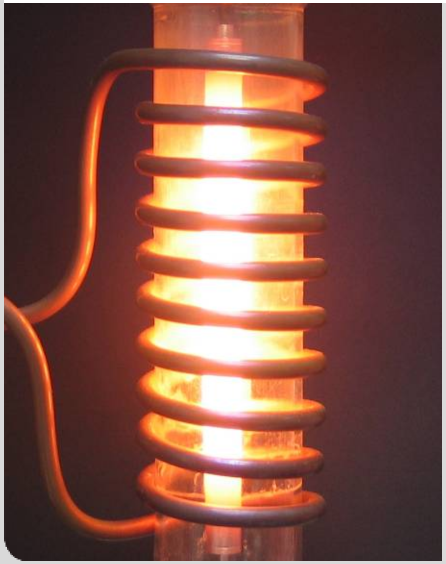
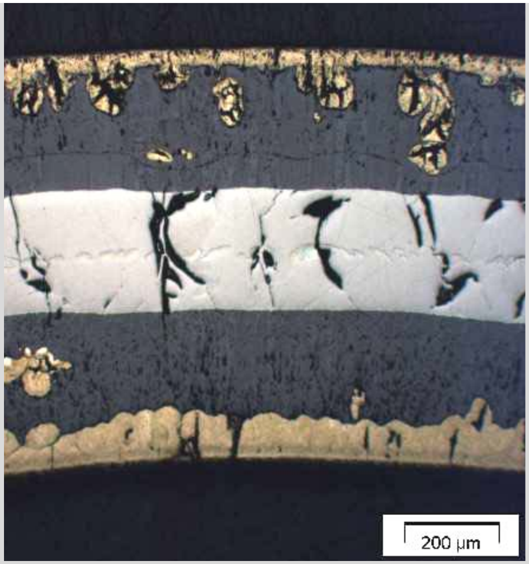
Oxidation of zirconium alloys in mixed atmospheres containing nitrogen

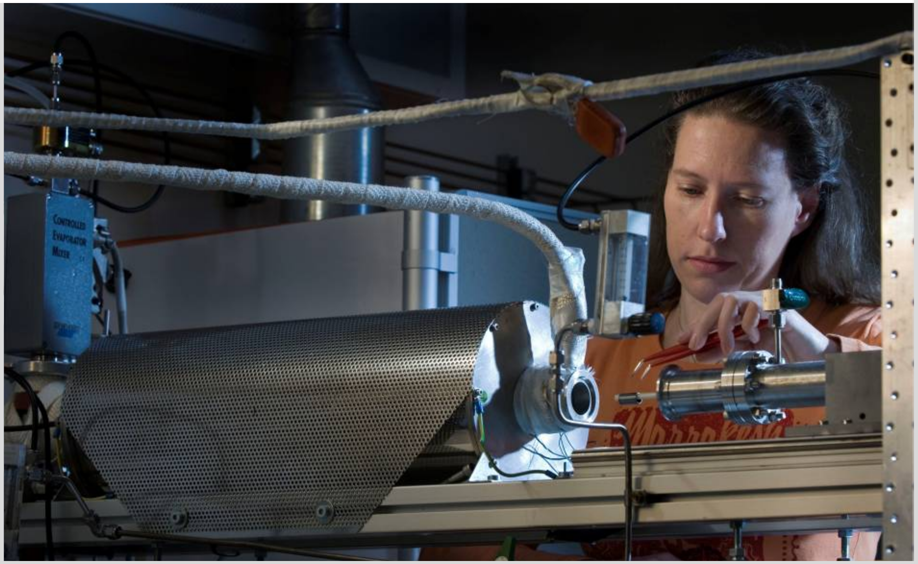
Martin Steinbrück, Karlsruhe Institute of Technology, Institute for Applied Materials

EFC Workshop „Beyond Single Oxidants“, 19-21 September 2012, Frankfurt/M., Germany

Institute for Applied Materials, IAM-AWP / Program NUKLEAR







Karlsruhe Institute of Technology

Founded in 2009

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

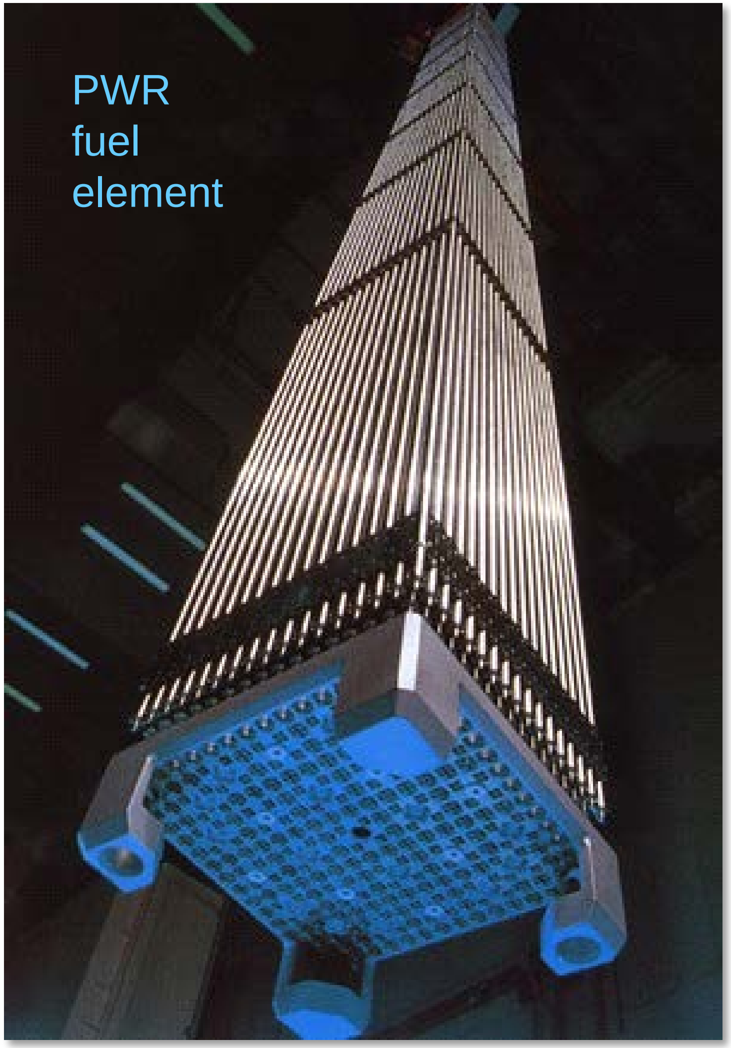
= 9000 employees

= 23 000 students

Motivation

- Zirconium alloys are used as cladding materials in nuclear reactors worldwide
- Especially advanced cladding alloys (e.g. M5®, ZIRLO™) exhibit excellent mechanical and corrosion properties during operation till high burnup
- But, at high temperature, existing during LOCA and severe accidents, strong oxidation occurs, causing:
  - Cladding degradation
  - Hydrogen release
  - Energy release
- Oxidizing atmospheres:
  - **Steam**
  - Air
  - Nitrogen
  - Mixtures of them

