr}$
- Fuel value of mineral oil: $12\ \mathrm{MJ/kg}_{oil}$
- Fuel value of black coal: $30\ \mathrm{MJ/kg}_{coal}$

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°C

Fukushima Daiichi NPPs:

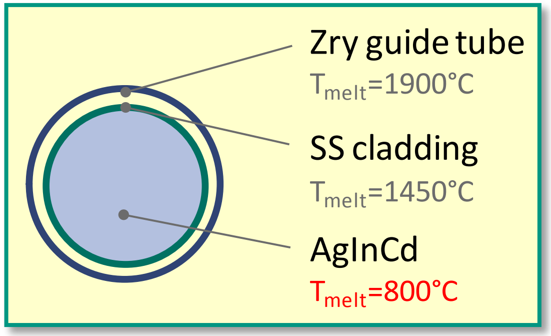
- Unit 1: 97 control blades
- Unit 2-4: 137 control blades

- Complete oxidation of B_4C inventory by steam:
- ➡ 195/275 kg H_2
- ➡ 2700/3800 kWh (10/14 GJ)

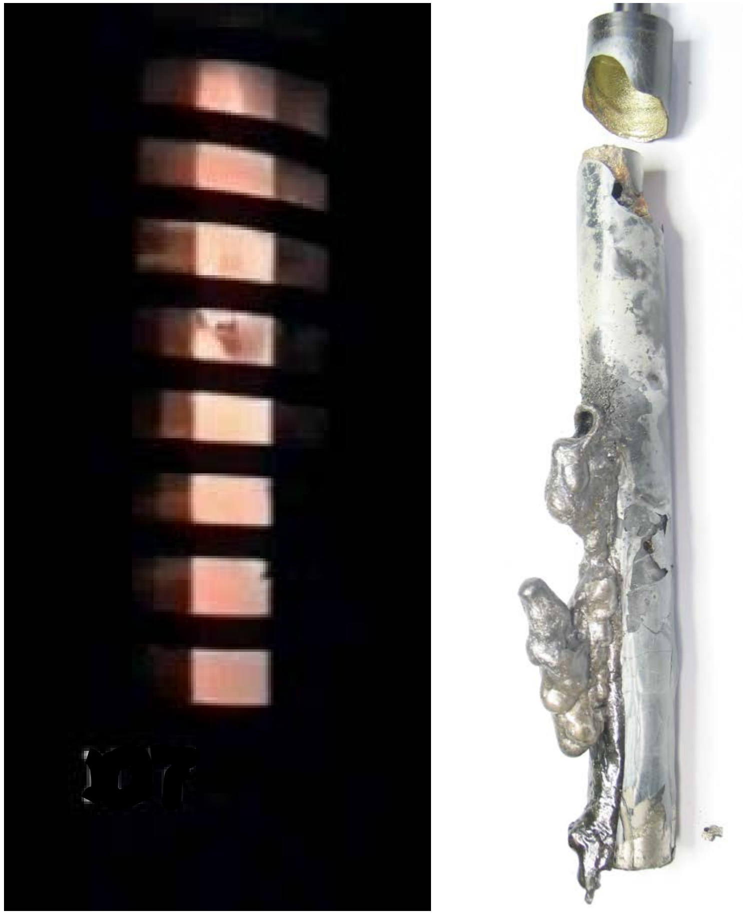
BWR control rod

Failure of AgInCd absorber rod

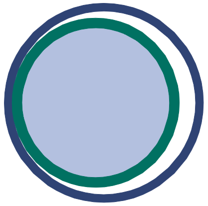
- Ag-In-Cd control rods fail at temperatures above 1200°C due to the eutectic interaction between SS and Zry-4
- Failure is very stochastic (from local to explosive) with the tendency to higher temperatures for symmetric samples and specimens with inner oxidation
- No ballooning of the SS cladding tube was observed before rupture
- Burst release of cadmium vapour is followed by continuous release of indium and silver aerosols and absorber melt

