Comparative View on High-Temperature Oxidation of Zirconium Alloys in Various Atmospheres

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GfKORR-Arbeitskreis „Korrosionsschutz bei erhöhten Temperaturen“
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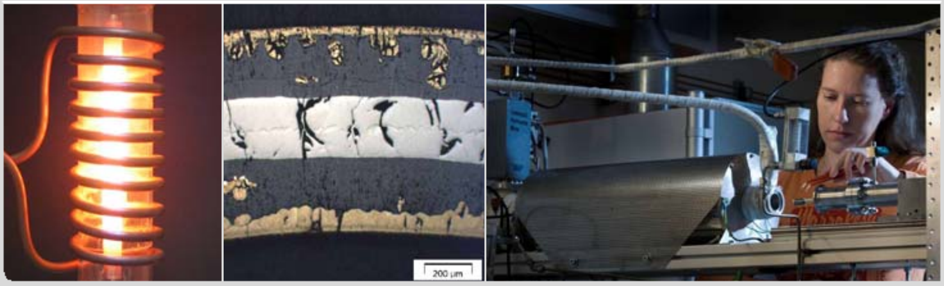
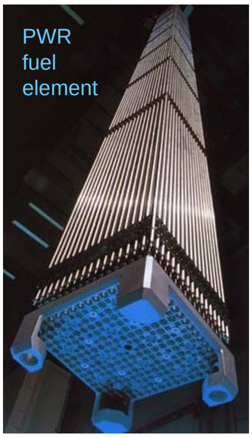
Institute of Applied Materials, IAM-AWP / Program NUKLEAR



Introduction

- 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
- Possible atmospheres:
  - Steam
  - Air
  - Nitrogen
  - Mixtures of them
- Fukushima