after failure of RPV



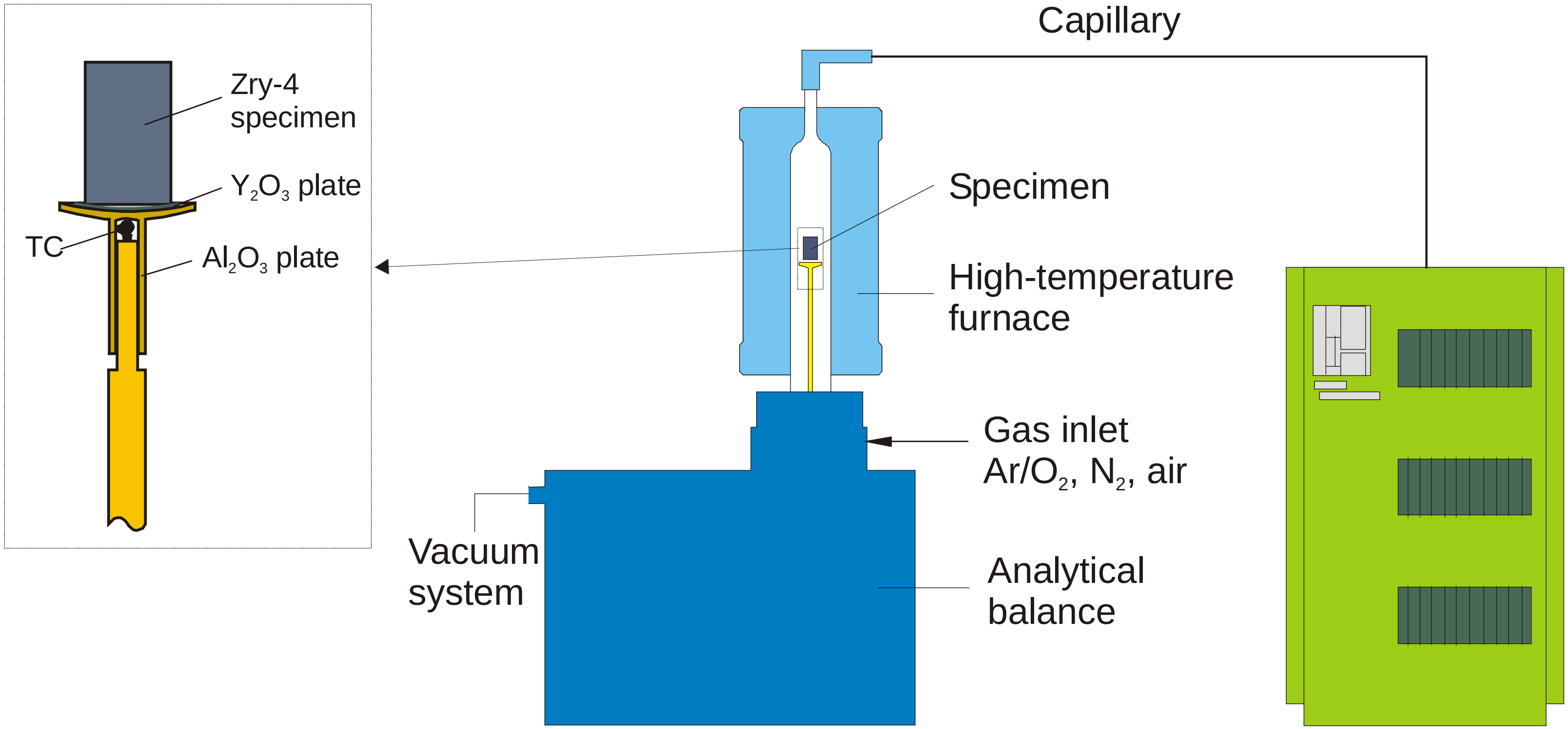
Specimens

- 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

Test rig with thermal balance and mass spectrometer



Zry-4 specimen

Y_2O_3 plate

TC

Al_2O_3 plate

Capillary

Specimen

High-temperature furnace

Gas inlet Ar/O_2, N_2, air

Vacuum system

Analytical balance

TG measuring head

Thermobalance

Mass spectrometer

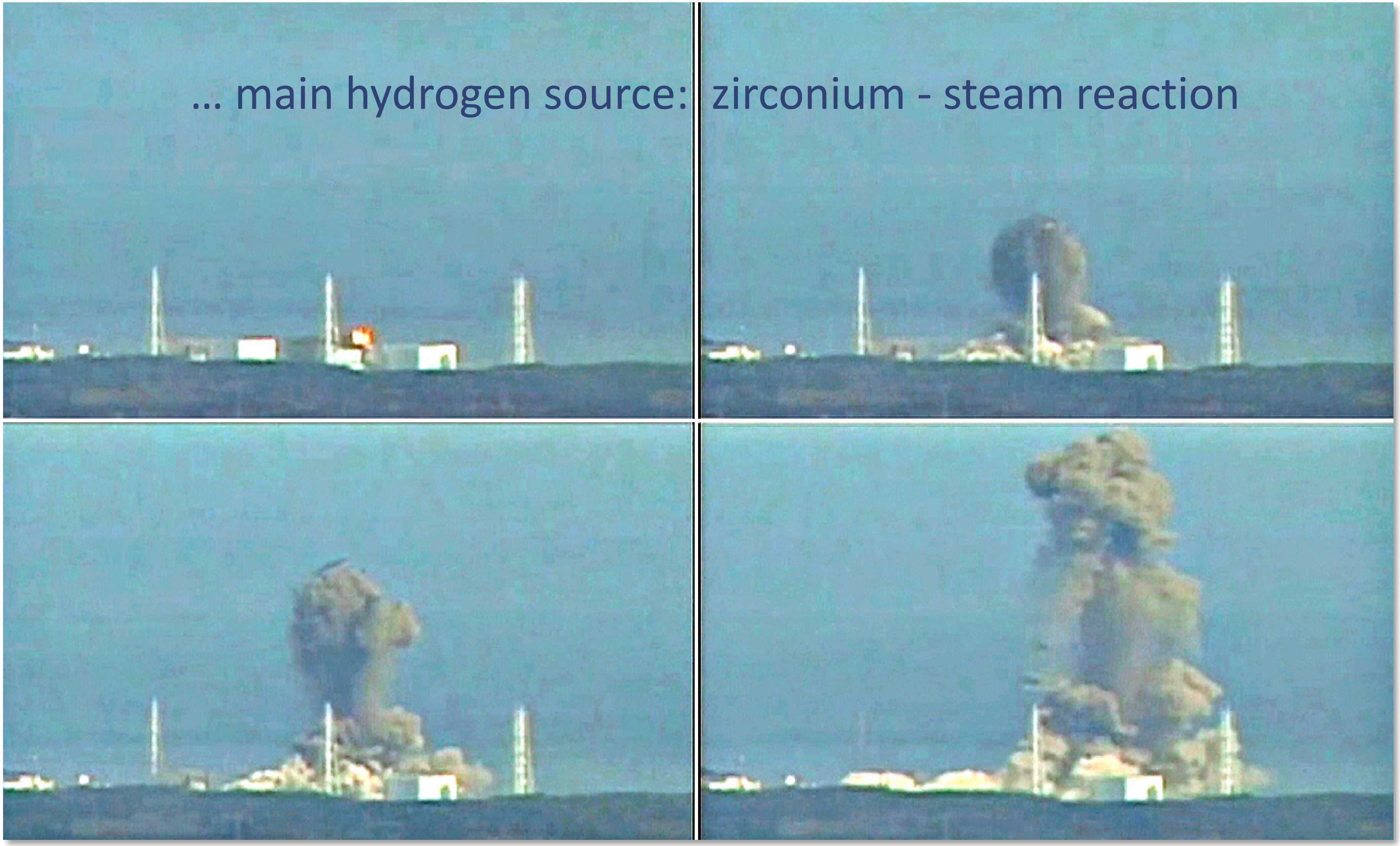
Basics – chemical reactions

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

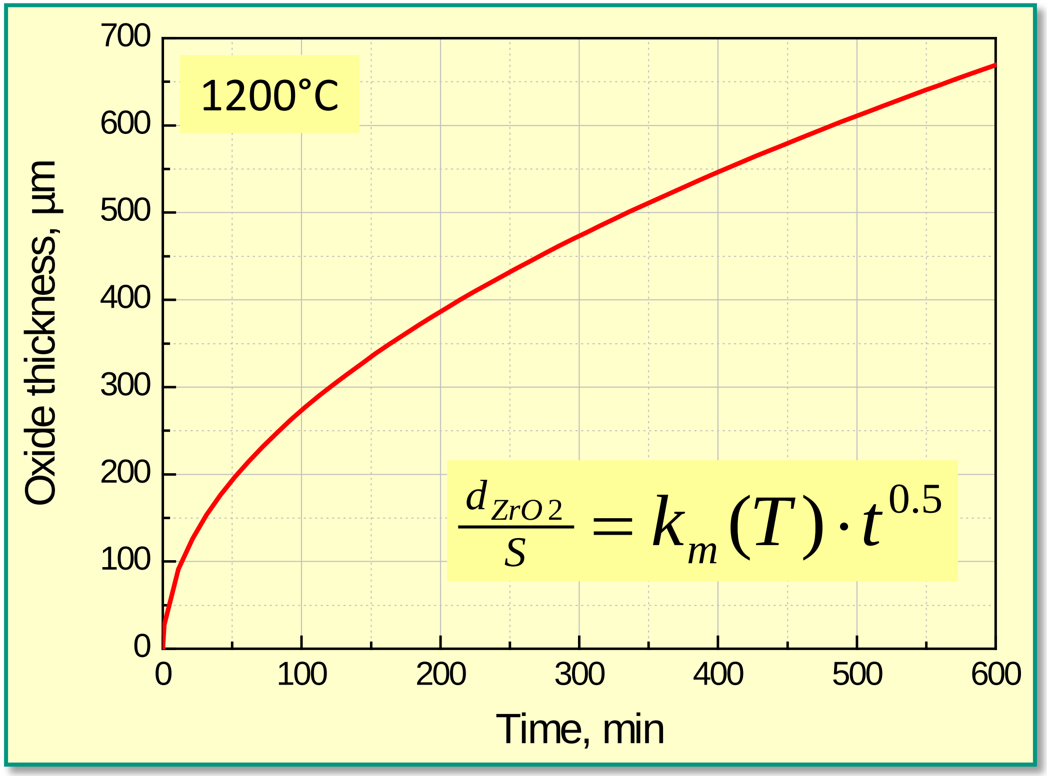
- Release of hydrogen and heat
- Hydrogen either released to the environment or absorbed by Zr metal

Hydrogen detonation in Fukushima Dai-ichi NPPs …


… main hydrogen source: zirconium - steam reaction

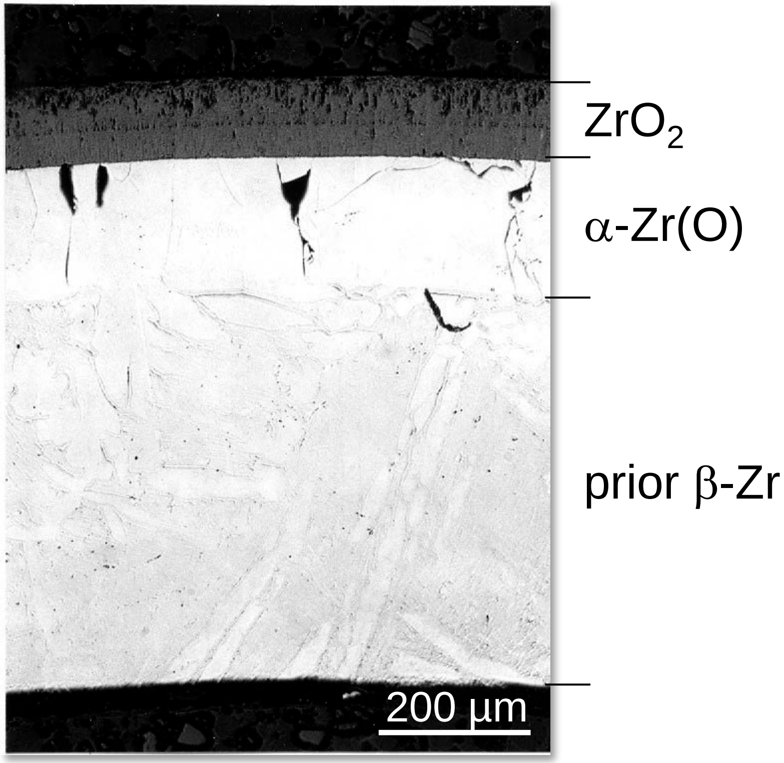
Oxidation in steam (oxygen)

