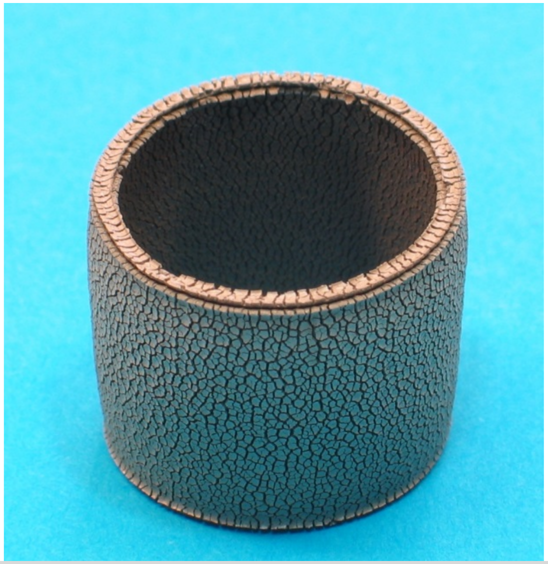
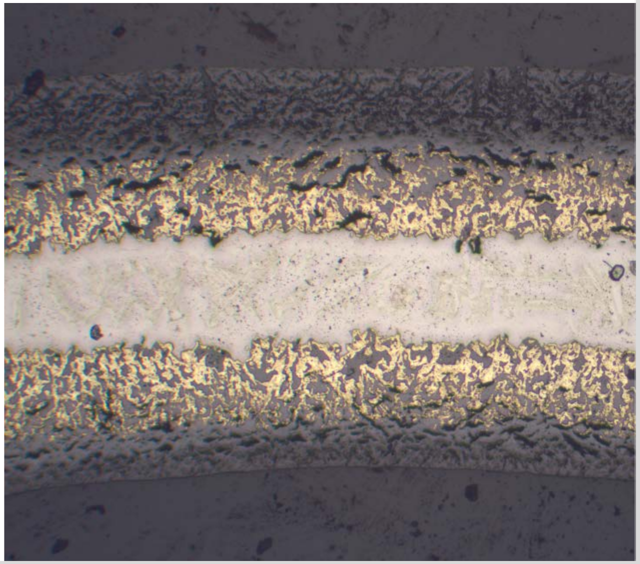
Zry-4 oxidation in mixed steam-nitrogen atmospheres

M. Steinbrück, F. Oliveira da Silva, H.J. Seifert

NuMat 2014*: The Nuclear Materials Conference, 27-30 October 2014, Clearwater Beach, Florida, USA*

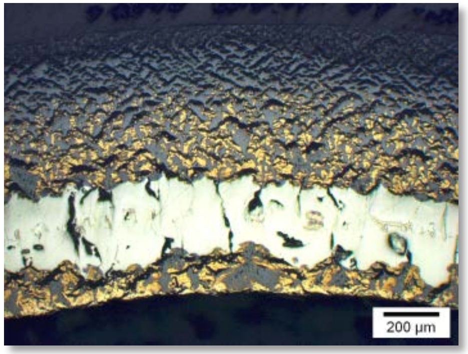
Institute for Applied Materials IAM-AWP & Program NUKLEAR

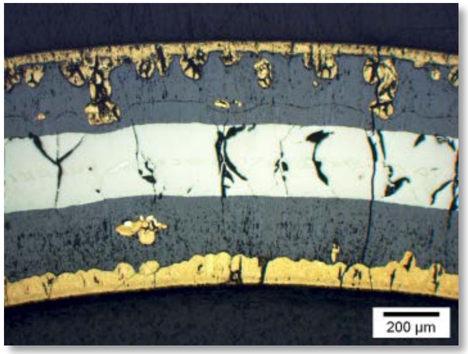


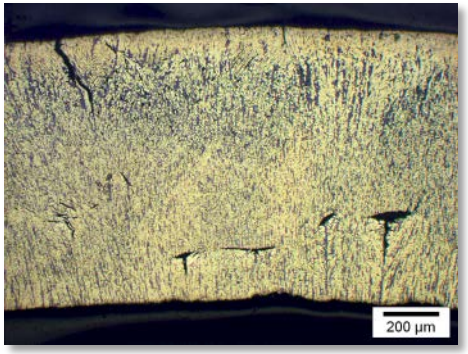


Motivation

- Air ingress and Zr oxidation in atmospheres containing nitrogen is of actual interest in many countries
- The mechanism of oxidation of Zr alloys in atmospheres containing nitrogen is very complex
- Nitrogen is used for inerting BWR containments and for pressurization of ECCS; hence steam-nitrogen mixtures are prototypic for reactor and SFP accident scenarios
- No systematic study of the oxidation of Zr alloys in steam-nitrogen mixtures was available, especially for the edge regions in composition







Experimental setup

Thermal balance

(STA-409)

