KIT
Karlsruhe Institute of Technology

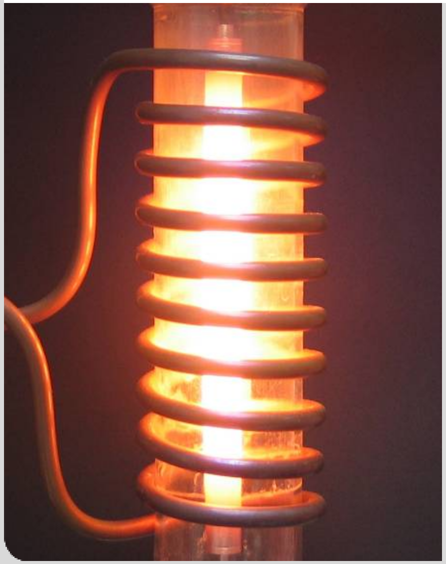
IAM
Institute for Applied Materials

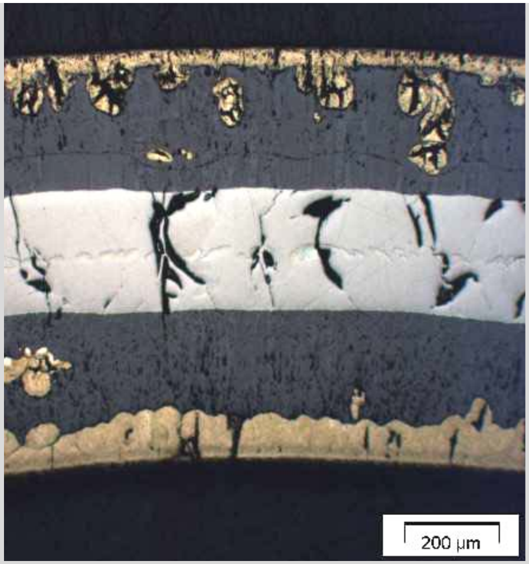
Early core degradation with special emphasis on oxidation and B_4C control rod failure

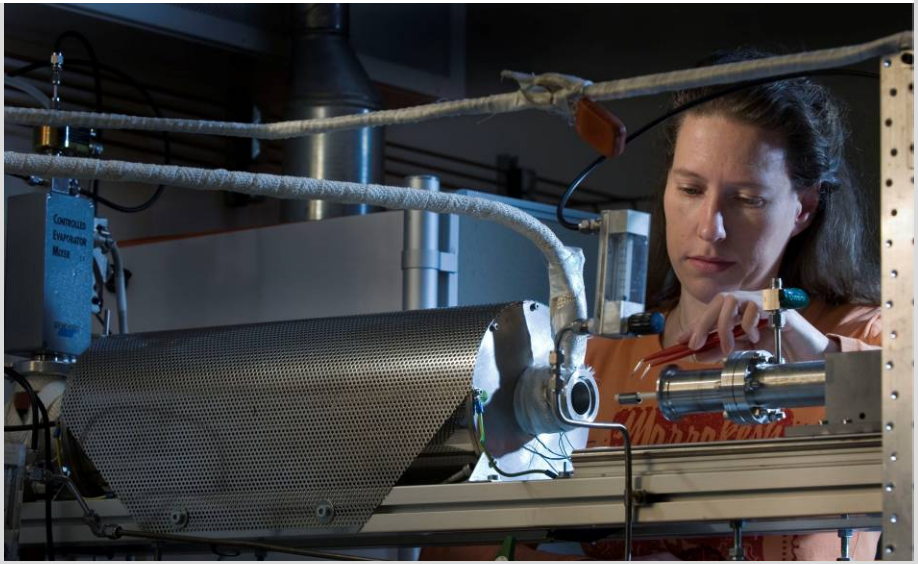
Martin Steinbrück

International Seminar on Fuel Degradation Methodology in Severe Accidents - Tokyo, Japan, 26 October 2012

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 research center (1956) + University Karlsruhe (1825)

= 9000 employees

= 23 000 students

Outline

- Phenomenology of severe accidents in light water reactors (LWR)
- Experimental facility and setups at KIT
- High-temperature oxidation of zirconium alloys in various atmospheres
  - Steam
  - Air
  - Mixtures
- Behavior of boron oxide control rods during severe accidents
  - Degradation
  - Eutectic interactions
  - Oxidation

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

LWR severe accident scenario - II

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

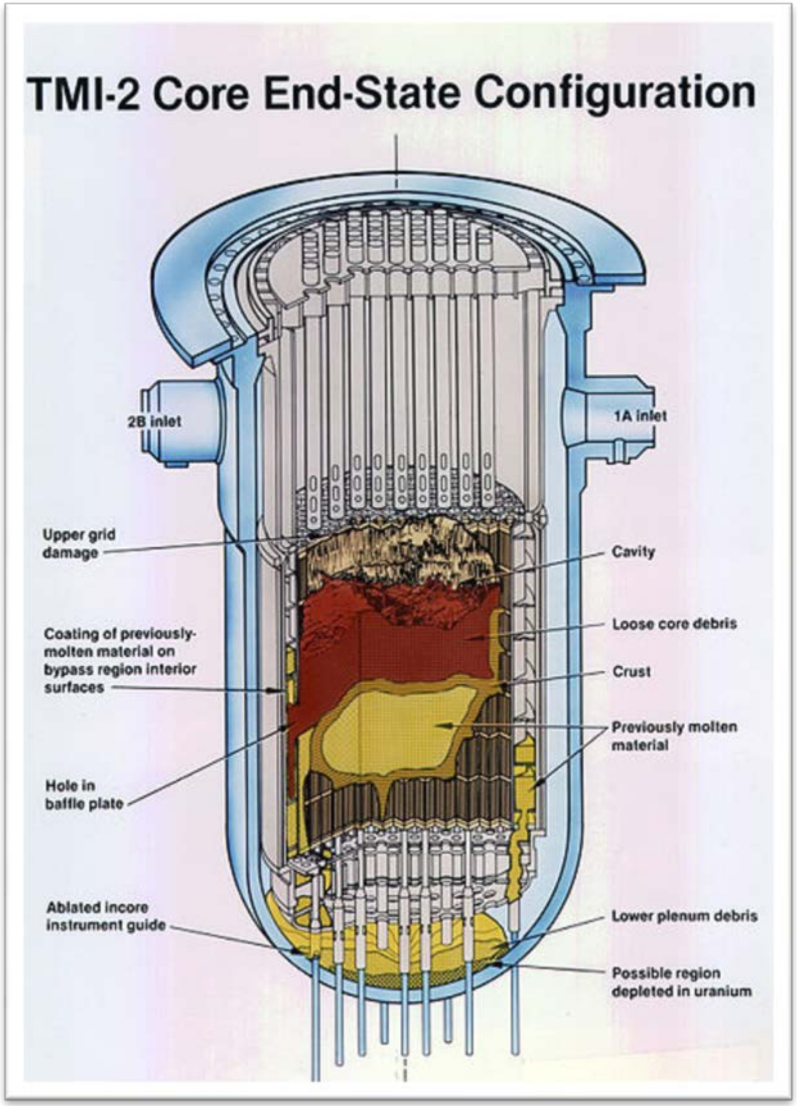
- Reflood and cooling as early as possible.

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).
- Subsequently, failure of the RPV and release of corium melt into the containment (ex-vessel, see Chernobyl, Fukushima)



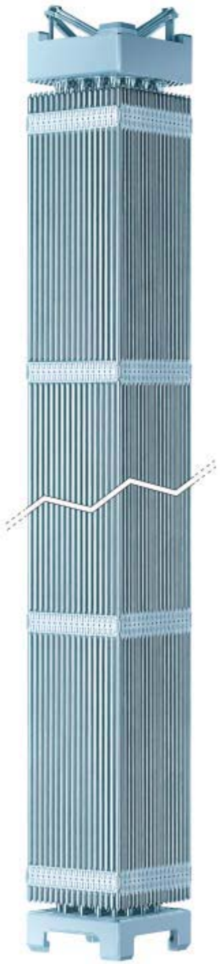
Core materials in Light Water Reactors

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 (including RPV)
B_4C absorber (BWR, VVER, …):	0.3-2 t
AgInCd absorber (PWR):	3-5 t

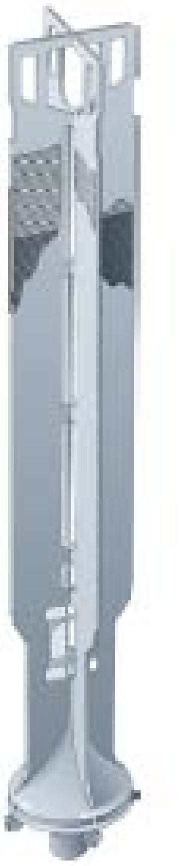
Environment

- **Water, steam**
- Air
- Nitrogen

} After failure of RPV/primary circuit



PWR fuel assembly

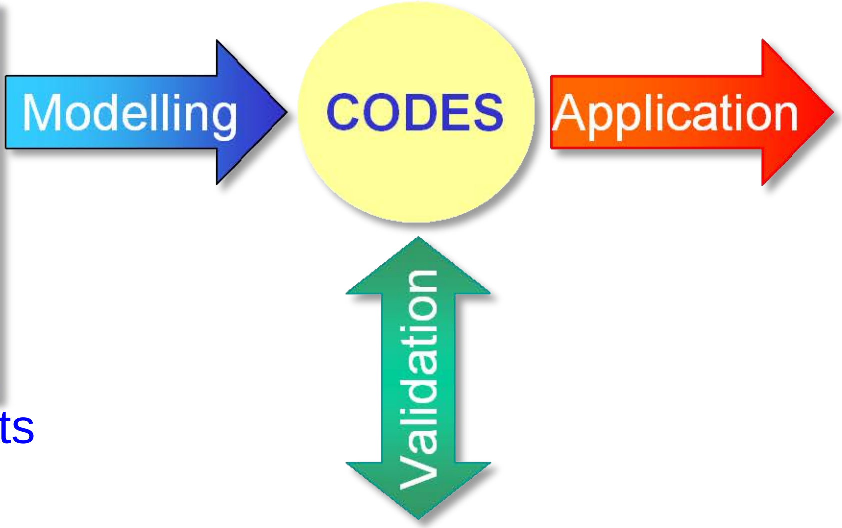


BWR control blade

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



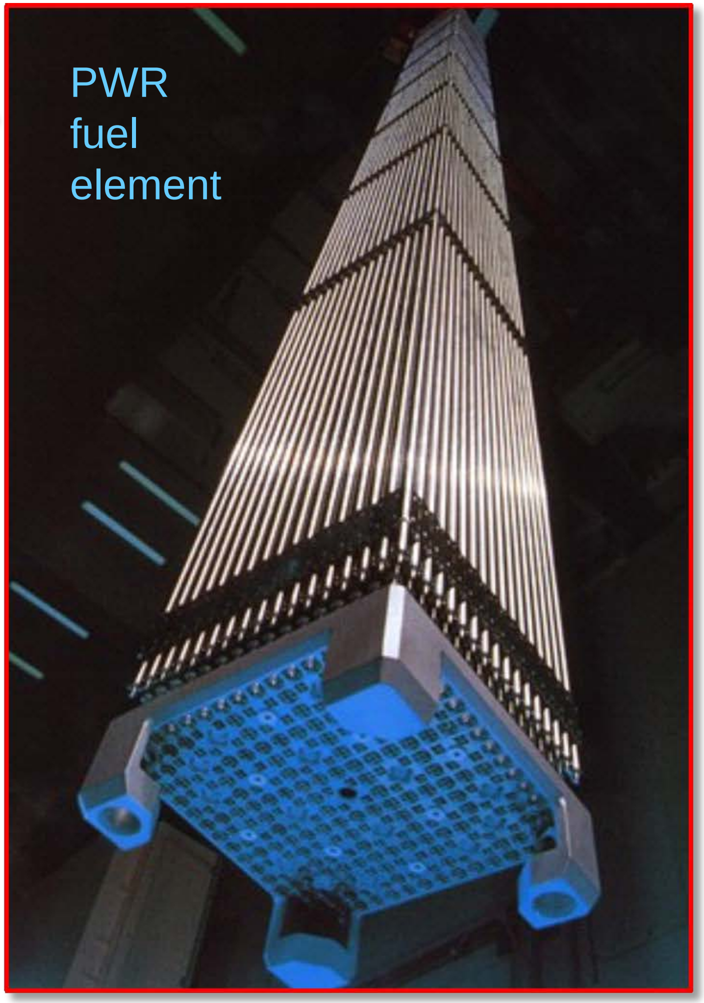
Modelling

CODES

Application

Validation

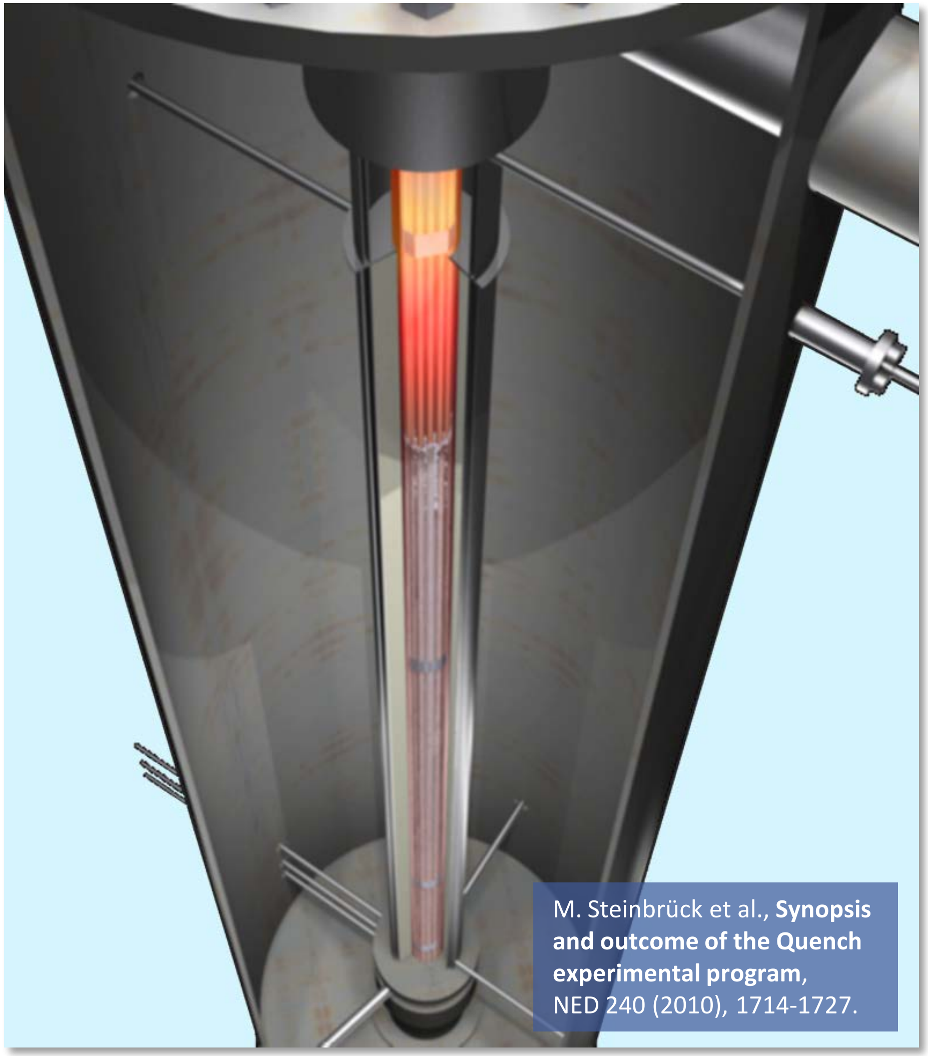
Bundle experiments



PWR
fuel
element

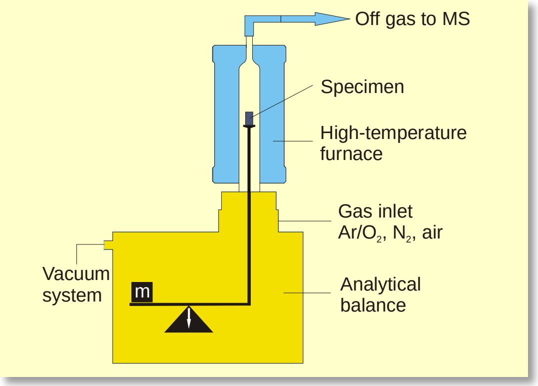
QUENCH Facility

- 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, 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
- Part of the validation matrix of most SA codes



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

QUENCH Separate-effects tests: Main setups

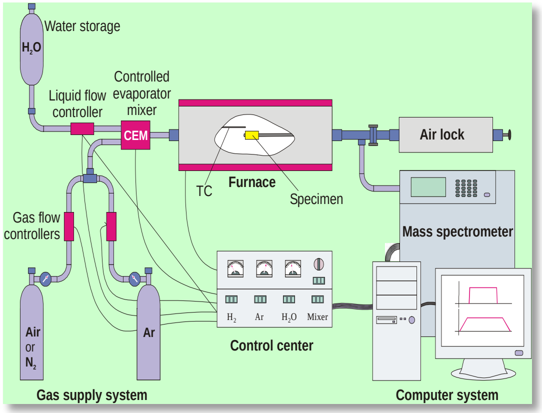


Thermobalance

1600 °C
1250 °C (steam)

Specimens: 0-2 cm

MS coupling



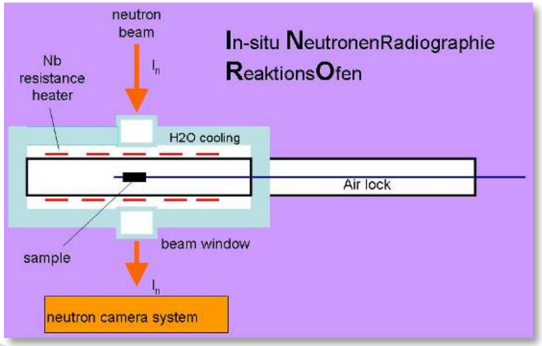
BOX Facility

1700 °C

Oxidising, reducing atmosphere (incl. steam)

