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Deviations from the parabolic kinetics during oxidation of zirconium alloys

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17th International Symposium on Zirconium in the Nuclear Industry, 03.-07.02.2013, Hyderabad, India

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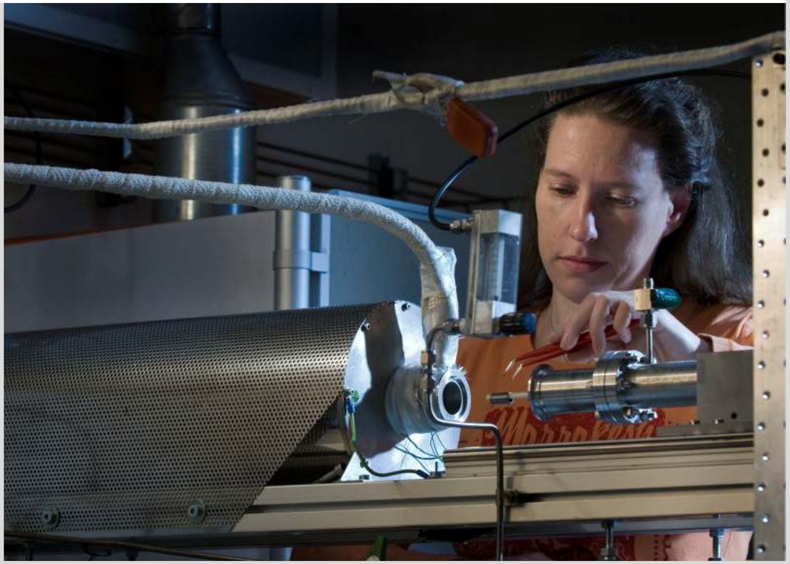
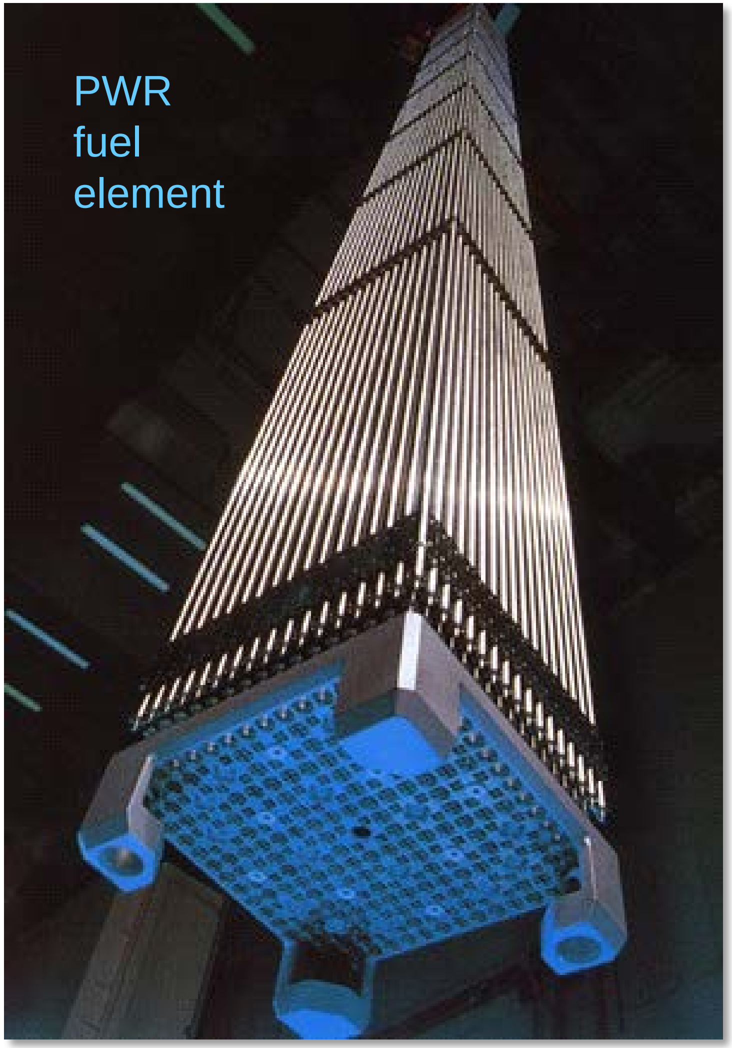


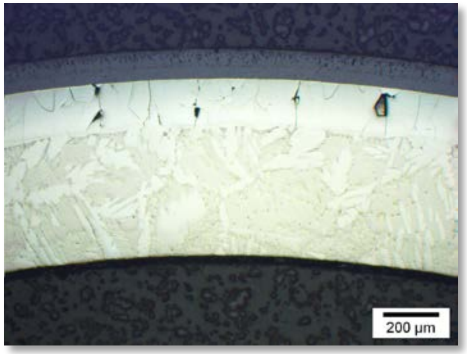
Motivation

- Oxidation of zirconium alloy claddings during severe accidents causes degradation of cladding and loss of barrier effect as well as production of hydrogen and heat
- Oxidation kinetics and corresponding hydrogen source term have to be known for appropriate accident management measures
- At KIT extensive investigations on oxidation of zirconium alloys in various atmospheres have been performed in the framework of the QUENCH program including integral bundle tests and small-scale separate-effects experiments

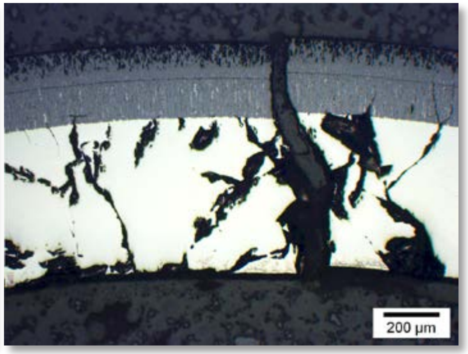

PWR fuel element

Motivation

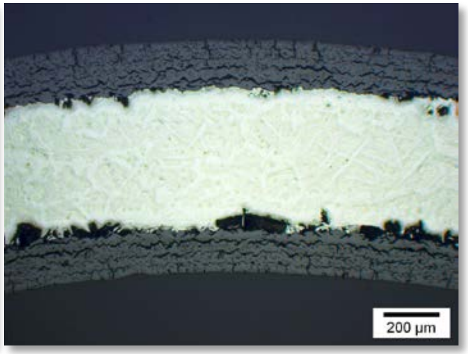
Post-test appearance of Zry samples oxidized in various atmospheres