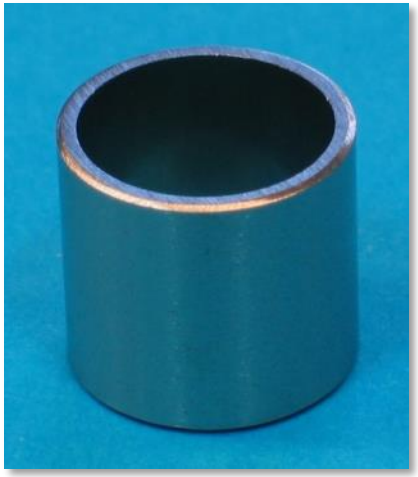
Mass spectrometer

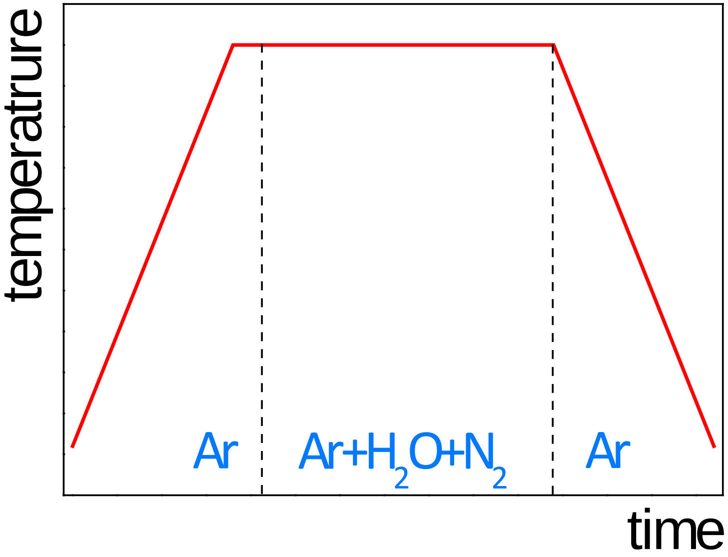
MFCs

Samples, test matrix, and test conduct

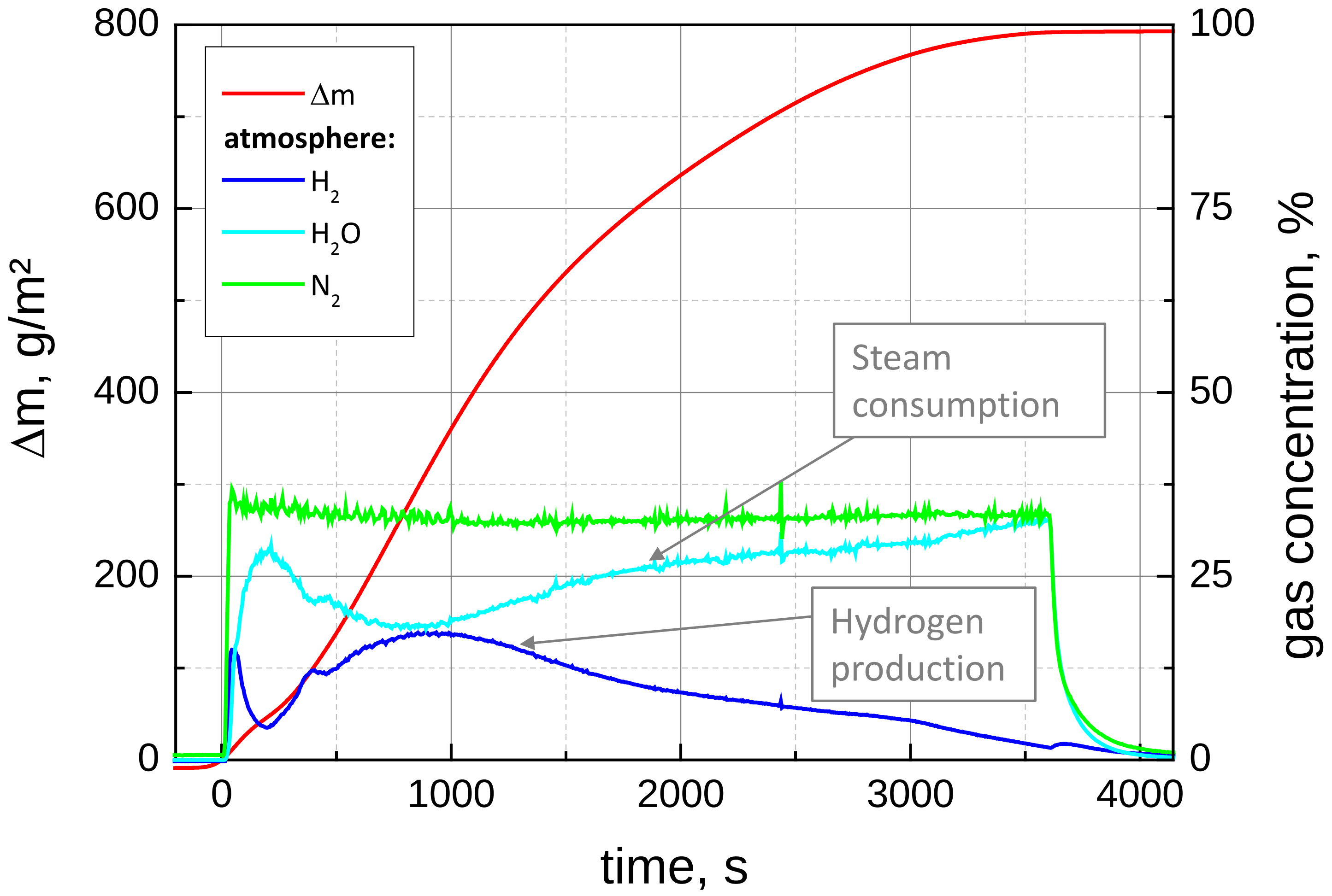
- 1 cm cladding tube segments made of Zircaloy-4
- Isothermal tests
- Temperatures and times:

  20 h @ 600°C
  6 h @ 800°C
  1 h @ 1000°C
  15 min @ 1200°C
- Atmospheres:
  0-100% nitrogen incl. 0.1 and 90%
- Flow rates:
  0.28 mol/h H_2O+N_2, 0.13 mol/h Ar





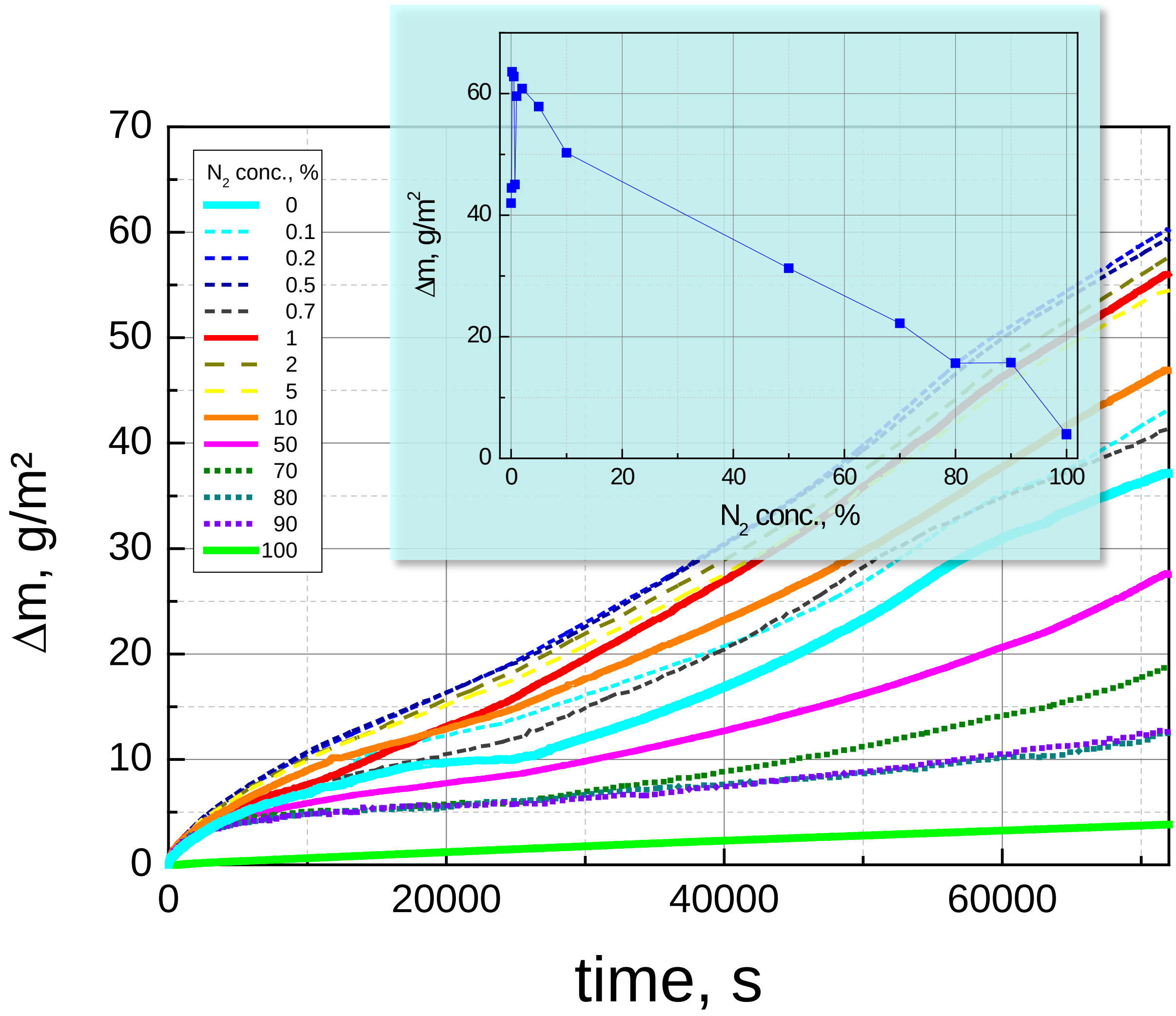
Test conduct; example 1000°C, 50% H_2O + 50% N_2