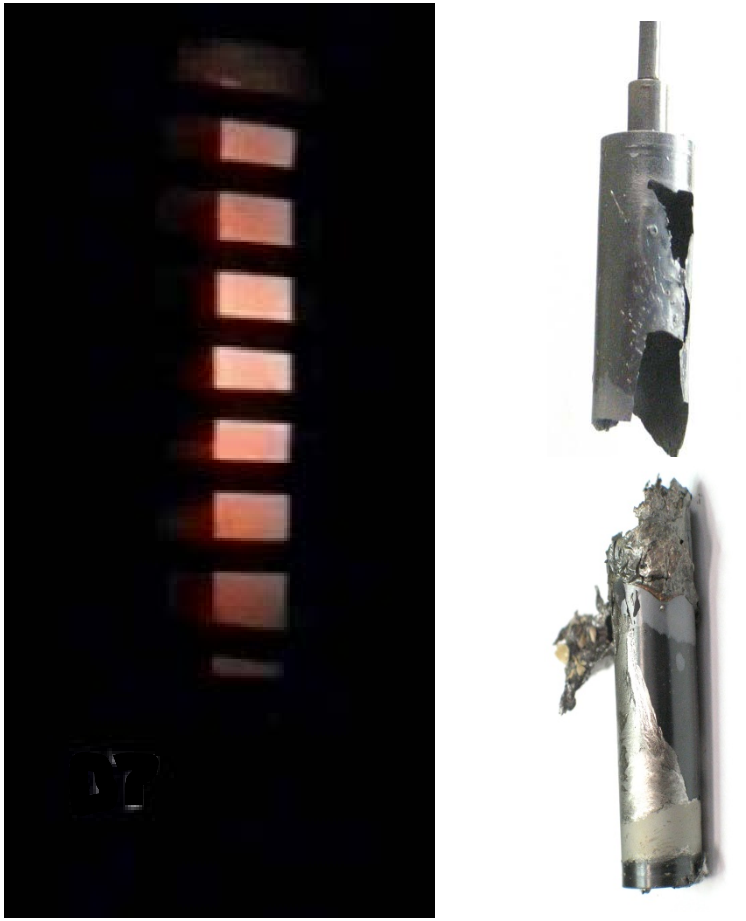


Different failure types of AgInCd absorber rod

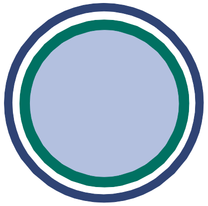


SIC-02 (asym. rod)
Local failure at 1230°C

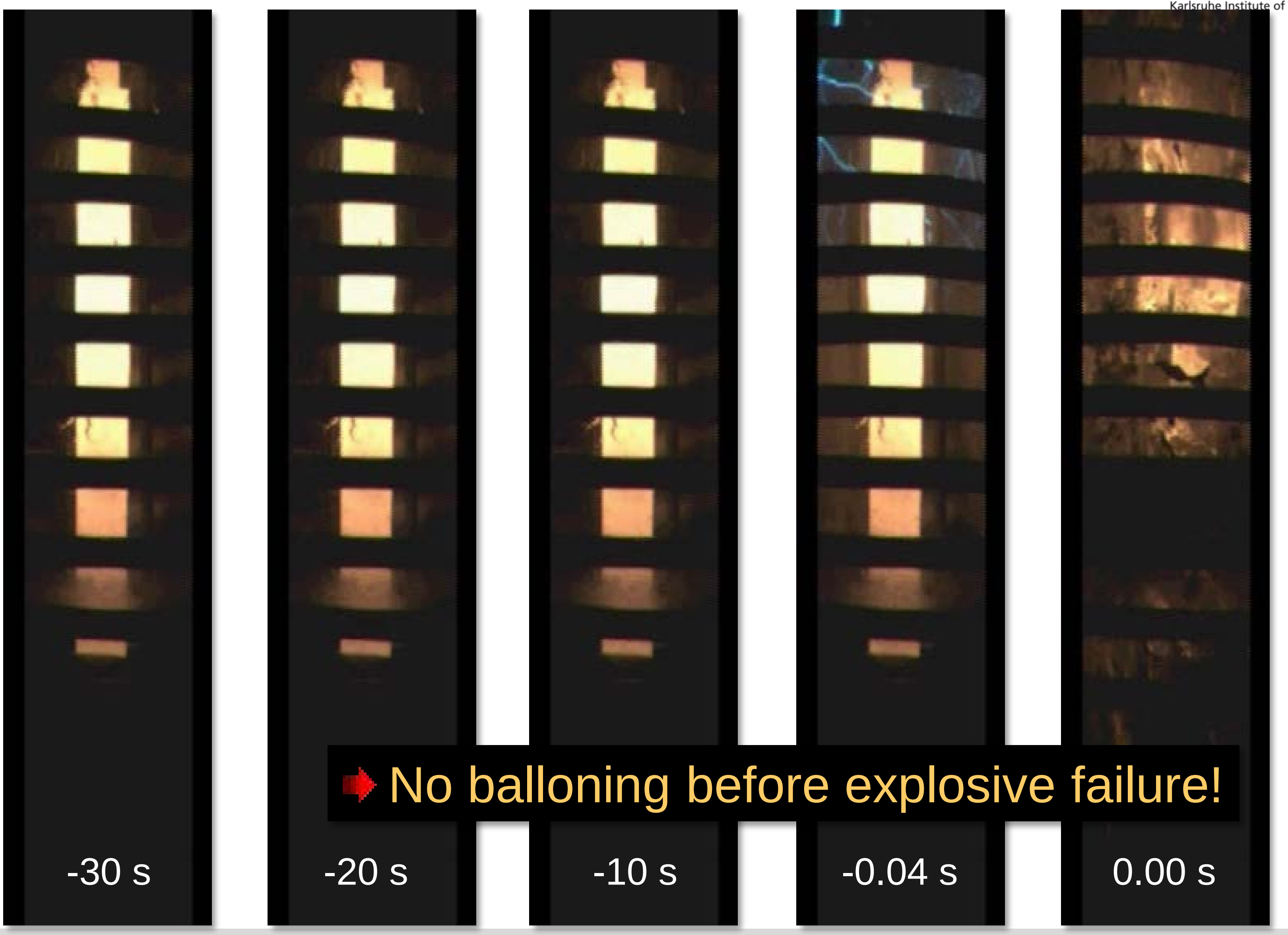




SIC-05 (symmetric rod)
Global failure at 1350°C

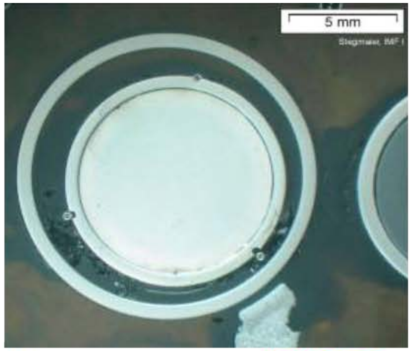


Explosive failure of SIC-11 w/o Zry guide tube

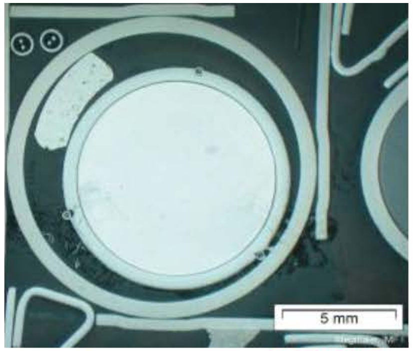


➧ No balloning before explosive failure!

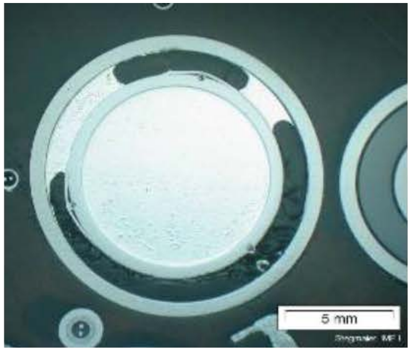
QUENCH-13 control rod appearance



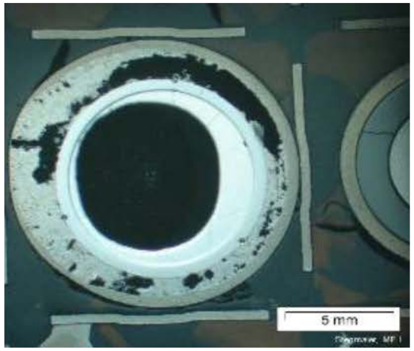
50 mm 540°C



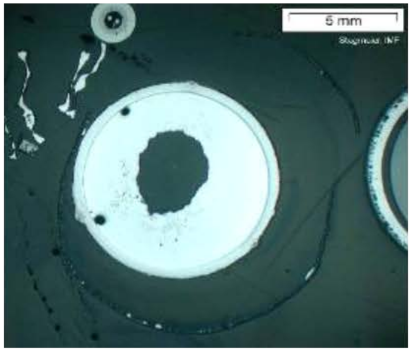
170 mm 650°C



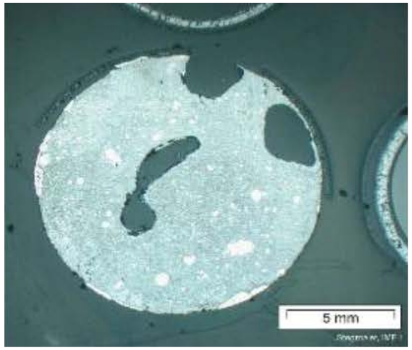
350 mm 850°C



550 mm 1026°C

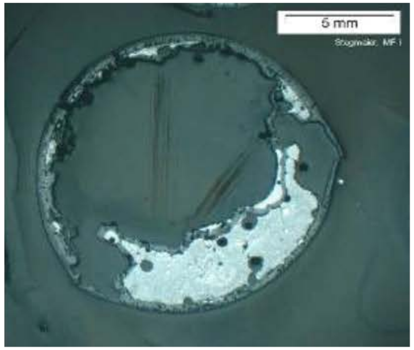


750 mm 1280°C



850 mm 1437°C

950 mm 1418°C

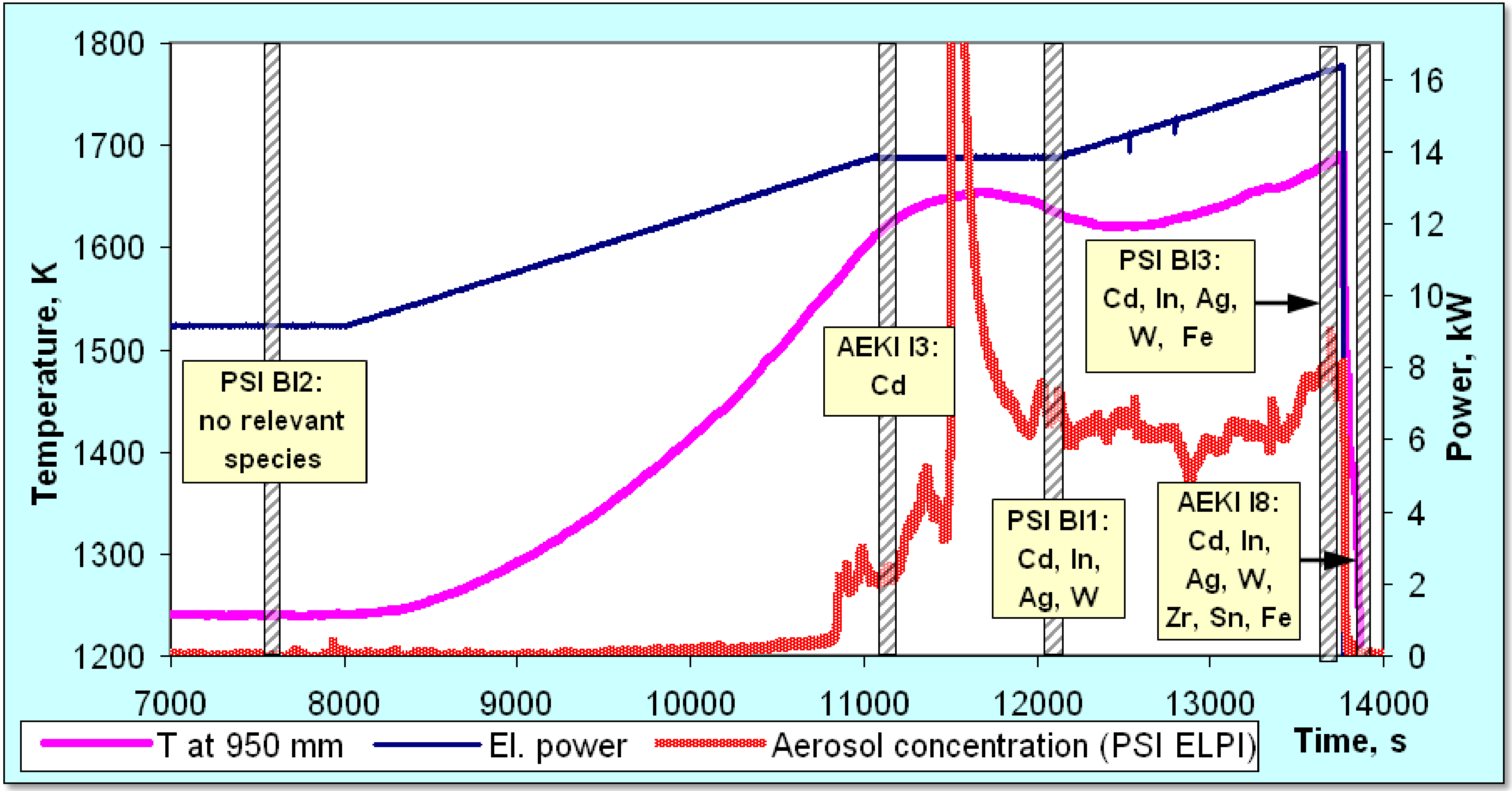


1050 mm 1216°C

- 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. B_4C-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