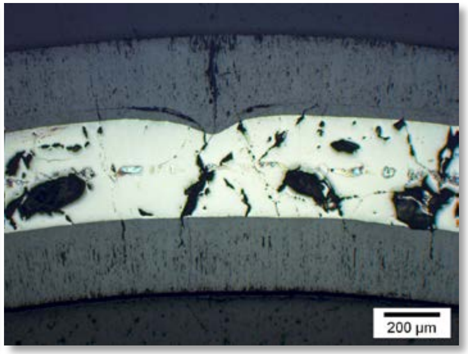
20min, 1200°C, steam



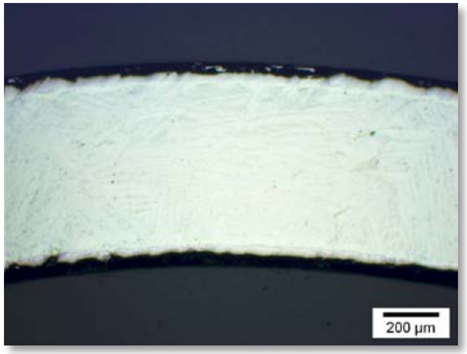
3min, 1600°C, steam



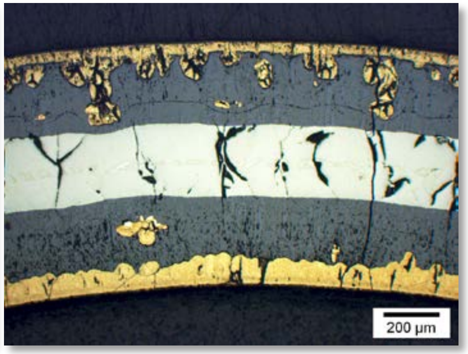
1.5h, 980°C, steam



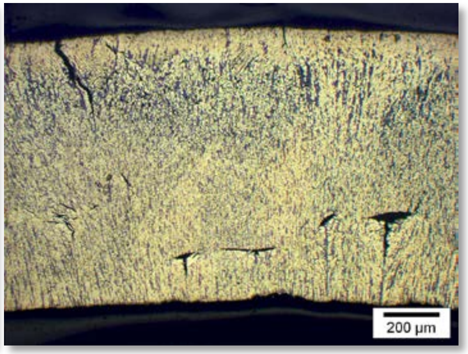
1.5h, 1200°C, oxygen



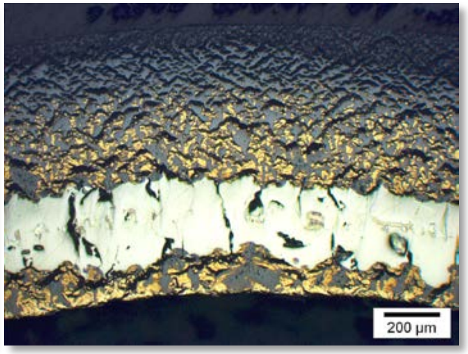
3h, 1200°C, nitrogen



10min O_2, then 50min N_2, 1200°C



α-Zr(O), 1h N_2, 1200°C

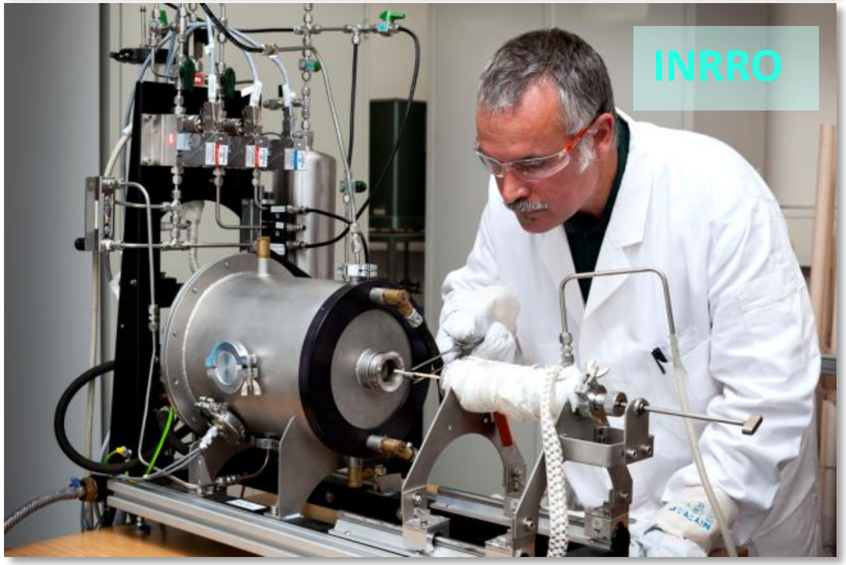


15min, 1200°C, air

➡ **Very complex reaction behavior depending on conditions (temperature, atmosphere)**

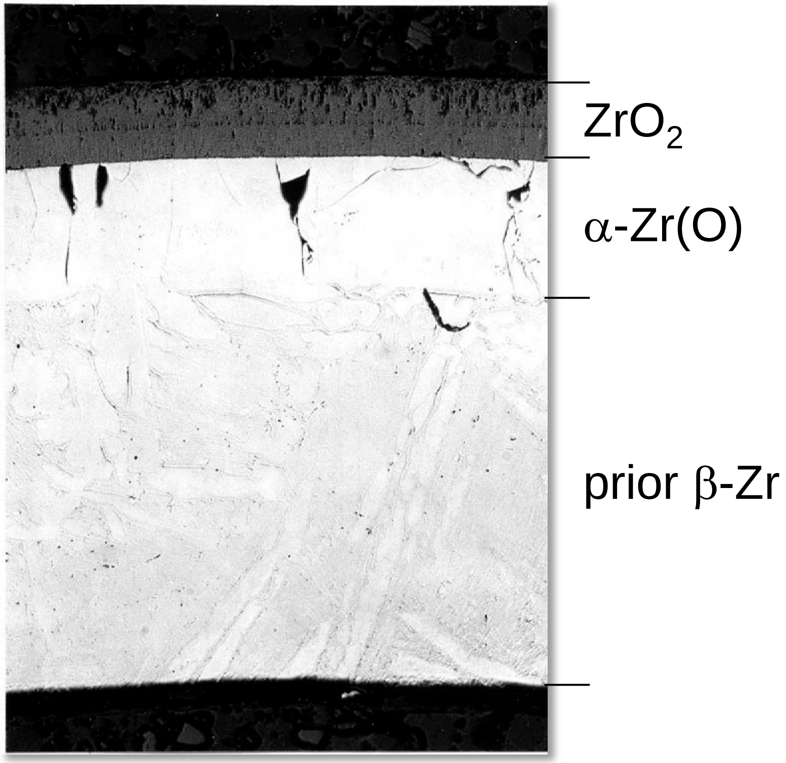
Experimental

- Most tests were conducted in a NETZSCH STA409 coupled with steam injector and mass spectrometer; some in horizontal tube furnace with air lock
- Typical temperature range: 600-1600°C
- Zr alloys:
  Zry-4, Zry-2, Duplex DX-D4, M5®, E110, Zirlo^{TM}
- Atmospheres:
  steam, oxygen, air, nitrogen, mixtures of these
- Mostly isothermal tests, some transient experiments

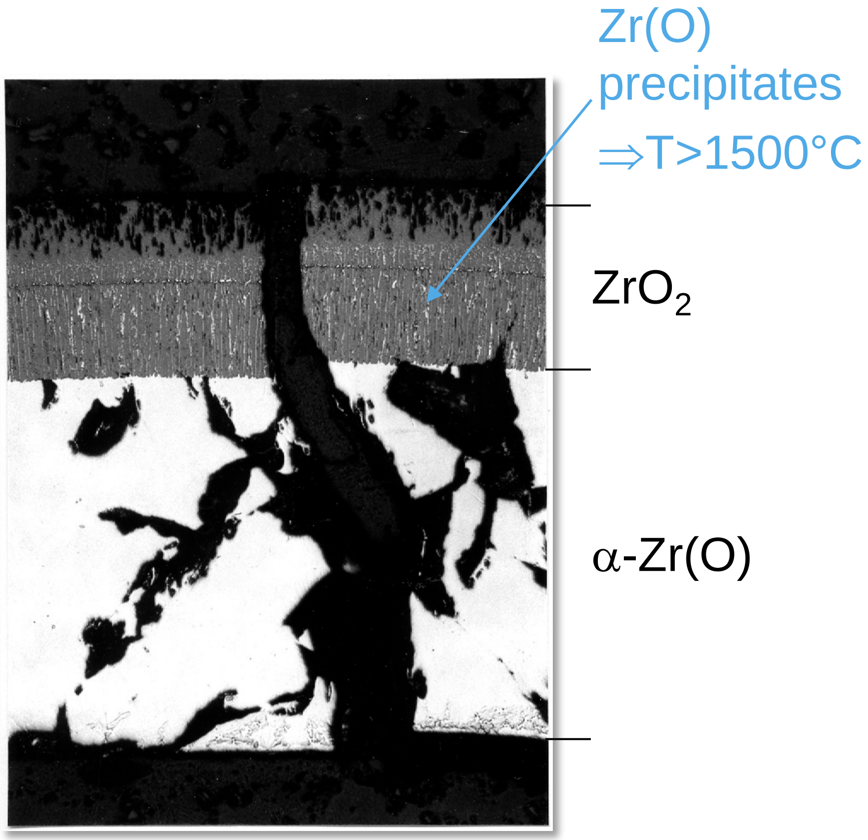


Oxidation in steam (oxygen)

- Most LOCA and SFD codes use parabolic oxidation correlations, (i.e. n=1/2 in $\Delta m / S = k_m \cdot t^n$)



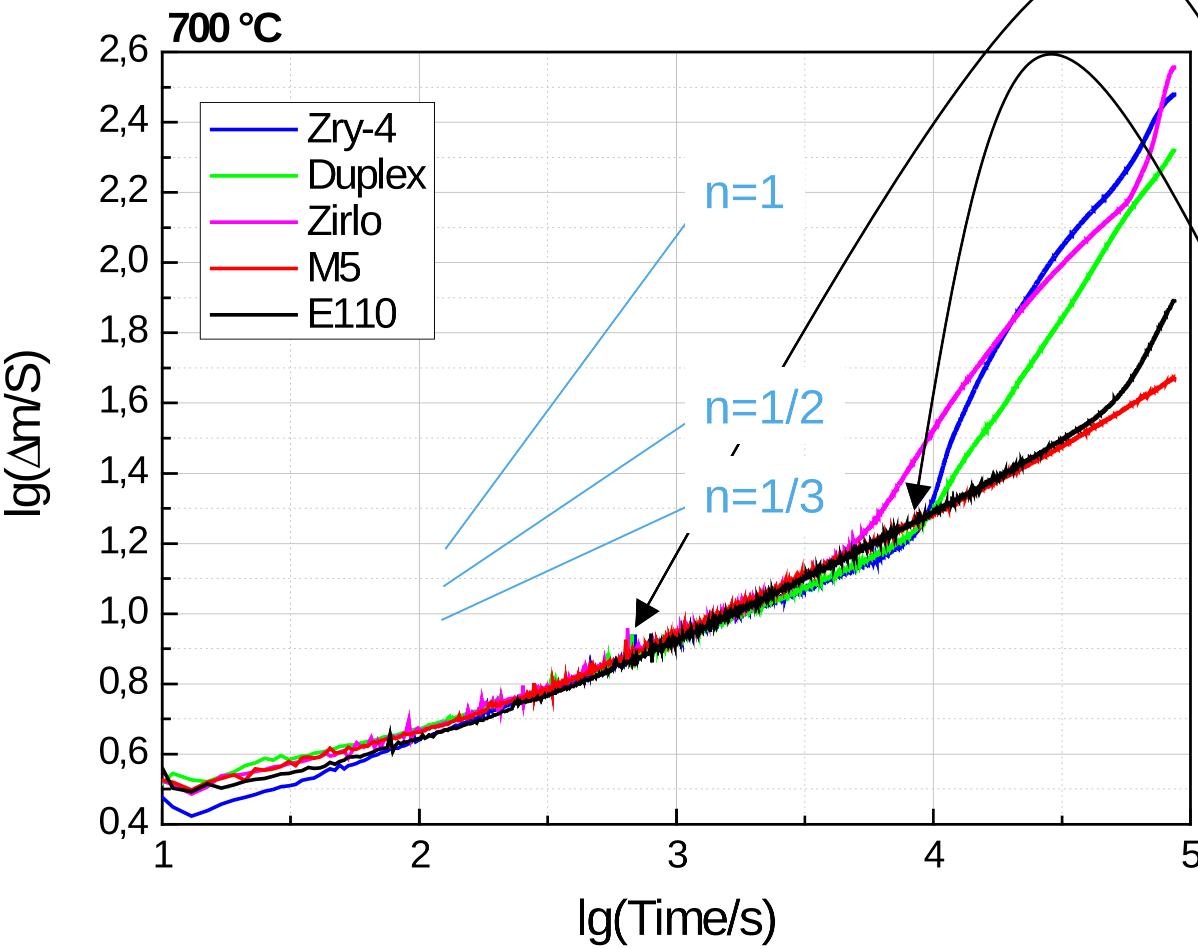
1200 °C, quench



1600 °C, quench

Oxidation in steam (oxygen)