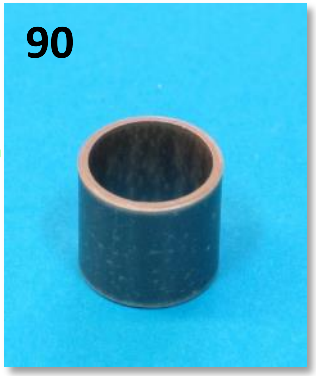


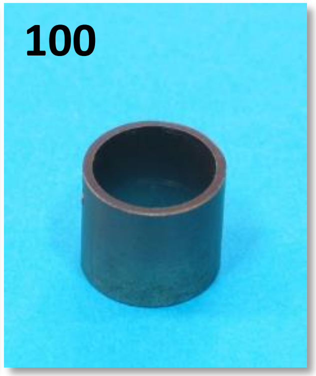
Steam consumption

Hydrogen production

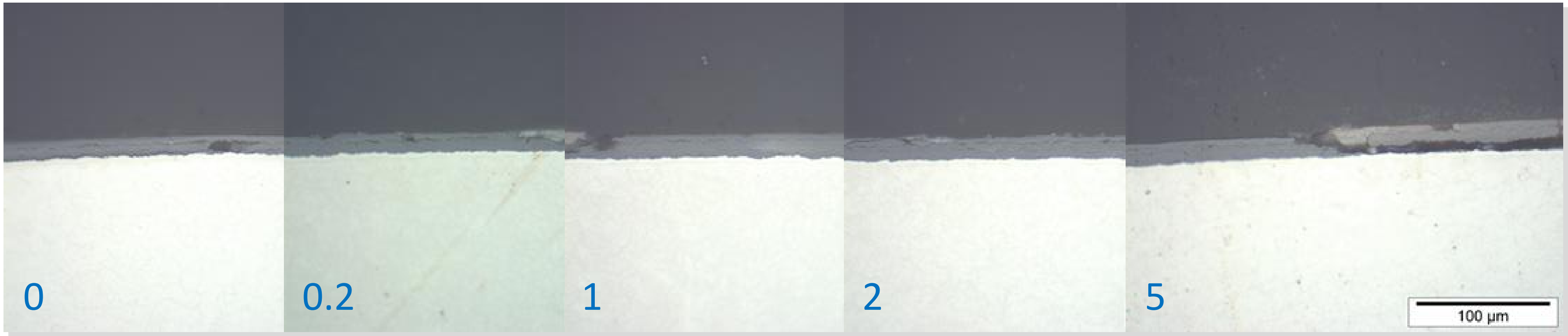
TG results at 600°C, 20 hours

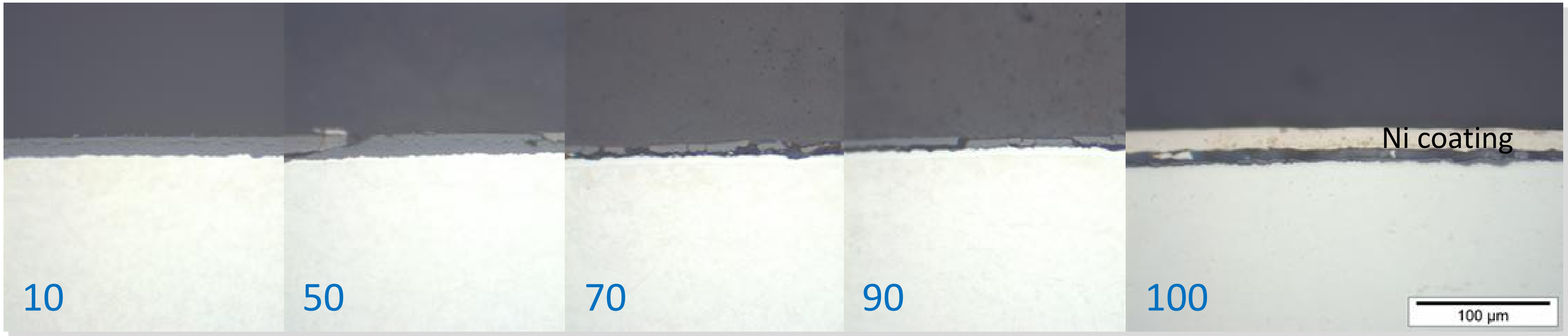






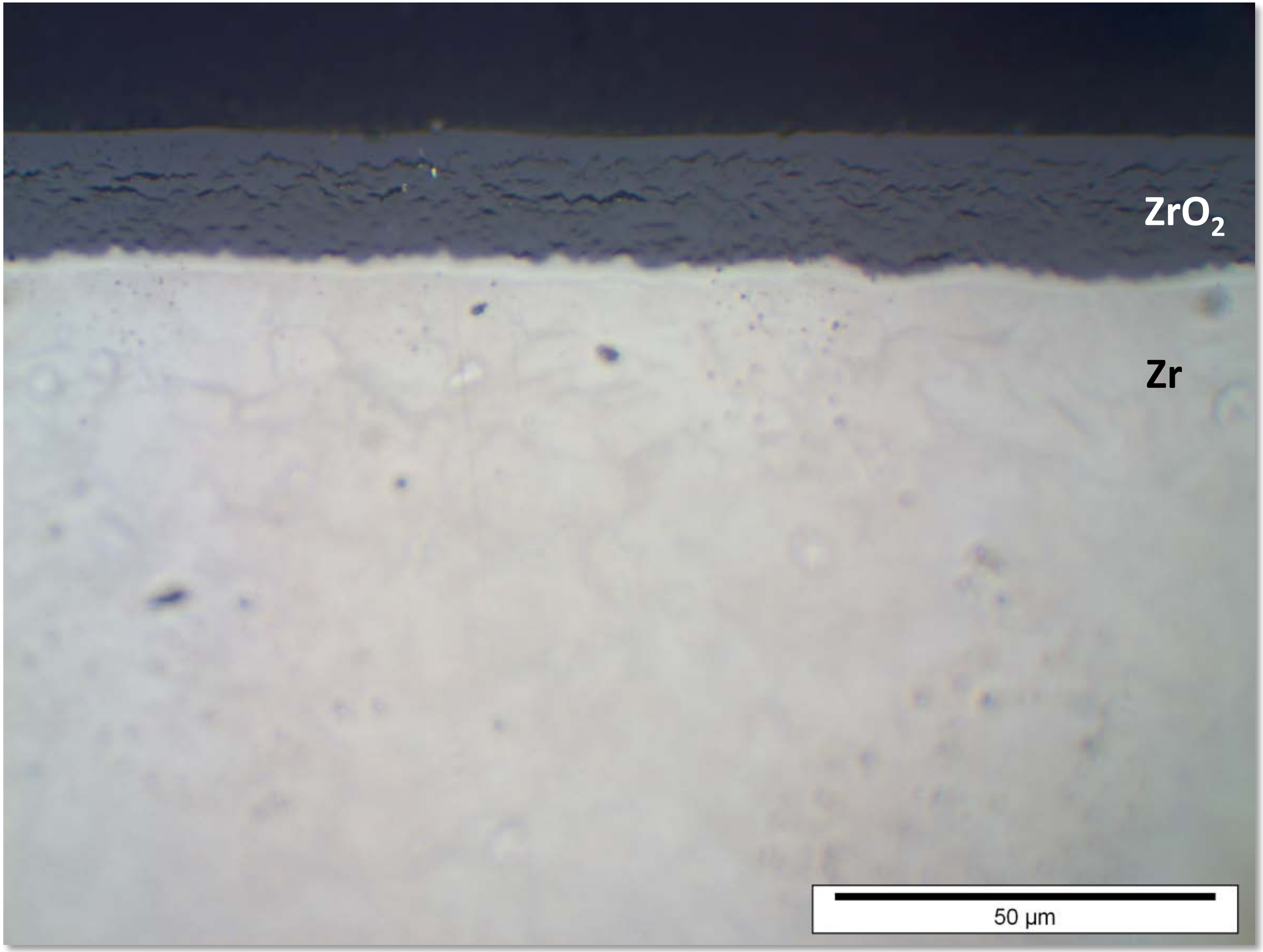
Micrographs of 600°C samples