- Most textbooks: Parabolic kinetics of HT oxidation of Zr alloys determined by the diffusion of oxygen through growing oxide scale
- Most LOCA and SFD codes use parabolic oxidation correlations



$$\frac{d_{ZrO2}}{S} = k_m(T) \cdot t^{0.5}$$

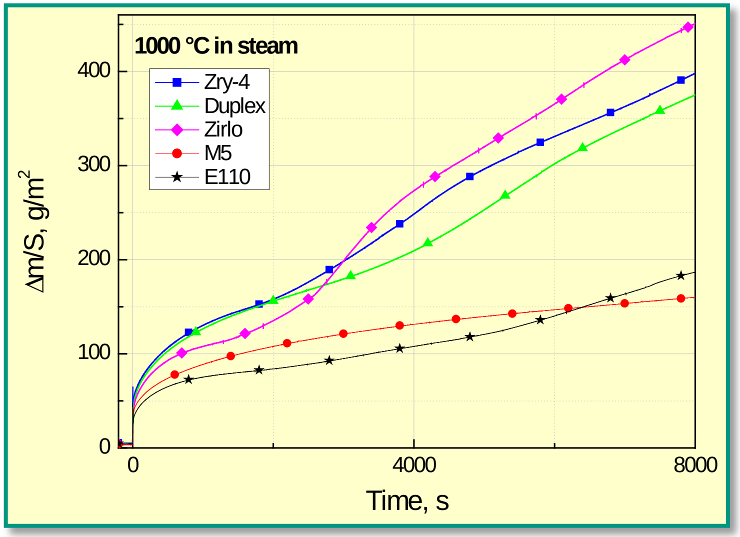
Calculated oxide thickness during oxidation of Zry at 1200°C in steam

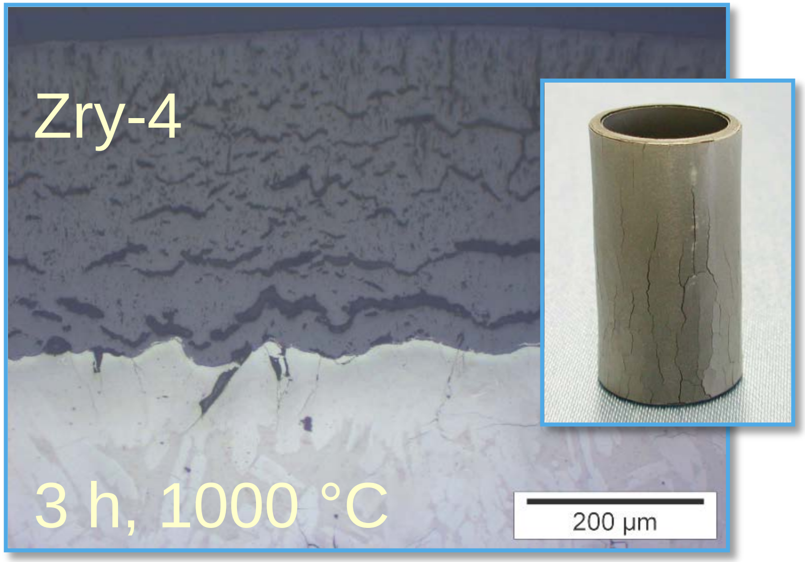


20 min at 1200°C in steam

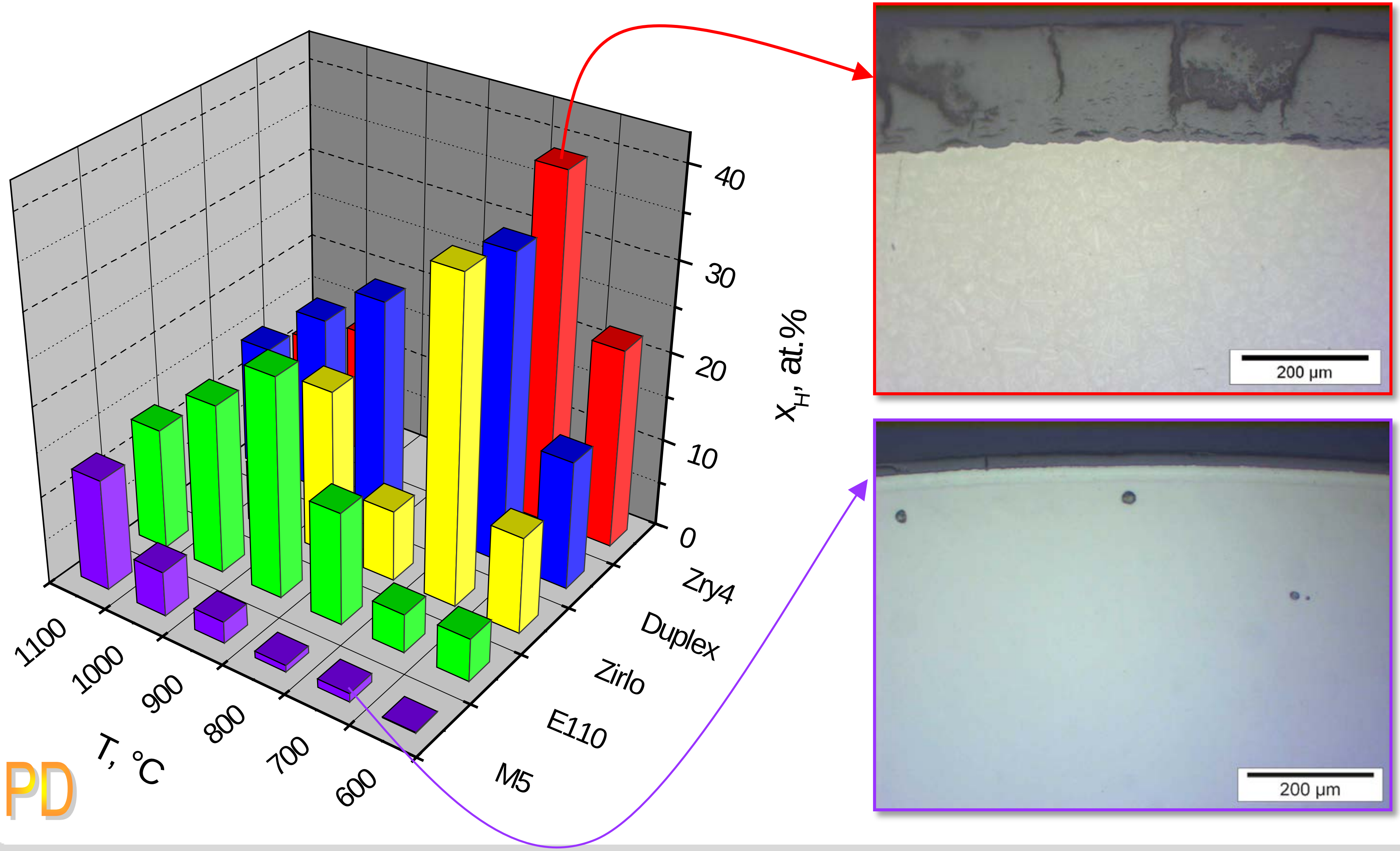
Breakaway oxidation

- 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”).

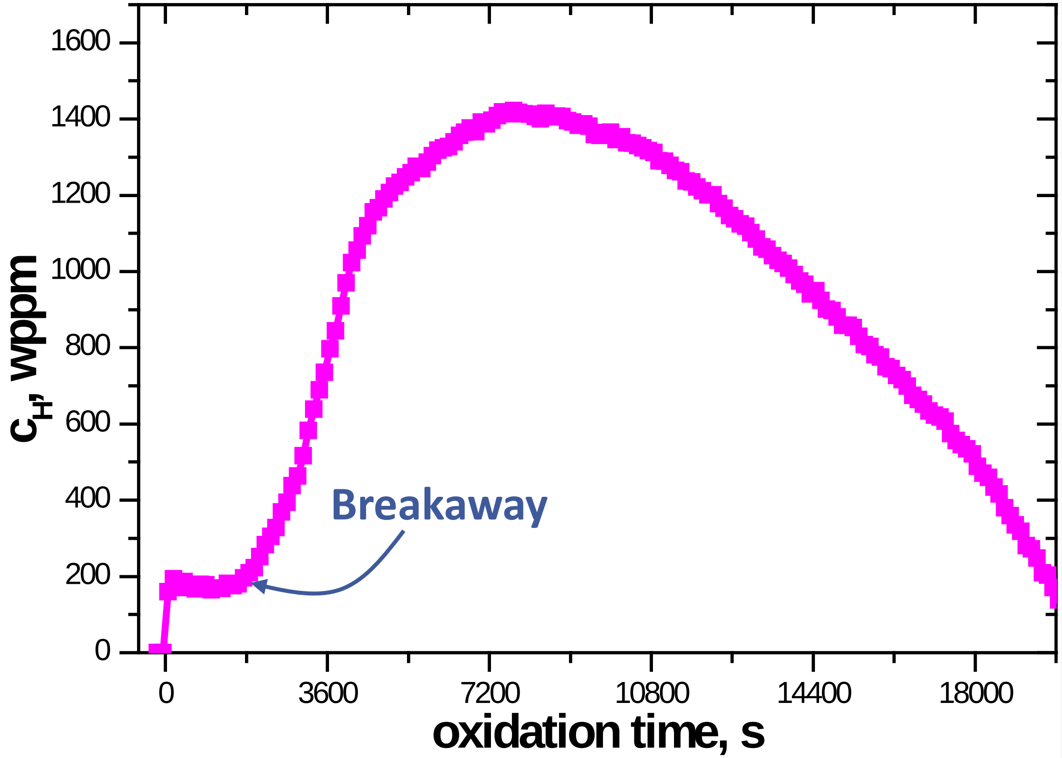




Correlation of H absorption and oxide morphology



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



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

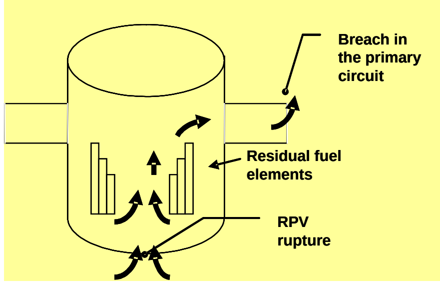
- Rapid initial hydrogen uptake
- Further strong hydrogen absorption after transition to breakaway