Specimens: 1-2 cm

MS coupling

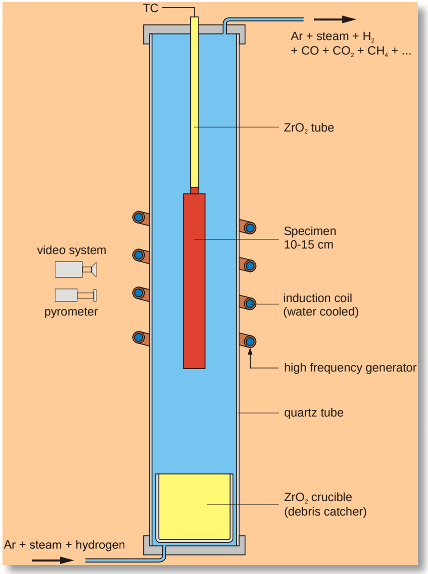


INRRO Facility

1500°C

Specimens: 1-2 cm

Transparent for neutrons



QUENCH-SR Rig

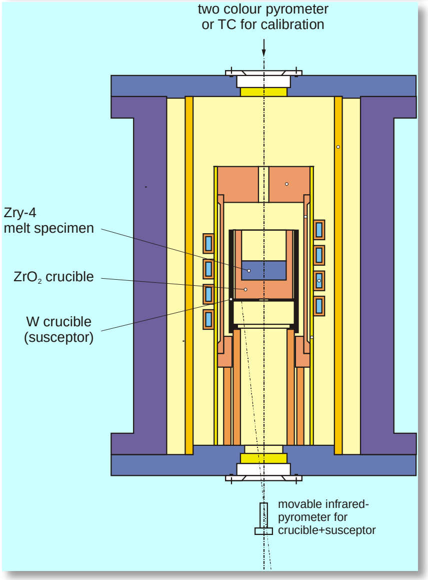
2000 °C

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

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
- Hydrogen behavior

Composition of cladding alloys for nuclear fuel rods

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

Oxidation of zirconium alloys – chemical reactions

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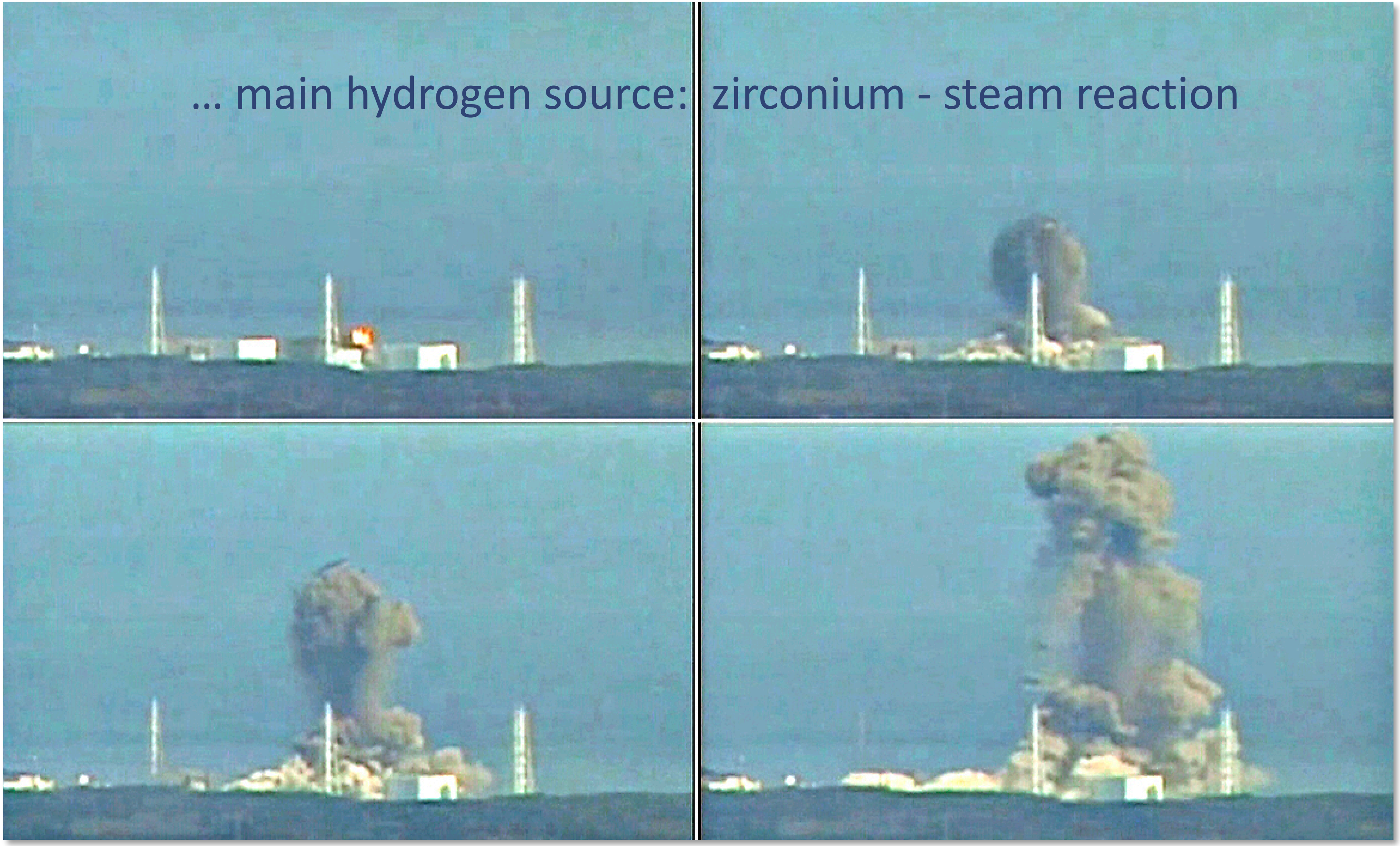
	ΔH_f at 1500 K
$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$	-585 kJ/mol
$Zr + O_2 \rightarrow ZrO_2$	-1083 kJ/mol
$Zr + 0.5N_2 \rightarrow ZrN$	-361 kJ/mol

- Release of hydrogen and heat
- Hydrogen either released to the environment or absorbed by Zr metal

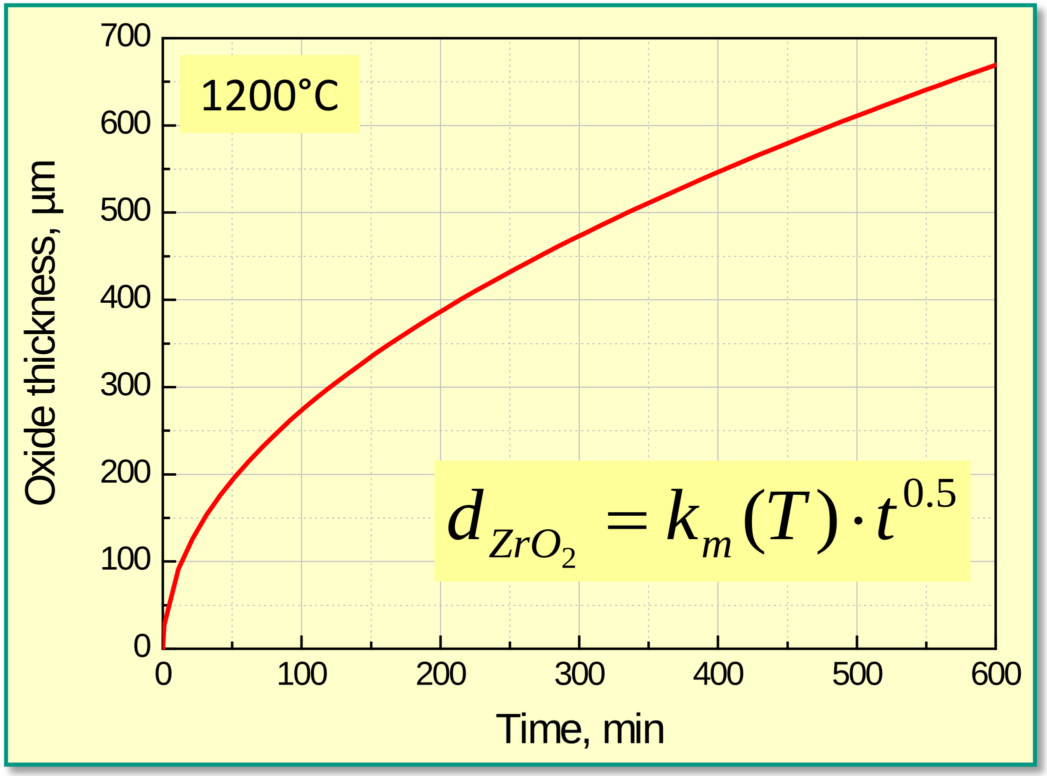
Hydrogen detonation in Fukushima Dai-ichi NPPs …



… main hydrogen source: zirconium - steam reaction

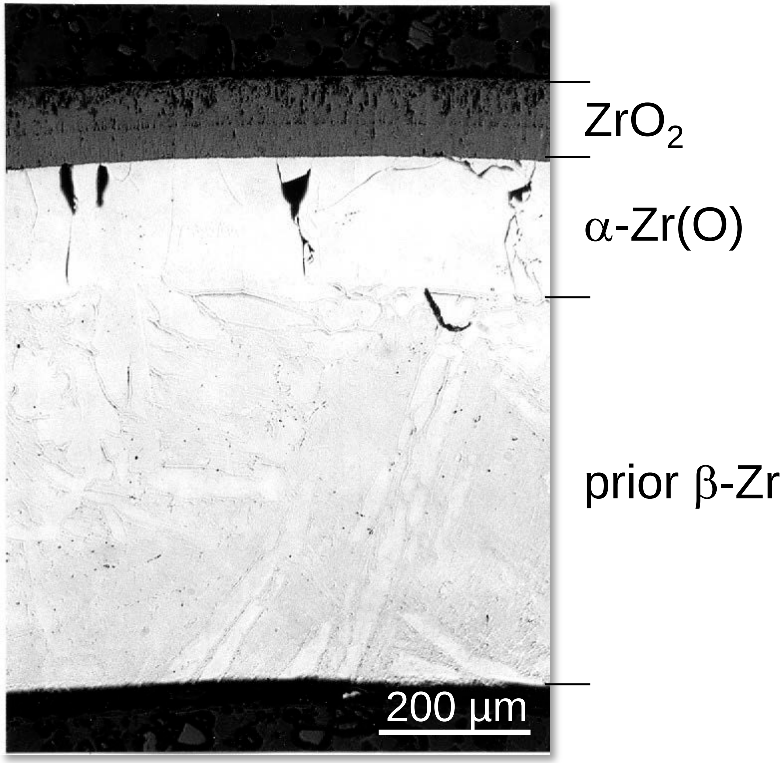
Oxidation in steam (oxygen)

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



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

Calculated oxide thickness during oxidation of Zry at 1200°C in steam

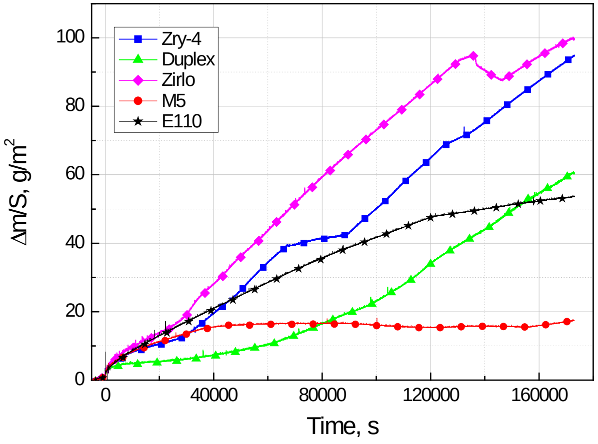


20 min at 1200°C in steam

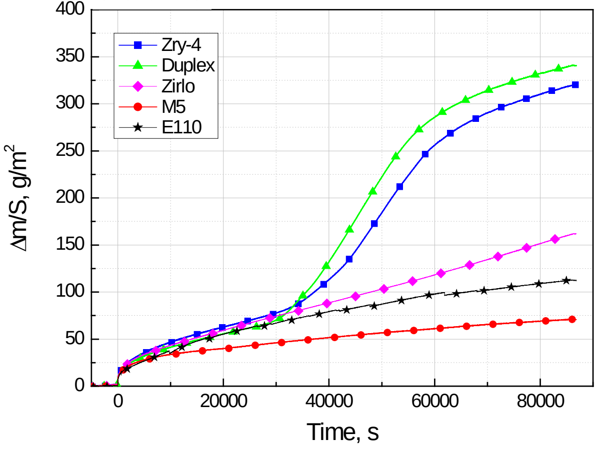
Isothermal oxidation of Zr alloys in steam

- 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).

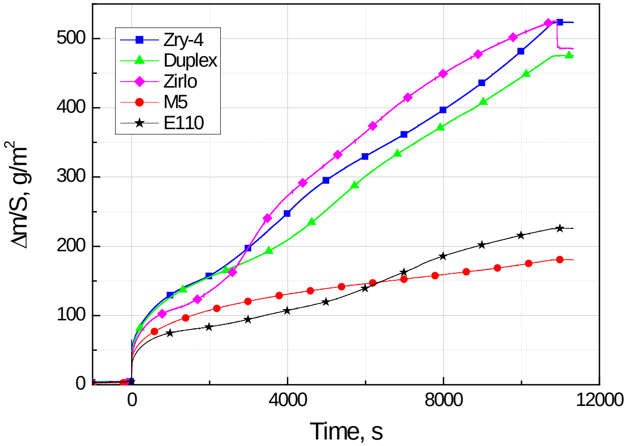
600°C



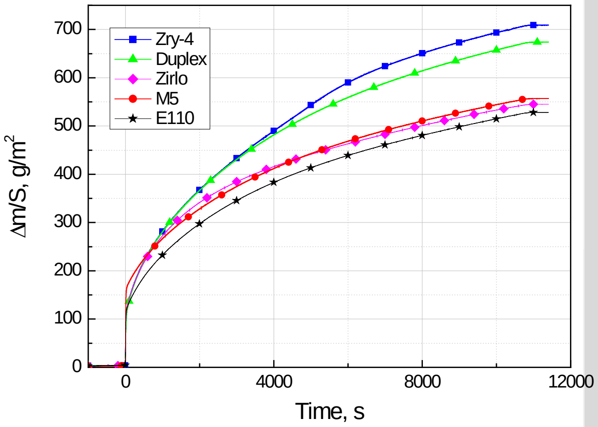
800°C



1000°C

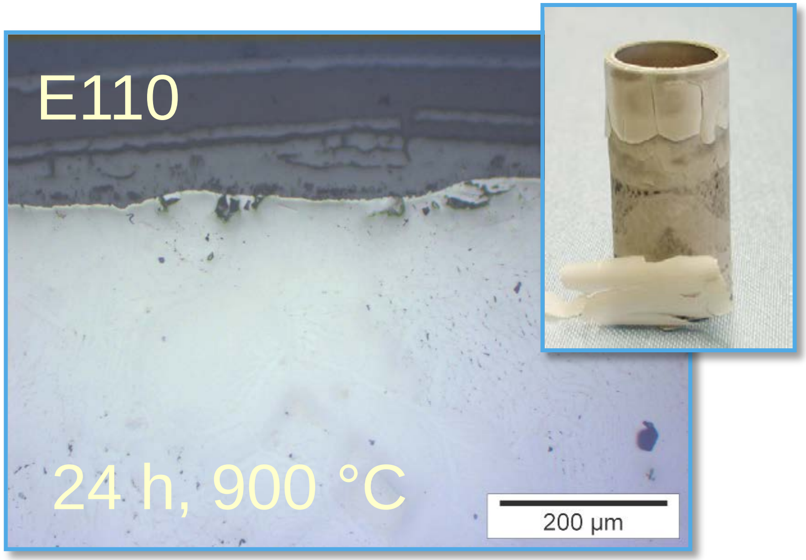


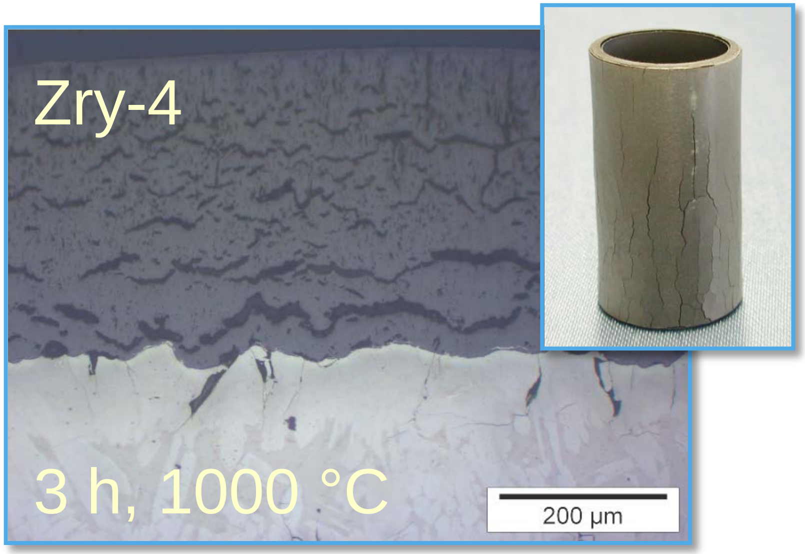
1100°C



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”).