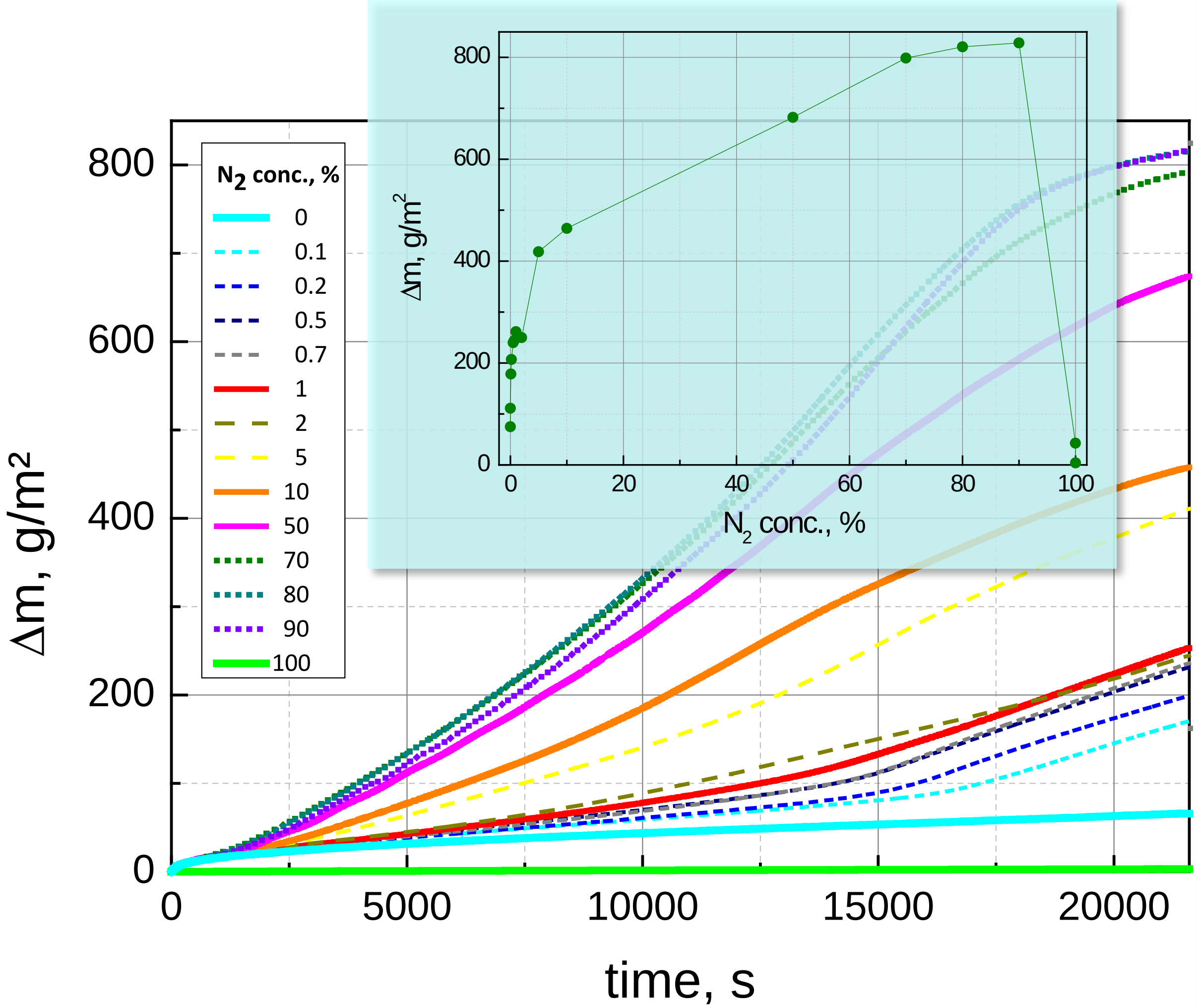


N_2 content in the mixture

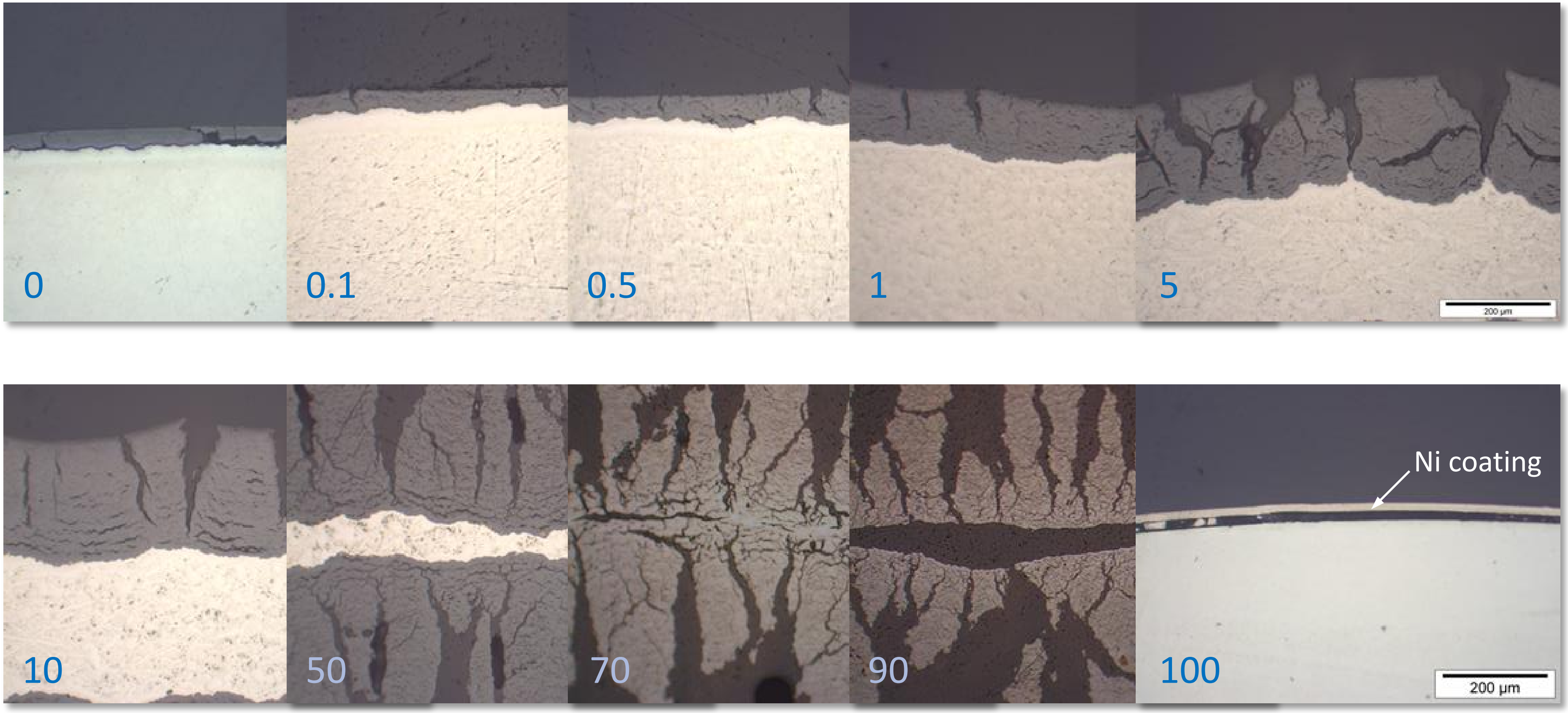
Micrograph: 600°C, 2% nitrogen



TG results at 800°C, 6 hours

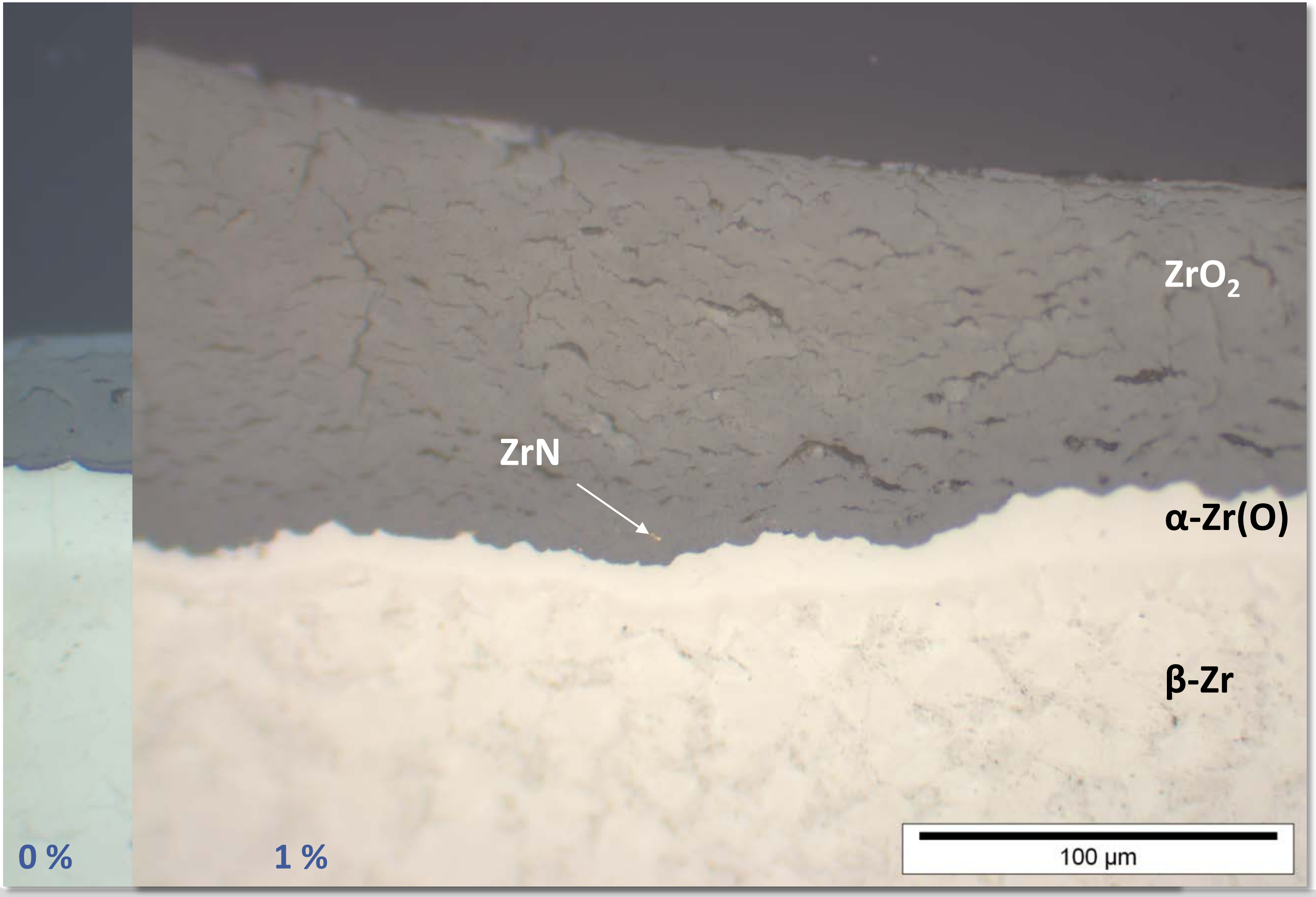


Micrographs of 800°C samples

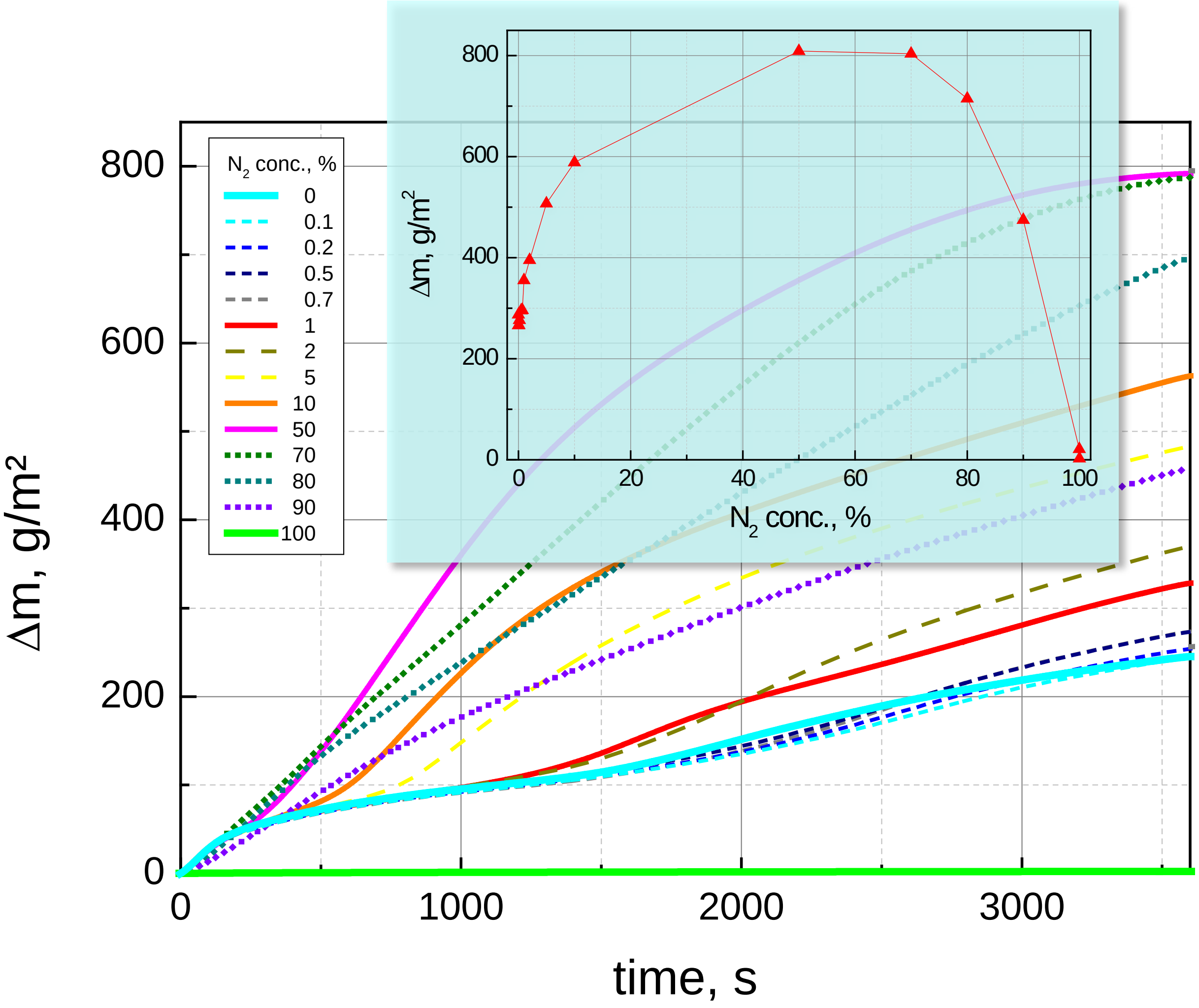


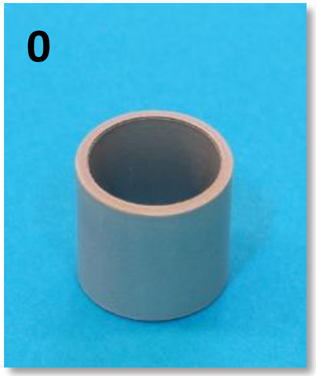
N_2 content in the mixture