Oxidation in atmospheres containing nitrogen

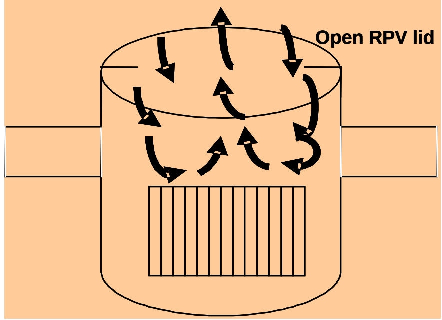
- Air ingress reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

- 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

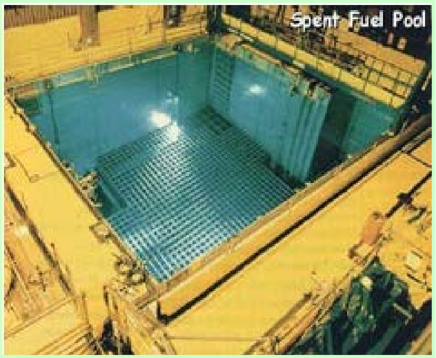
Late phase after RPV failure



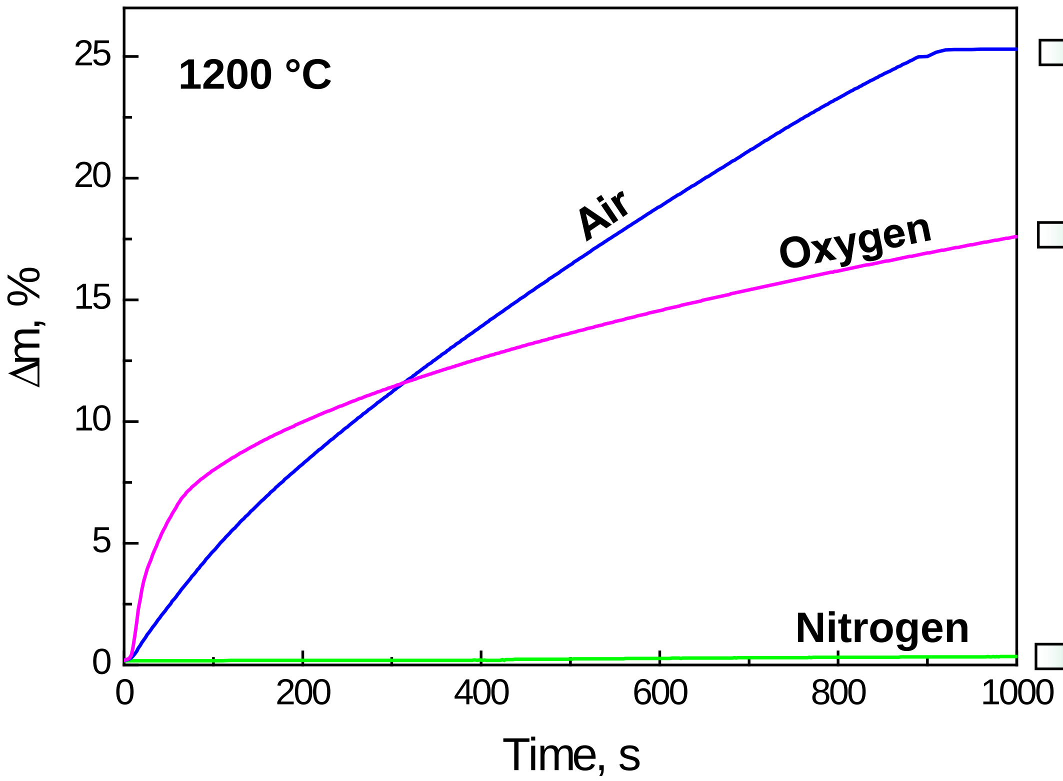
Mid loop operation



Spent fuel storage pool accident



Oxidation of Zr alloys in N_2, O_2 and air



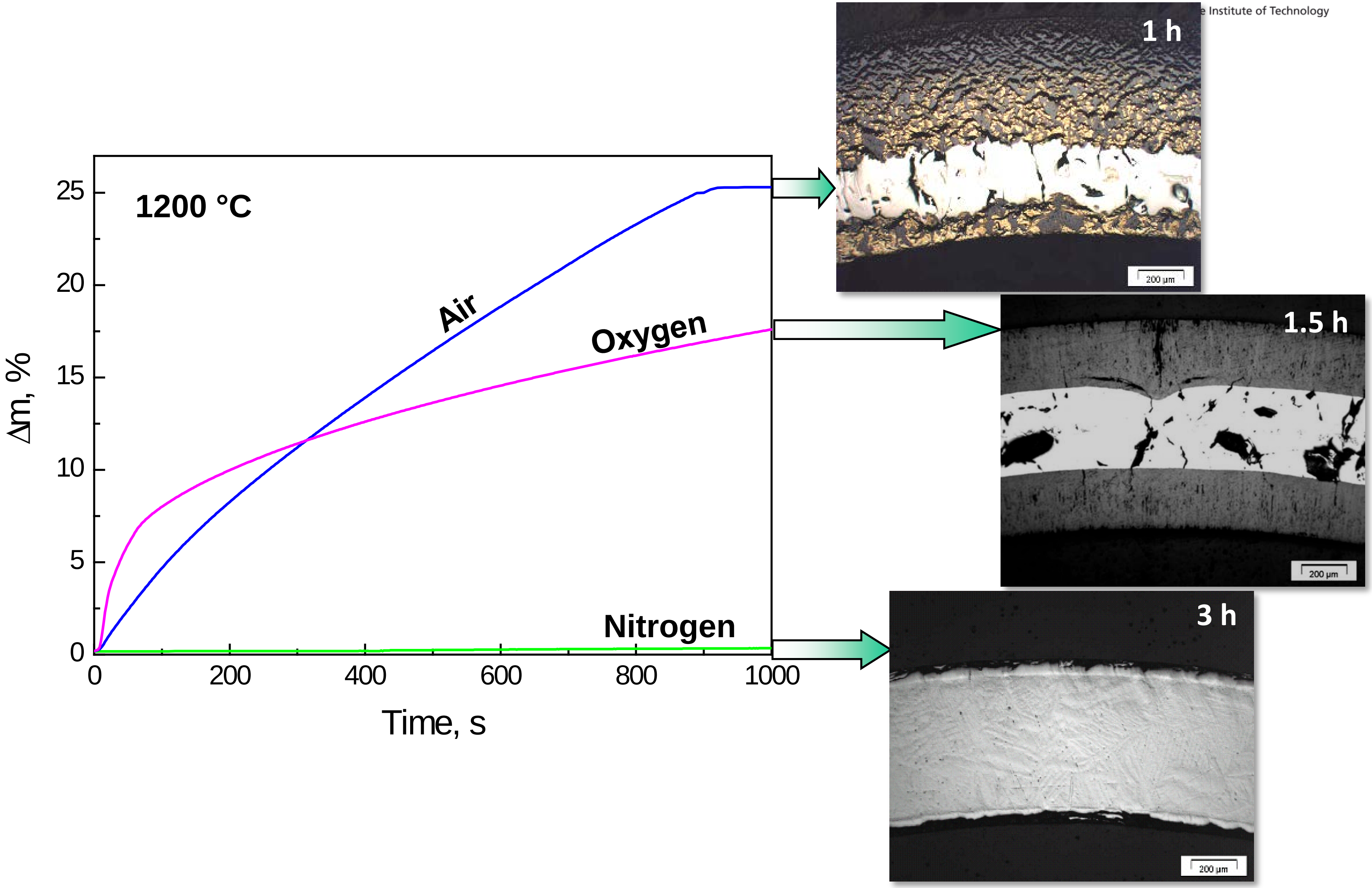