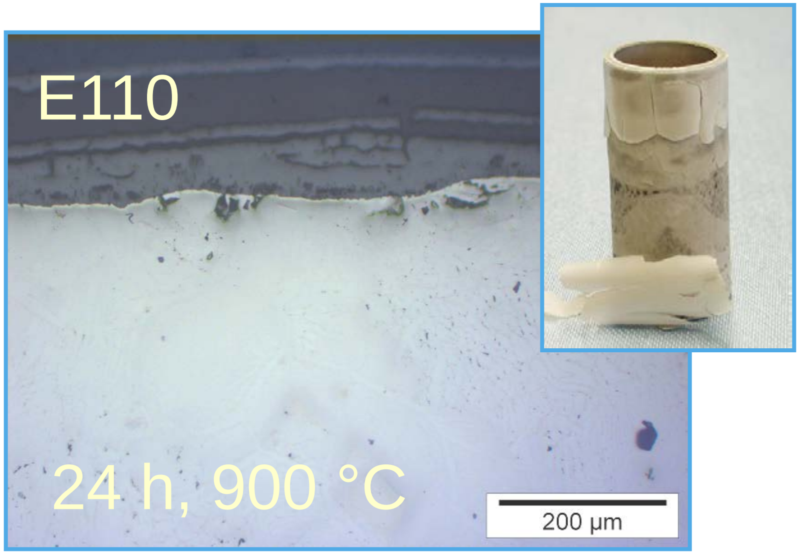
- Deviations from parabolic kinetics at temperatures <1100°C

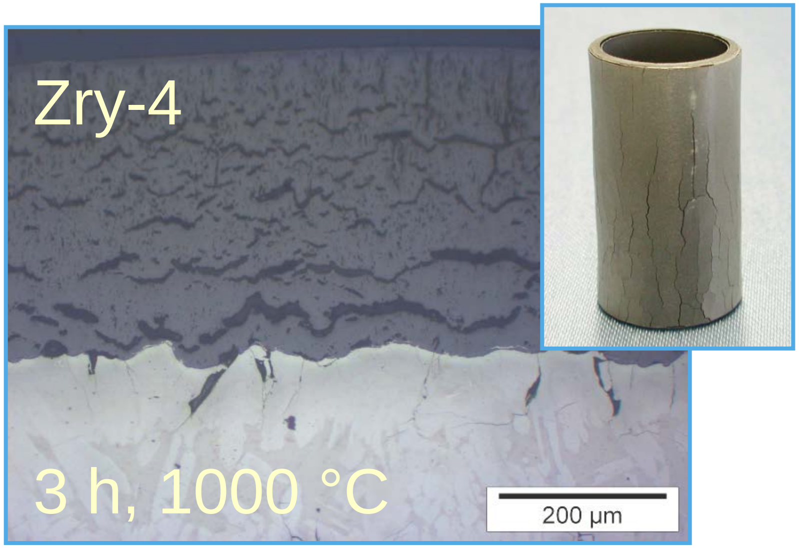


- Sub-parabolic (cubic) kinetics
- Transition from (sub-) parabolic to linear kinetics after critical time / oxide thickness due to <u>breakaway</u>
- Similar kinetics of all alloys before transition, but strongly varying behavior at and after transition

Breakaway oxidation

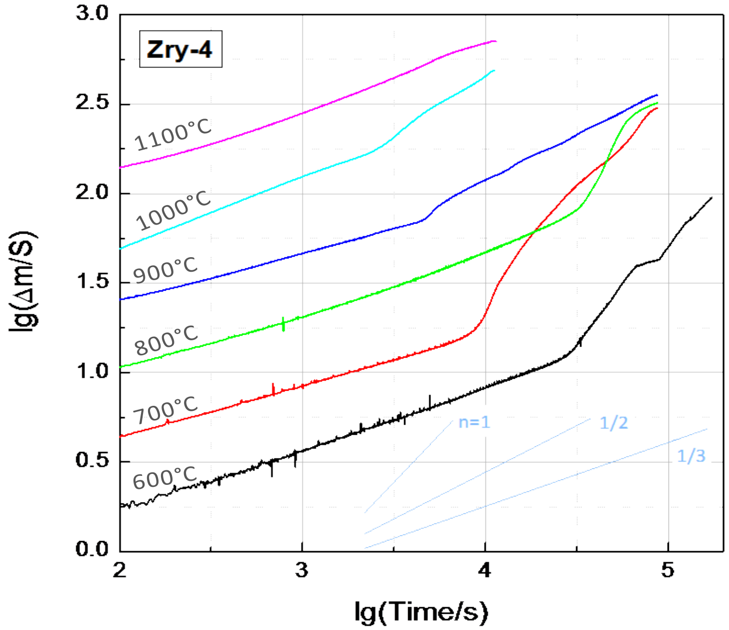
- Loss of protective properties of oxide scale due to its mechanical failure.
- Breakaway is caused by phase transformation from meta-stable tetragonal to monoclinic oxide and corresponding change in density up to ca. 1050°C.
- Critical times and oxide thicknesses for breakaway strongly depend on type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

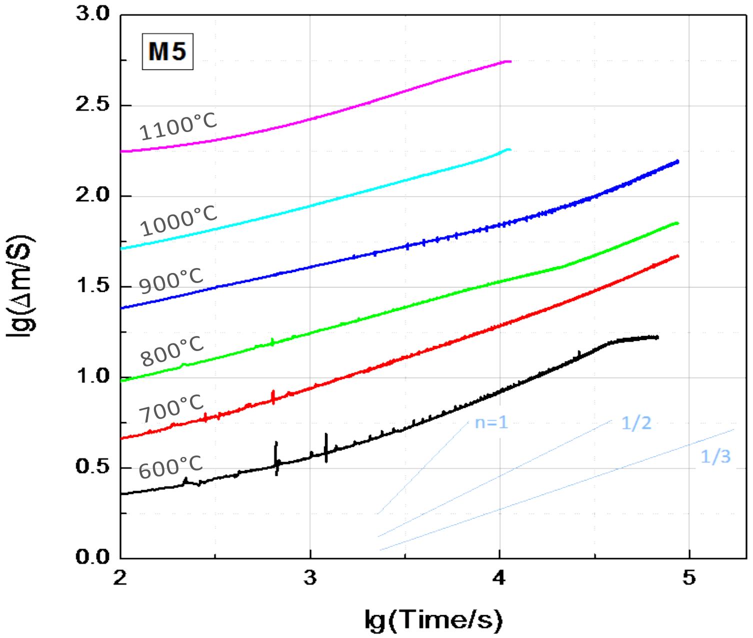




Transition times (h) and corresponding critical oxide scale thickness (µm) during oxidation in steam