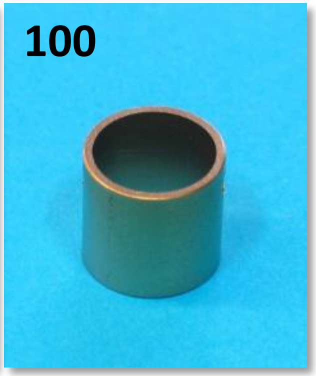
Micrograph: 800°C, 1% nitrogen



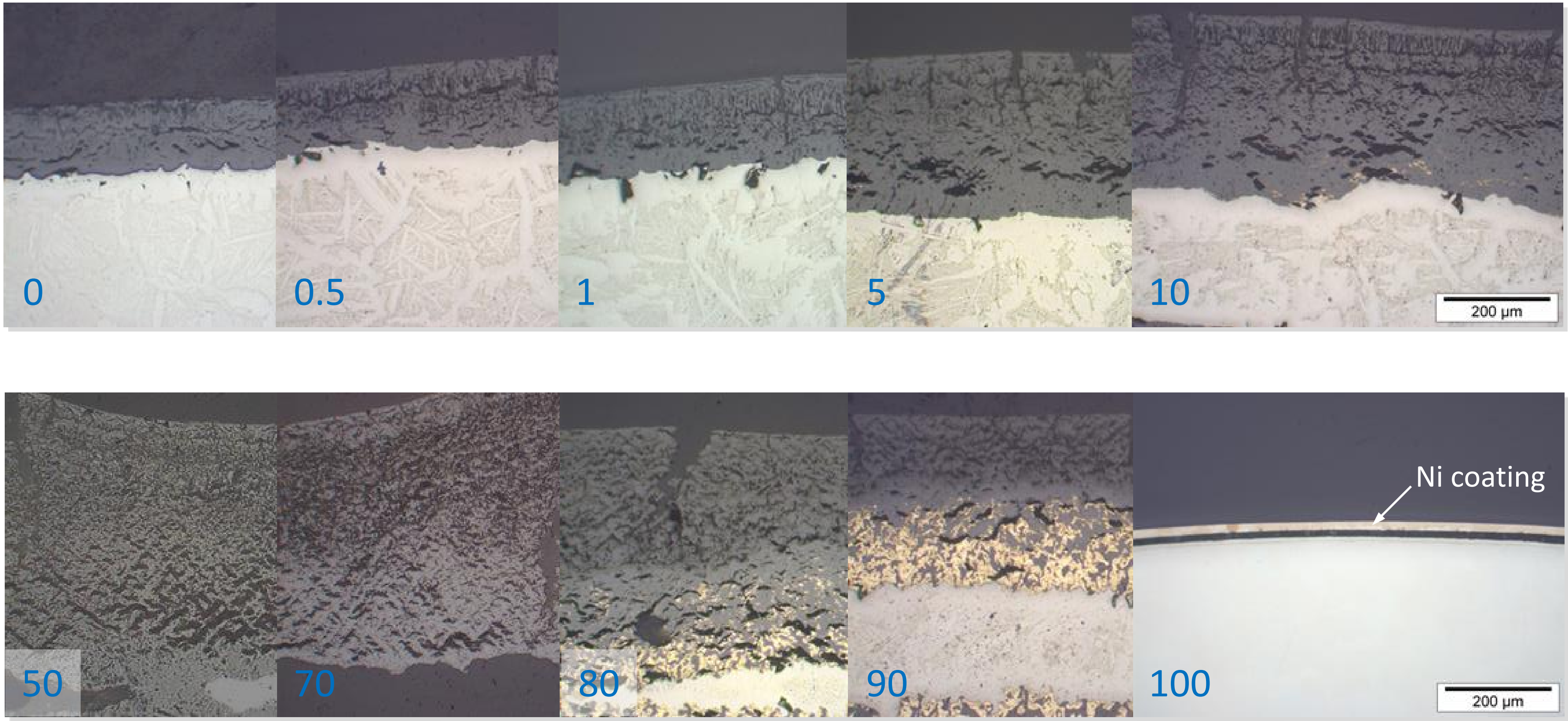
TG results at 1000°C, 1 hour





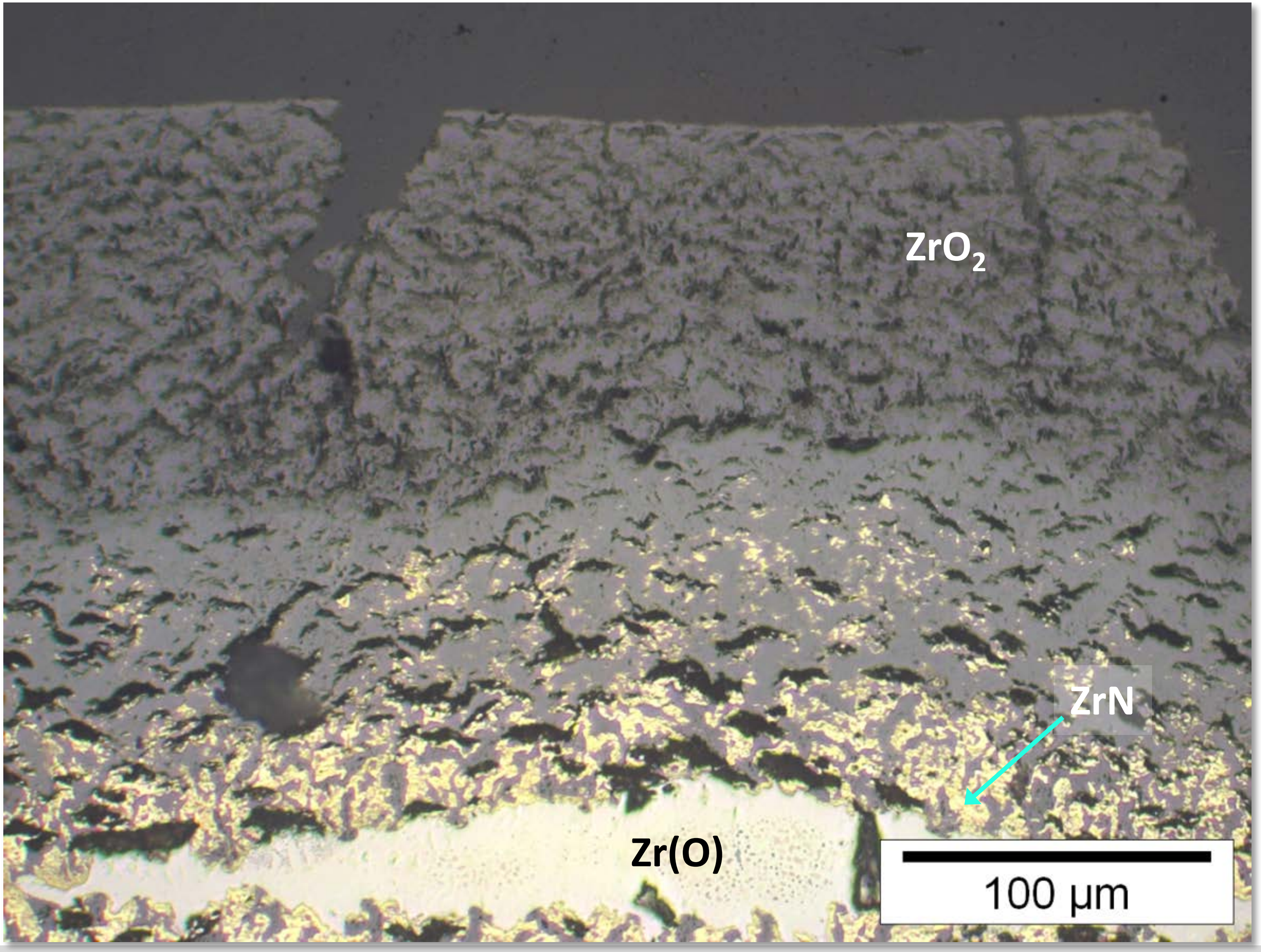


Micrographs of 1000°C samples

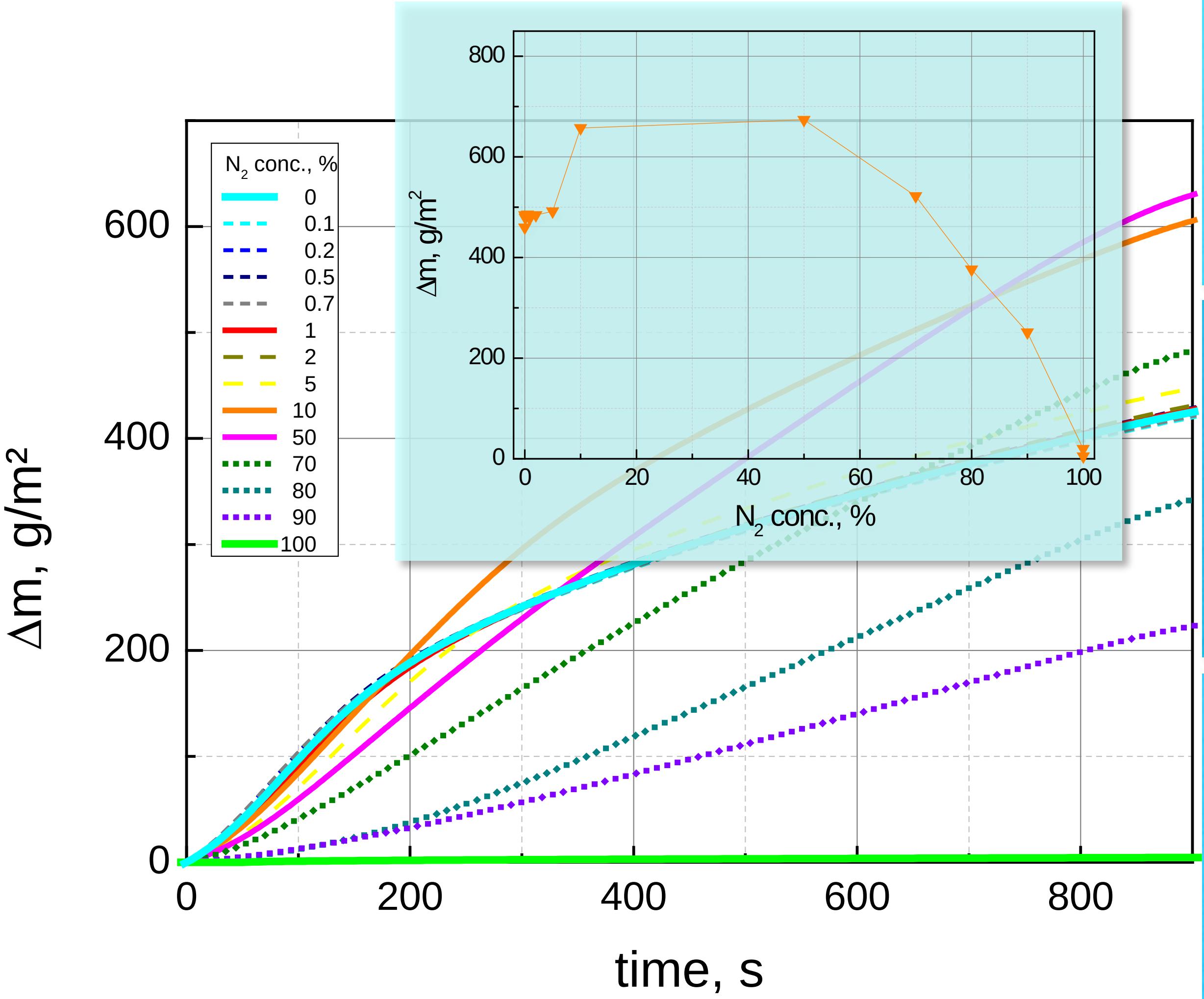


N_2 content in the mixture

Micrograph: 1000°C, 80% nitrogen