~ Linear oxidation kinetics

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

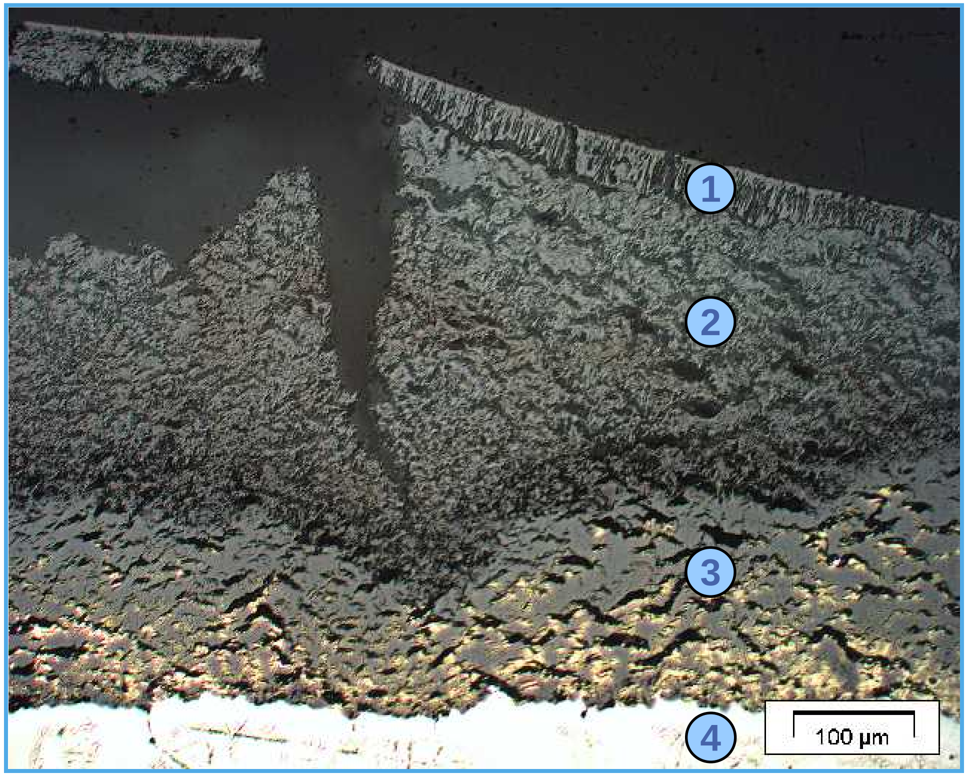
1 hour at 1200°C in air

→ 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



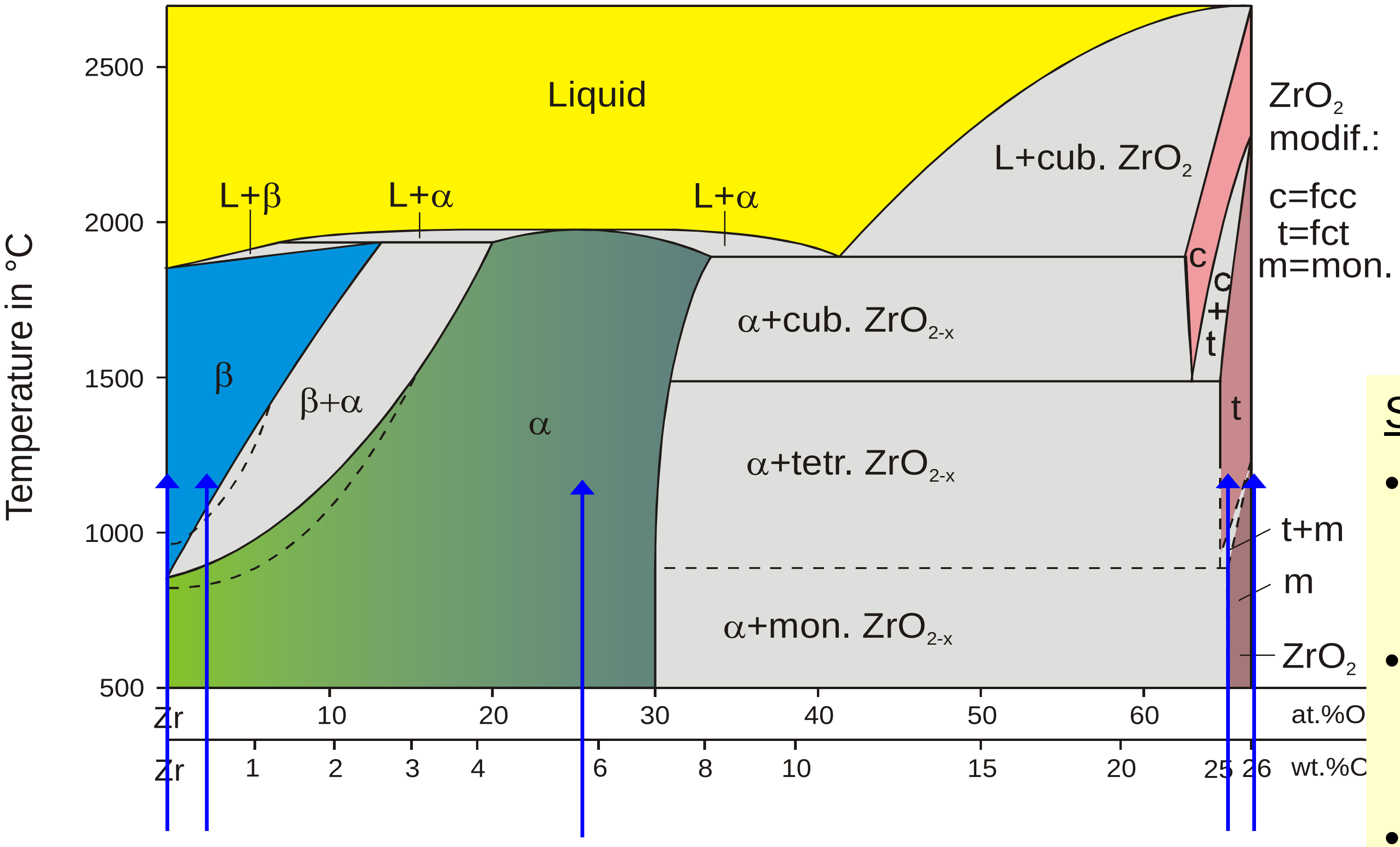
1 – initially formed dense oxide ZrO_2

2 – porous oxide after oxidation of ZrN

3 – ZrO_2 / ZrN mixture

4 – α-Zr(O)

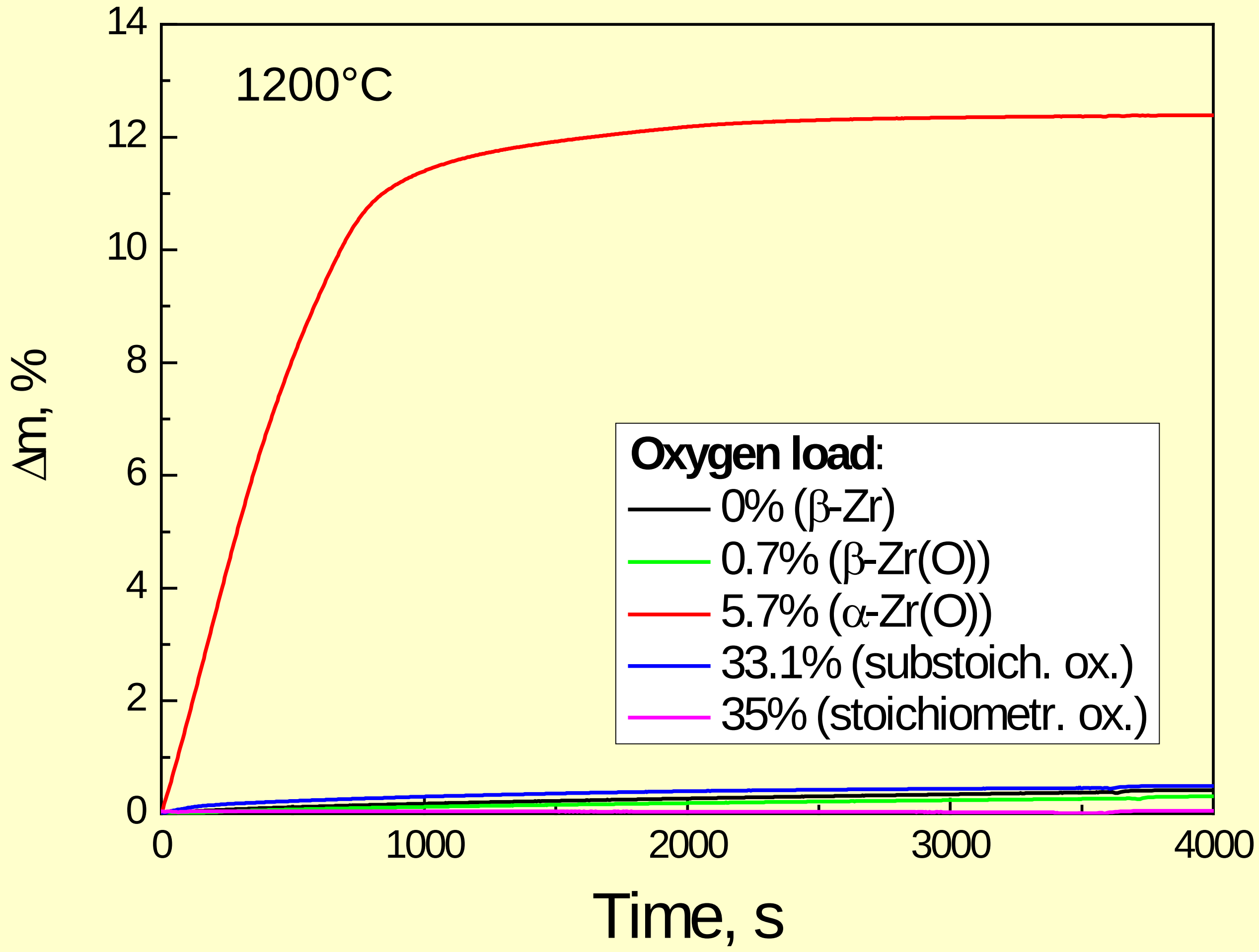
Experiments on mechanism of nitrogen attack