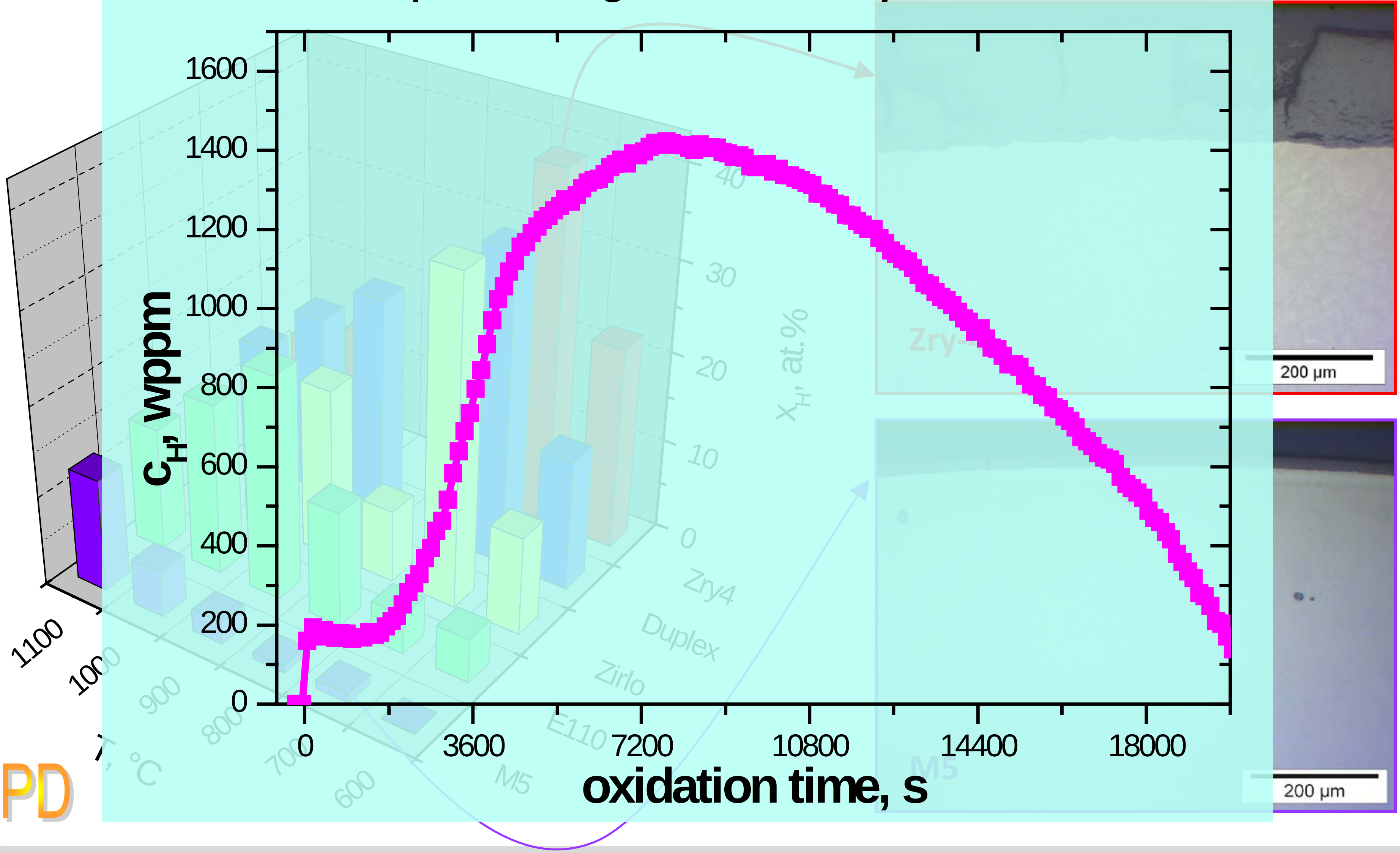
T, °C	Zircaloy-4	Duplex-D4	Zirlo™	M5®	E110
600	8.2 *(7)*	7.7 *(3)*	6.3 *(8)*	nt	nt
700	2.2 *(9)*	2.2 *(9)*	1.4 *(9)*	nt	13 *(21)*
800	7.4 *(41)*	7.3 *(35)*	5.2 *(32)*	nt	0.9 *(12)*
900	1.3 *(40)*	1.4 *(38)*	2.1 *(40)*	nt	0.8 *(24)*
1000	0.6 *(89)*	0.9 *(105)*	0.6 *(76)*	nt	0.6 *(48)*
≥1100	nt	nt	nt	nt	nt





Correlation of H absorption and oxide morphology

In-situ NR of H uptake during oxidation of Zry-4 at 1000°C in steam

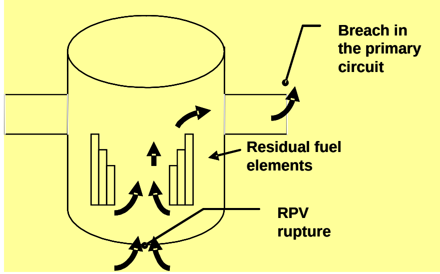


Oxidation in atmospheres containing nitrogen

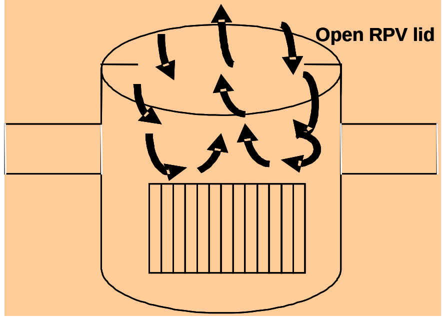
- Air ingress reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