Basics – chemical reactions

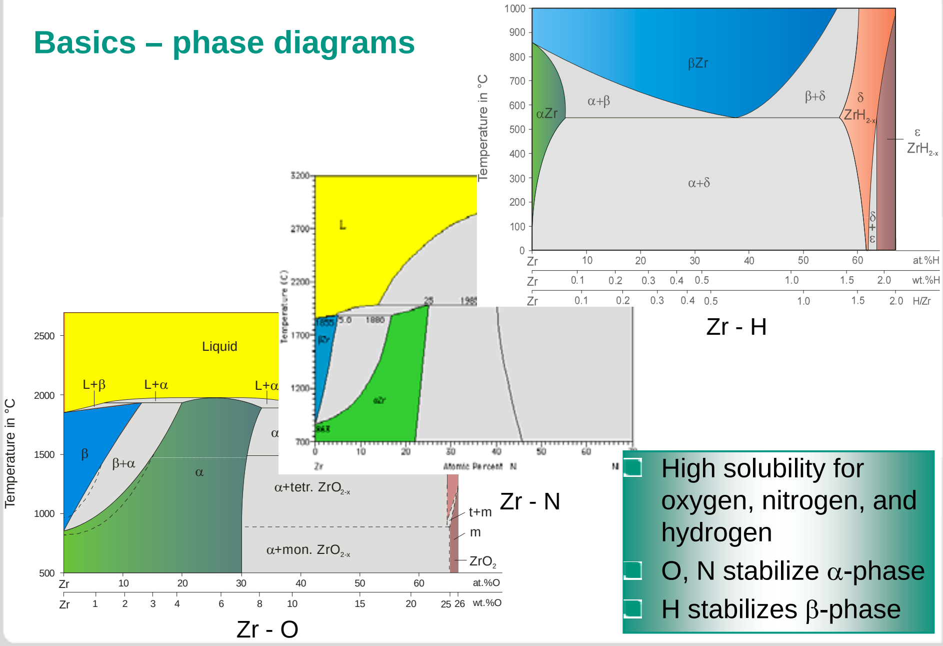
ΔH_f at 1500 K

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$ -585 kJ/mol

$$Zr + O_2 \rightarrow ZrO_2$$ -1083 kJ/mol

$$Zr + \frac{1}{2}N_2 \rightarrow ZrN$$ -361 kJ/mol

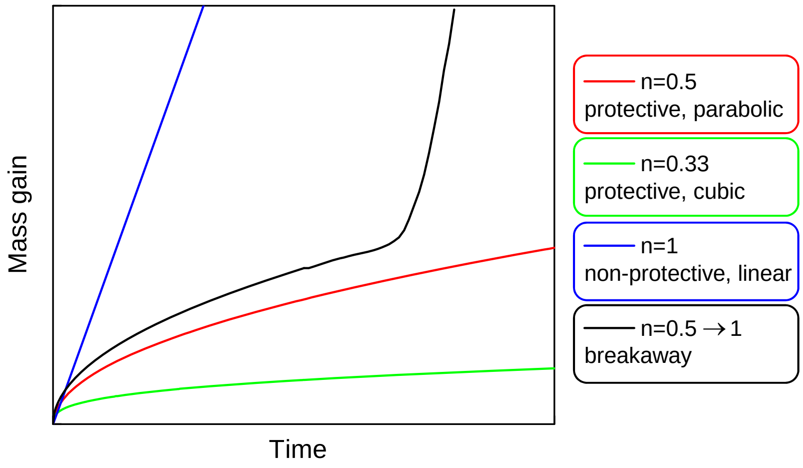
Basics – phase diagrams



- High solubility for oxygen, nitrogen, and hydrogen
- O, N stabilize α-phase
- H stabilizes β-phase

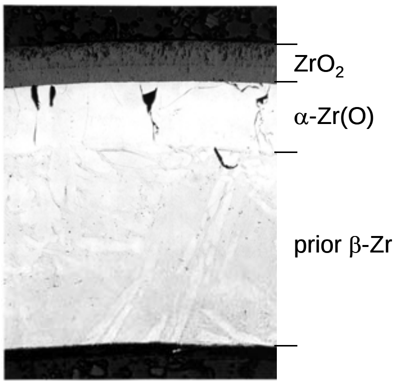
Basics – kinetics

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

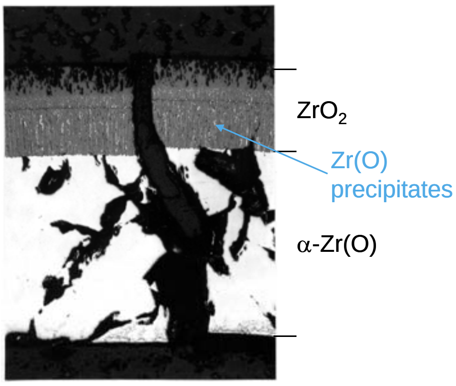


Oxidation in steam (oxygen)

- Most LOCA and SFD codes use parabolic oxidation correlations (n=1/2)



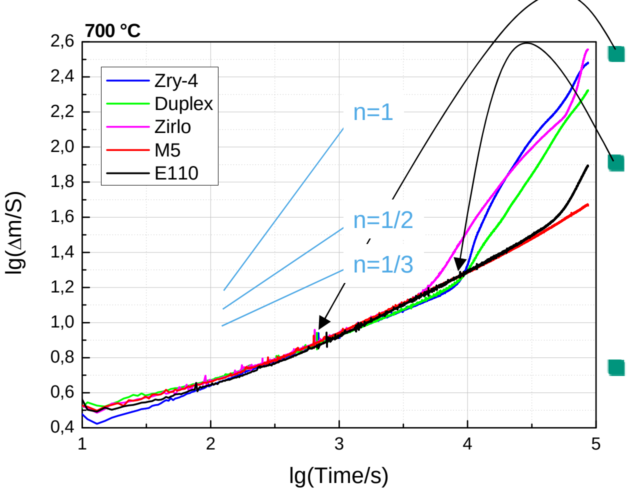
1200 °C, quench



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 breakaway
- Similar kinetics of all alloys before transition, but strongly varying behavior at and after transition

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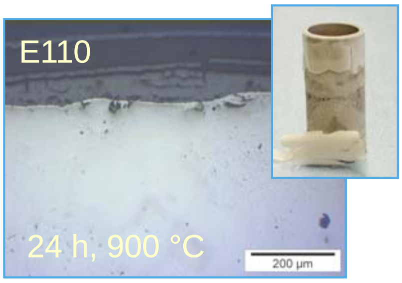
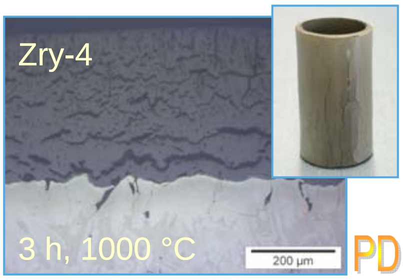
Breakaway oxidation