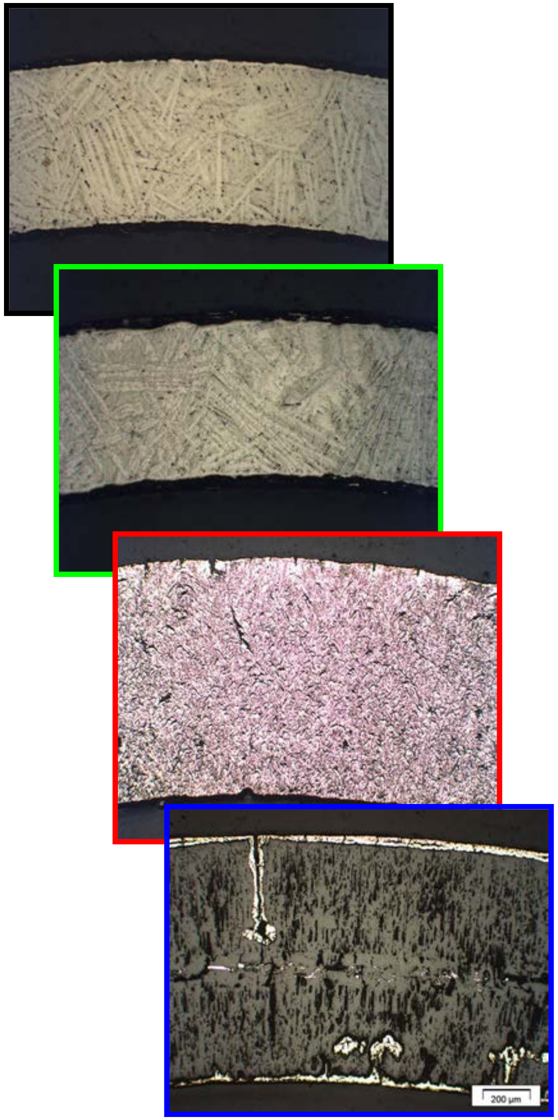


Specimens:

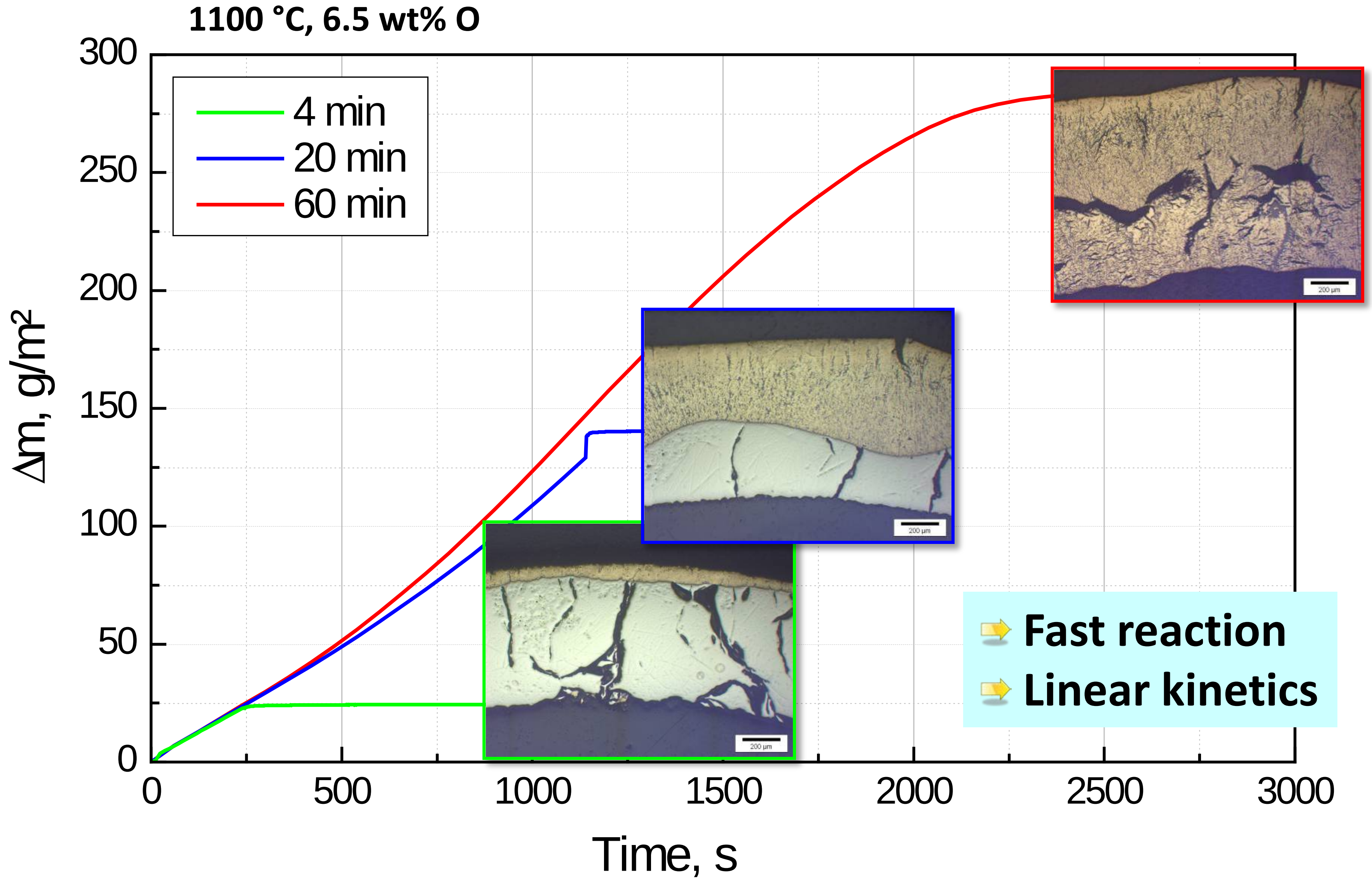
- Pre-oxidized on O_2 at 1200 °C (↑)
- Homogenized 3h at 1400 °C in Ar
- Reaction in N_2 1h at 1200 °C

Reaction of ZrO_x with nitrogen



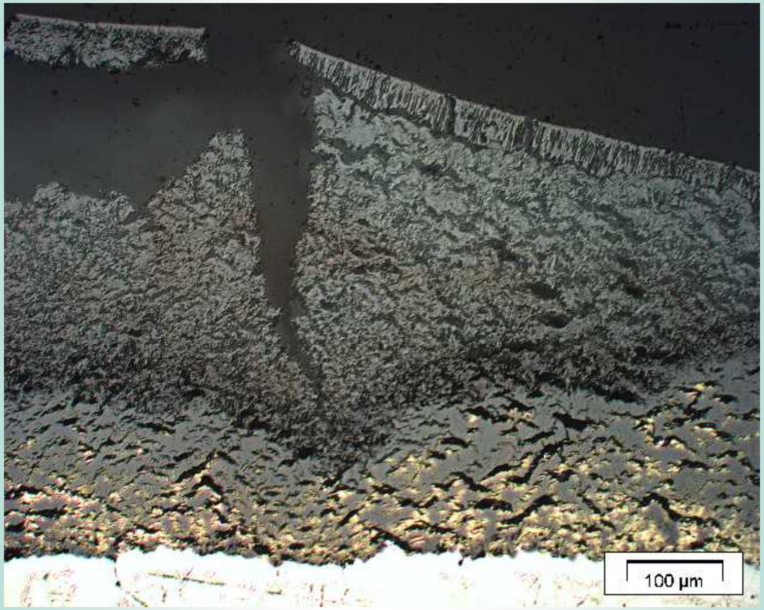


α-Zr(O) – nitrogen reaction kinetics

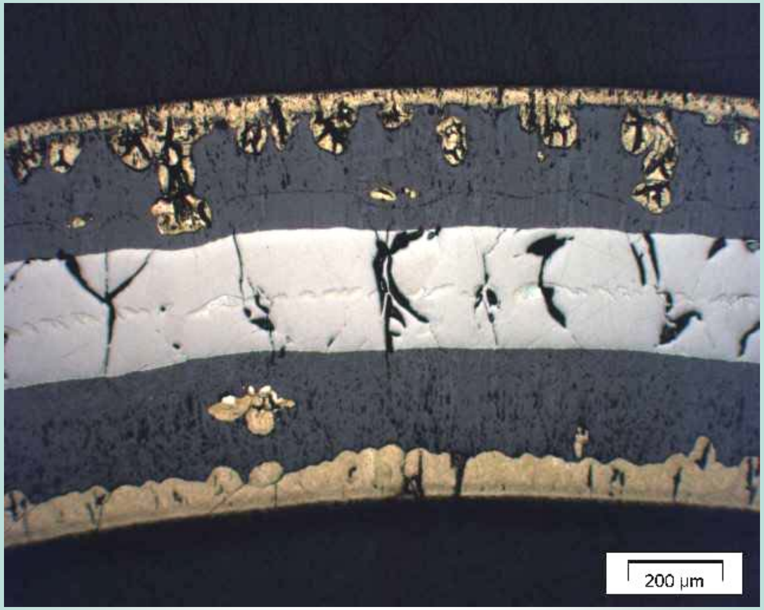


- Fast reaction
- Linear kinetics

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!