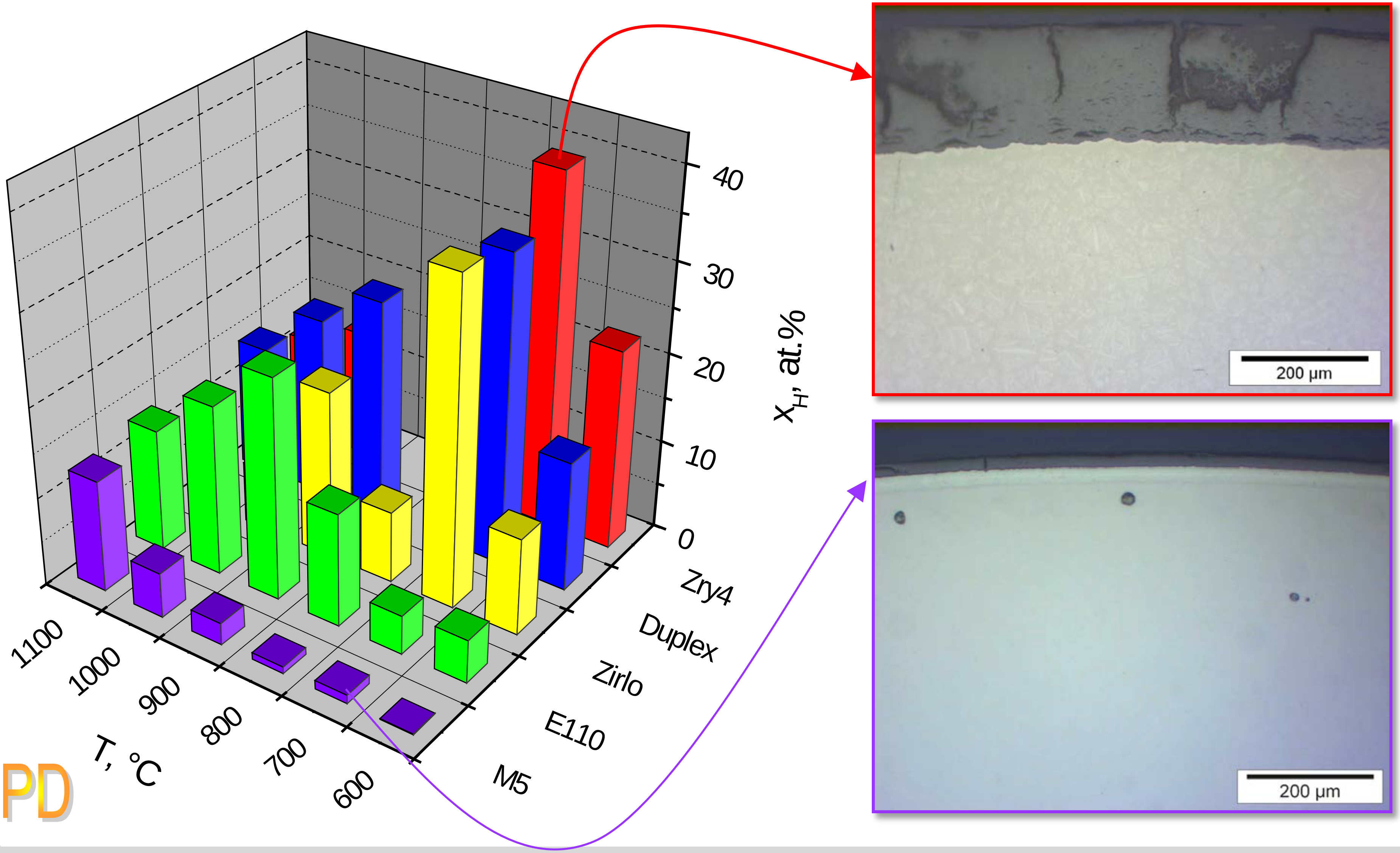


Transition to breakaway

Temperature °C	Time at transition h	Oxide at transition µm
600	6-8	3-8
700	1-10	7-17
800	1-7	11-37
900	0.6-1.5	18-33
1000	0.3-0.7	43-85

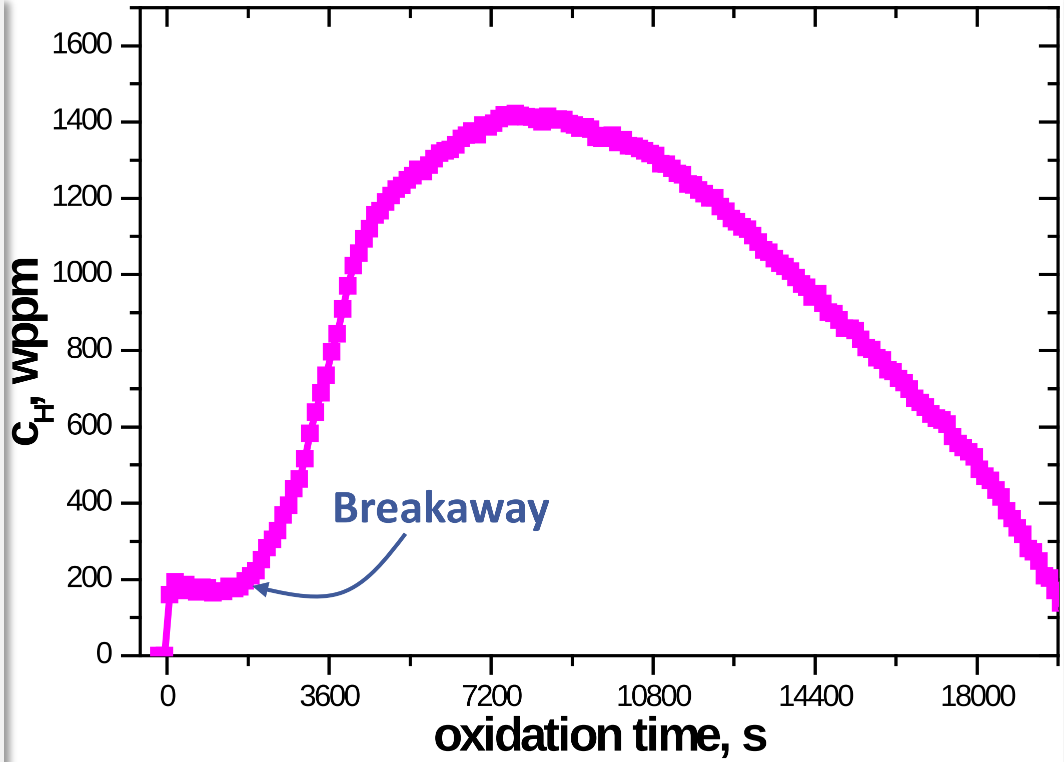
- Important for long-term scenarios!
- Insignificant during fast transients and LOCAs

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



Breakaway

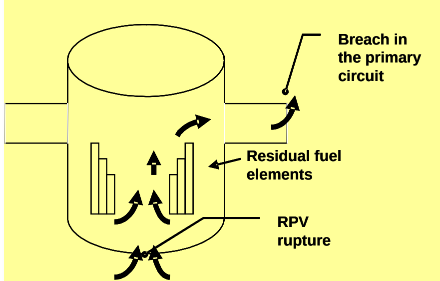
- Rapid initial hydrogen uptake
- Further strong hydrogen absorption after transition to breakaway

Oxidation in atmospheres containing nitrogen

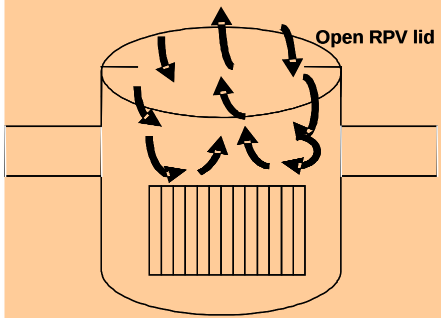
- Air ingress reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

- 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

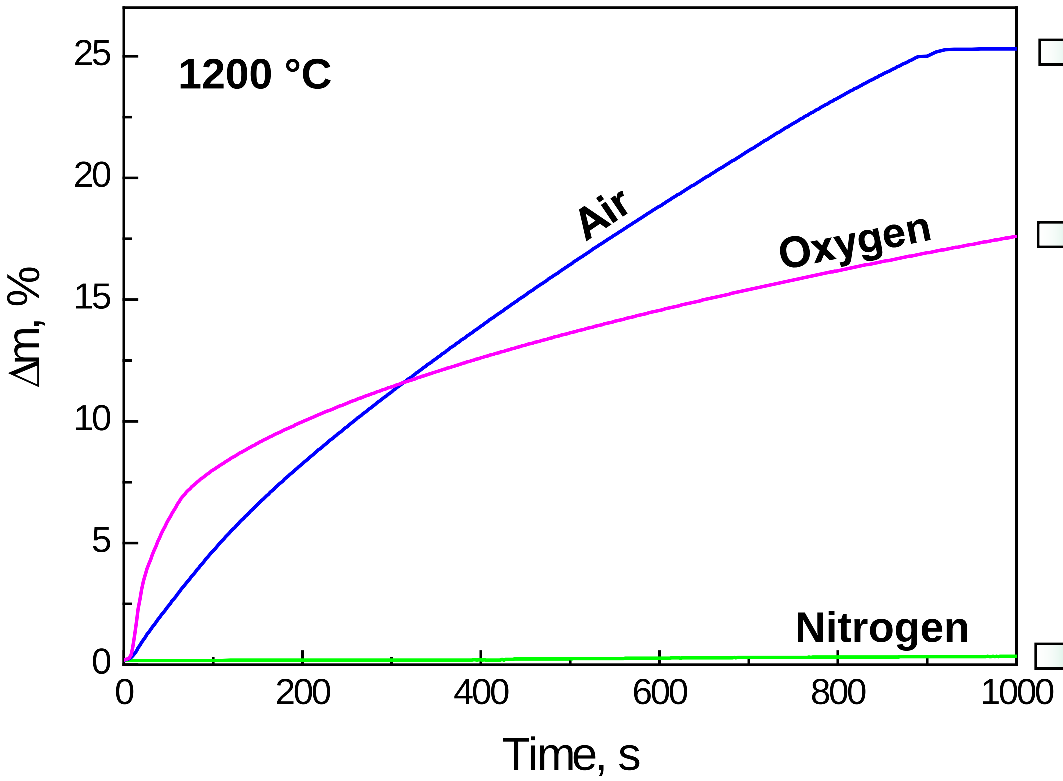


Mid loop operation



Spent fuel storage pool accident

Oxidation of Zr alloys in N_2, O_2 and air



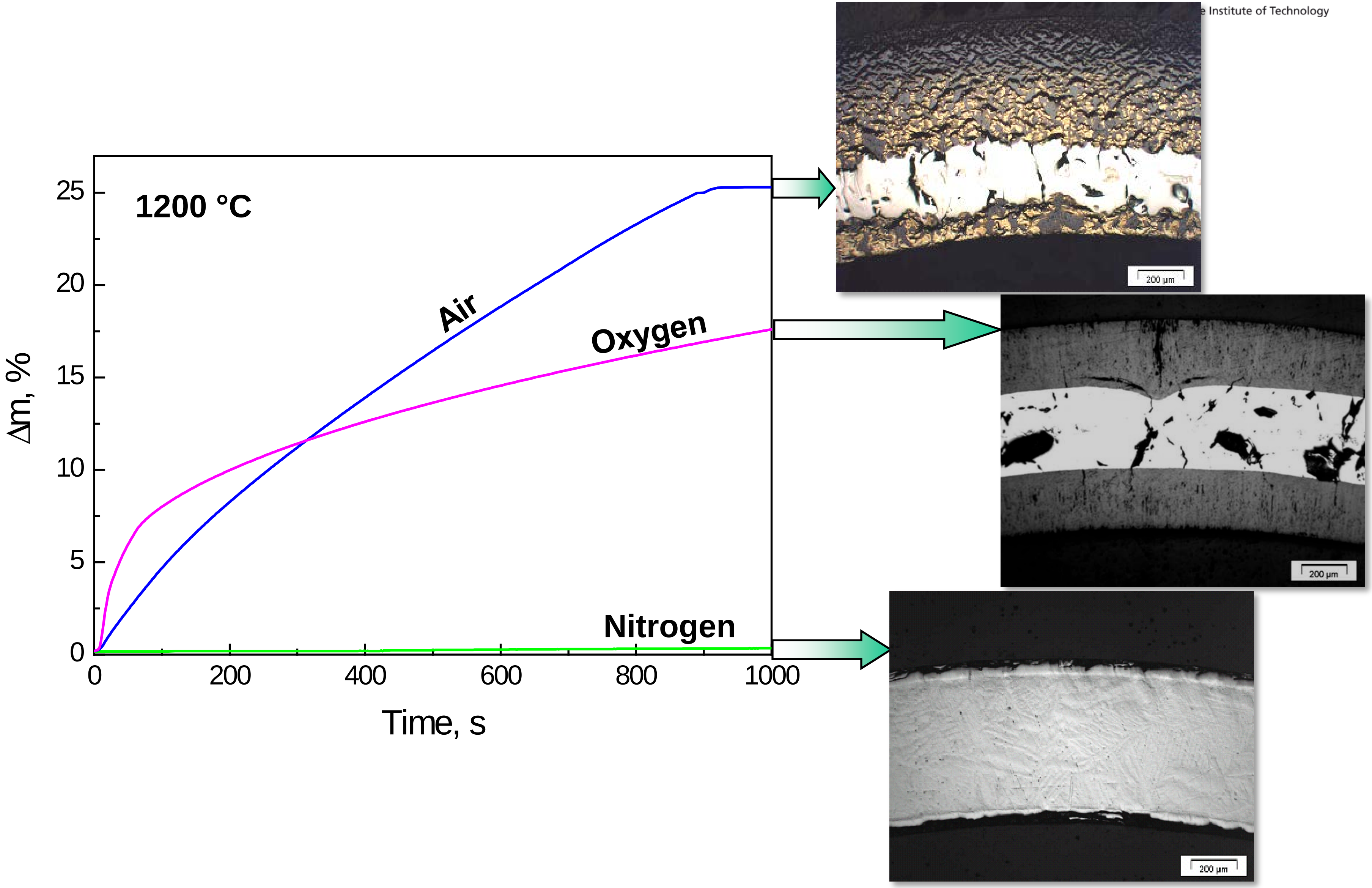
~ Linear oxidation kinetics

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

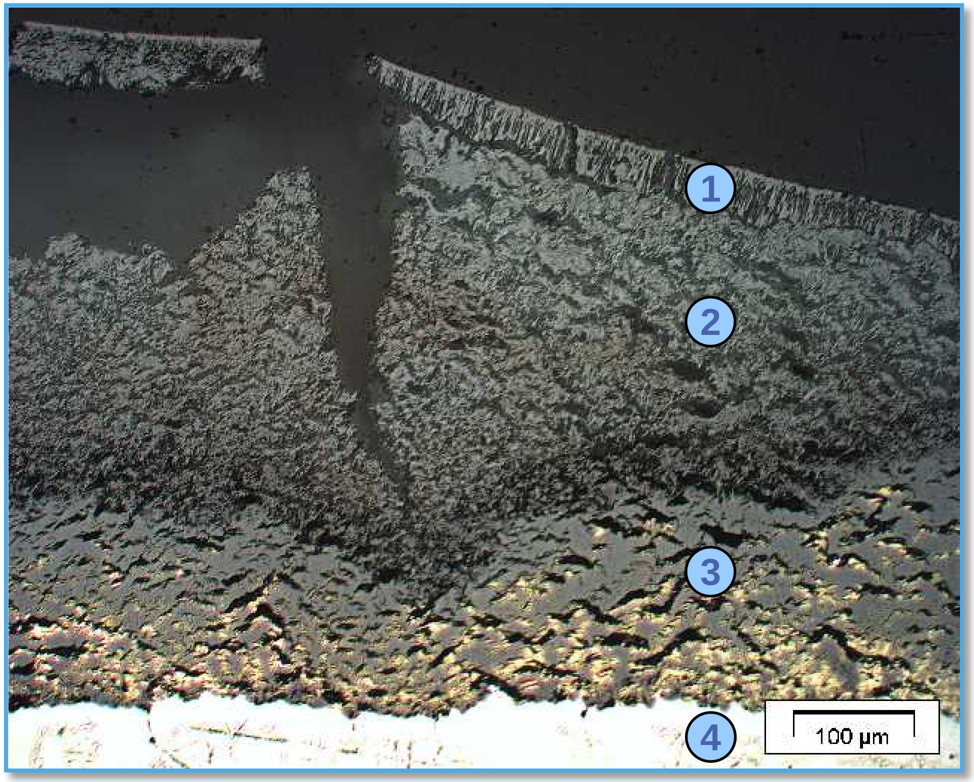
1 hour at 1200°C in steam

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 steam-air atmospheres

Zry-4, 1 hour at 1200°C

H_2O

0.7 H_2O
0.3 air

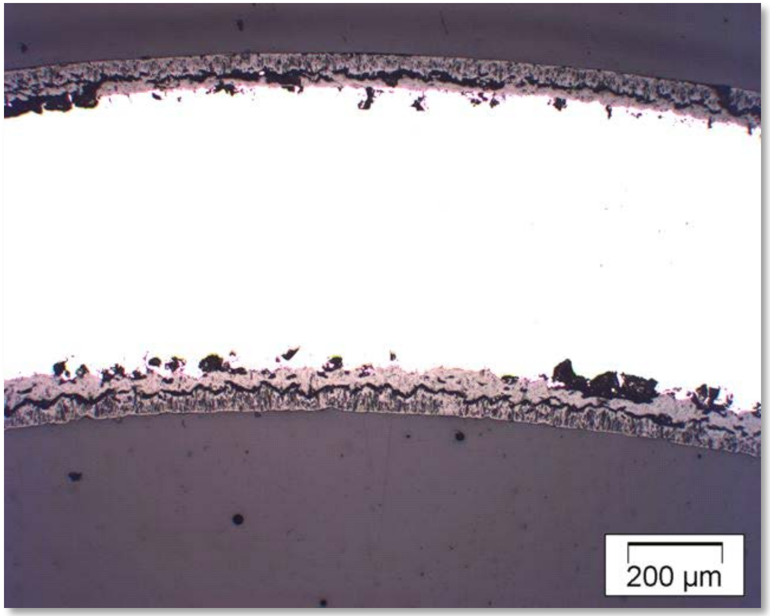
0.3 H_2O
0.7 air

0.1 H_2O
0.9 air

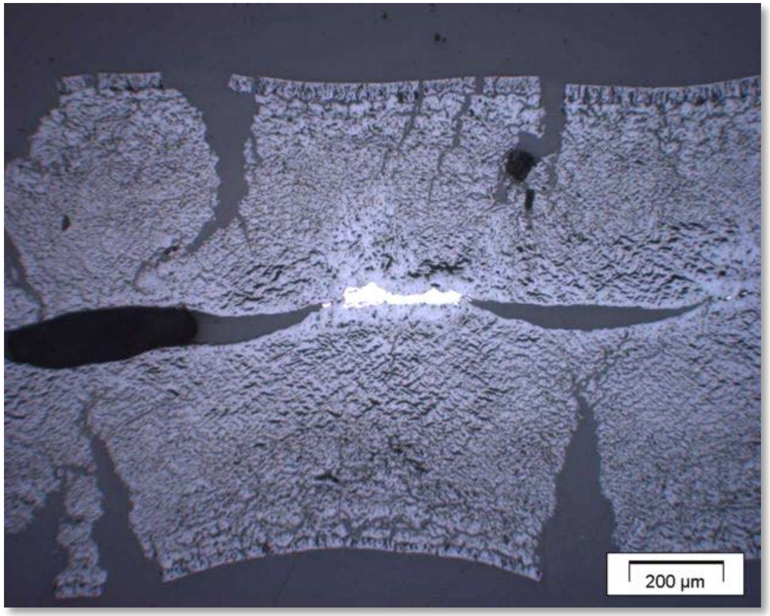
- Increasing degradation with raising content of air in the mixture