- 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

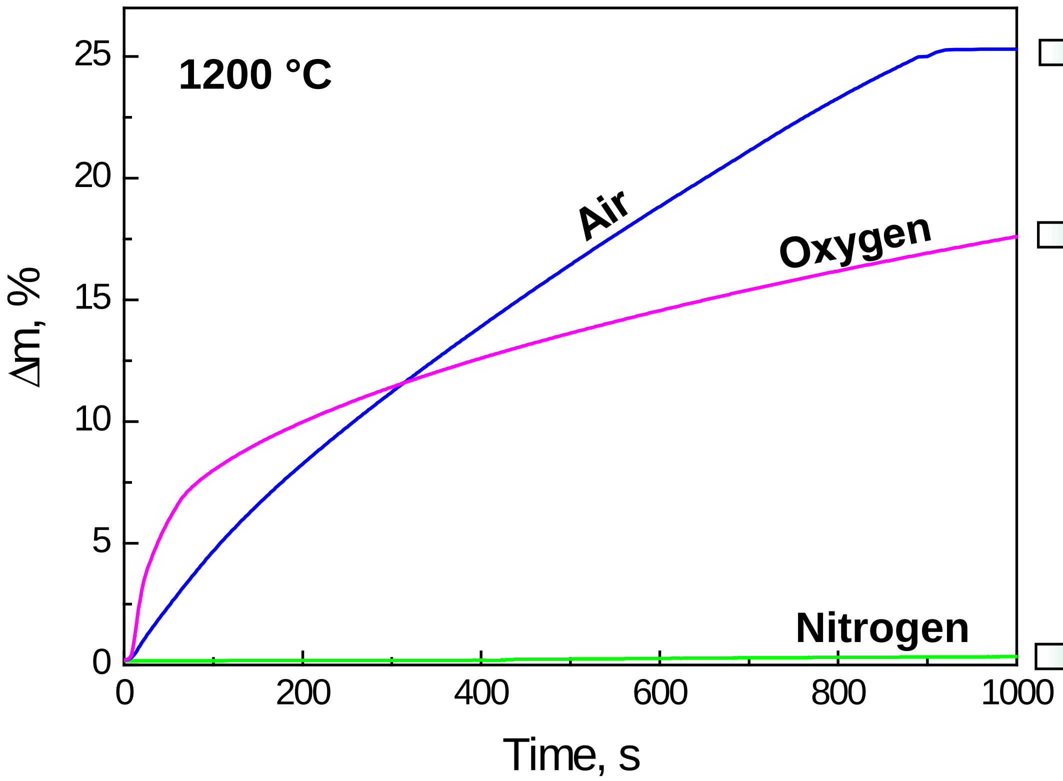


Mid loop operation



Spent fuel storage pool accident

Oxidation of Zr alloys in N_2, O_2 and air



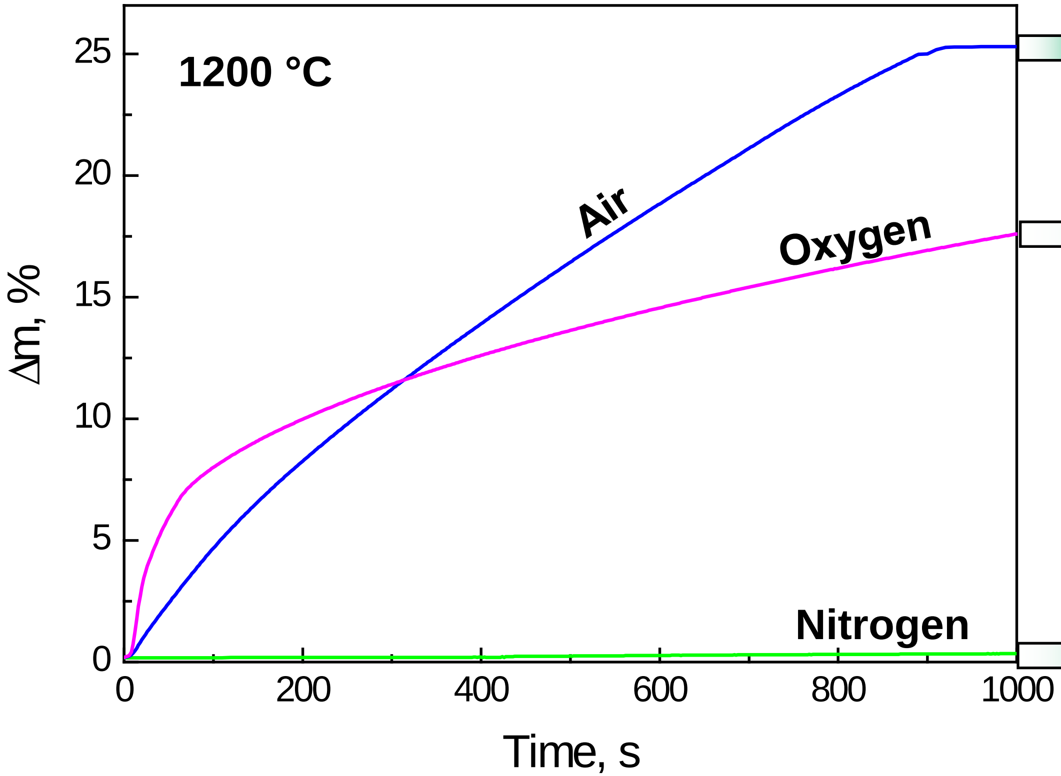
~ Linear oxidation kinetics

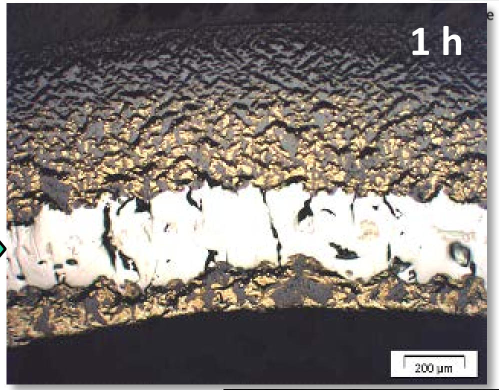
Parabolic oxidation kinetics

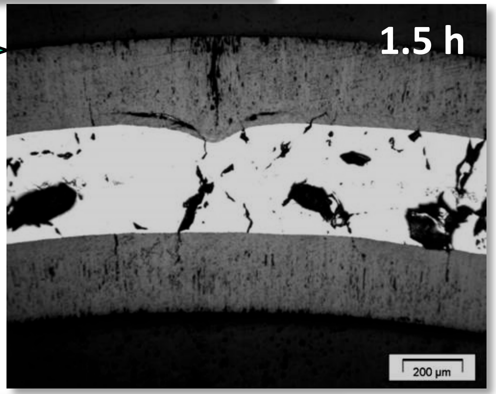
Parabolic reaction kinetics

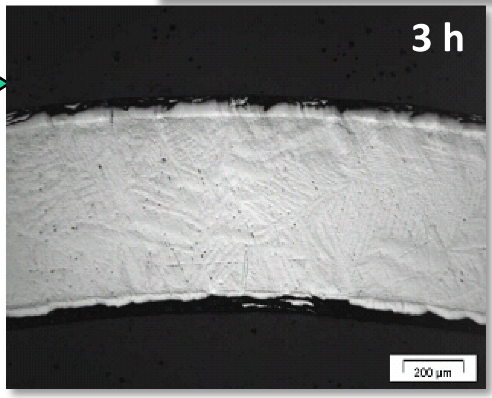
Oxidation rate in air is much higher than in oxygen or steam

Oxidation of Zr alloys in N_2, O_2 and air









Consequences of air ingress for cladding

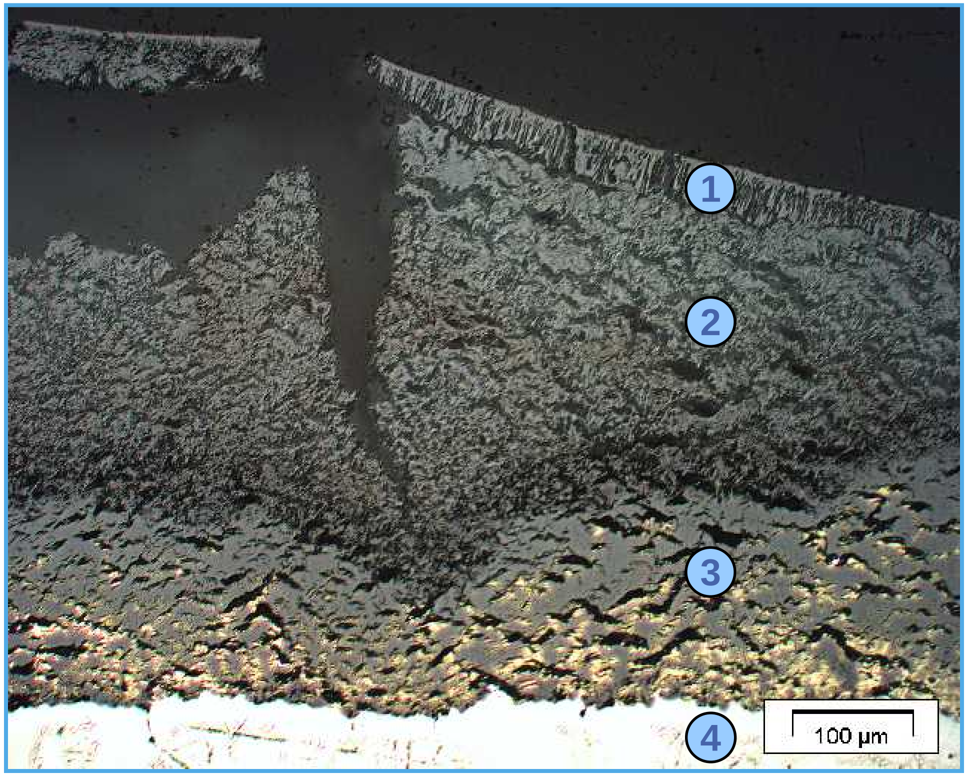
1 hour at 1200°C in steam

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 interface
- Consumption of oxygen
- Remaining nitrogen reacts with zirconium and forms ZrN
- ZrN is re-oxidized by fresh air with progressing reaction associated with a volume increase by 48%
- ➡ Formation of porous and non-protective oxide scales



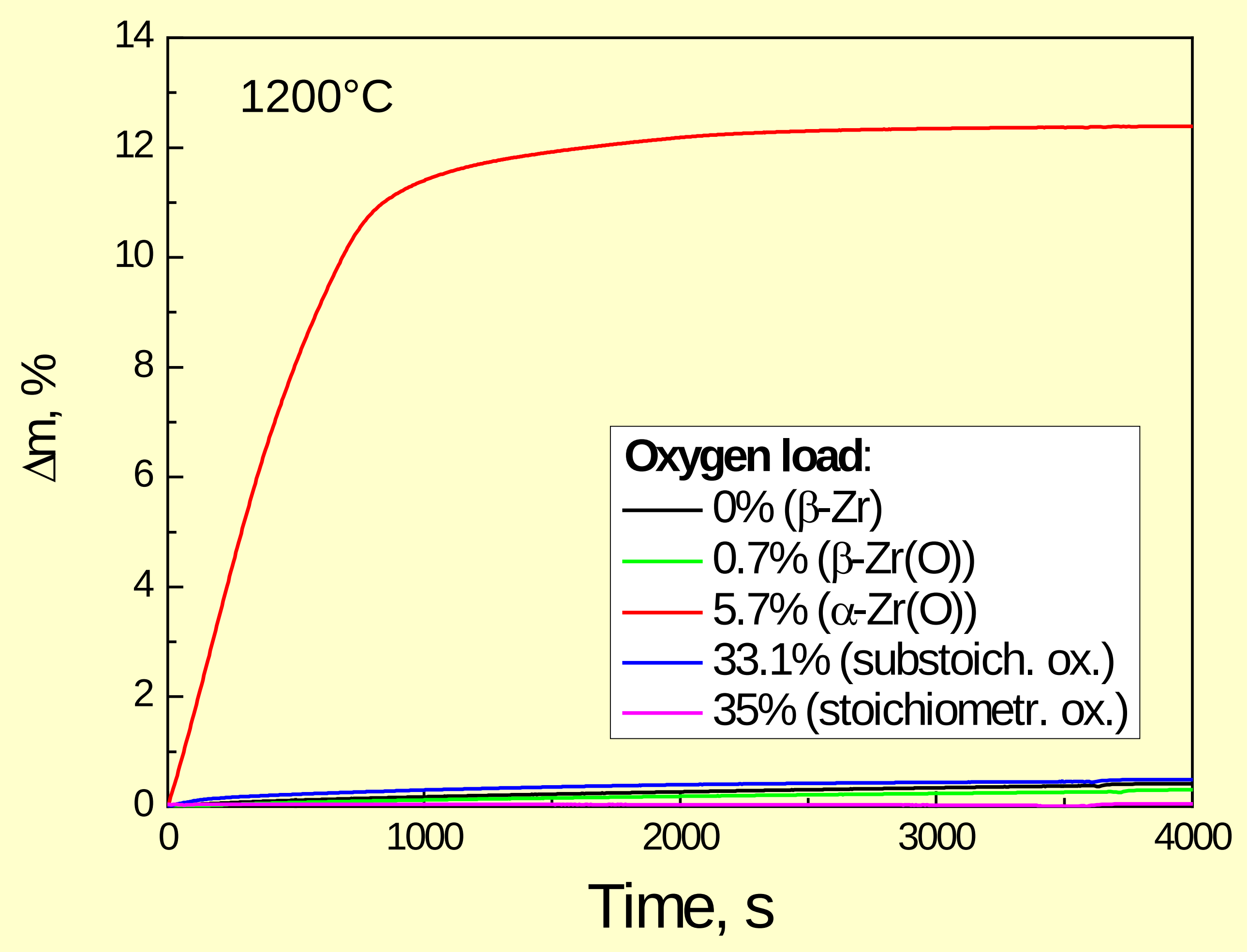
1 – initially formed dense oxide ZrO_2

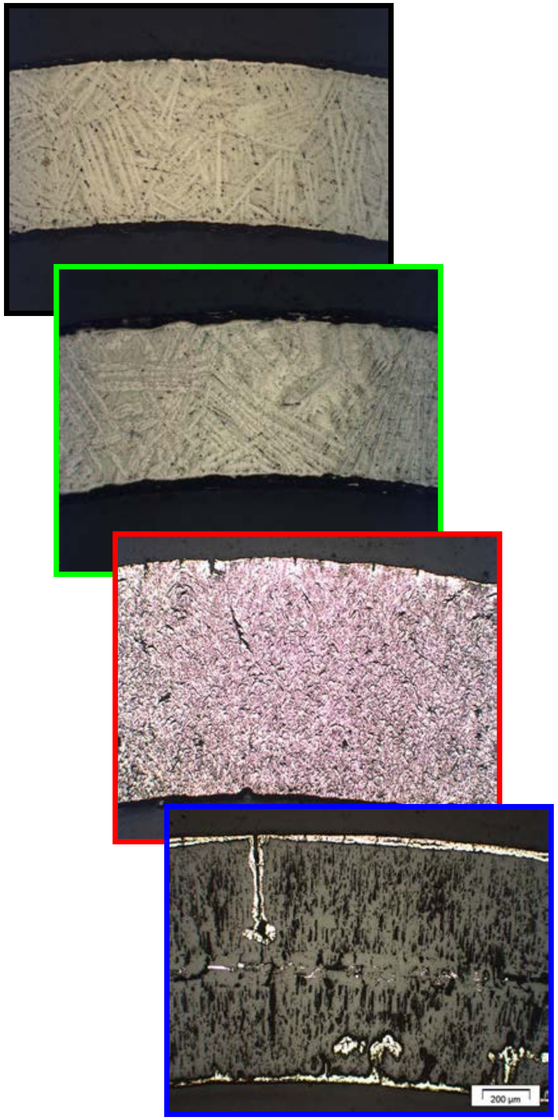
2 – porous oxide after oxidation of ZrN

3 – ZrO_2 / ZrN mixture

4 – α-Zr(O)