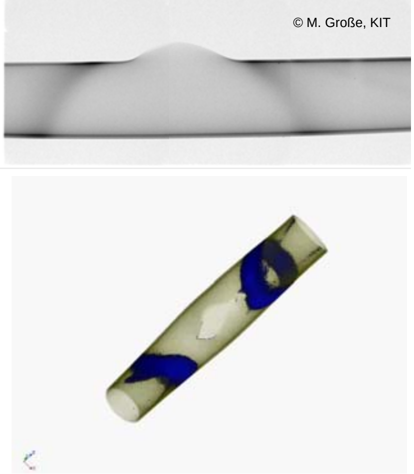
- Loss of protective properties of oxide scale due to its mechanical failure.
- Breakaway is caused by phase transformation from pseudo-stable tetragonal to monoclinic oxide and corresponding density change.
- Critical times and oxide thicknesses for breakaway strongly depend on type of alloy and boundary 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").





Secondary hydriding during LOCA

- Hydrogen enrichment near burst position was already observed e.g. by ANL *(NUREG/CR-6967)* and is one reason for the re-evaluation of the LOCA embrittlement criterion
- Mechanism:
  (1) enhanced oxidation of inner clad surface after rupture
  (2) enrichment of hydrogen in the gap between cladding and pellets
  (3) absorption of hydrogen through non-oxidized inner clad surface
- New results with neutron methods obtained in the framework of the recent QUENCH-LOCA program



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Neutron radiography and tomography of hydrogen bands near burst position after QUENCH-L0 bundle test

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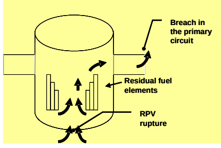
Oxidation in atmospheres containing nitrogen

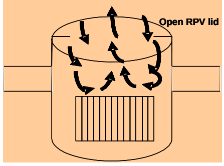
- Air ingress reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