Oxidation in mixed steam-air atmospheres

Zry-4, 1 hour at 1200°C

H_2O

0.7 H_2O
0.3 air

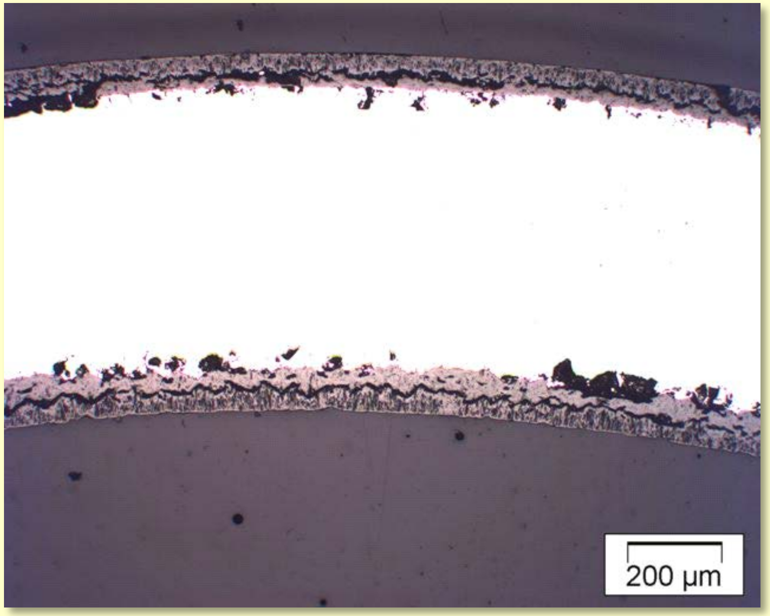
0.3 H_2O
0.7 air

0.1 H_2O
0.9 air

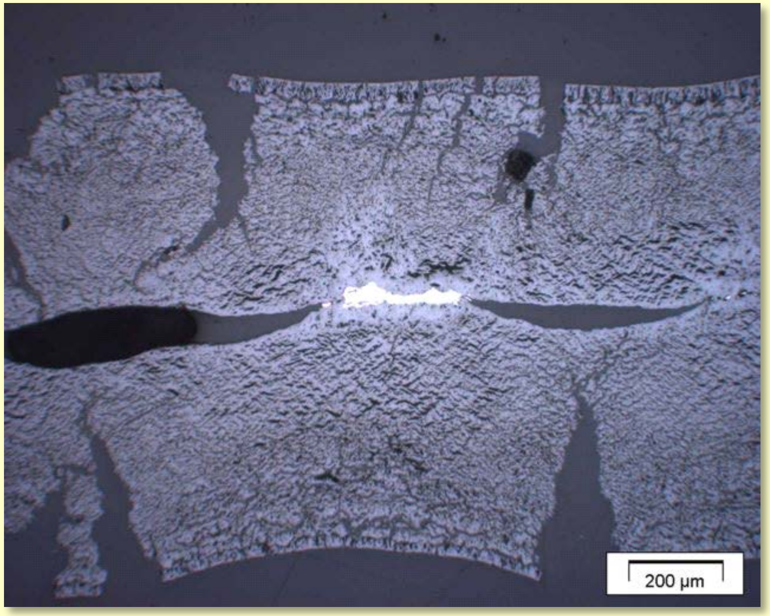
- ➧ Increasing degradation with raising content of air in the mixture

Oxidation in mixed steam-nitrogen atmosphere

1 hour at 1000 °C in steam

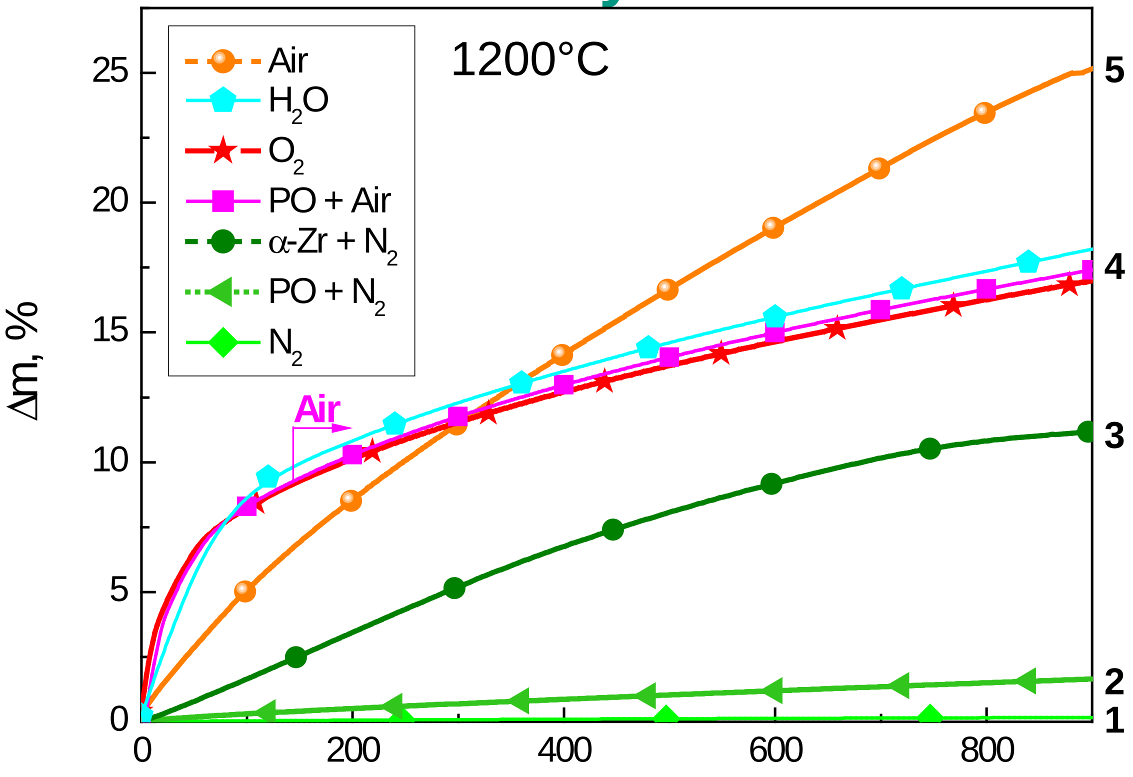


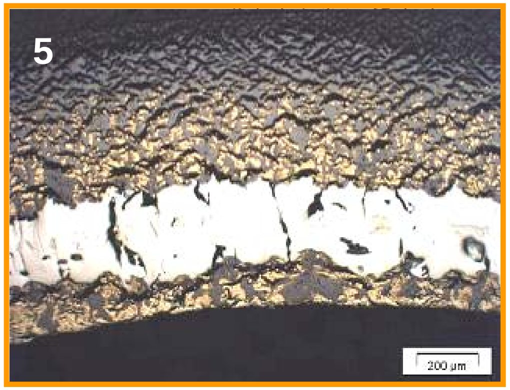
1 hour at 1000 °C in 50/50 steam/N_2

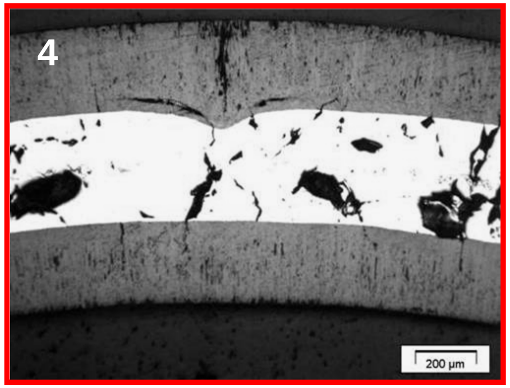


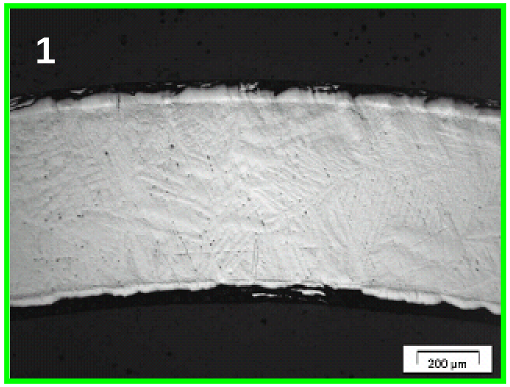
- Strong effect of nitrogen on oxidation and degradation
- Nitrogen acts like a catalyst (NOT like an inert gas)
- Enhanced hydrogen source term by oxidation in mixtures containing nitrogen

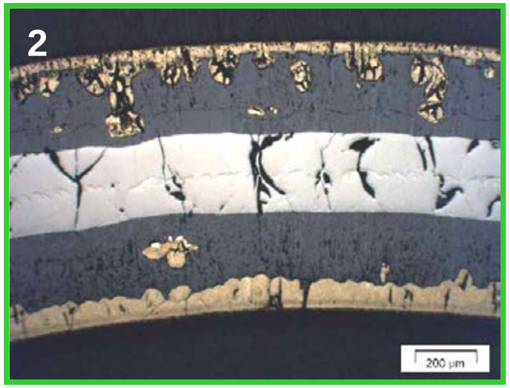
Oxidation of Zr alloys in various atmospheres

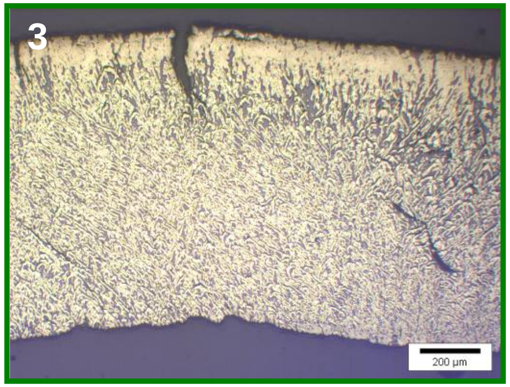












Conclusions

- The usually applied parabolic correlation for the high-temperature oxidation of zirconium alloys are not valid under all conditions

- Breakaway has to be taken into account at temperatures below 1100°C especially for slow transients and long duration scenarios

- Nitrogen is not an inert gas under the conditions of a nuclear accident

- Zirconium nitride ZrN is formed when (1) oxygen is absent in the atmosphere and (2) oxygen is present in the solid phase