TG results at 1200°C, 15 min

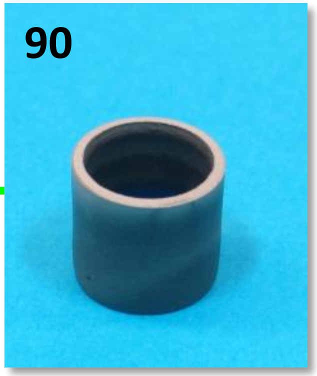



0


1

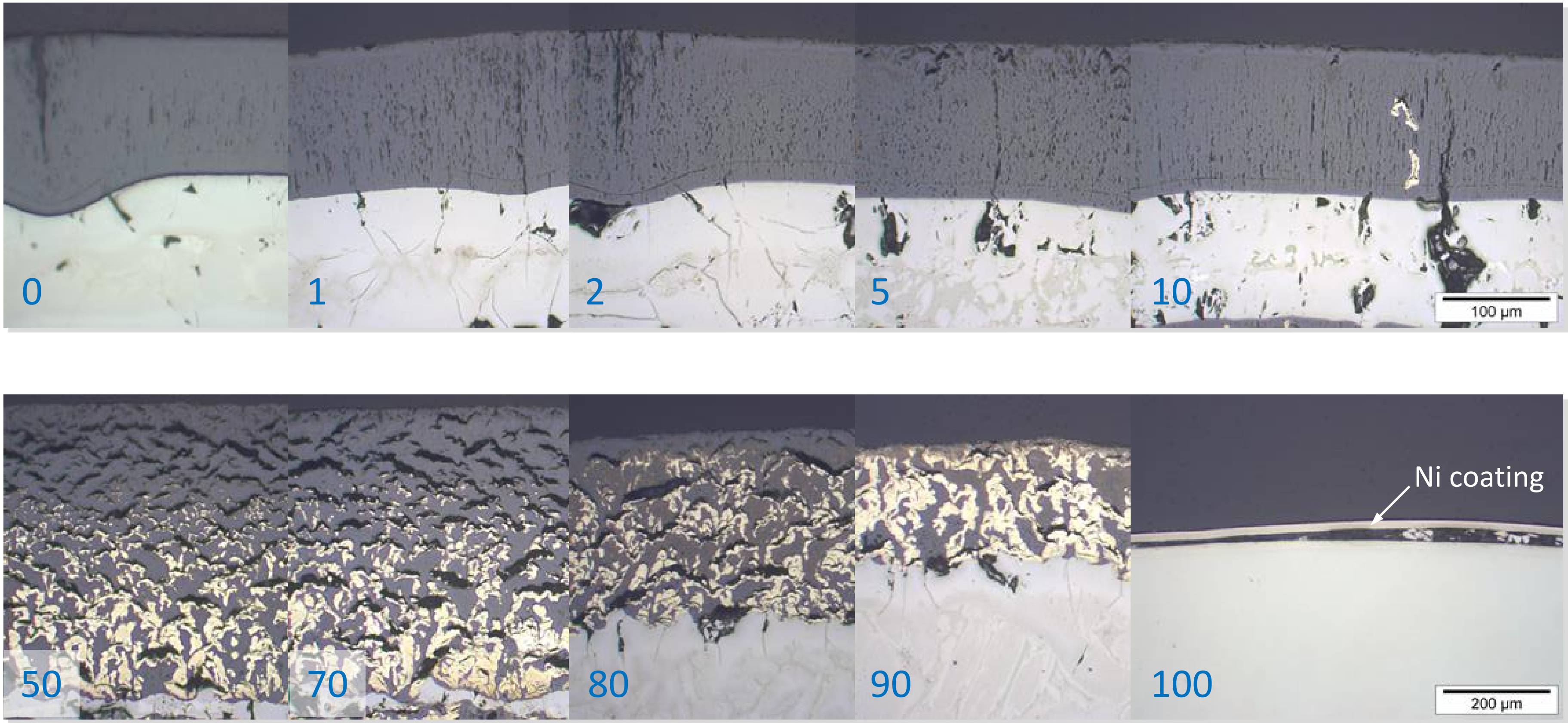

10


50


90

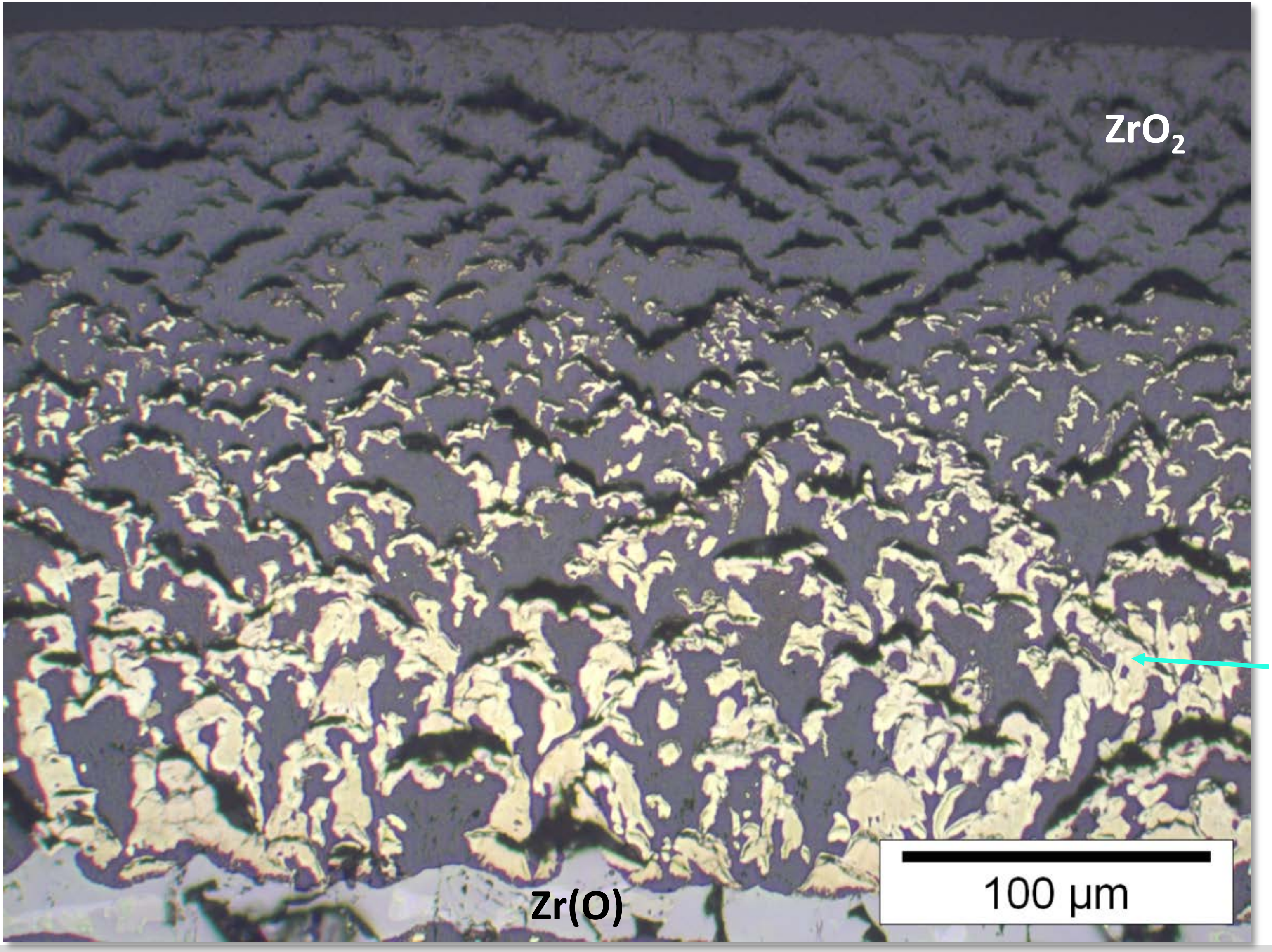

100

Micrographs of 1200°C samples



N_2 content in the mixture

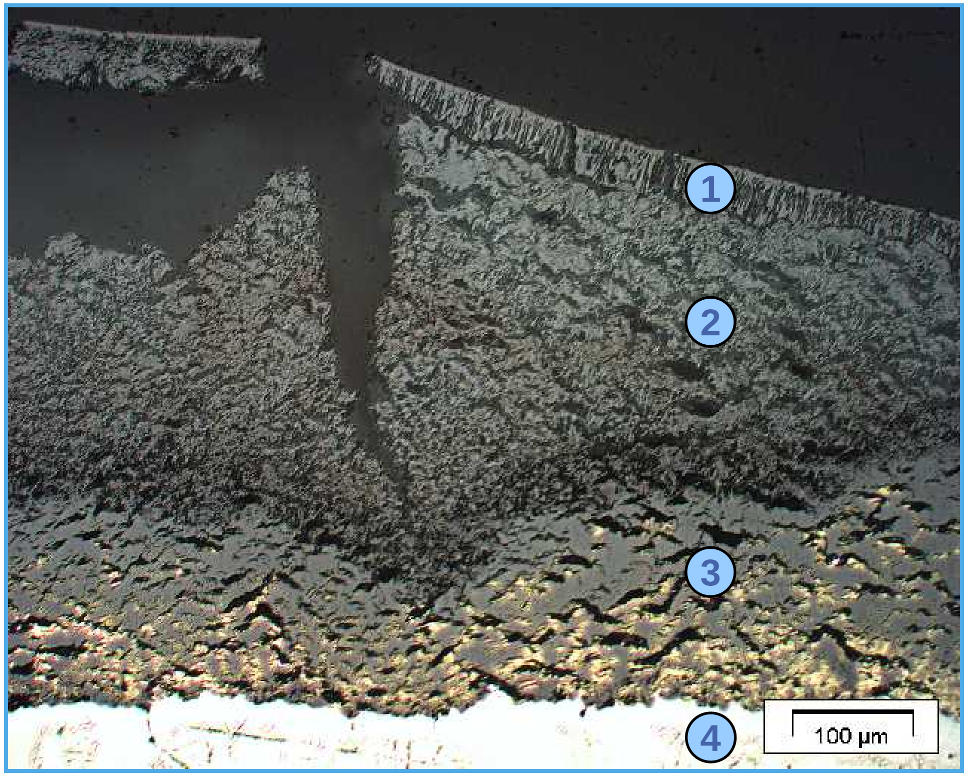
Micrograph: 1200°C, 50% nitrogen



Oxidation mechanism in steam-nitrogen mixtures

- Diffusion of gas through imperfections in the oxide scale to the metal/oxide boundary
- Consumption of steam; production of hydrogen
- Remaining nitrogen reacts with zirconium and forms “ZrN”
- ZrN is re-oxidized by fresh steam with continuing reaction associated with a volume increase by 48%