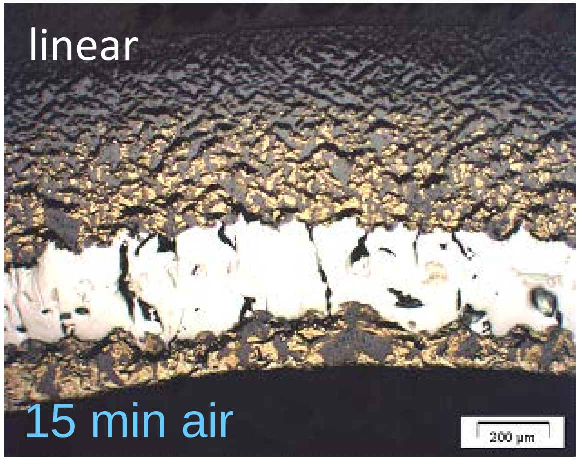
Reaction of ZrO_x with nitrogen

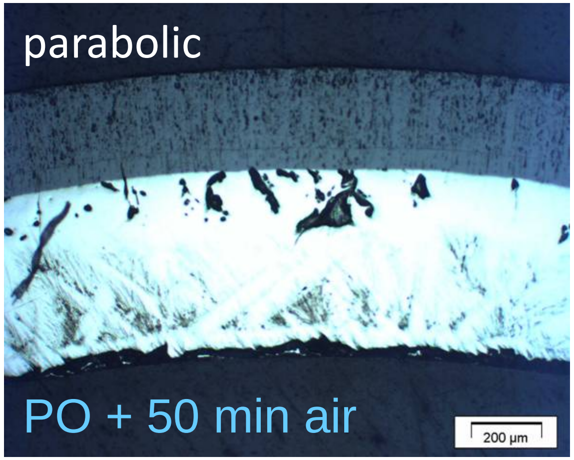




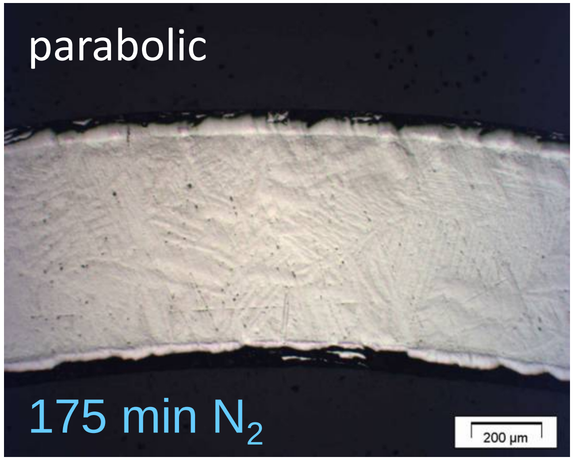
Influence of pre-oxidation (PO) in steam on subsequent reaction in air and nitrogen

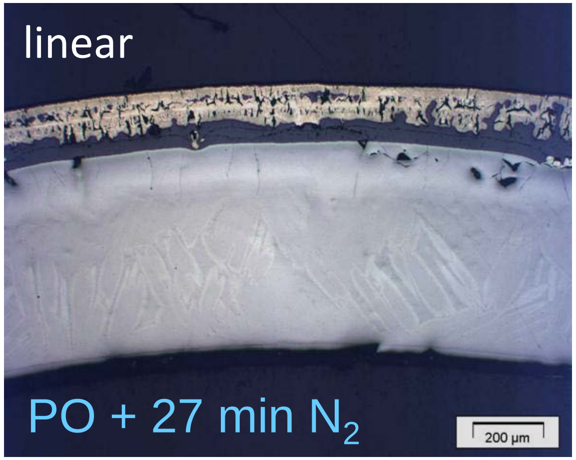
Example: Zry-4, 1200°C





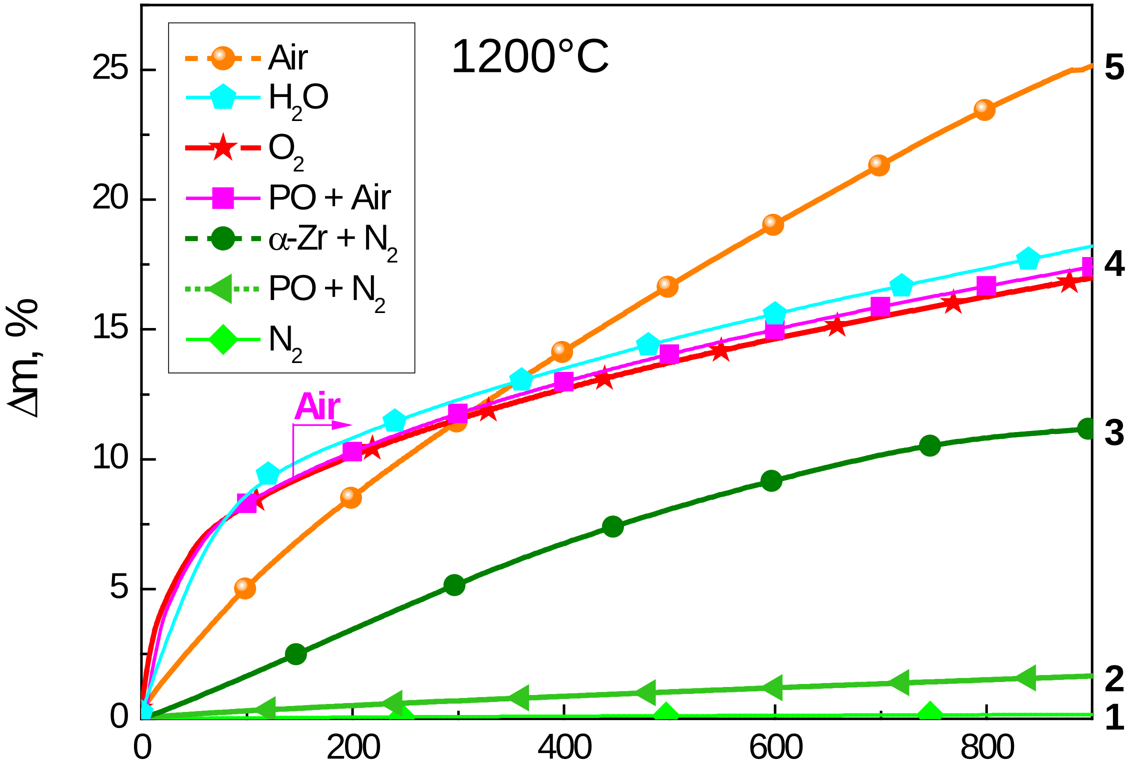
Protective effect of PO on subsequent oxidation in air as long as oxide scale is intact



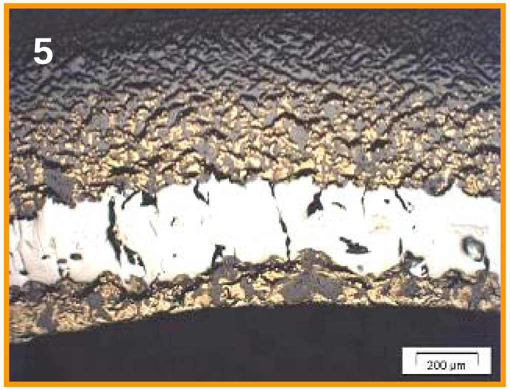


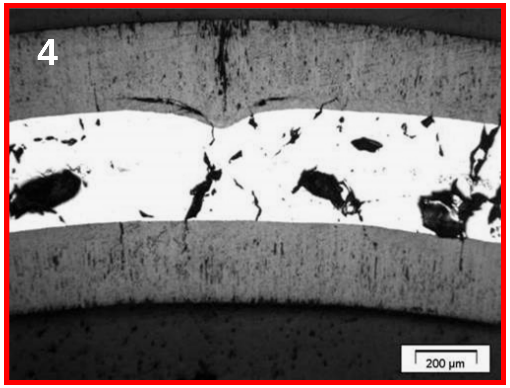
Accelerating effect of PO on subsequent reaction in nitrogen

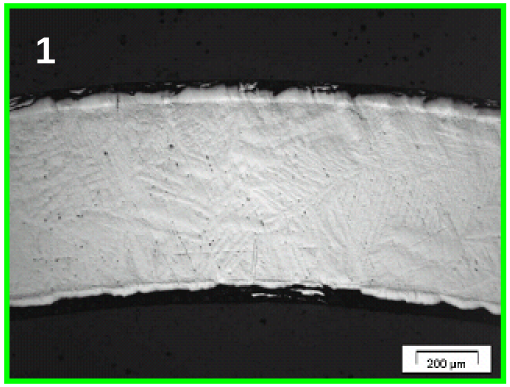
Oxidation of Zr alloys in various atmospheres