THANKS to …

- The QUENCH team at KIT
- Michèle Pijolat for inviting me and hospitality
- YOU … for your attention

KIT
Karlsruhe Institute of Technology

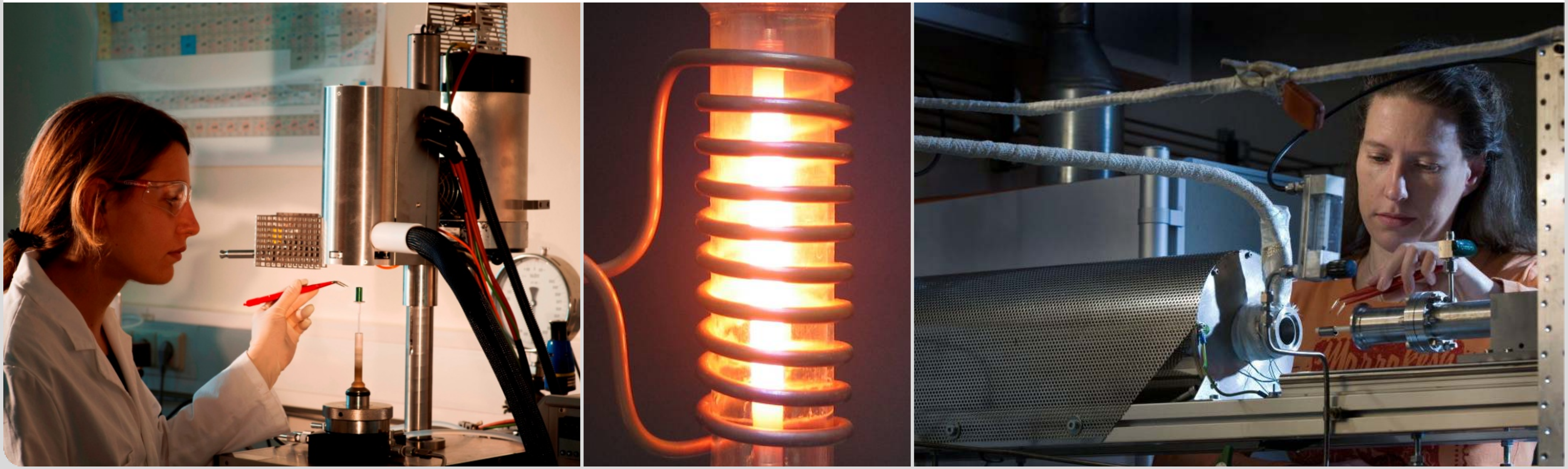
IAM
Institute for Applied Materials

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

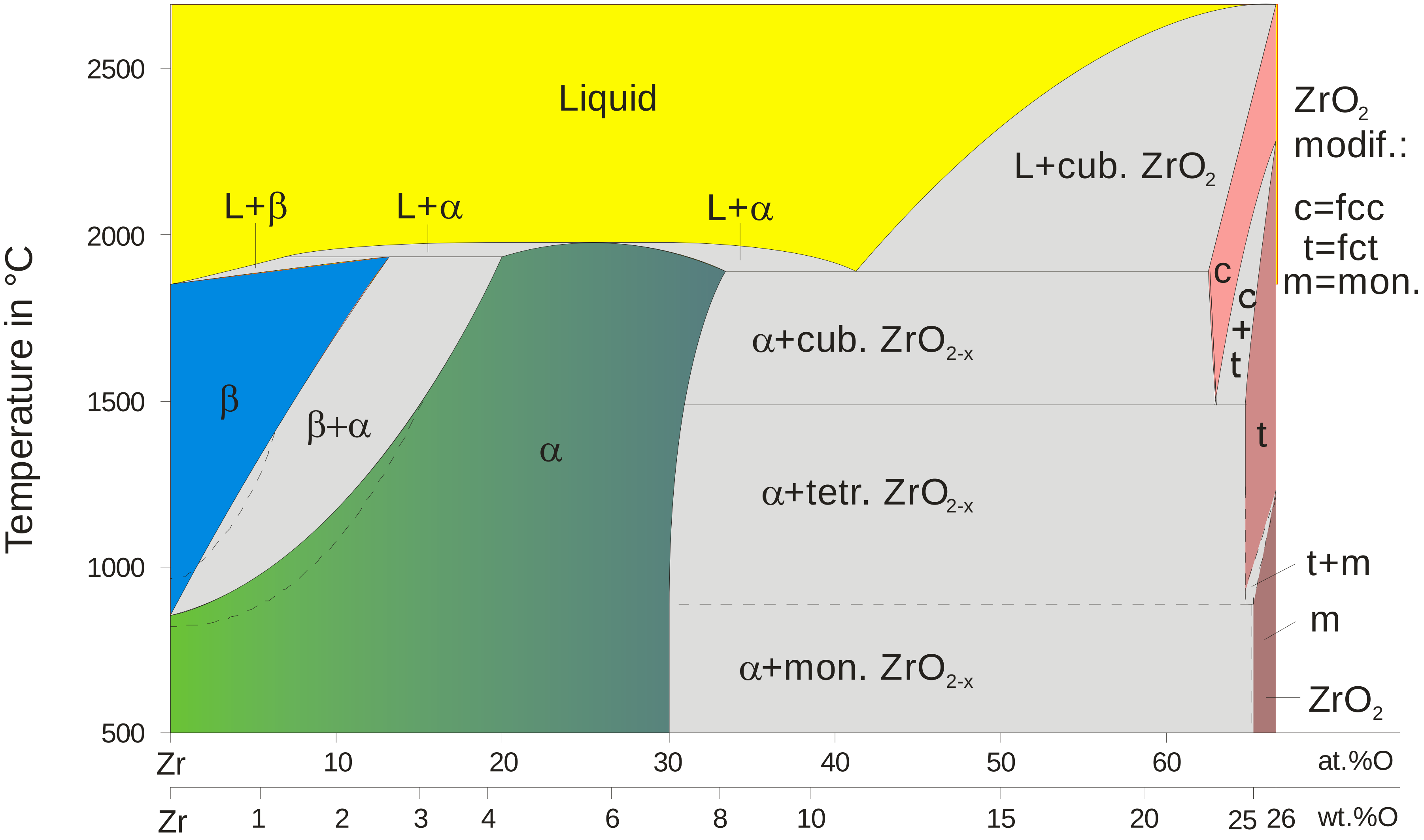
Martin Steinbrück

EMSE Seminar, 18 December2013, St. Etienne, France

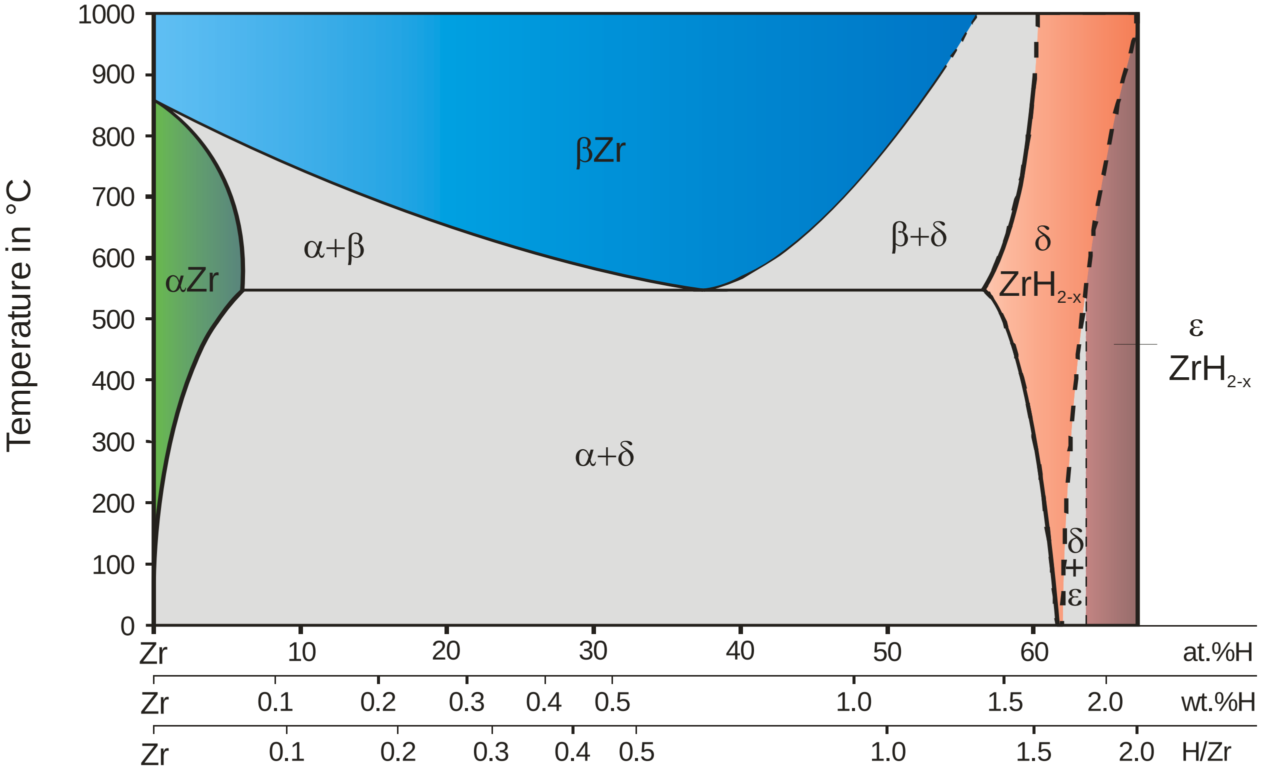
Institute for Applied Materials IAM-AWP & Program NUSAFE