- 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

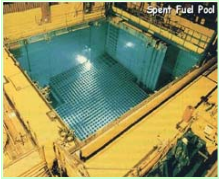
Late phase after RPV failure



Mid loop operation



Spent fuel storage pool accident



Consequences of air ingress for cladding

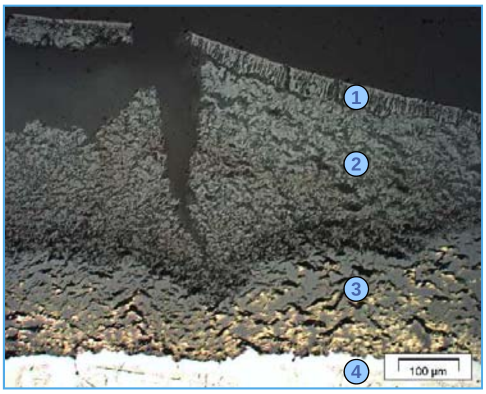
1 hour at 1200°C in steam

1 hour at 1200°C in air

→ Loss of barrier effect of cladding

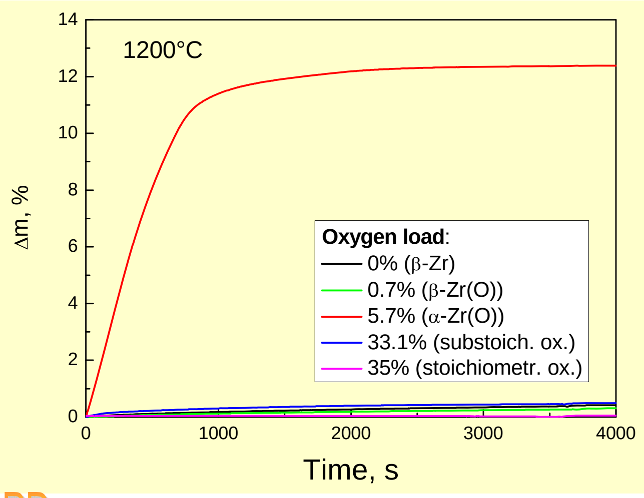
Mechanism of air oxidation

- 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



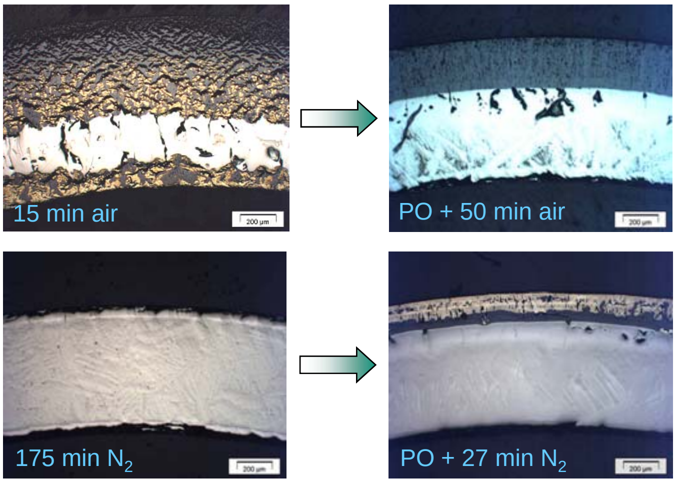
1 – initially formed dense oxide ZrO_2
2 – porous oxide after oxidation of ZrN
3 – ZrO_2 / ZrN mixture
4 – α-Zr(O)

Reaction of ZrO_x with nitrogen



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

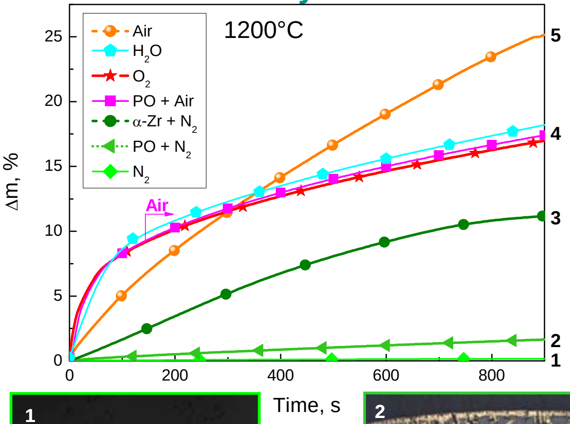
Example: Zry-4, 1200°C

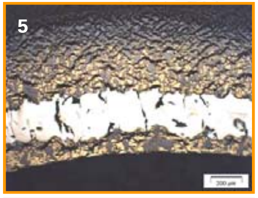


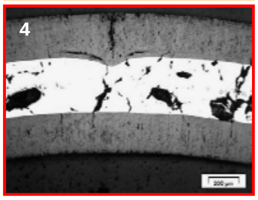
Protective effect of PO on subsequent oxidation in air as long as oxide scale is intact

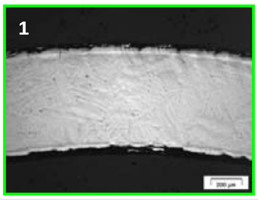
Accelerating effect of PO on subsequent reaction in nitrogen

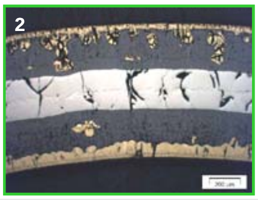
Oxidation of Zr alloys in various atmospheres

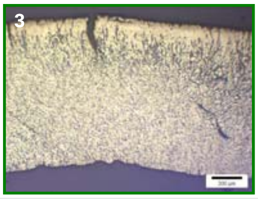












Oxidation of Zr alloys in various atmospheres

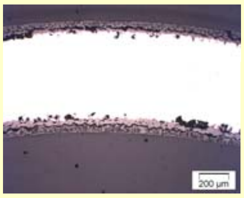
Reaction of Zry-4 in	Kinetic rate law	Relative reaction rate, a.u.
N_2	parabolic	1
N_2 after pre-oxidation in O_2	linear	10
N_2 with oxygen-stabilized α-Zr(O)	linear	70
O_2, H_2O	parabolic	100
Air after pre-oxidation in O_2	parabolic	100
Air	linear	150

Oxidation in mixed atmospheres

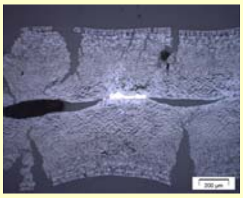
Zry-4, 1 hour at 1200°C

H_2O | 0.7 H_2O 0.3 air | 0.3 H_2O 0.7 air | 0.1 H_2O 0.9 air

1 hour at 1000 °C in



steam



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

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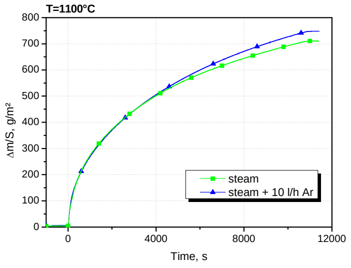
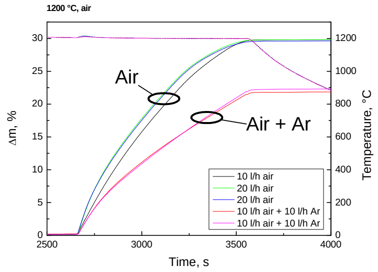
Influence of inert gases