Oxidation in mixed atmospheres

1 hour at 1000 °C in steam



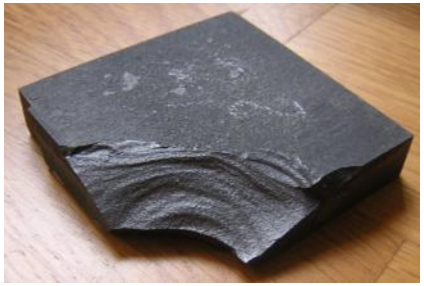
1 hour at 1000 °C in 50/50 steam/N_2



- 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

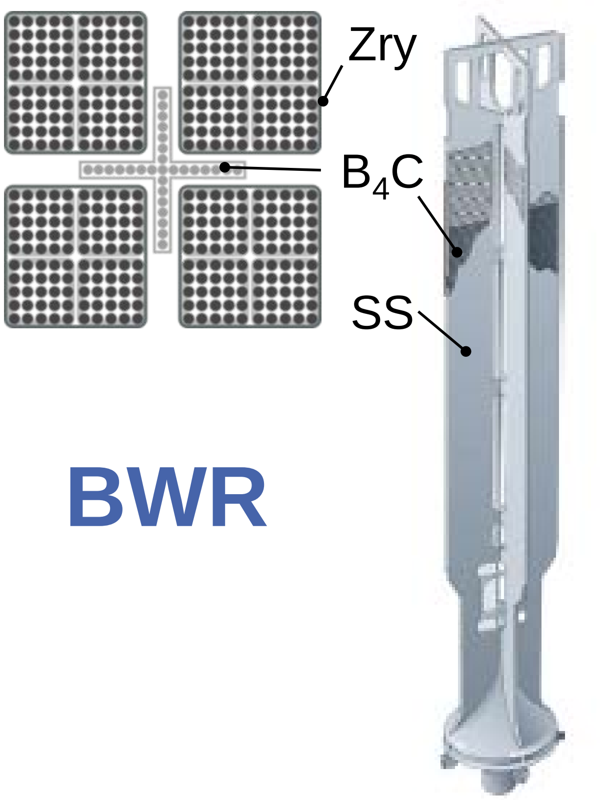
Boron carbide oxidation and interactions

- B_4C is widely used as control material in BWRs, VVERs, RBMKs, and some PWRs
- Integral tests (e.g. CORA, QUENCH, Phebus FPT3) have shown a strong influence of B_4C control rods on bundle degradation
- Oxidation of B_4C (containing melts) in steam produces large amounts of hydrogen and heat
- B_4C oxidation causes the formation of gas phase carbon (CO, CO_2, CH_4) and boron (H_3BO_3, HBO_2) compounds which affect the FP chemistry



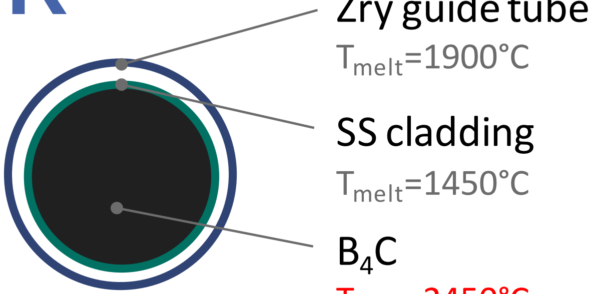
Boron carbide in LWRs

Reactor	Mass B_4C, kg
German BWR line 69	1200
German BWR line 72	1700
GE BWR-3 (Fukushima Daiichi, unit 1)	680
GE BWR-4 (Fukushima Daiichi, unit 2-4)	960
VVER 1000	250
FRAMATOME PWR 1300MW	320
FRAMAROM PWR 1450MW	340
EPR	440



BWR

PWR



Zry guide tube

T_{melt}=1900°C

SS cladding

T_{melt}=1450°C

B_4C

T_{melt}=2450°C

Degradation of B_4C control rods (1-pellet)

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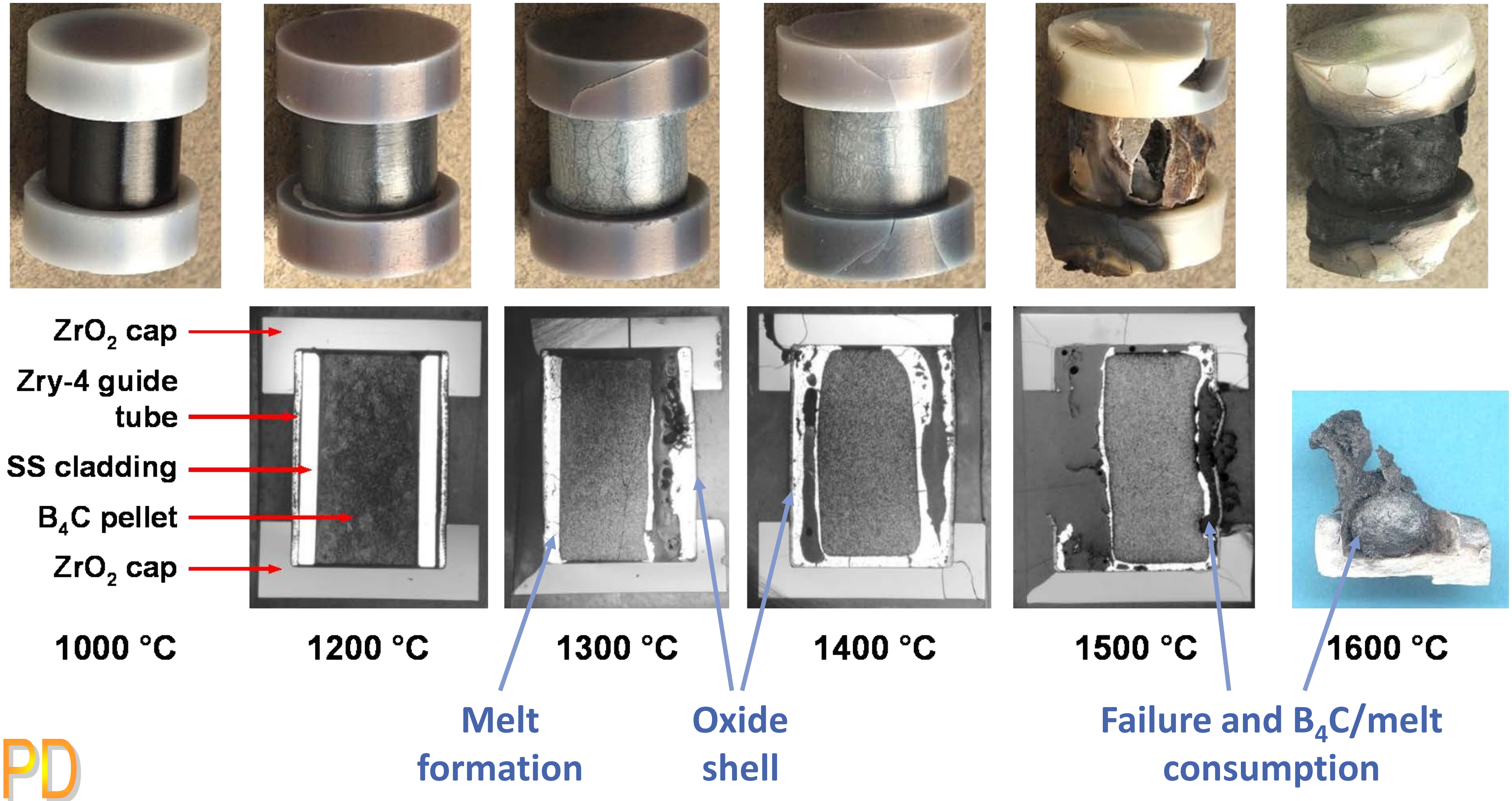
Post-test appearance and axial cross section of B_4C/SS/Zry specimens after 1 hour isothermal tests at temperatures between 1000 and 1600 °C



ZrO_2 cap

Zry-4 guide tube

SS cladding

B_4C pellet

ZrO_2 cap

1000 °C

1200 °C

1300 °C

1400 °C

1500 °C

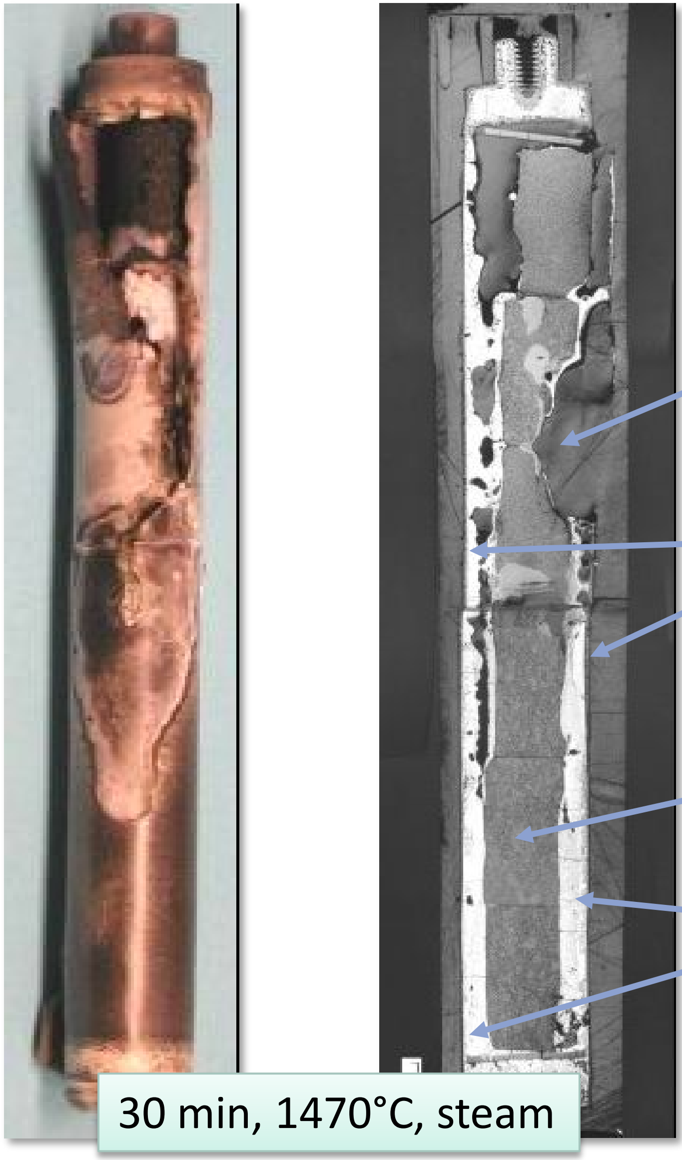
1600 °C

Melt formation

Oxide shell

Failure and B_4C/melt consumption

Degradation of B_4C control rods (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

Degradation of B_4C control rods (PWR bundle test)

Bundle cross sections

QUENCH-07
with B_4C
CR failure at 1312°C

QUENCH-08
w/o B_4C

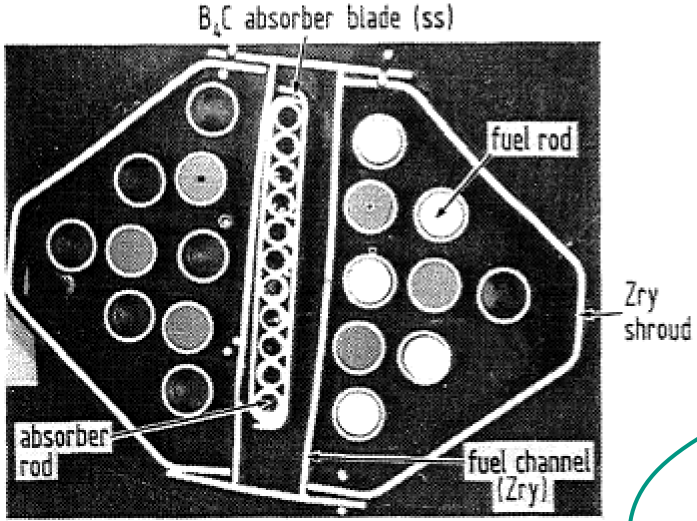
550 mm (T_{max}≈1000°C)

750 mm (T_{max}≈1300°C)

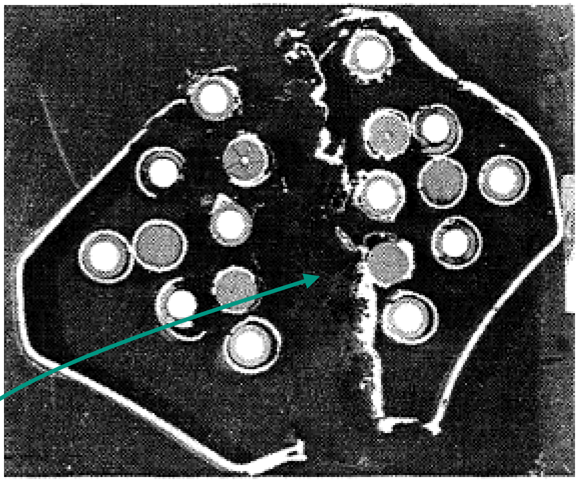
950 mm (T_{max}≈1500°C)

Degradation of B_4C control blade (BWR bundle test)