Phase diagram Zr - O



Phase diagram Zr - H



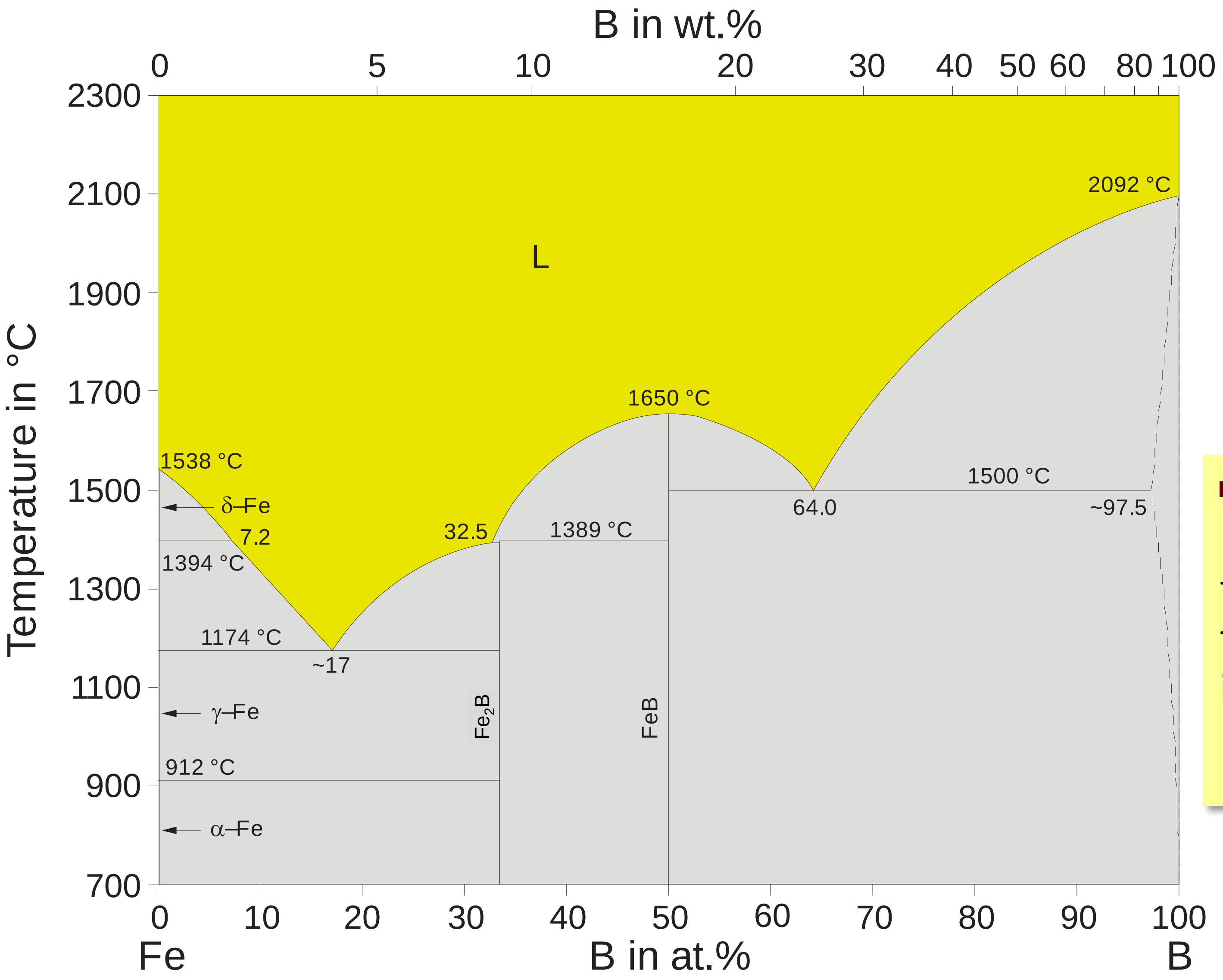
Sieverts' law:

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

with

$$k_S = A \cdot e^{\frac{-B}{RT}}$$

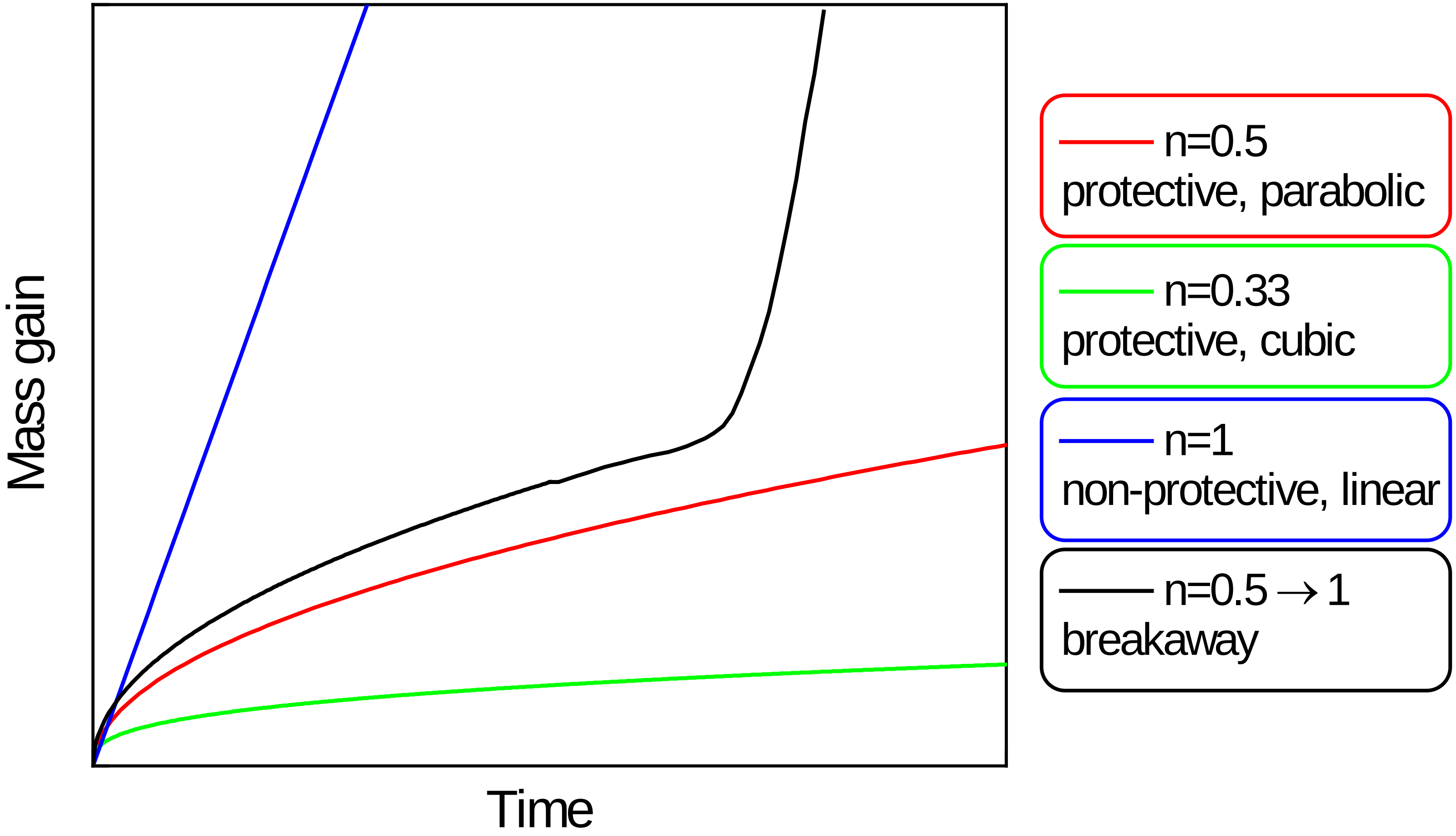
Phase diagram iron - boron



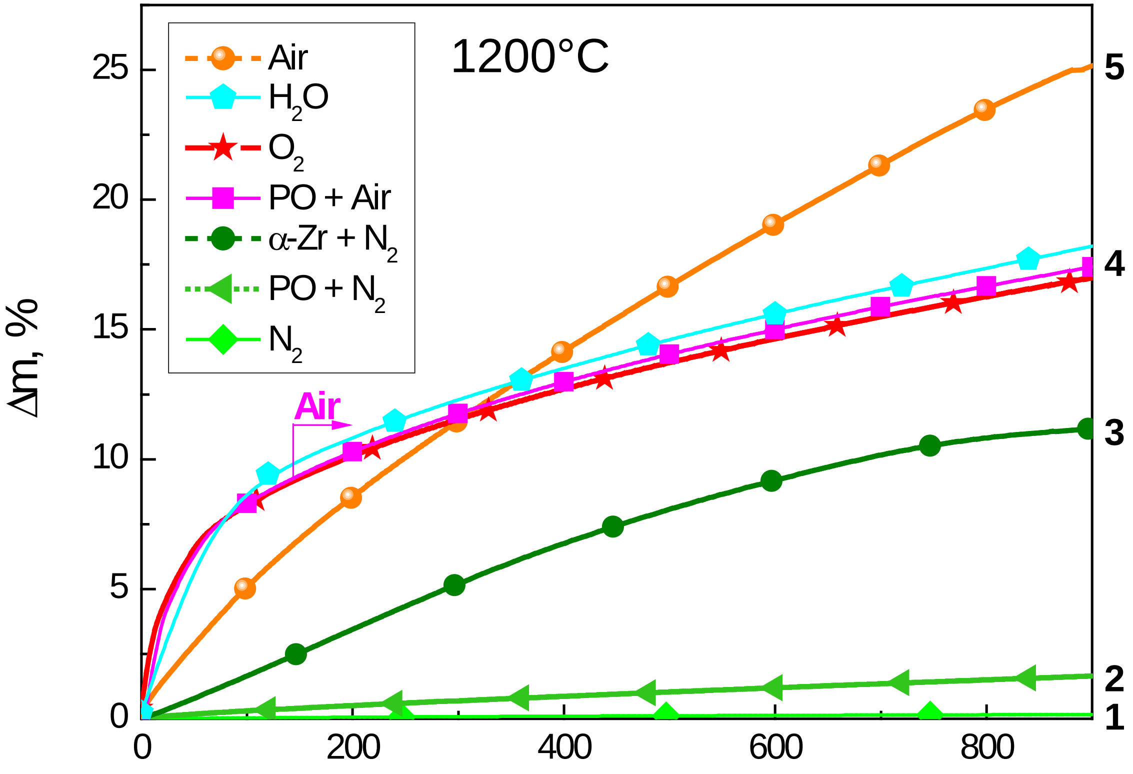
Decrease of melting temperatures due to eutectic interactions

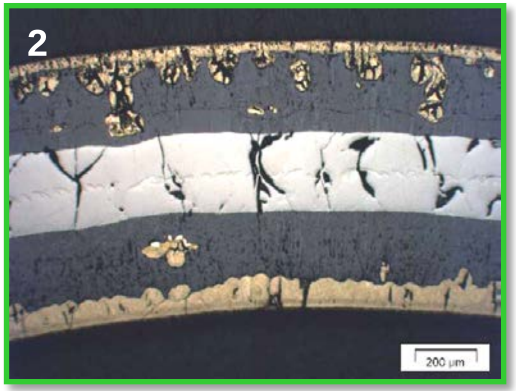
Basics – kinetics

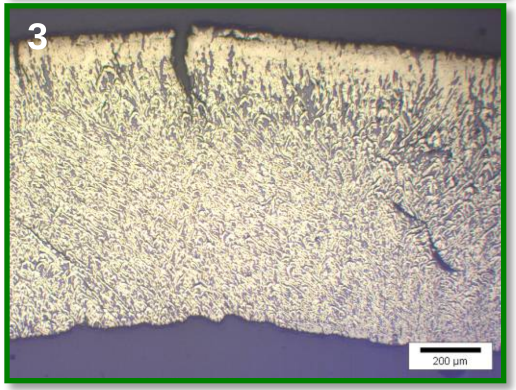
$$\frac{\Delta m}{S} = k_m(T) \cdot t^n$$

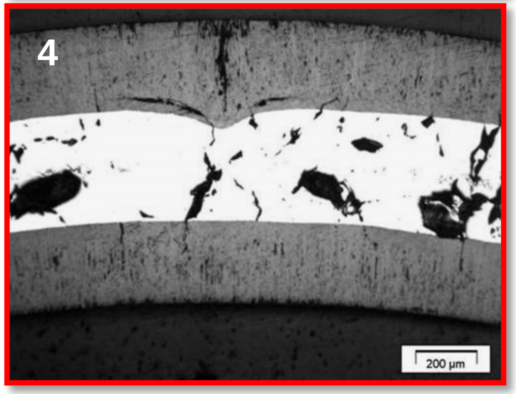


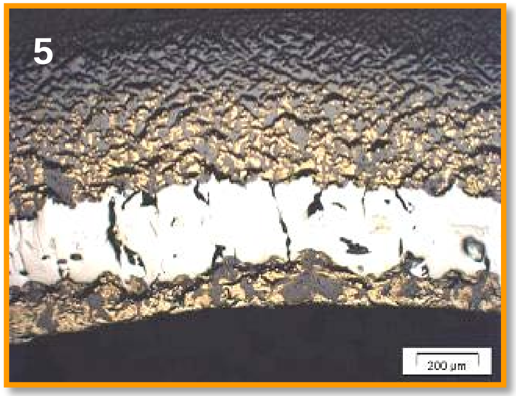
Oxidation of Zr alloys in various atmospheres