- Inert gases like argon and helium are often used as carrier or reference gases in experiments simulating nuclear accidents.
- They have only insignificant influence on oxidation kinetics as long as the oxide scale is dense and oxidation is determined by diffusion of oxygen through the ZrO_2 lattice.
- Inert gases may influence oxidation in case of porous oxide layers (breakaway, air oxidation), determined by gas phase diffusion through pores and cracks.





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).
- 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.
- Zirconium nitride ZrN is formed when (1) oxygen is absent in the atmosphere and (2) oxygen is present in the solid phase.
- The use of inert gases in simulation experiments for nuclear accidents may have an effect on the results.

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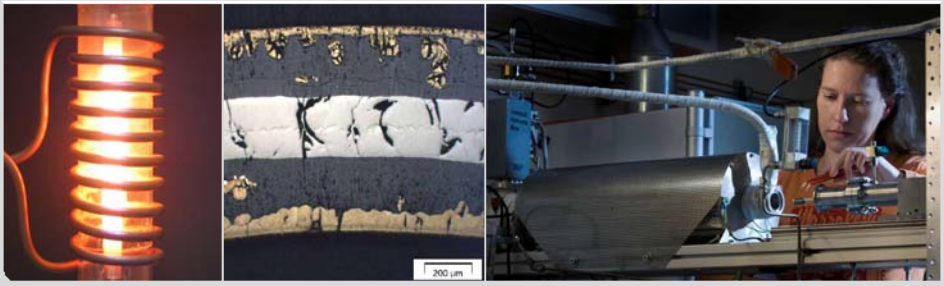
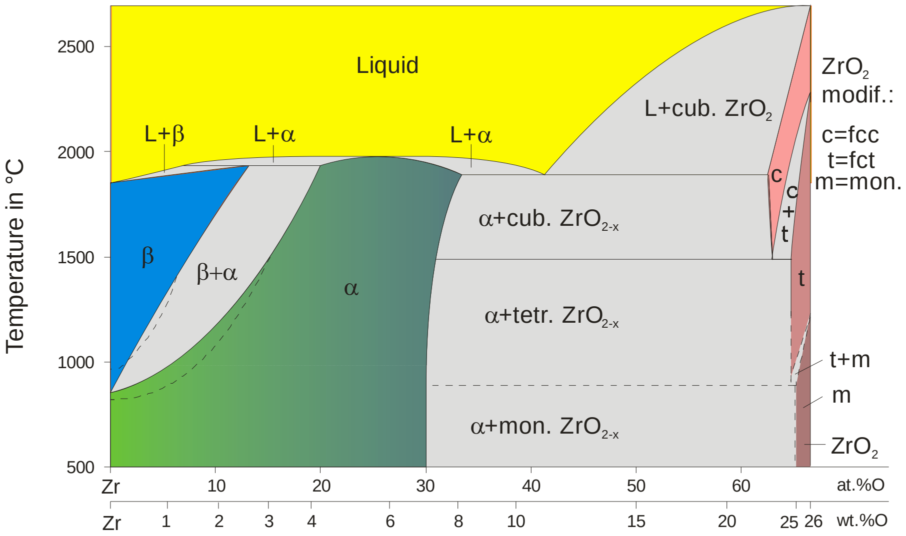