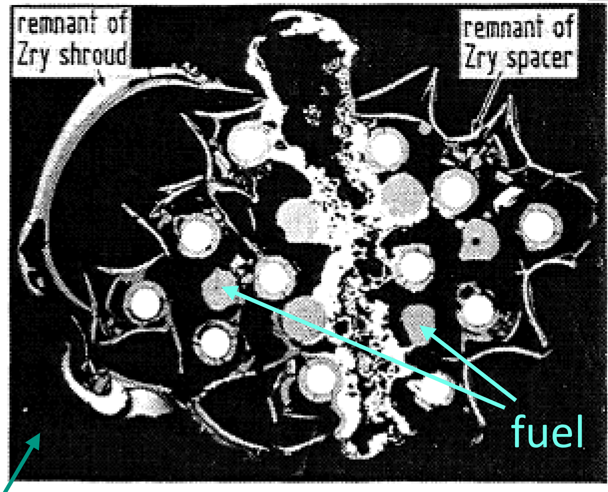
CORA-16



16-08 (1145mm), bottom view

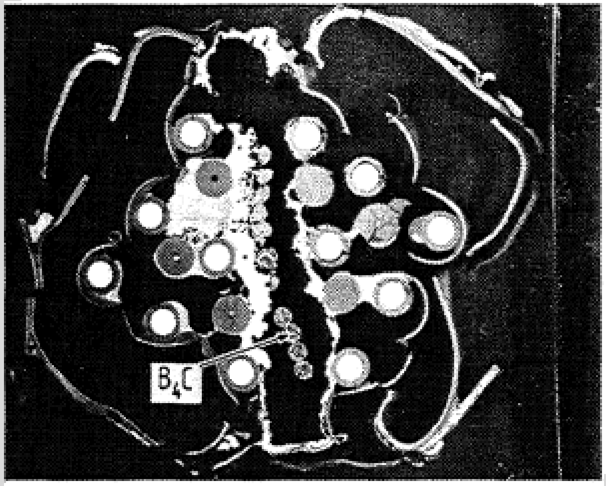


-07 (963mm), top view

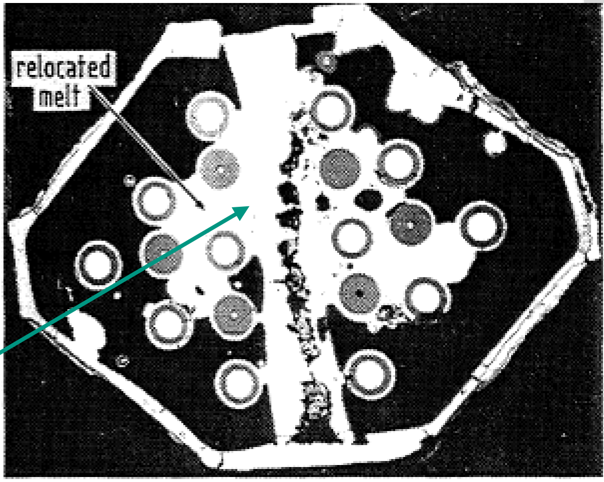


16-09 (525mm), top view
center grid spacer elevation

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



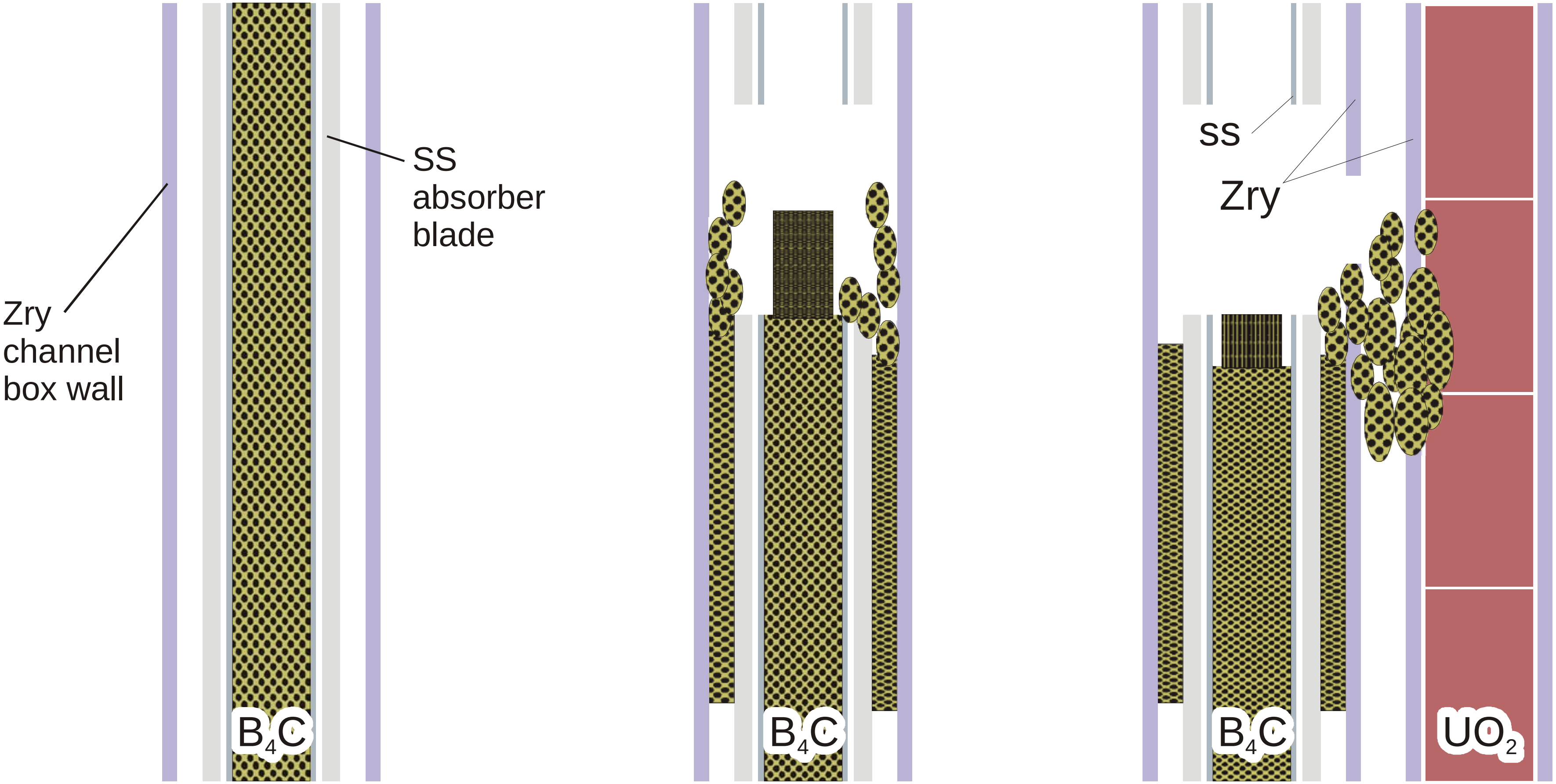
16-03 (310mm), top view



16-01 (110mm), top view

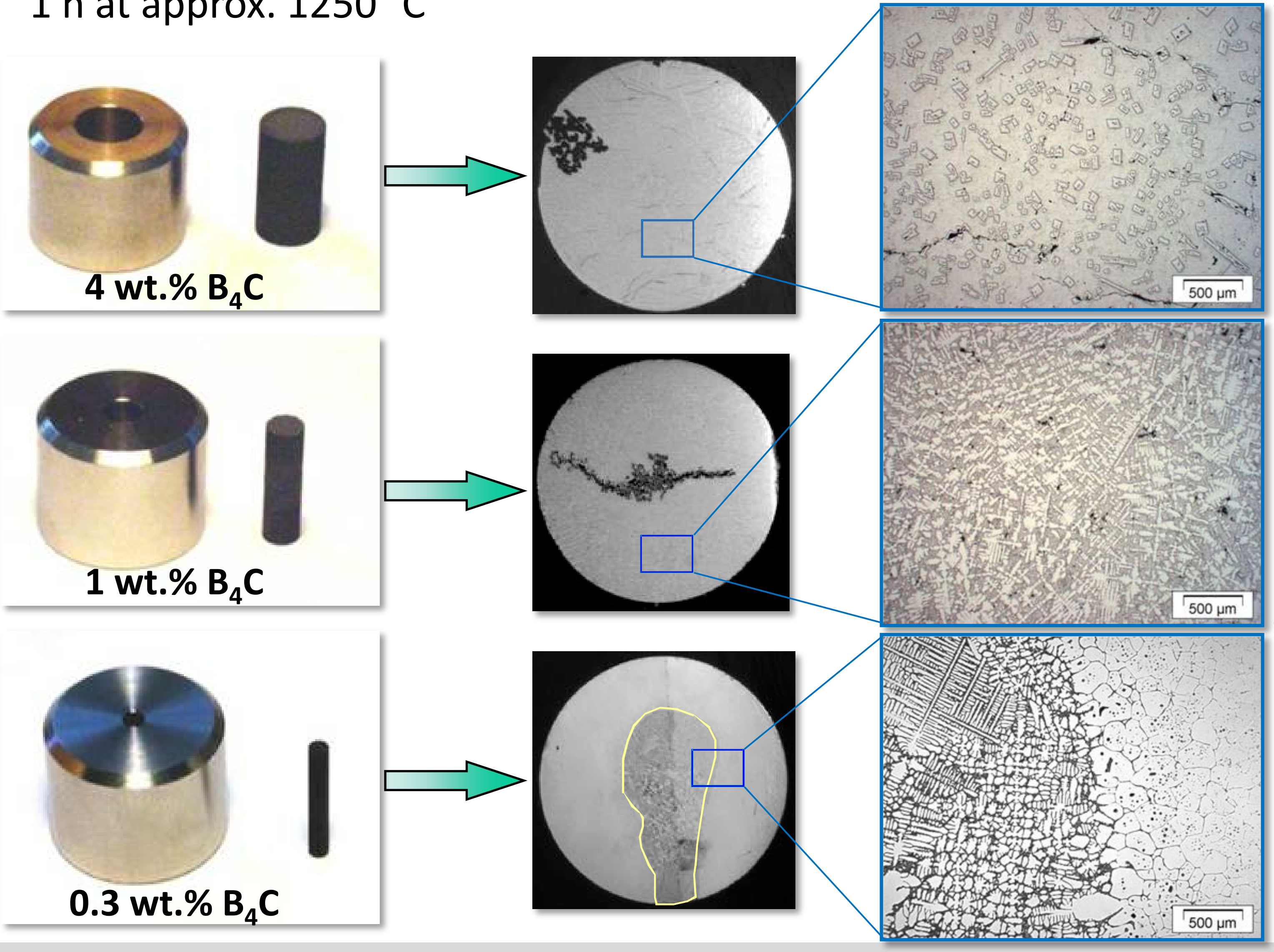
Degradation of BWR control blades

1. Interaction between B_4C and SS blade
2. Interaction between B_4C/SS melt and Zry channel box
3. Interaction between B_4C/SS/Zry melt with fuel rods + oxidation



Eutectic interaction of stainless steel with B_4C

1 h at approx. 1250 °C



4 wt.% B_4C

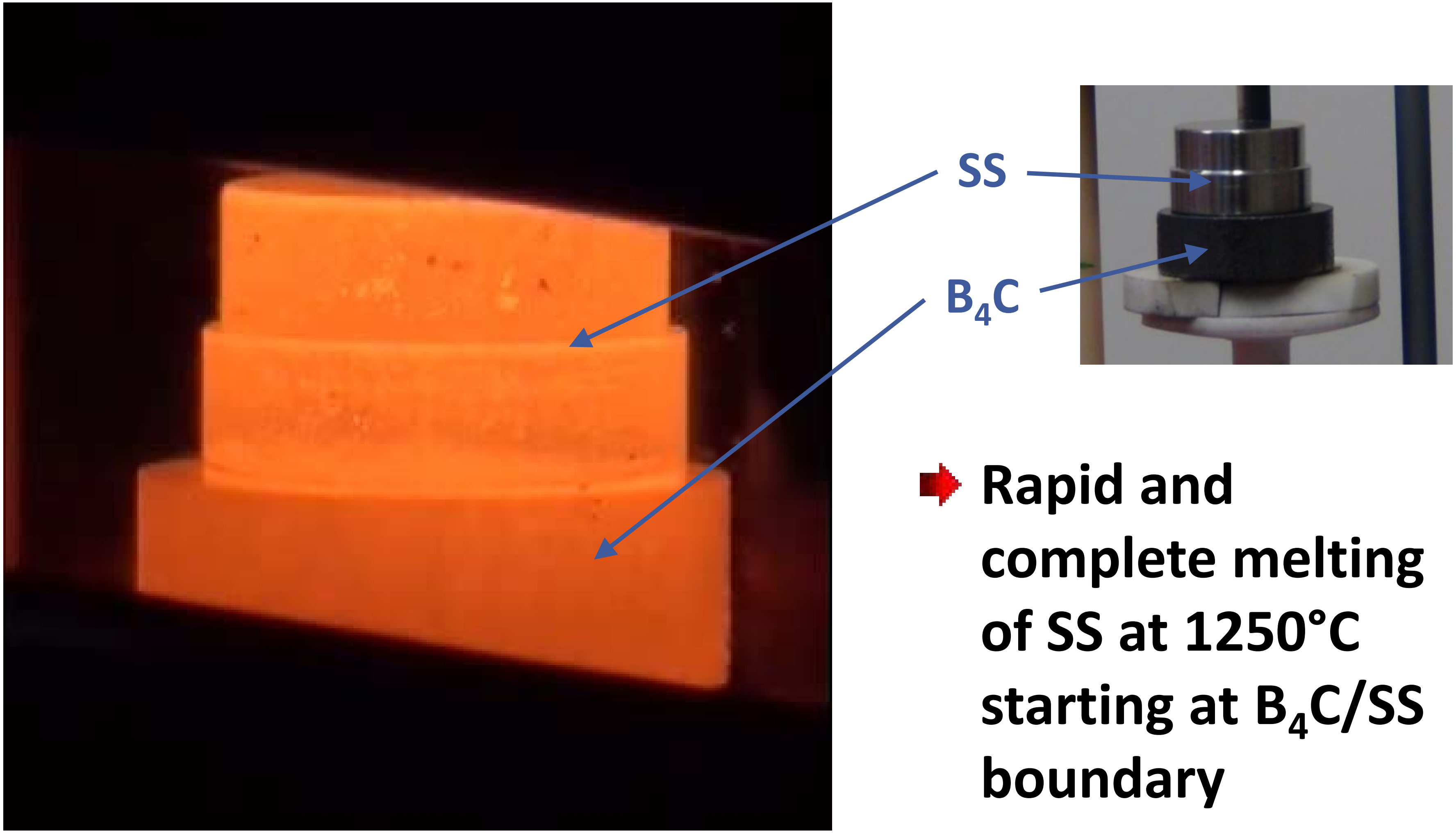
1 wt.% B_4C

0.3 wt.% B_4C

Complete liquefaction of stainless steel

1/3 of SS liquefied

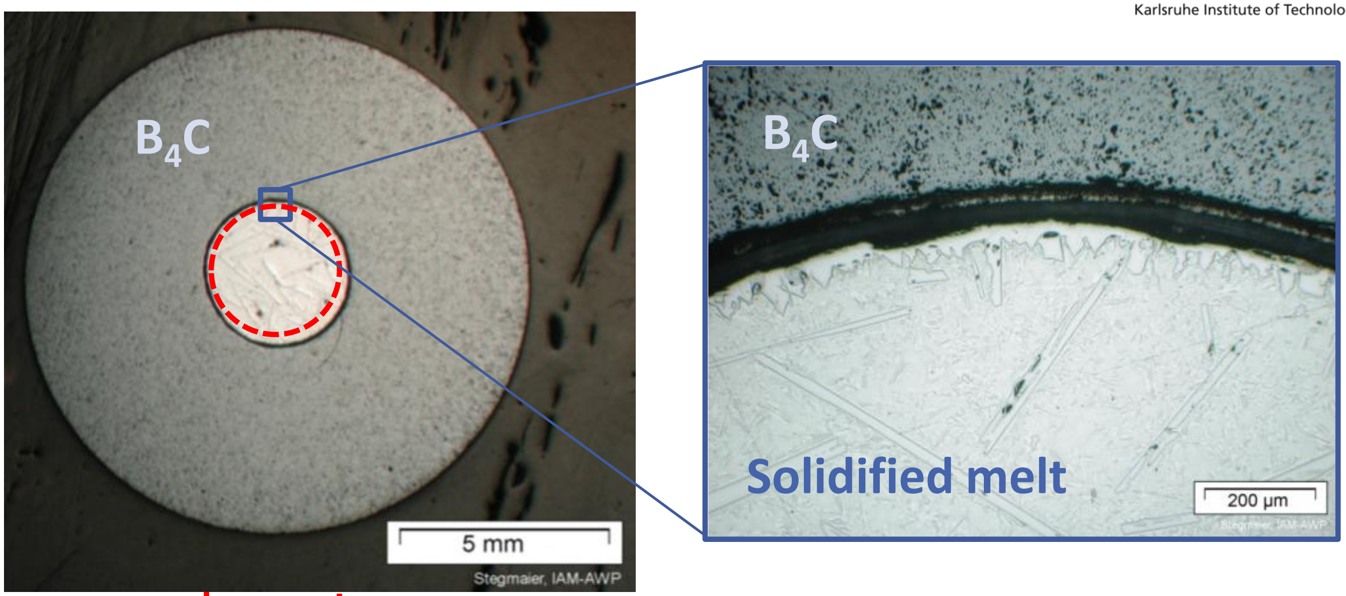
Eutectic interaction of stainless steel with B_4C

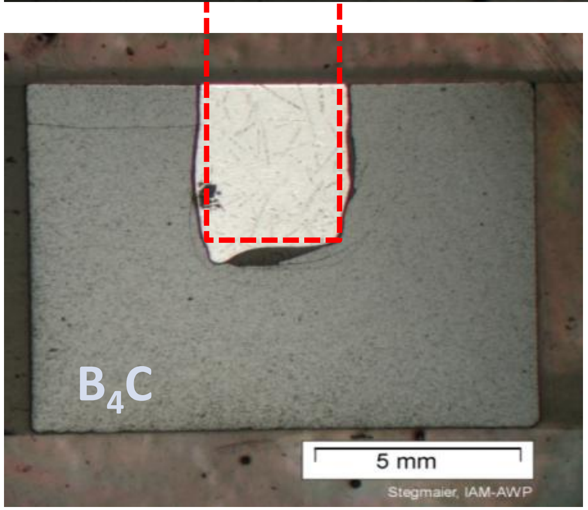


- **Rapid and complete melting of SS at 1250°C starting at B_4C/SS boundary**

Eutectic interaction of stainless steel with B_4C

1h @
1280°C





------- Initial geometry of B_4C crucible

- **Only little dissolution of B_4C**

Oxidation of B_4C: Main chemical reactions

$$B_4C + 7H_2O(g) \rightarrow 2B_2O_3(l) + CO(g) + 7H_2(g)$$

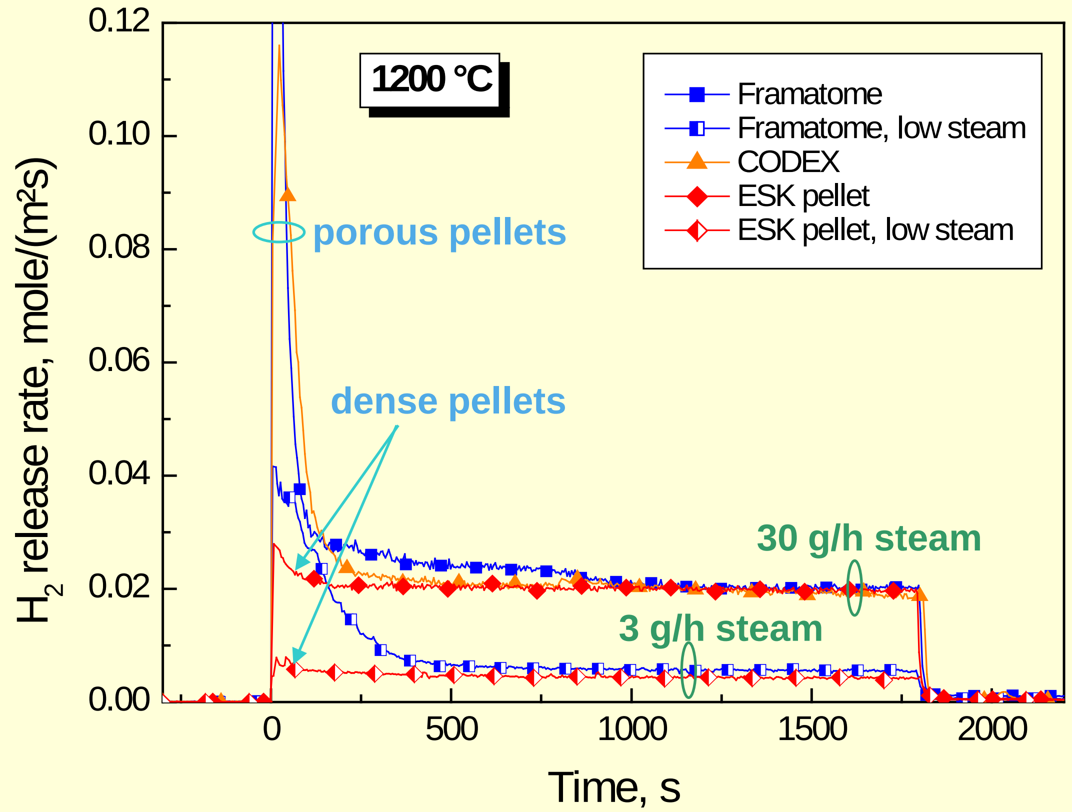
$$B_4C + 8H_2O(g) \rightarrow 2B_2O_3(l) + CO_2(g) + 8H_2(g)$$