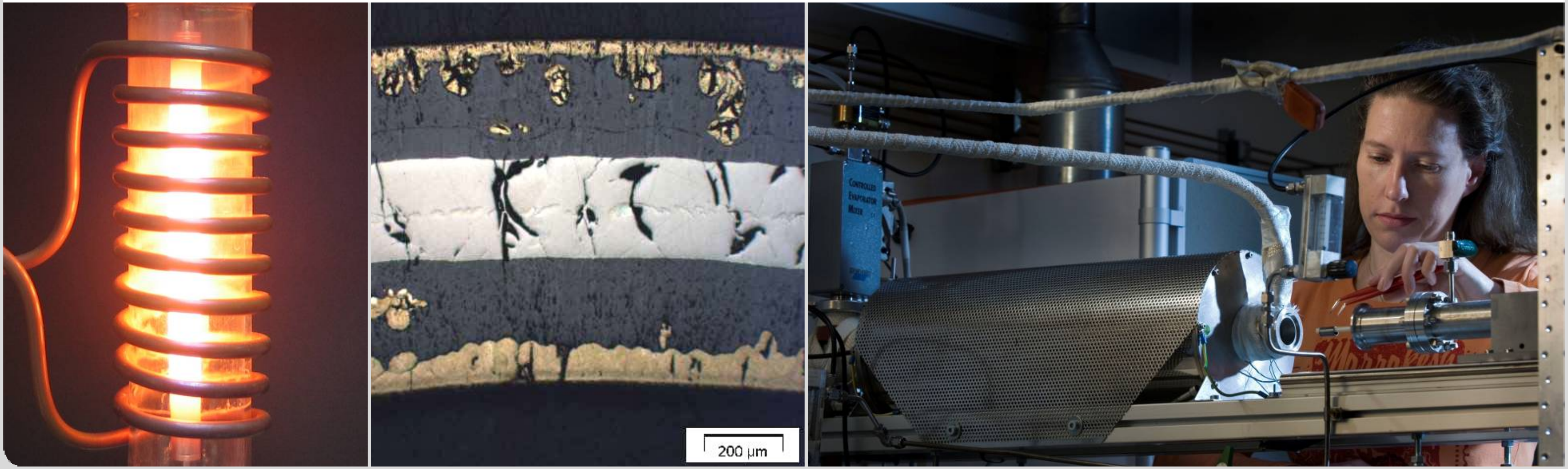
- Hydrogen produced by oxidation in steam is released to the environment (explosion risk) and absorbed by the remaining metal (degradation of mechanical properties)

Oxidation of zirconium alloys in mixed atmospheres containing nitrogen

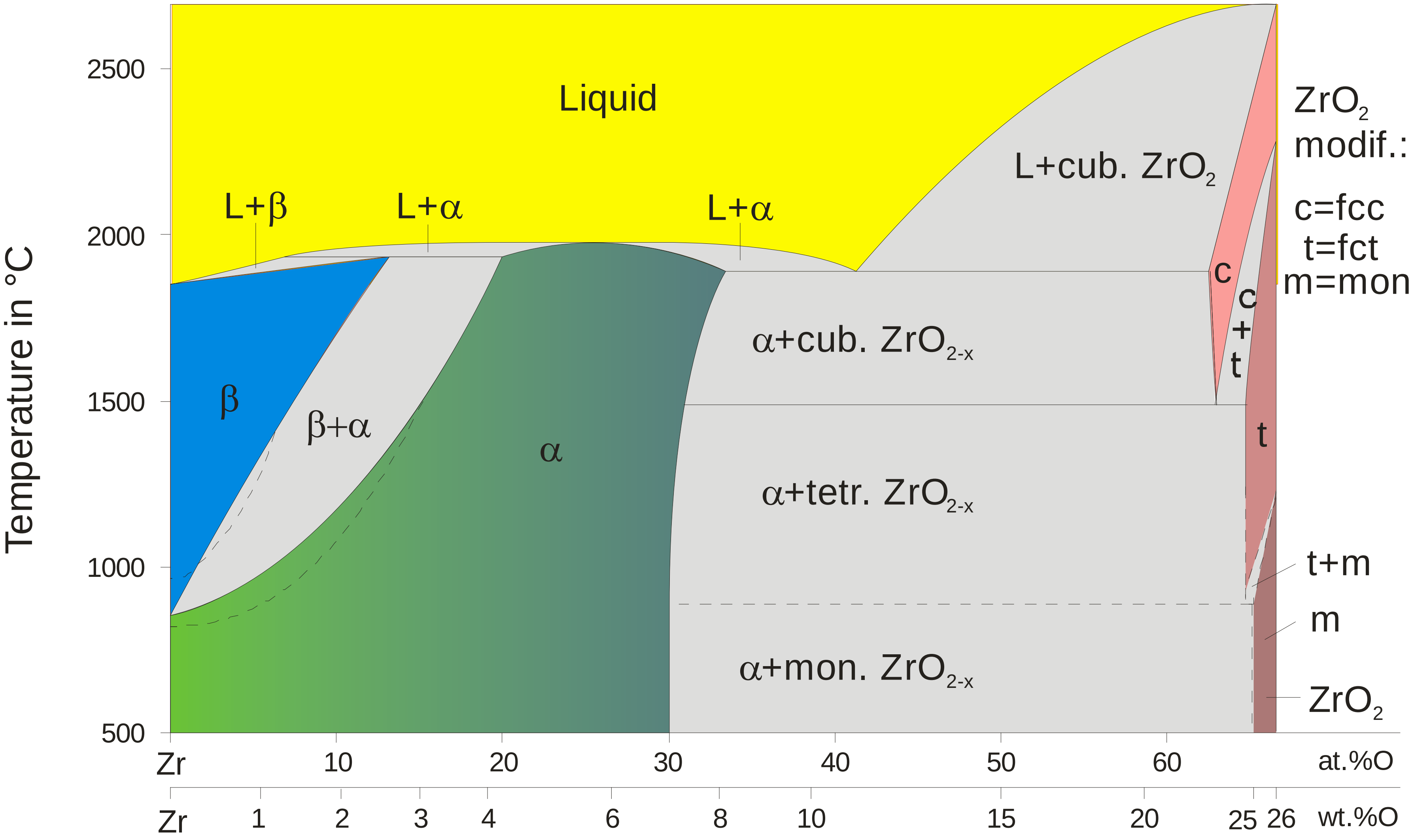
Martin Steinbrück, Karlsruhe Institute of Technology, Institute for Applied Materials

EFC Workshop „Beyond Single Oxidants", 19-21 September 2012, Frankfurt/M., Germany

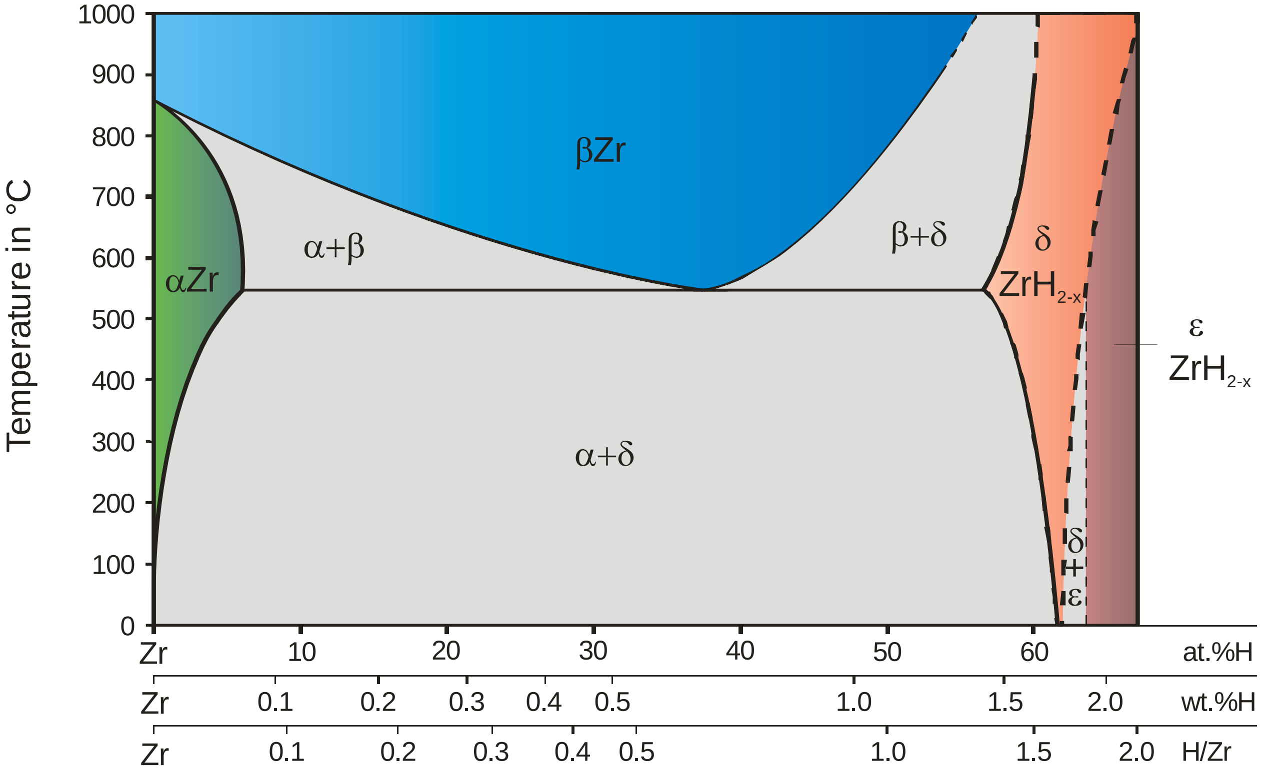
Institute for Applied Materials, IAM-AWP / Program NUKLEAR



Phase diagram Zr - O



Phase diagram Zr - H



Sieverts' law:

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

with

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

Reaction of α-Zr(O) with nitrogen