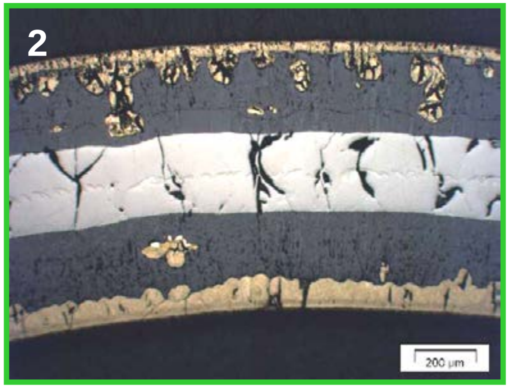


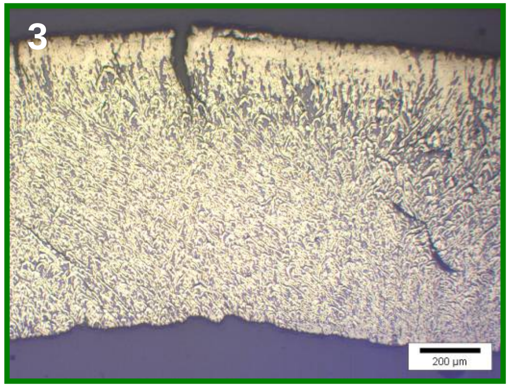
Time, s











Oxidation of Zr alloys in various atmospheres

Reaction of Zry-4 in	Kinetic rate law	Relative reaction rate*, a.u.
N_2	parabolic	1
N_2 after pre-oxidation in O_2	linear	10
N_2 with oxygen-stabilized α-Zr(O)	linear	70
O_2, H_2O	parabolic	100
Air after pre-oxidation in O_2	parabolic	100
Air	linear	150

* at 1200°C

Oxidation in mixed steam-air atmospheres

Zry-4, 1 hour at 1200°C

H_2O

$0.7\ H_2O$
0.3 air

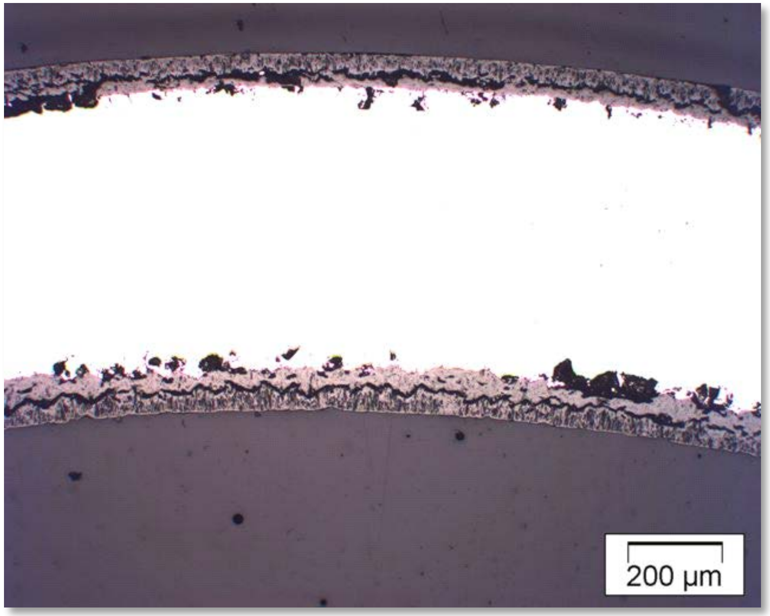
$0.3\ H_2O$
0.7 air

$0.1\ H_2O$
0.9 air

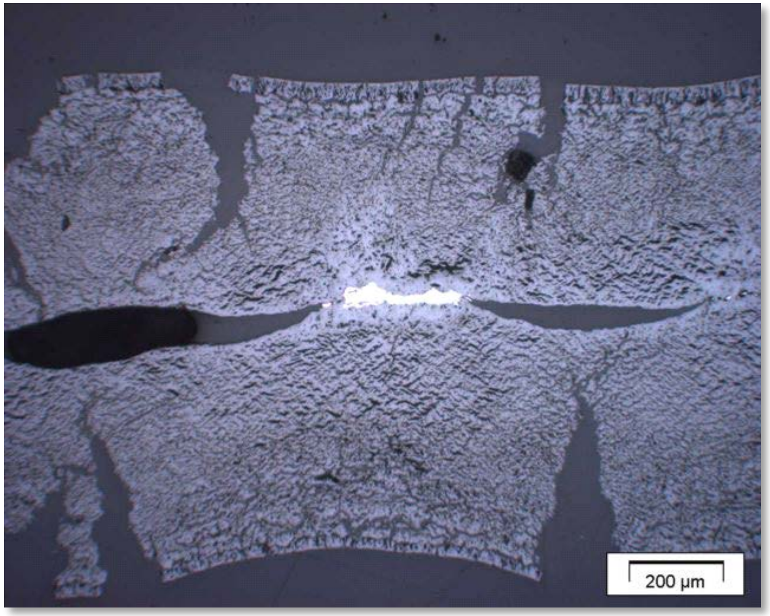
- Increasing degradation with raising content of air in the mixture

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

Conclusions

- The usually applied parabolic oxidation kinetics are, strictly speaking, only valid at temperatures above 1000°C and for fast transients (with fast passing of the breakaway region).
- Sub-parabolic kinetics is observed at temperatures below 1000°C.
- Breakaway has to be taken into account for slow transients and long duration scenarios at medium temperatures (600-1000°C).
- Nitrogen is not an inert gas under the conditions of a nuclear accident. It accelerates oxidation and causes rather linear kinetics.
- Computer codes simulating severe accident scenarios should take into account non-parabolic oxidation kinetics. Various activities are ongoing worldwide.