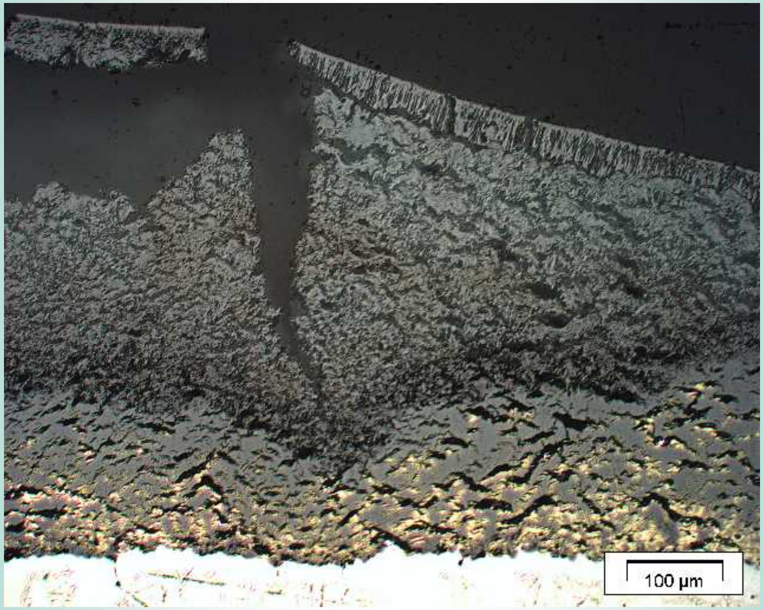




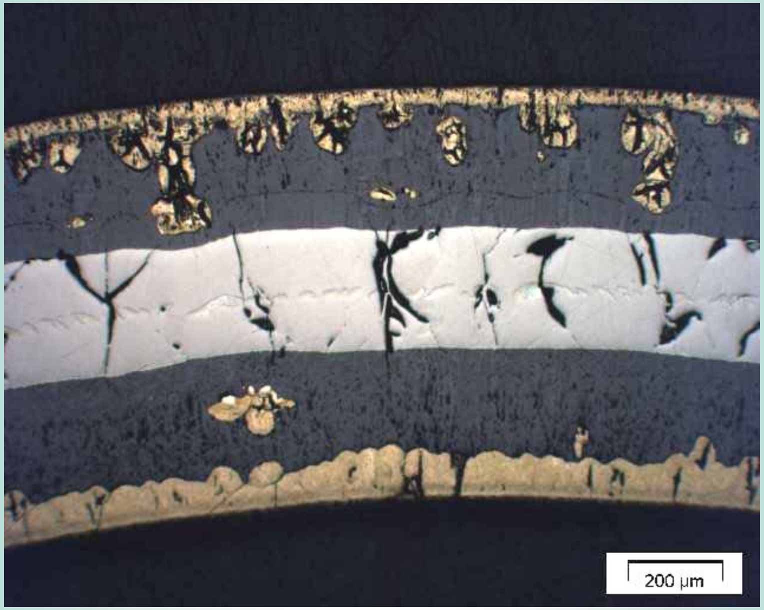




Nitride formation under local and global oxygen starvation conditions



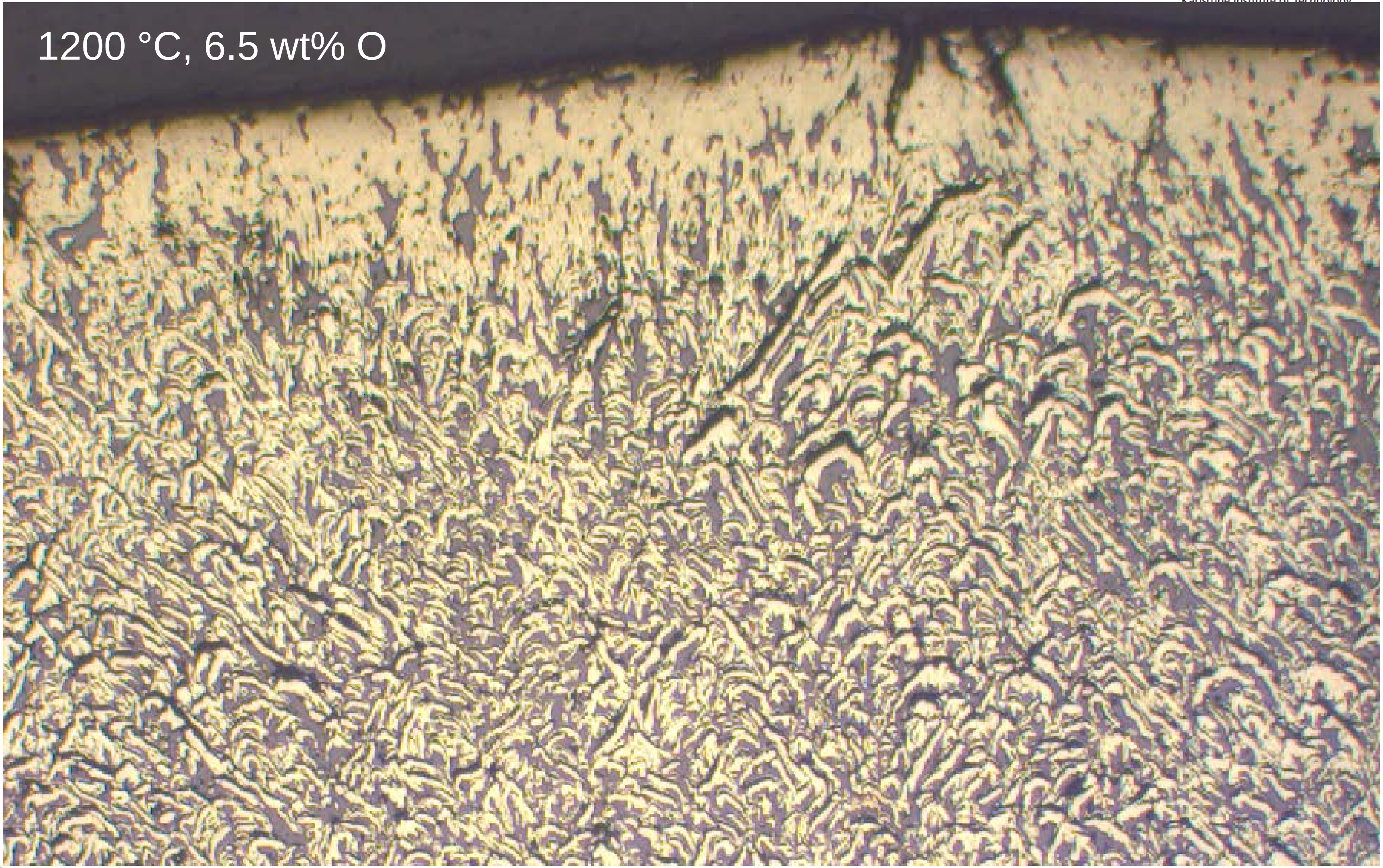
Local oxygen starvation:
Formation and re-oxidation of nitride phase at metal-oxide phase boundary



Global oxygen starvation:
Pre-oxidation in steam and subsequent reaction in pure nitrogen

Nitride formation only in the absence of oxygen in the gas phase and in the presence of oxygen in the solid phase!