Phase diagram Zr - O



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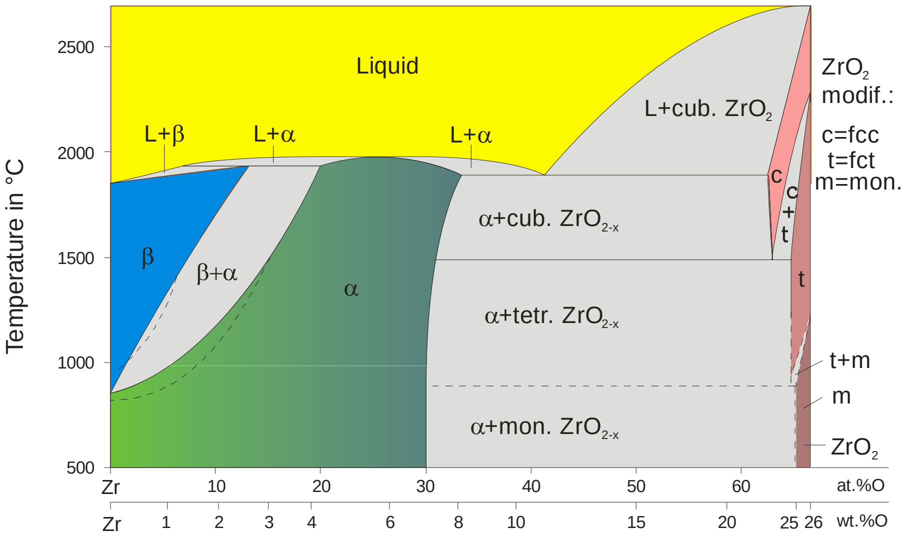

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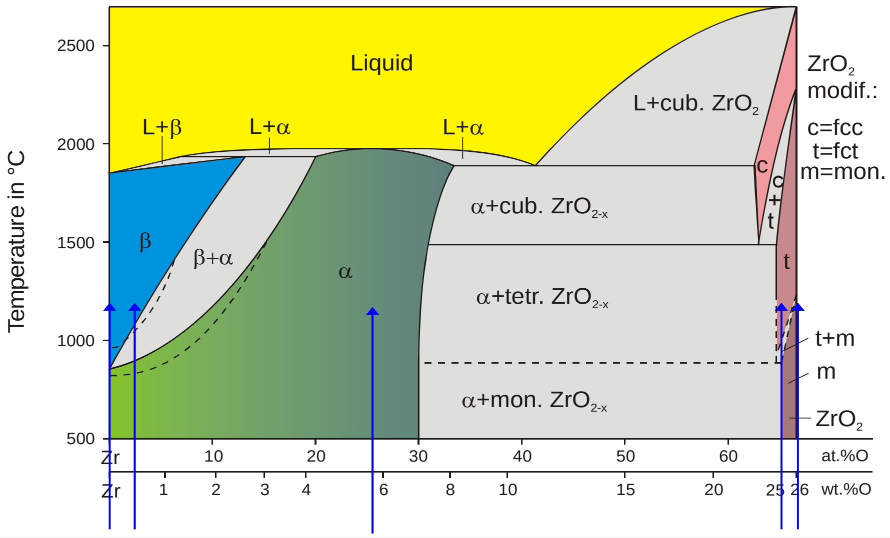
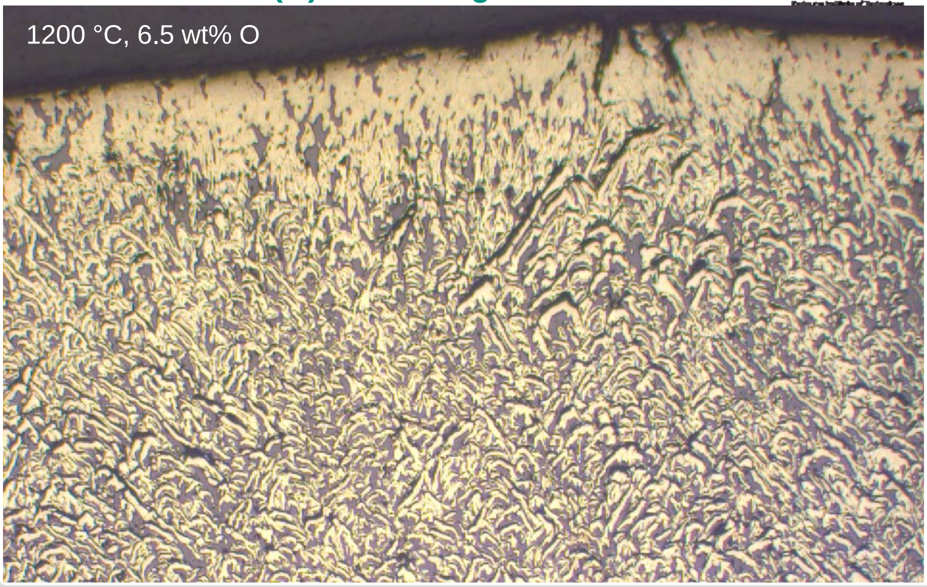


Reaction of α-Zr(O) with nitrogen


1200 °C, 6.5 wt% O