$$B_4C + 6H_2O(g) \rightarrow 2B_2O_3(l) + CH_4(g) + 4H_2(g)$$

$$B_2O_3 + H_2O(g) \rightarrow 2HBO_2(g)$$

$$B_2O_3 + 3H_2O(g) \rightarrow 2H_3BO_3(g)$$

Oxidation kinetics of B_4C in steam

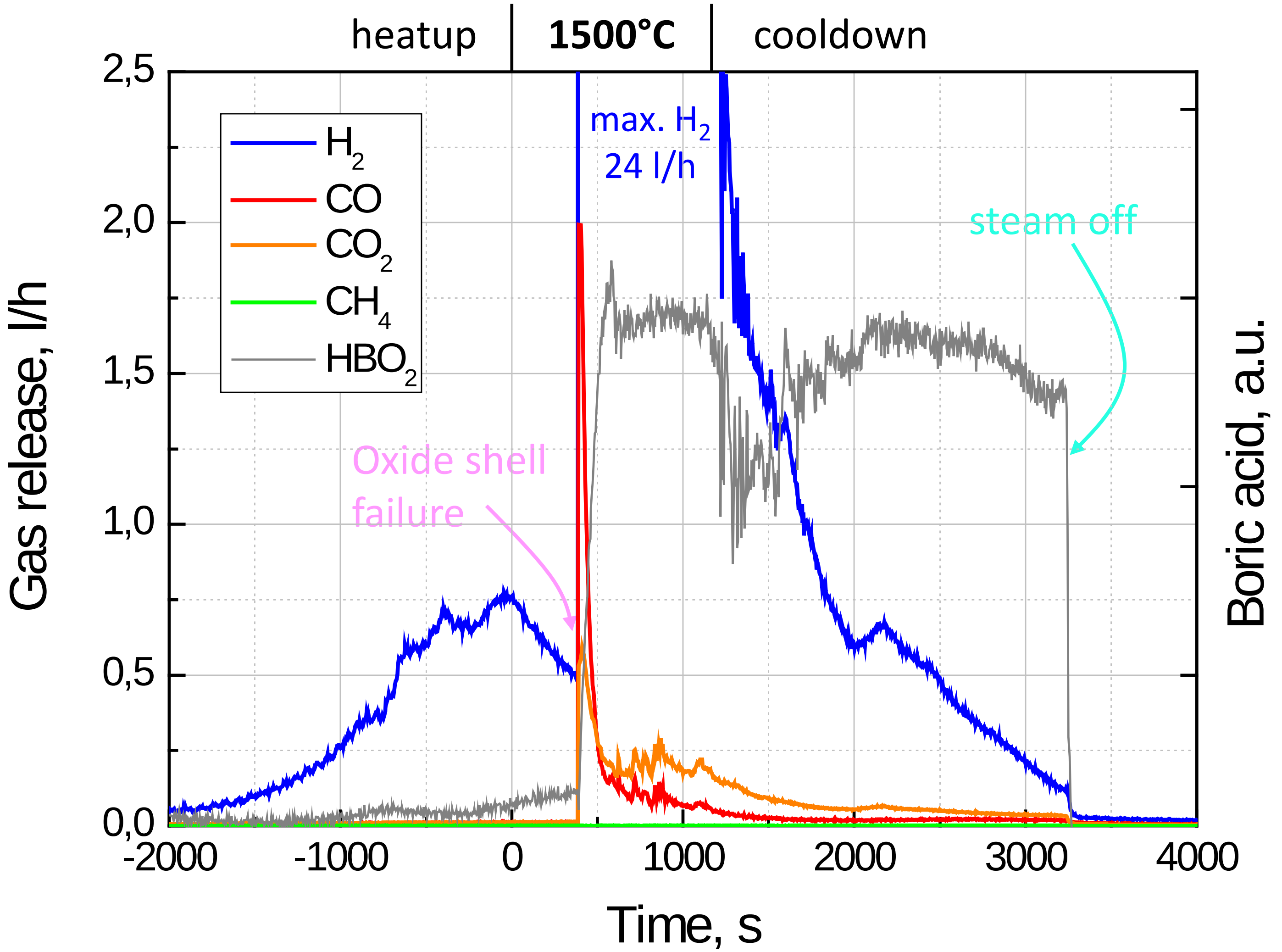


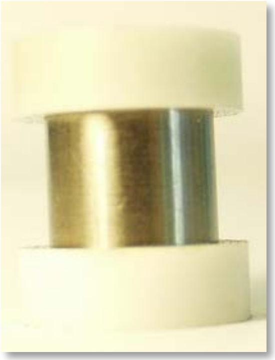
- Strongly dependant on B_4C structure and thermo hydraulic boundary conditions like pressure and flow rate

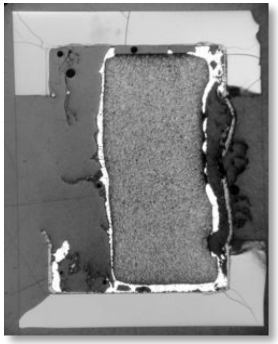
Gas release during oxidation of B_4C (melts)

- 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 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

Gas release after failure of B_4C CR segment

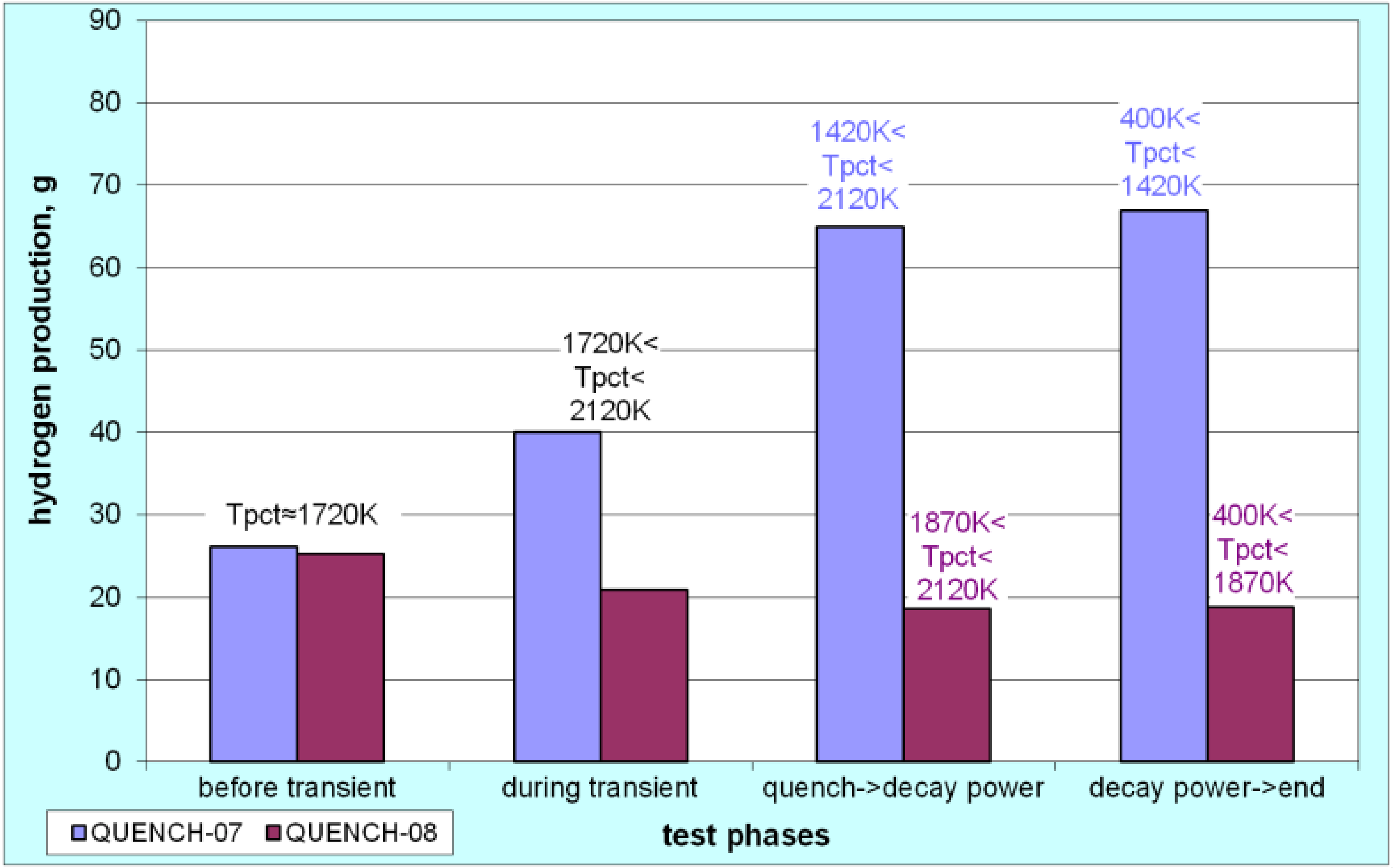






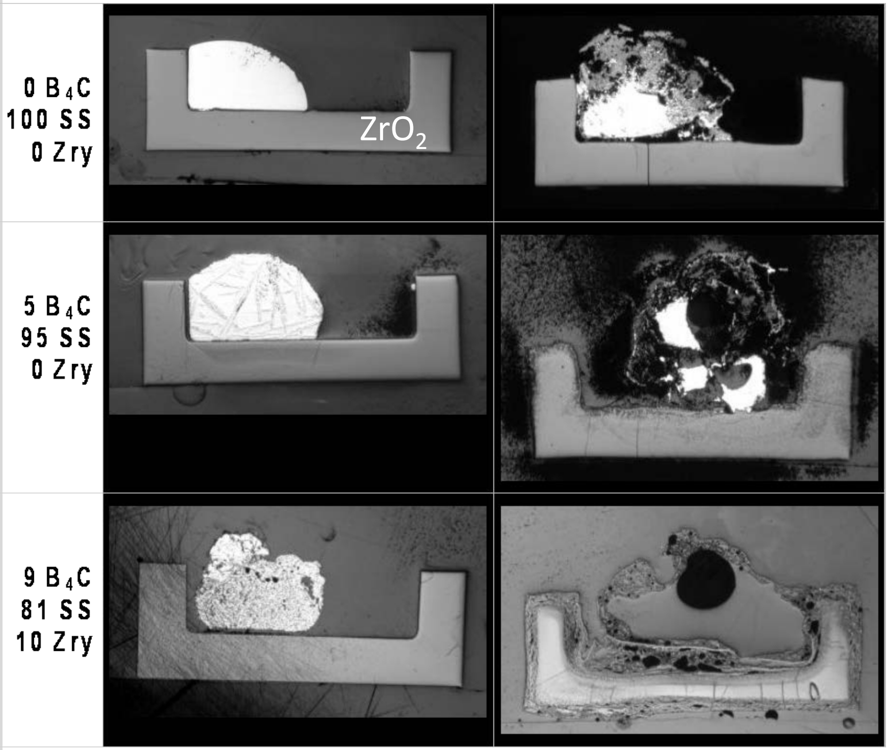
Hydrogen release in QUENCH bundle experiments

Comparison of hydrogen release during the various test phases of bundle tests QUENCH-07 (with B_4C) and QUENCH-08 (w/o B_4C)



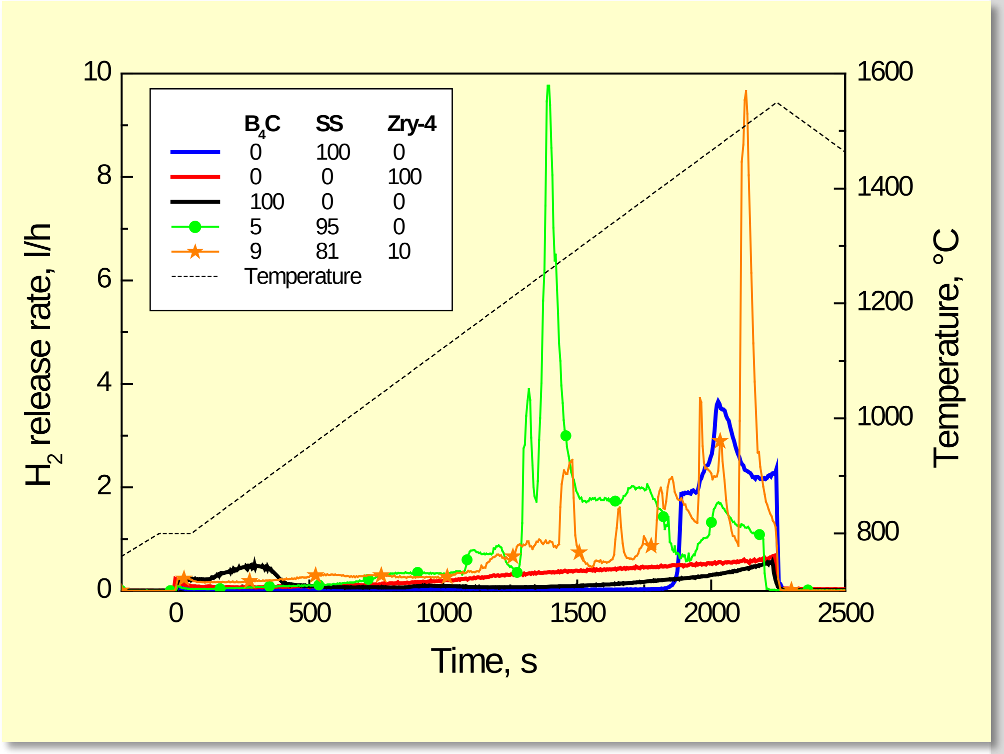
Oxidation of B_4C absorber melts

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



before oxidation

after oxidation



Hydrogen release (~ ox. rate) during oxidation of absorber melts and pure CR components

Energetic effects of B_4C oxidation

- Oxidation of B_4C in steam: 13 MJ/kg_{B4C}
- Oxidation of B_4C in oxygen: 50 MJ/kg_{B4C}
- ➡ Significant contribution to energy release in the core

For comparison:

- Oxidation Zr in steam: 6 MJ/kg_{Zr}
- Fuel value of mineral oil: 12 MJ/kg_{oil}
- Fuel value of black coal: 30 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

Summary

- Chemical interactions may strongly affect the early phase of a severe accident
- The main hydrogen source term is produced by metal (B_4C)-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, B_4C-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 …

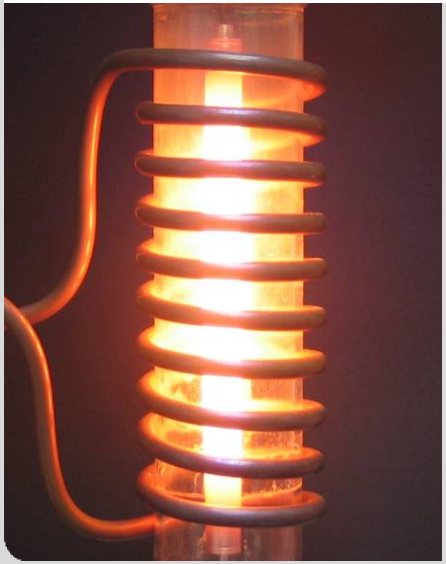
- The QUENCH team at KIT
- Masaki Kurata (JAEA) for inviting me
- YOU … for your attention

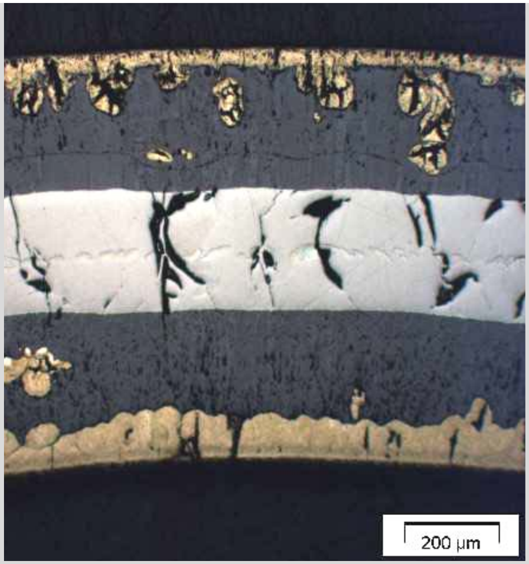
Early core degradation with special emphasis on oxidation and B_4C control rod failure

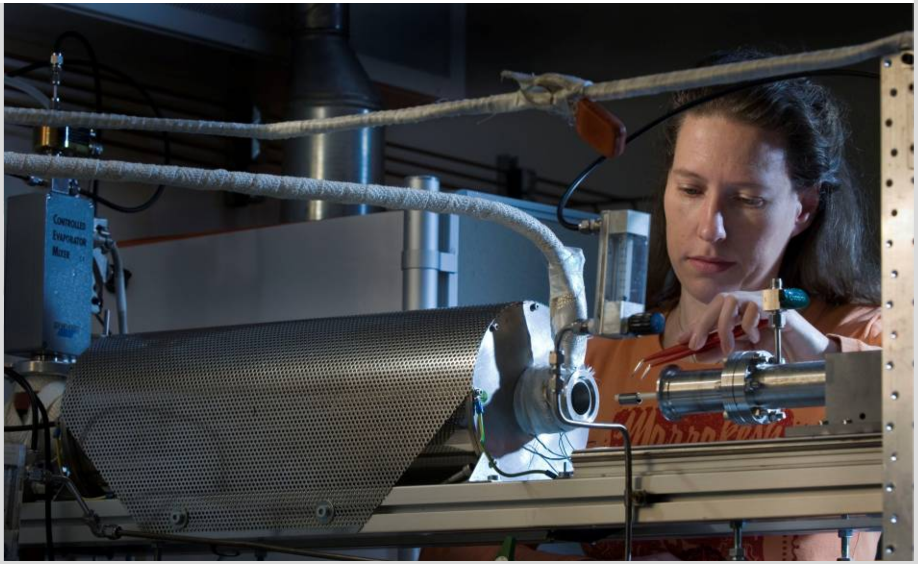
Martin Steinbrück

International Seminar on Fuel Degradation Methodology in Severe Accidents - Tokyo, Japan, 26 October 2012