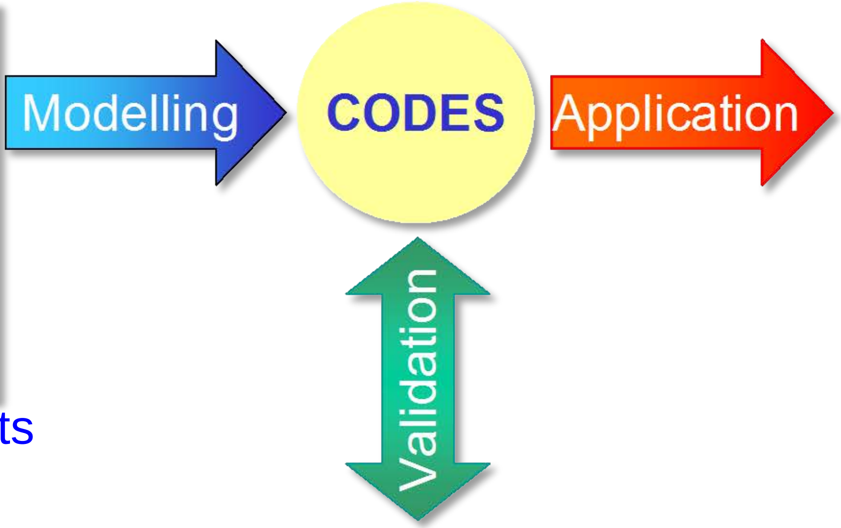
Reaction of α-Zr(O) with nitrogen



QUENCH Program at KIT

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

Separate-effects tests

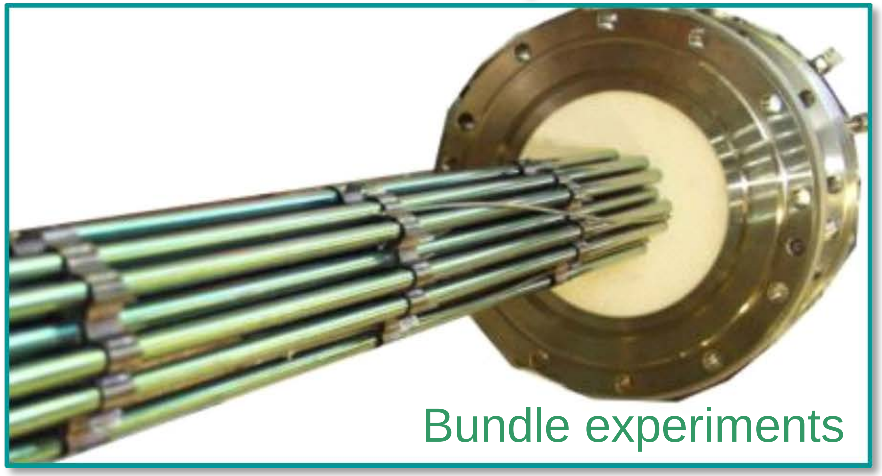


Modelling

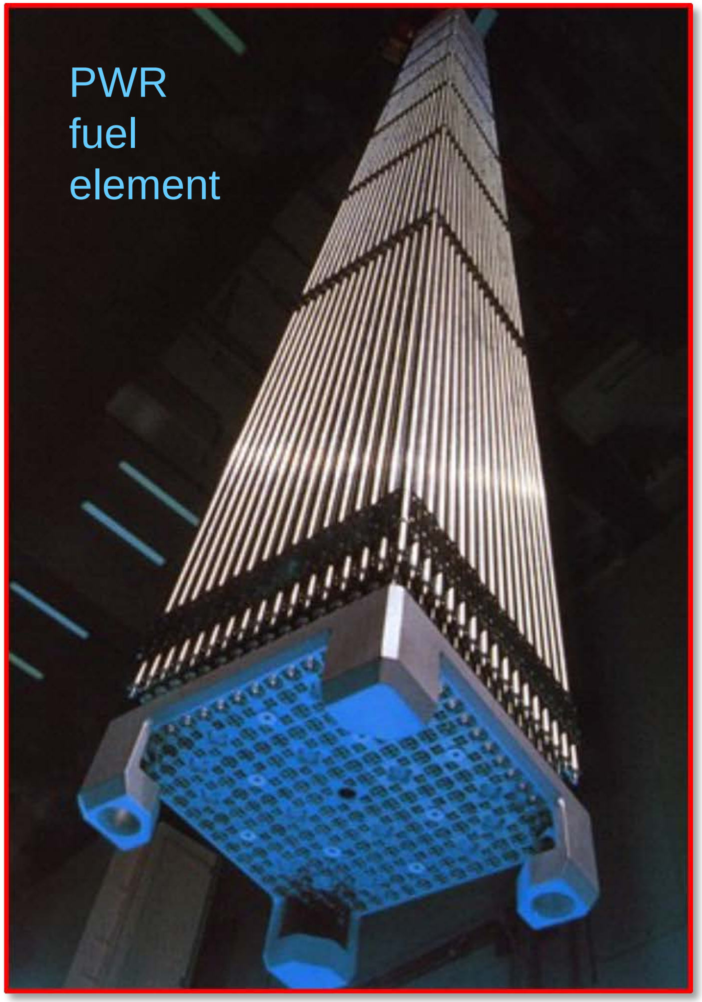
CODES

Application

Validation



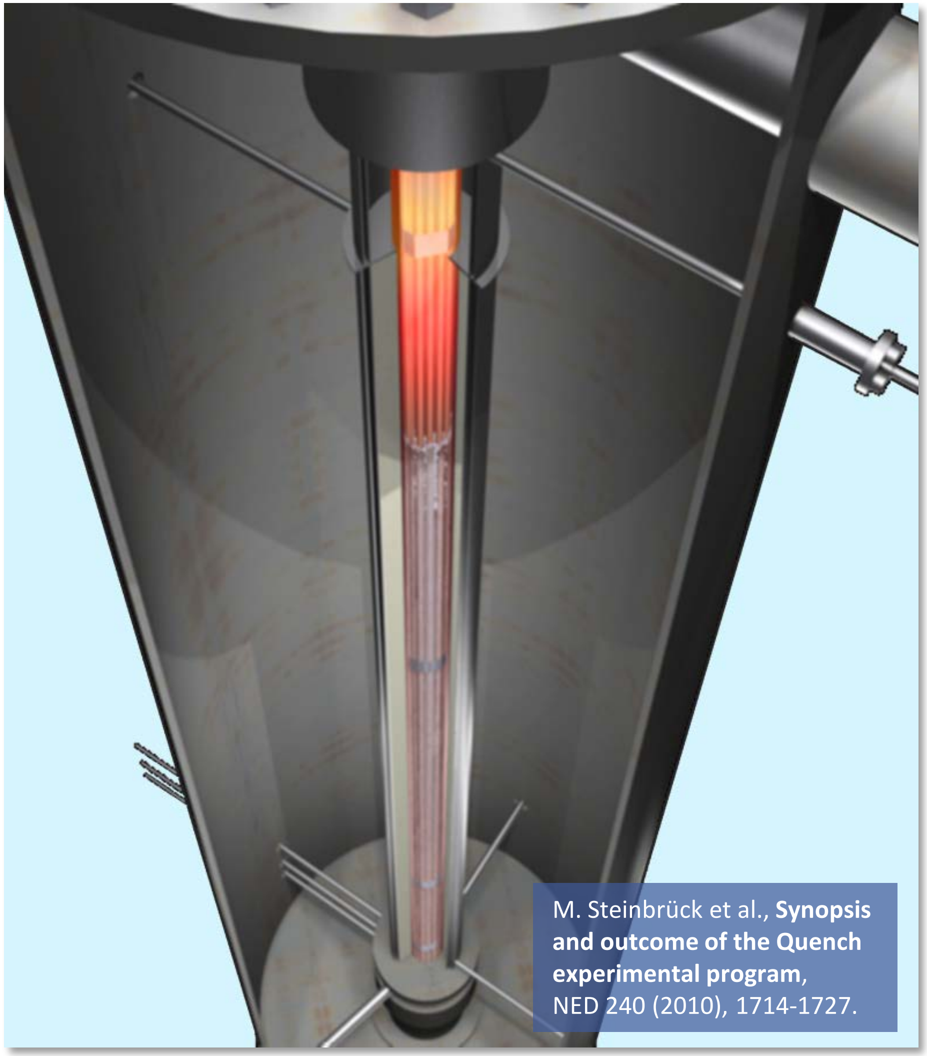
Bundle experiments



PWR fuel element

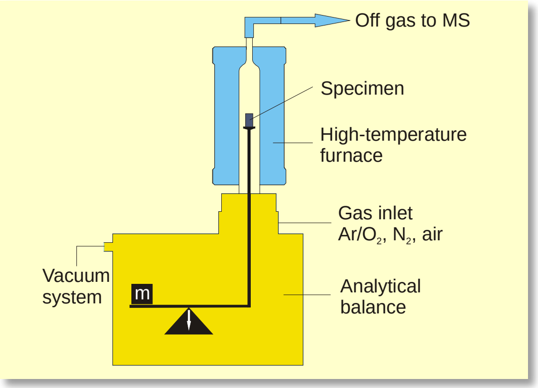
QUENCH Facility

- 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, 17 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
  - Debris formation and coolability



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

QUENCH Separate-effects tests: Main setups

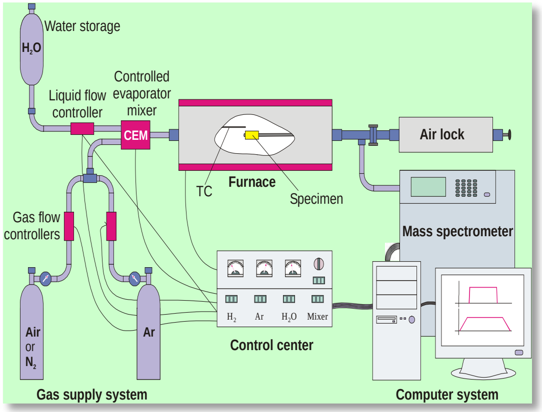


Thermobalance

1600 °C
1250 °C (steam)

Specimens: 0-2 cm

MS coupling



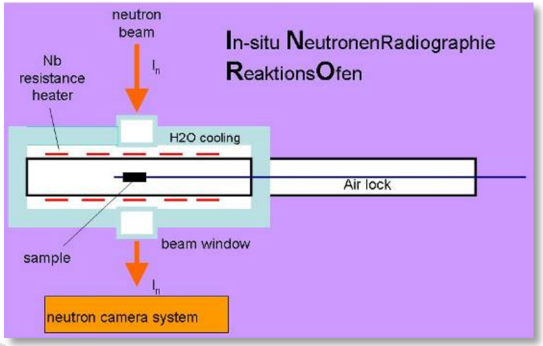
BOX Facility

1700 °C

Oxidising, reducing atmosphere (incl. steam)

Specimens: 1-2 cm

MS coupling

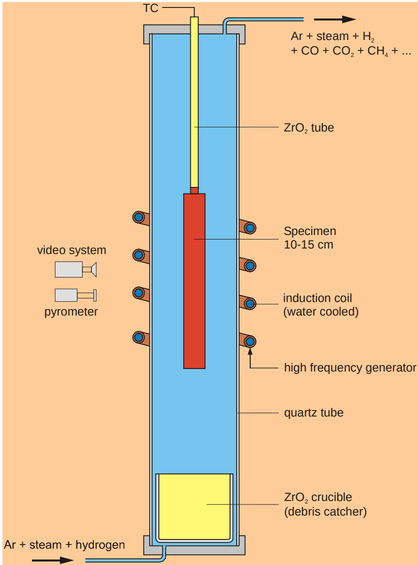


INRRO Facility

1500°C

Specimens: 1-2 cm

Transparent for neutrons



QUENCH-SR Rig

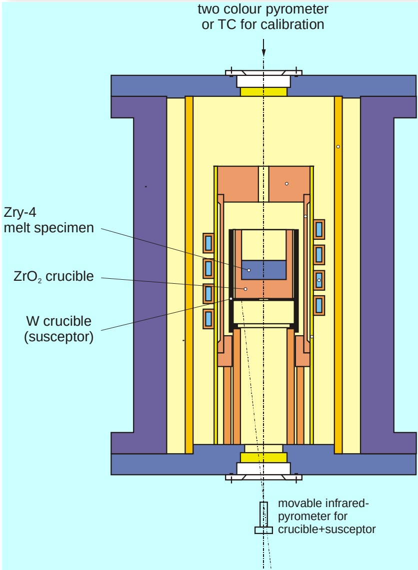
2000 °C

Induction heating

Oxidising, reducing atmosphere (incl. steam)