Deviations from the parabolic kinetics during oxidation of zirconium alloys

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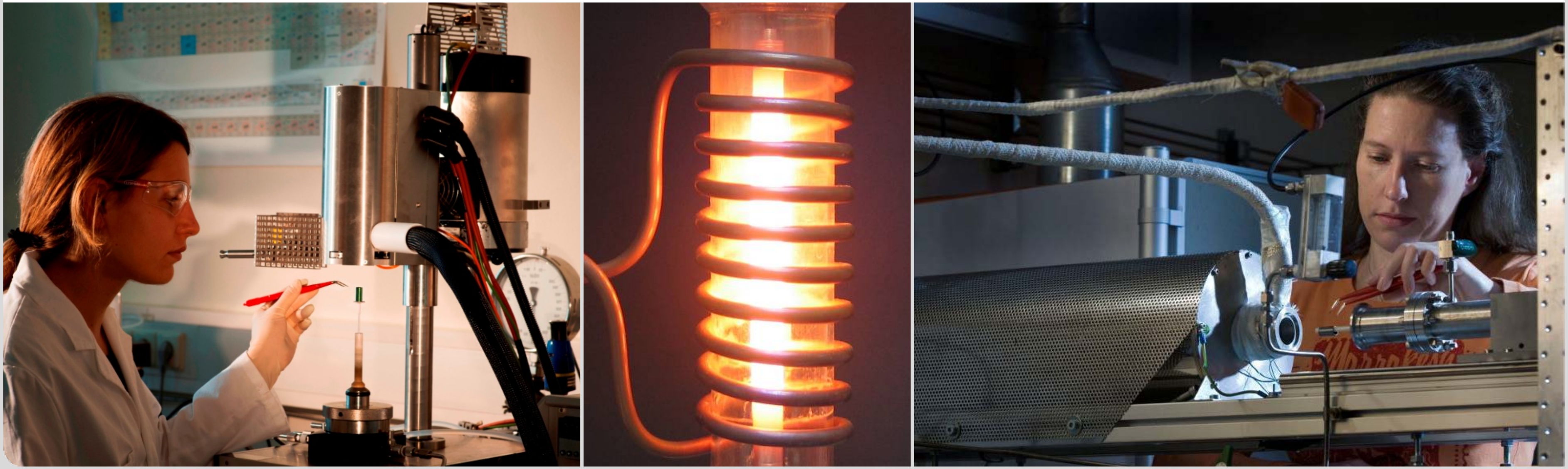
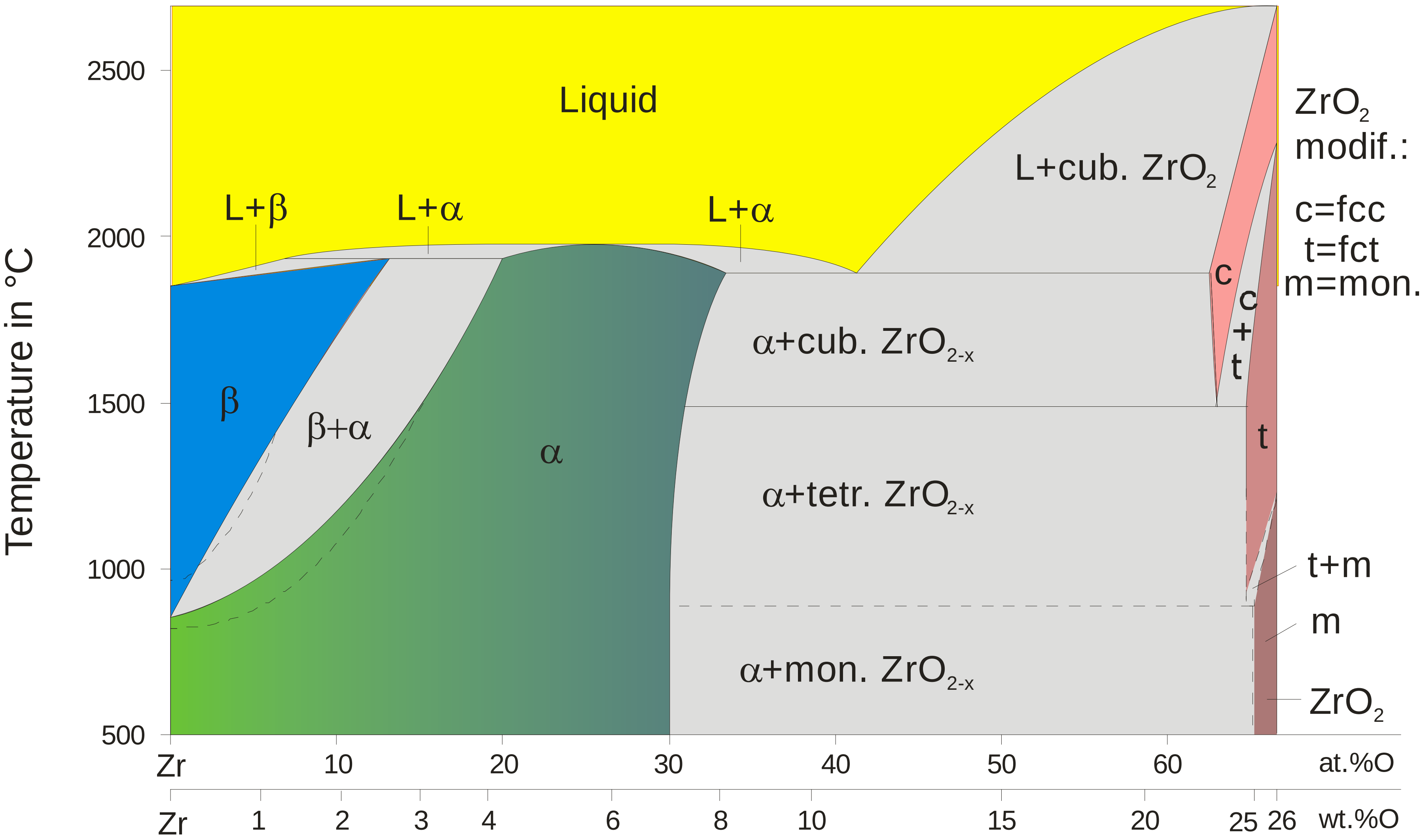
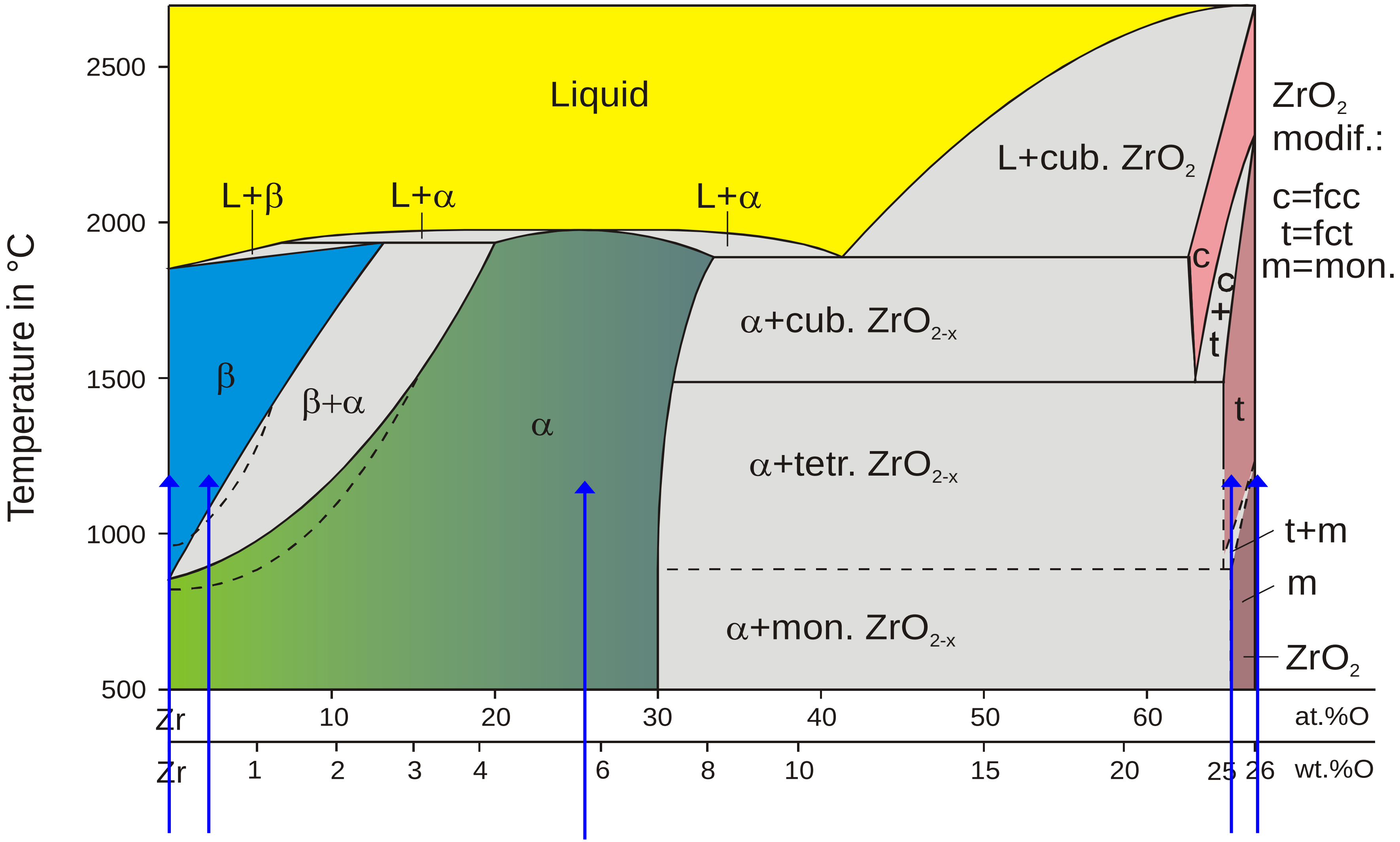


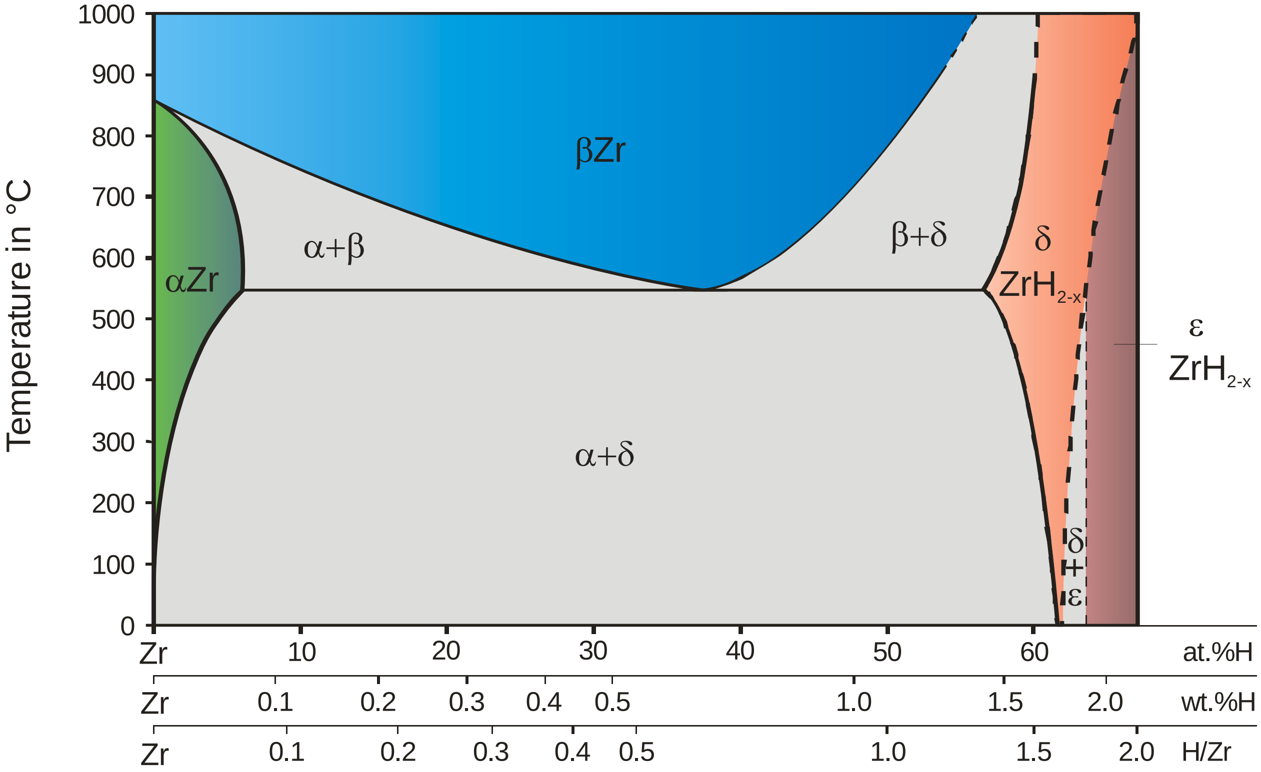
Phase diagram Zr - O



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