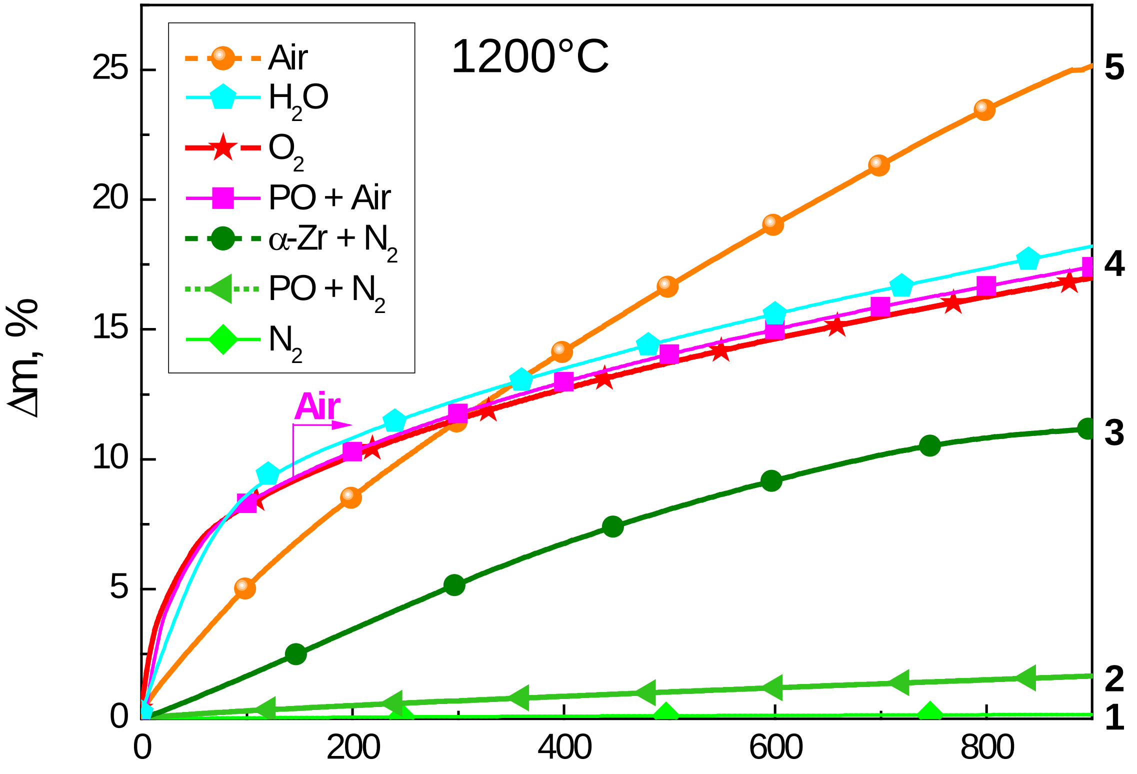
Institute for Applied Materials IAM-AWP & Program NUKLEAR

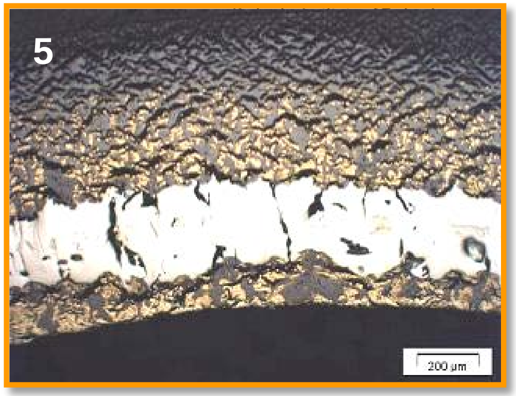


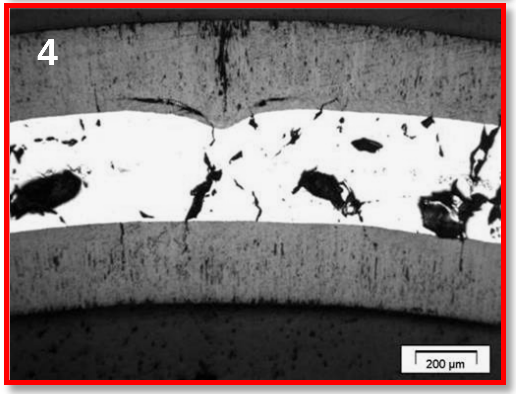


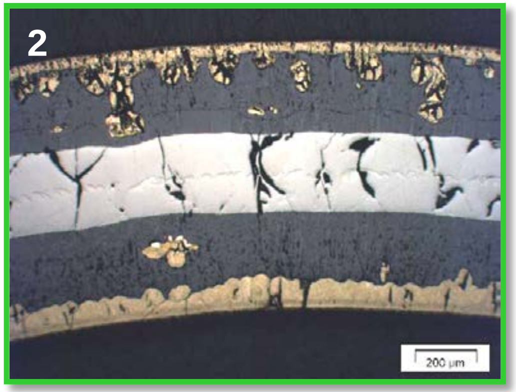


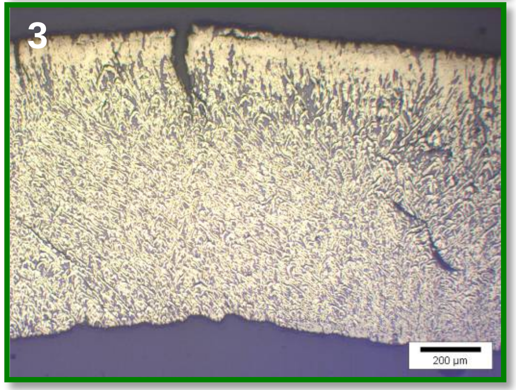
Oxidation of Zr alloys in various atmospheres



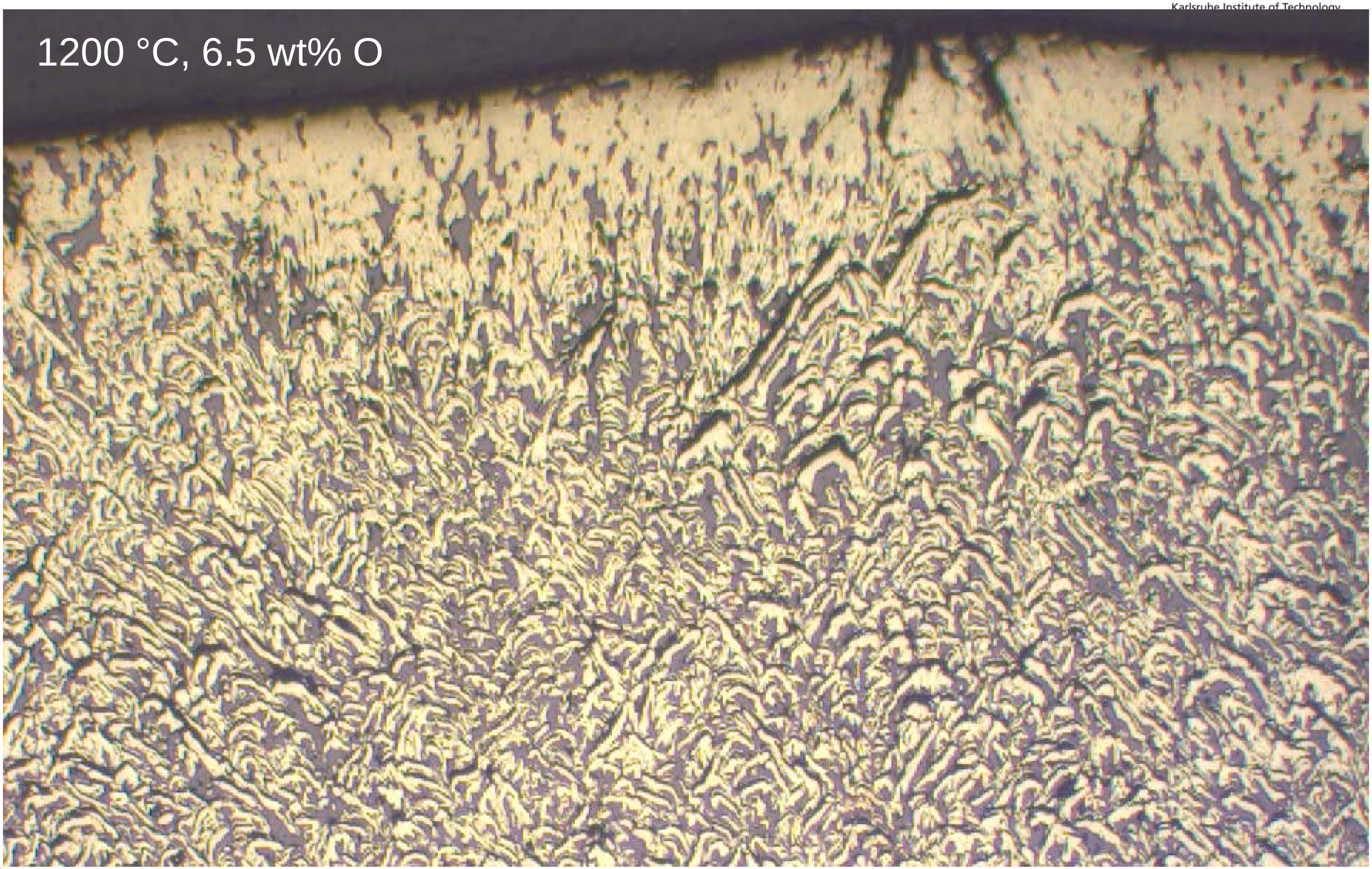






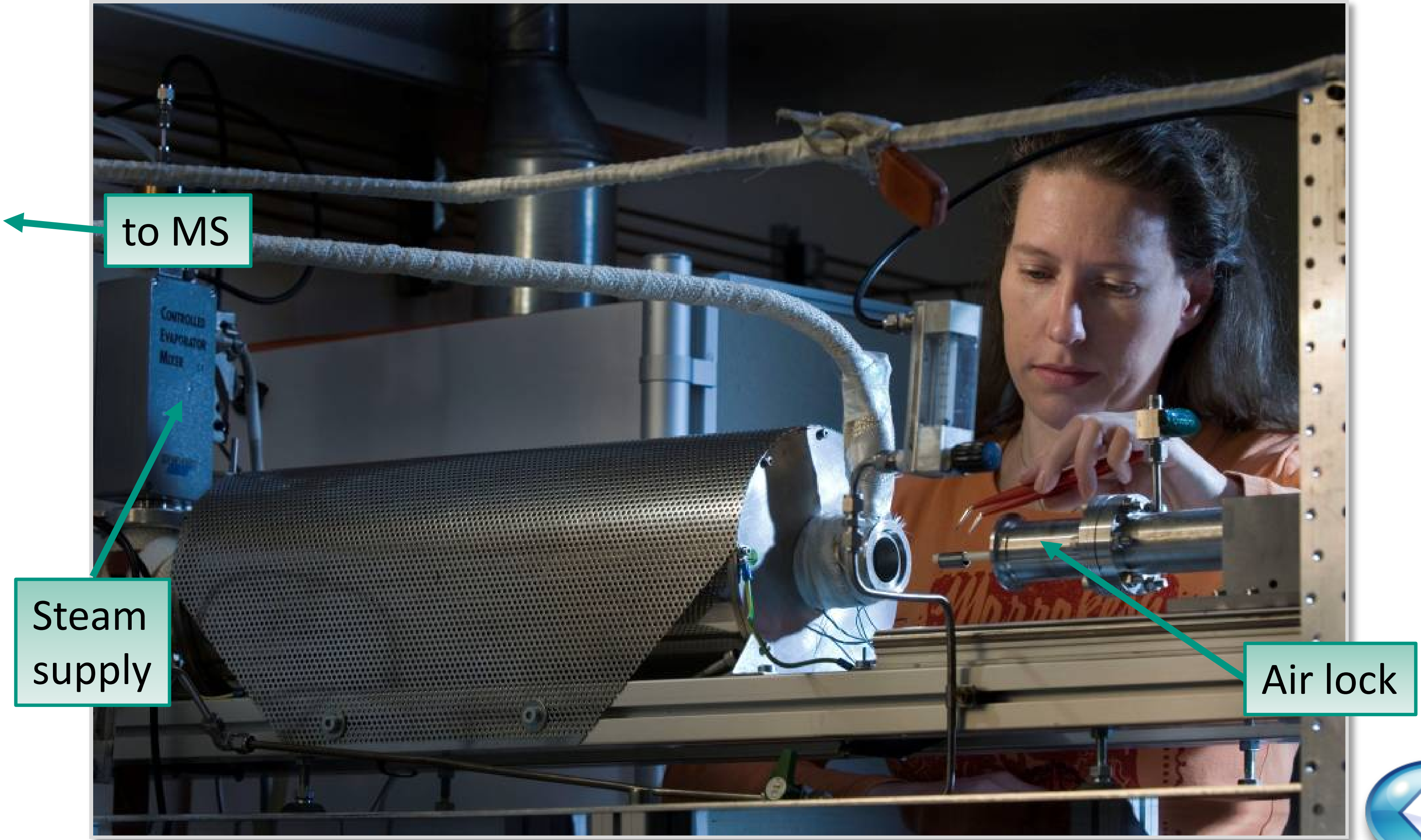


Reaction of α-Zr(O) with nitrogen

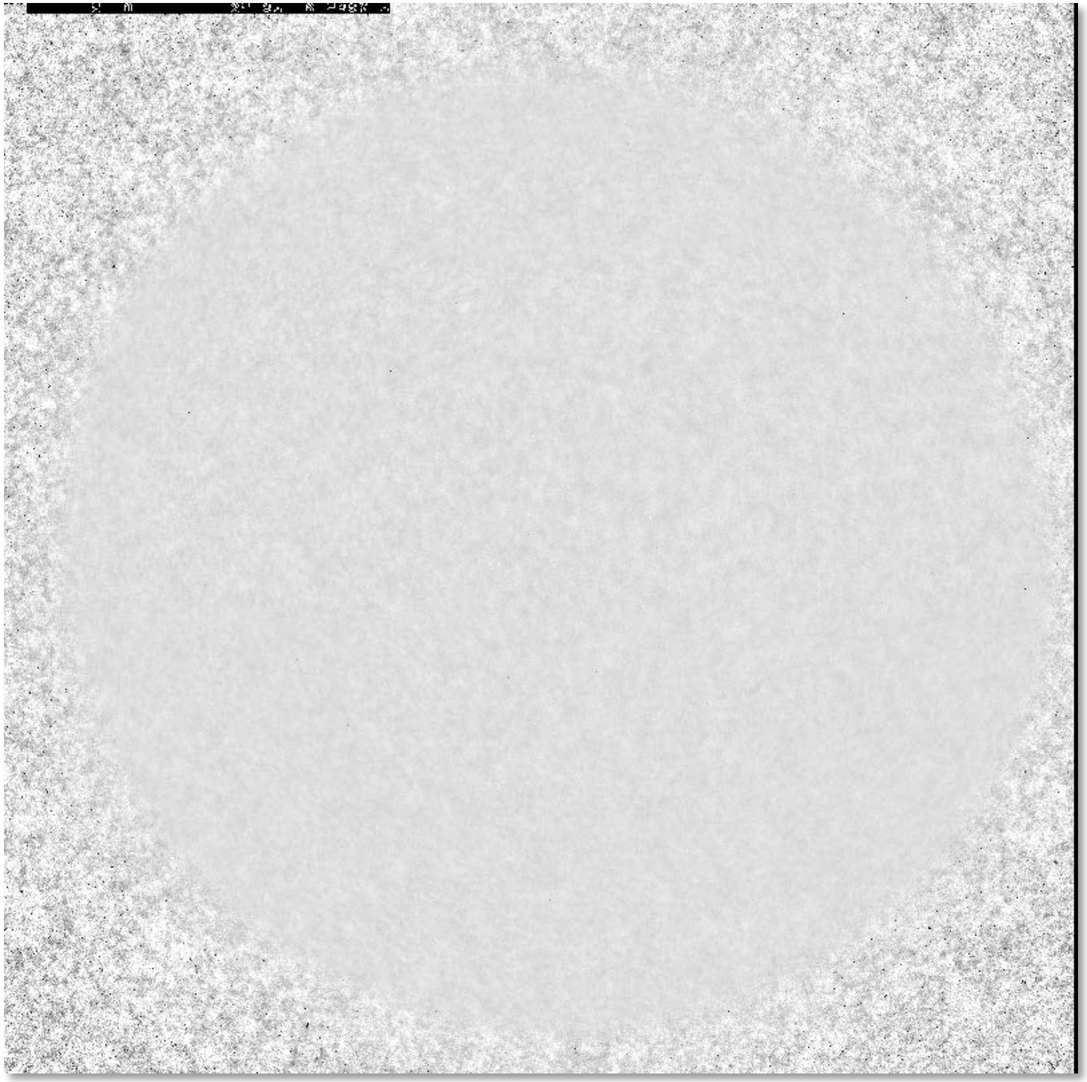


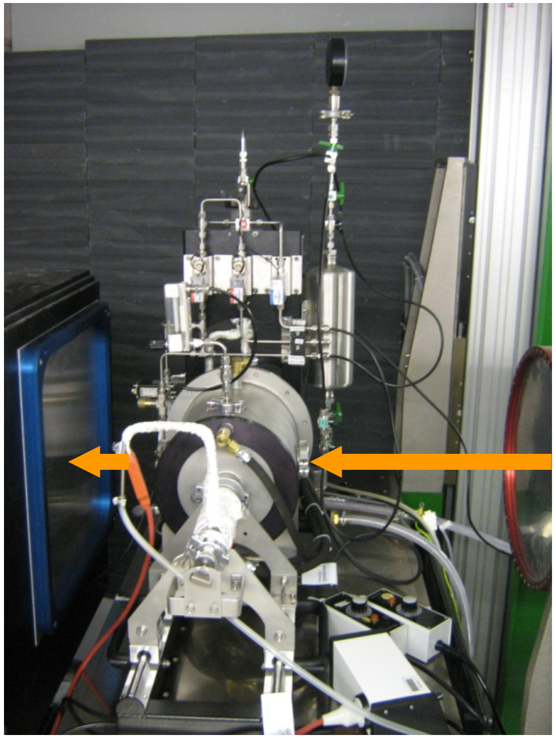
1200 °C, 6.5 wt% O

BOX rig for investigation of materials at high temperatures (1700°C) in defined atmospheres