Specimens: 15 cm

MS coupling



LAVA Furnace

2300 °C

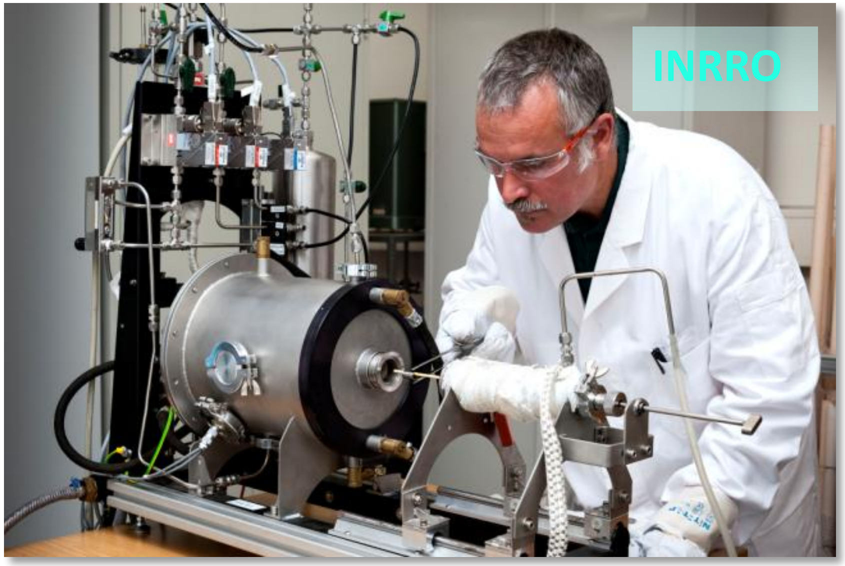
Induction heating

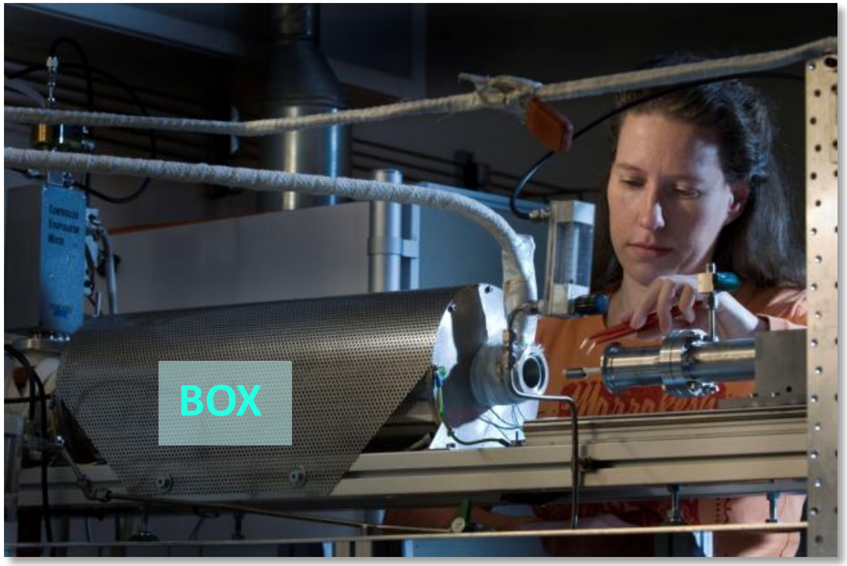
Inert, reducing atmosphere

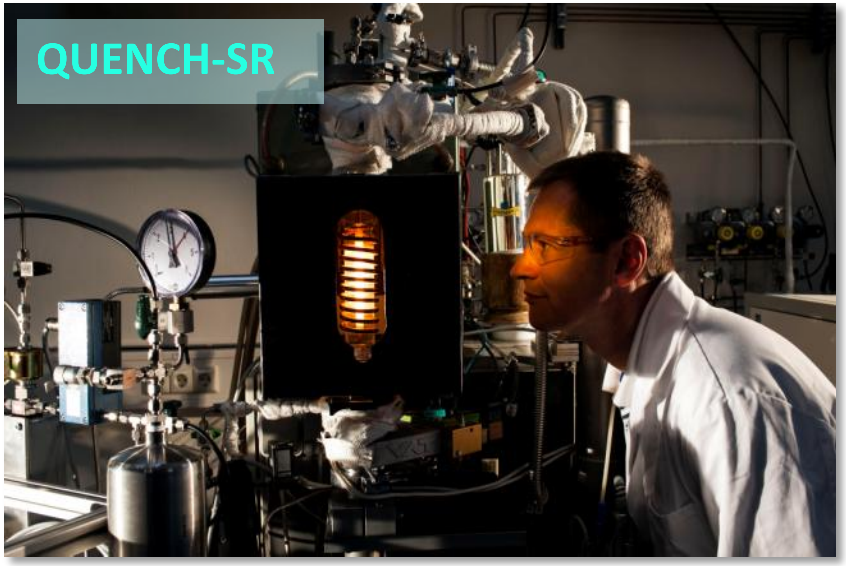
Specimens: 1-2 cm

MS coupling

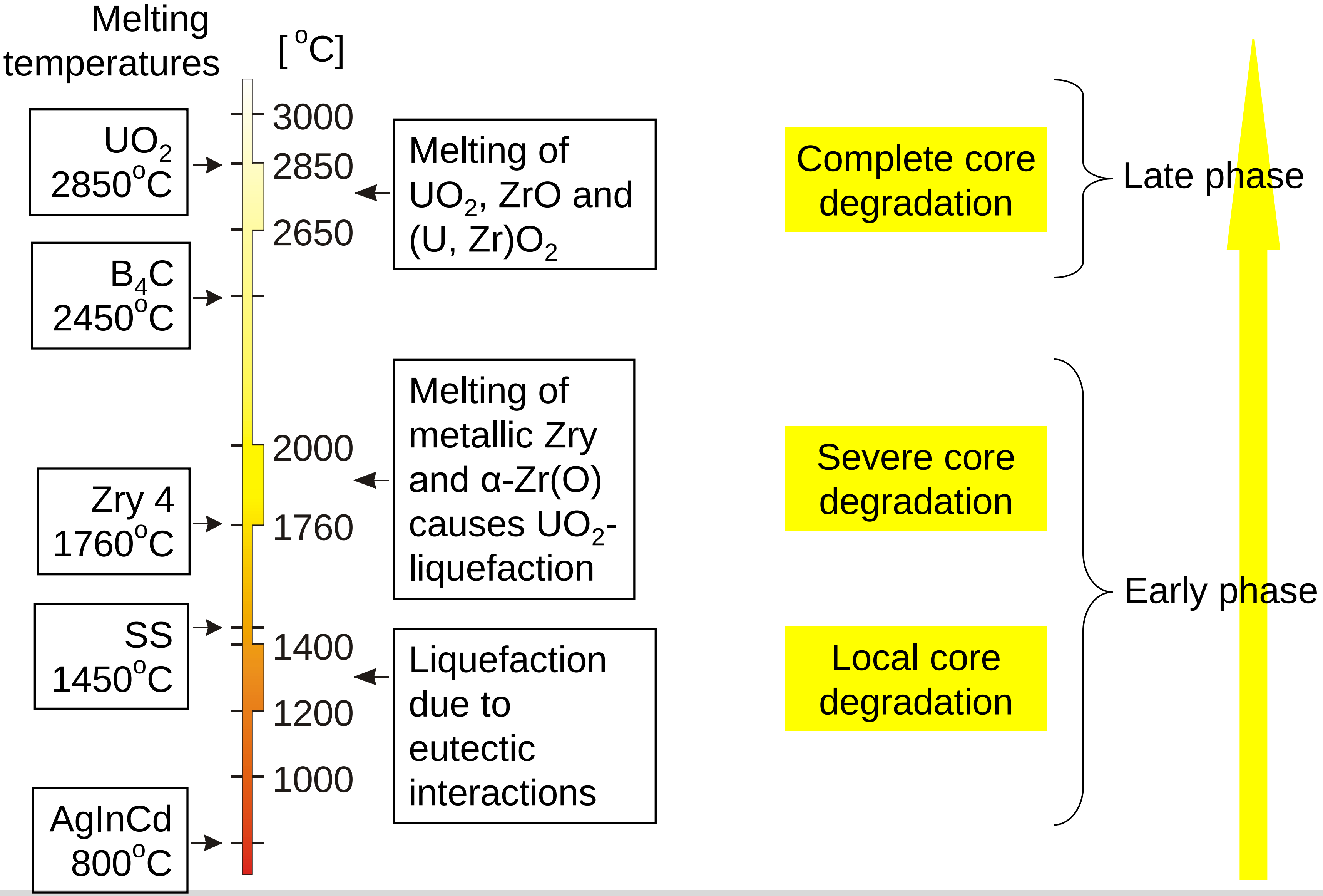
QUENCH Separate-effects tests: Main setups







Core degradation - summary



Melting temperatures

UO_2
$2850^{o}C$

B_4C
$2450^{o}C$

Zry 4
$1760^{o}C$

SS
$1450^{o}C$

AgInCd
$800^{o}C$

Melting of UO_2, ZrO 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