In-situ investigation of hydrogen diffusion in Zry





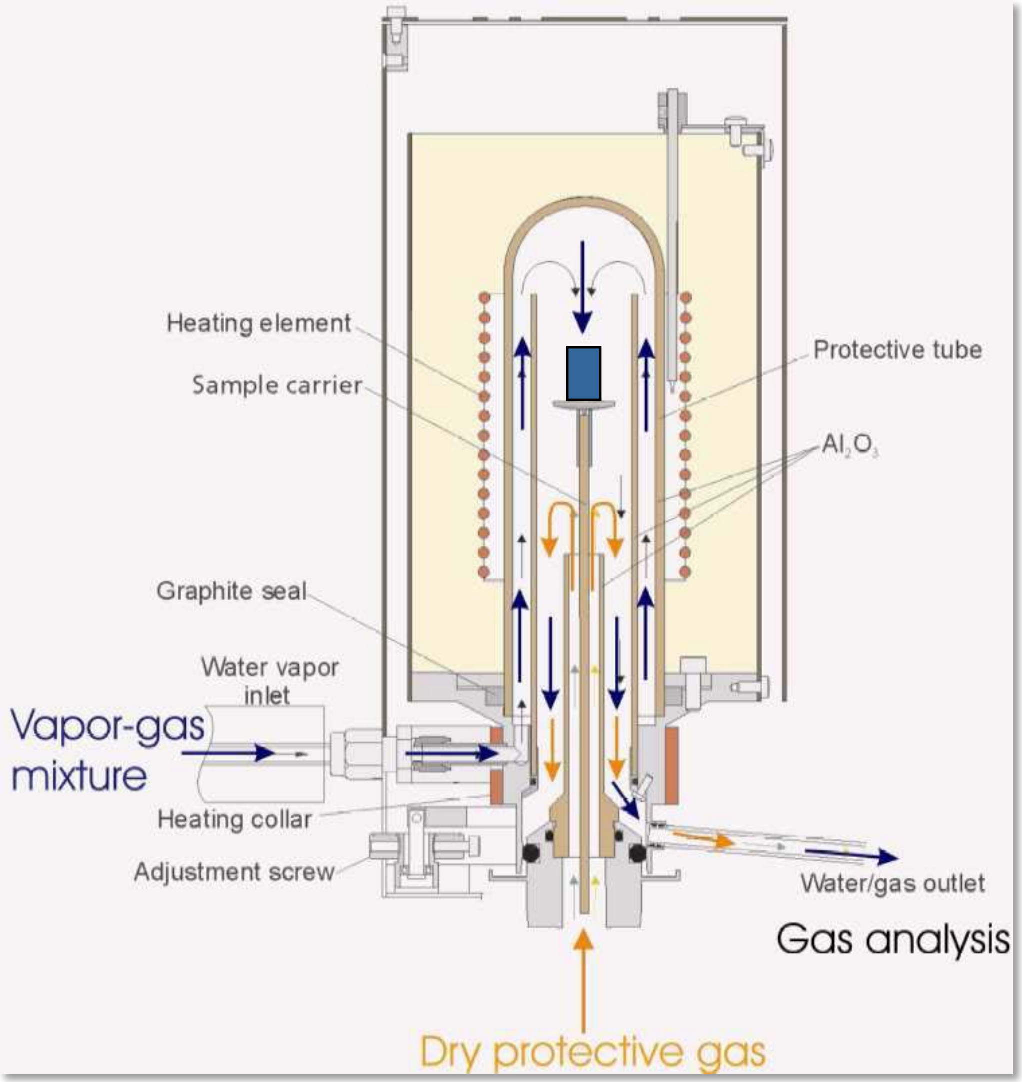
Example:

- Hydrogen diffusion into a Zry-4 cylinder
- Surface oxidized except one base
- Ø =12mm, l = 20 mm
- at 1100°C
- time ratio: 1:100

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

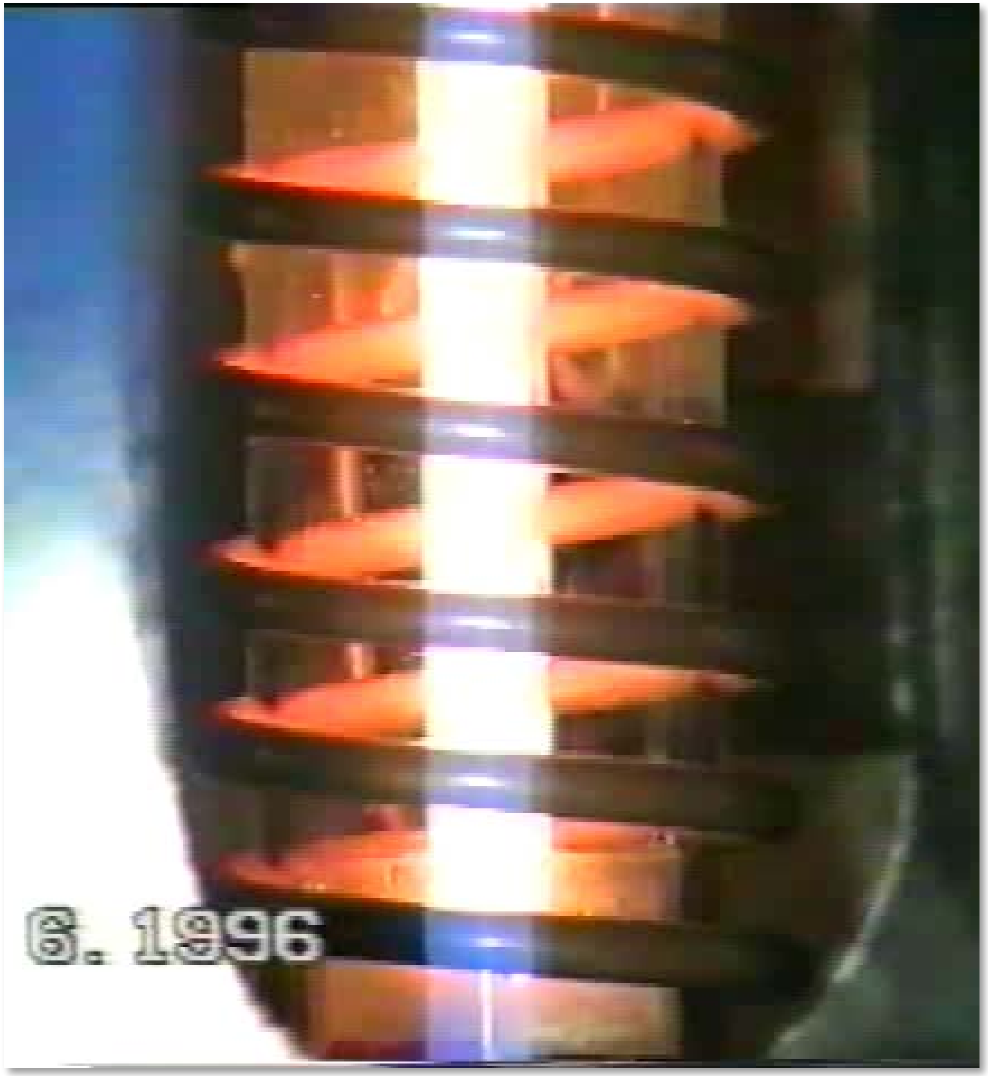
NETZSCH® steam furnace for TGA

- Up to 100% steam
- Up to 1250°C



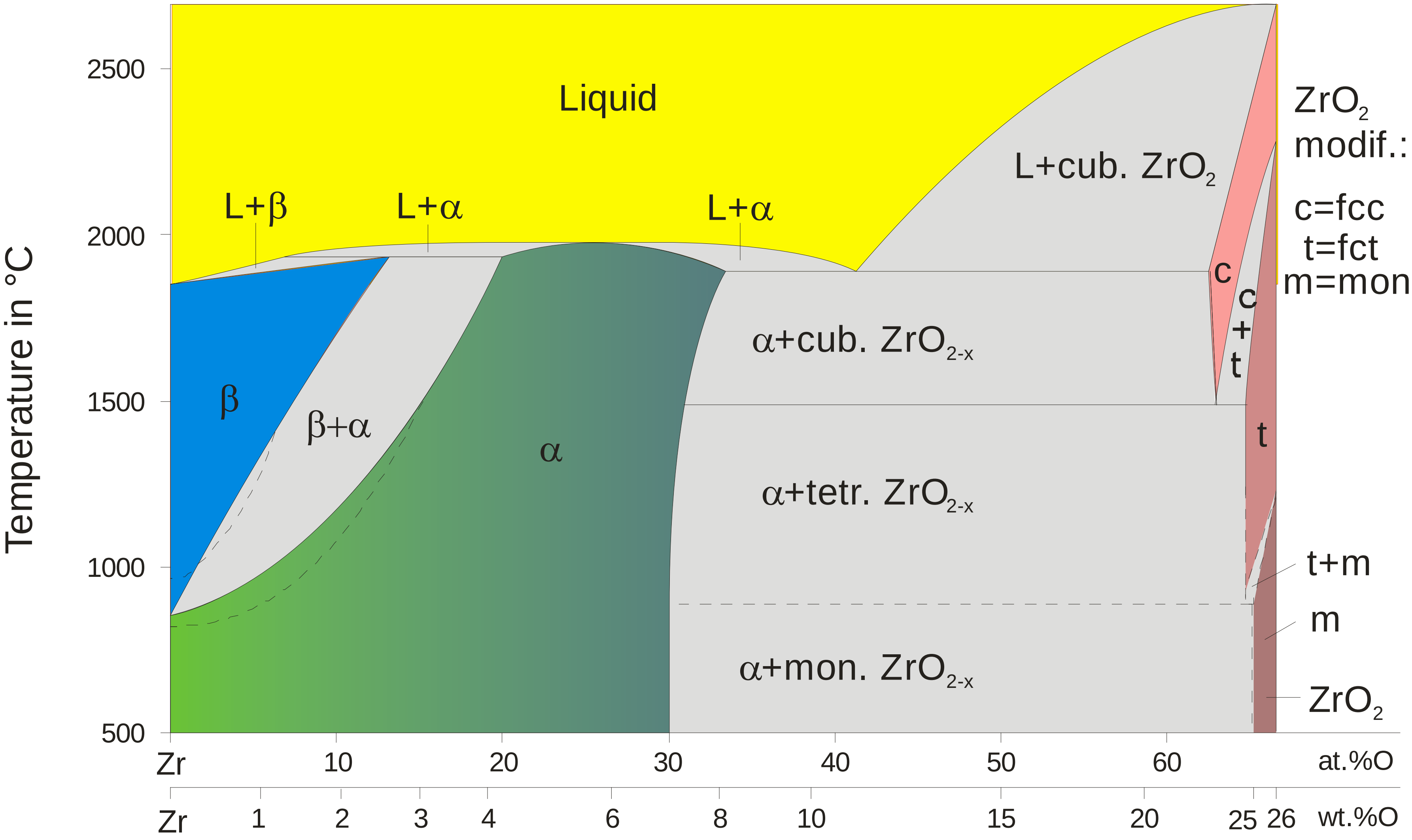
Single-rod QUENCH tests

- 15-cm rods filled with ZrO_2 pellets
- Direct inductive heating till melting temperatures
- Video recording
- Mass spectrometer for analysis of hydrogen release

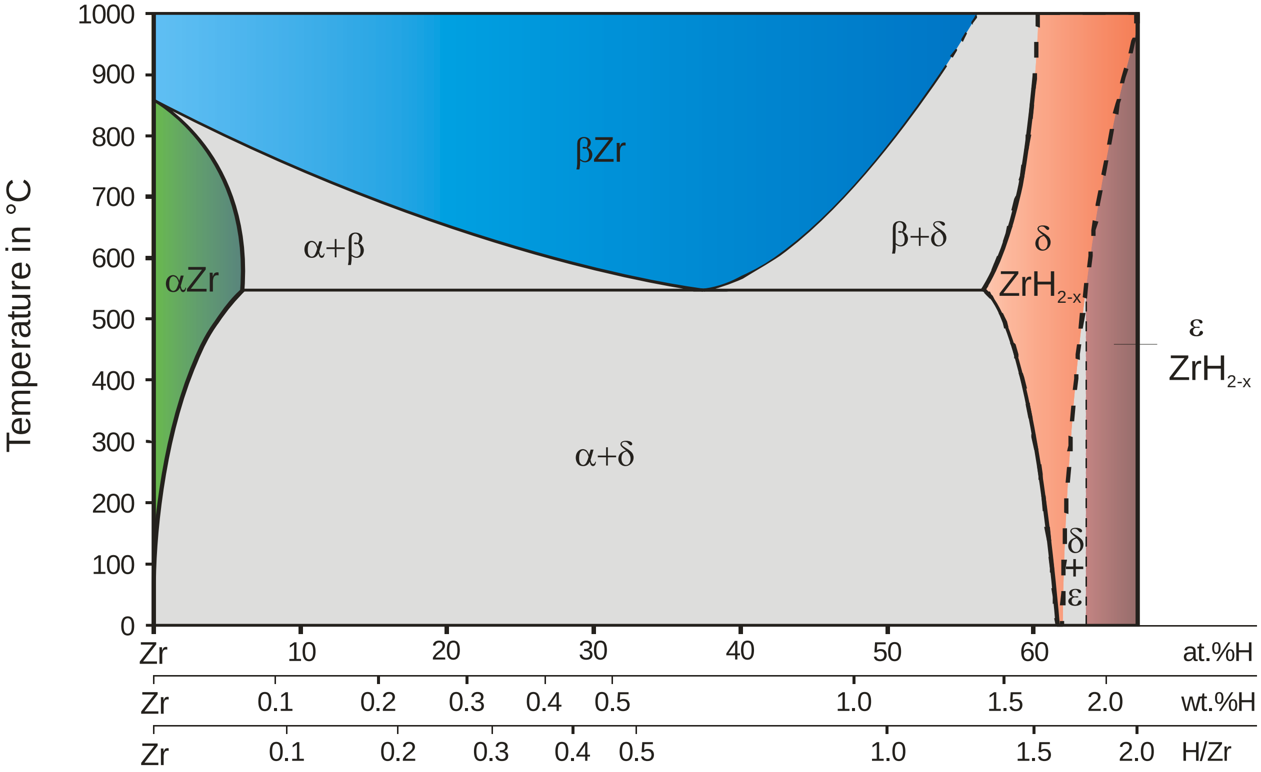


Reflood from 1400°C

Phase diagram Zr - O



Phase diagram Zr - H



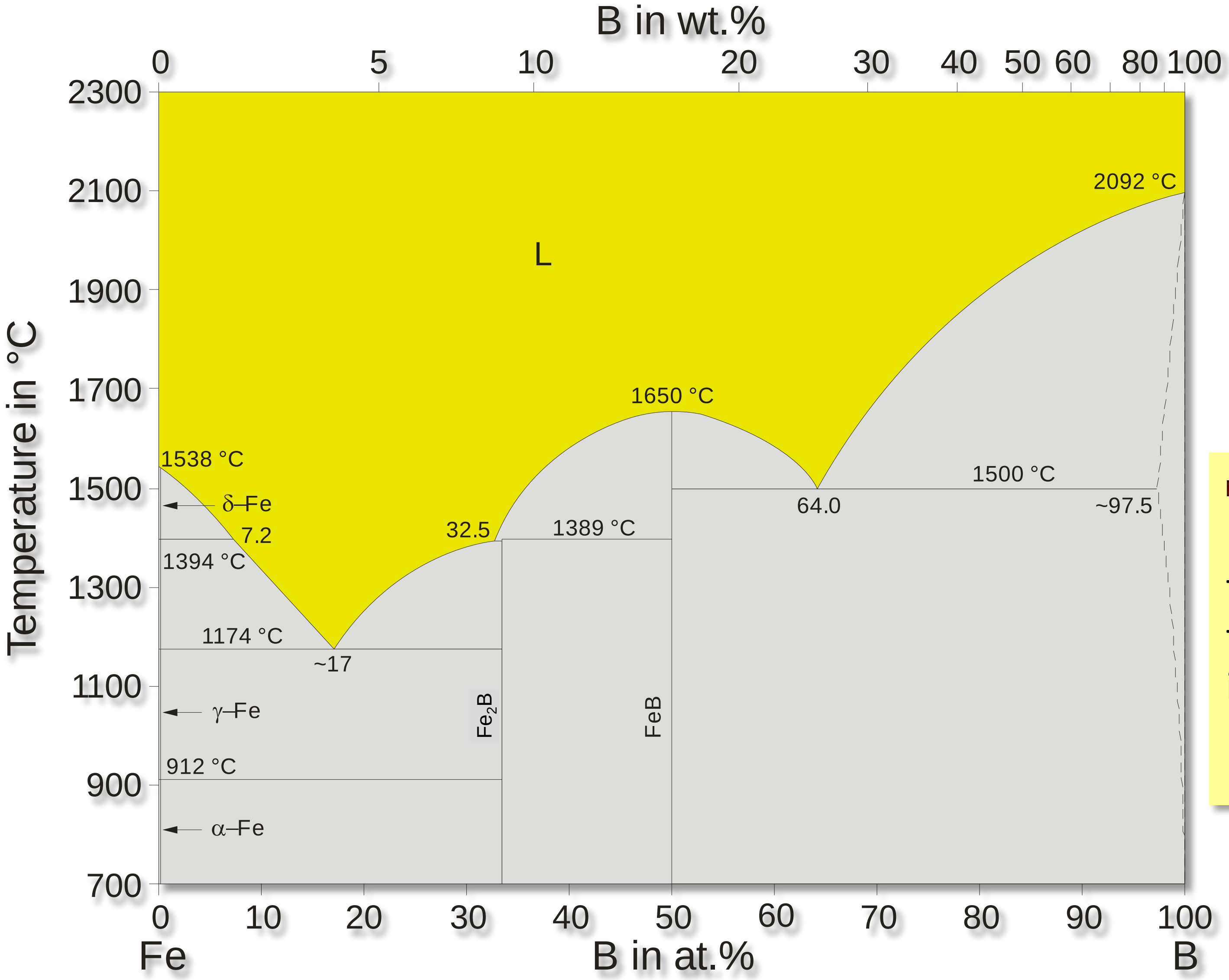
Sieverts' law:

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

with

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

Phase diagram iron - boron



Decrease of melting temperatures due to eutectic interactions