➡ Formation of porous and non-protective oxide scales



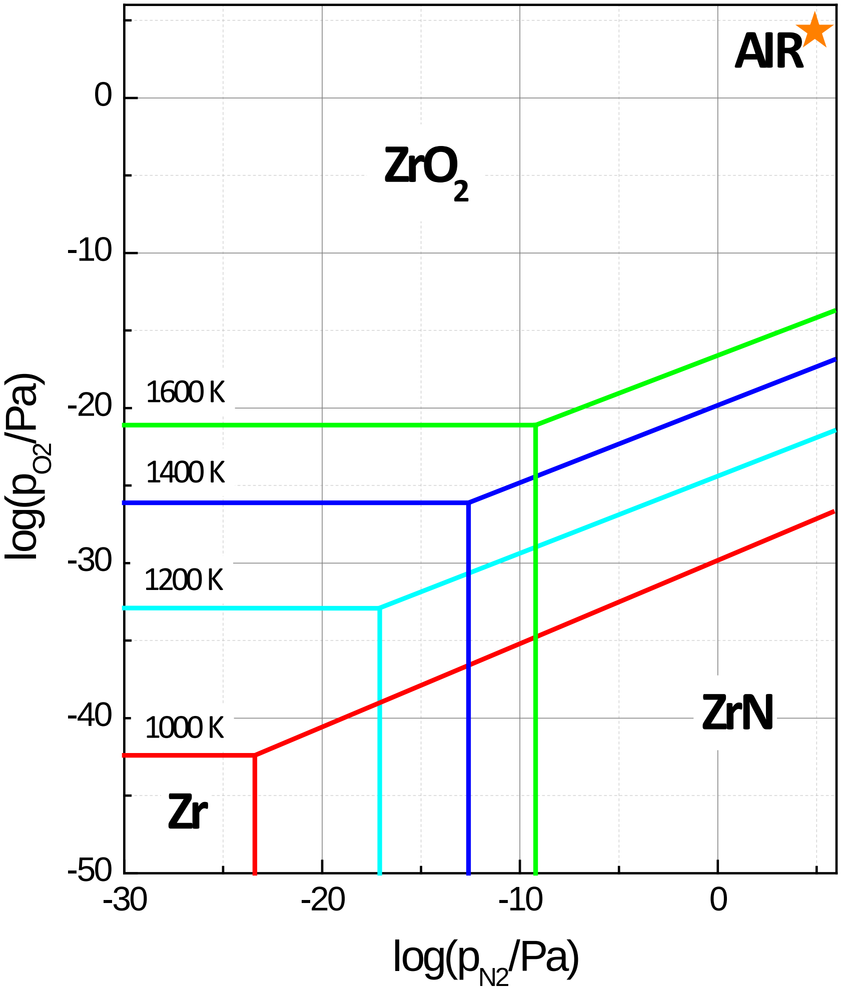
1 – initially formed dense oxide ZrO_2

2 – porous oxide after oxidation of ZrN

3 – ZrO_2 / ZrN mixture

4 – α-Zr(O)

ZrO_2-ZrN stability diagram



- ZrN is practically only stable in the absence of oxygen in the gas phase
- Nitrogen preferably reacts with saturated α-Zr(O)
- Both conditions are fulfilled locally at/near the metal-oxide interface
- ZrN is reoxidized when oxygen or steam are available again

Simple reaction scheme

O dissolution by the metal: $Zr + xH_2O \rightarrow ZrO_x^{abs} + xH_2$ *(1)*

Oxide scale formation: $ZrO_x + (2-x)H_2O \rightarrow ZrO_2 + (2-x)H_2$ (2.1)

Nitride formation: $ZrO_x + \left(\frac{1-{}^{x}/_{2}}{2}\right) N_2 \rightarrow \frac{x}{2} ZrO_2 + (1-{}^{x}/_{2})ZrN$ (2.2)

Nitride re-oxidation:

$(1-{}^{x}/_{2})ZrN + (2-x)H_2O \rightarrow (1-{}^{x}/_{2})ZrO_2 + \left(\frac{1-{}^{x}/_{2}}{2}\right) N_2 + (2-x)H_2$ (3)

Hydrogen absorption: $H_2(g) \leftrightarrow 2H_{abs}$ (4)

Complete oxidation:

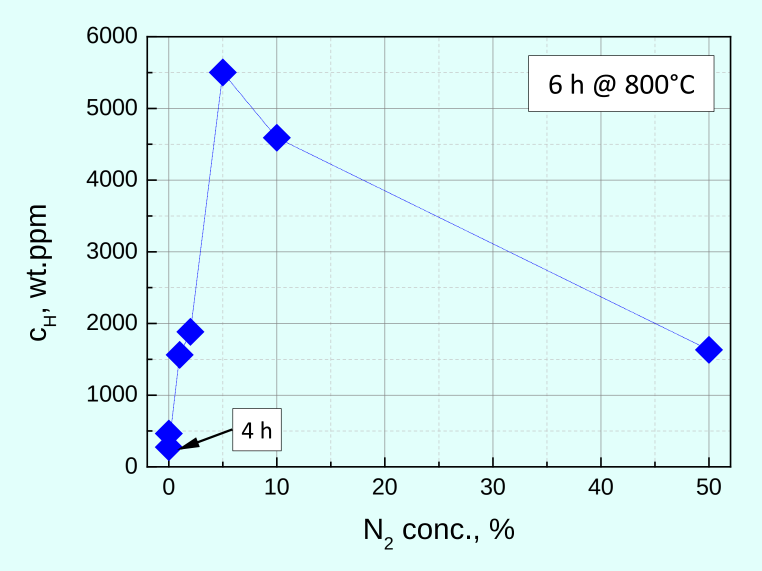
$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$ (1)+(2.1) / (1)+(2.2)+(3)

$H_2(g) \leftrightarrow 2H_{abs}$ (4)

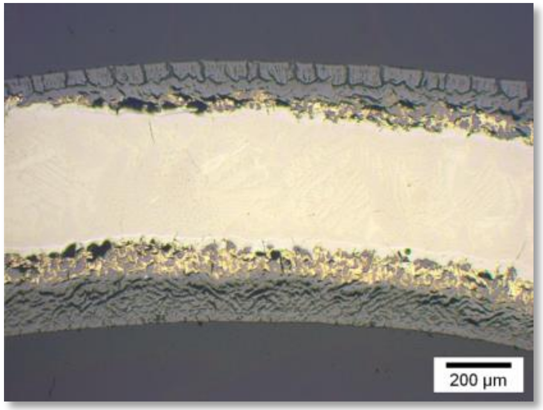
➡ Nitrogen acts like a catalyst

Effect of hydrogen

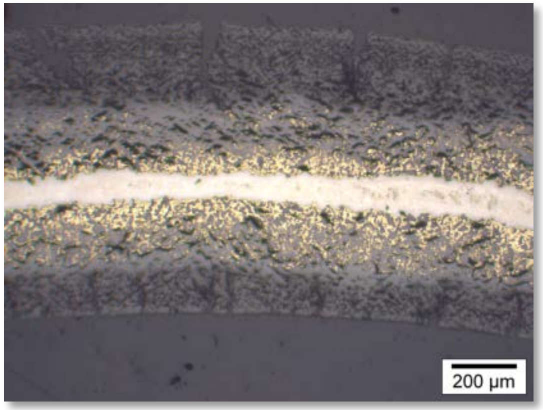
- Hydrogen produced by steam oxidation of Zr may be (i) released to the environment or (ii) absorbed by the metal
- Hydrogen stabilizes the β-Zr phase and may influence the oxygen/nitrogen solubility in the metal
- Hydrogen locally reduces the oxygen partial pressure in pores and cracks and hence affects the stability region of ZrN



H uptake by the metal



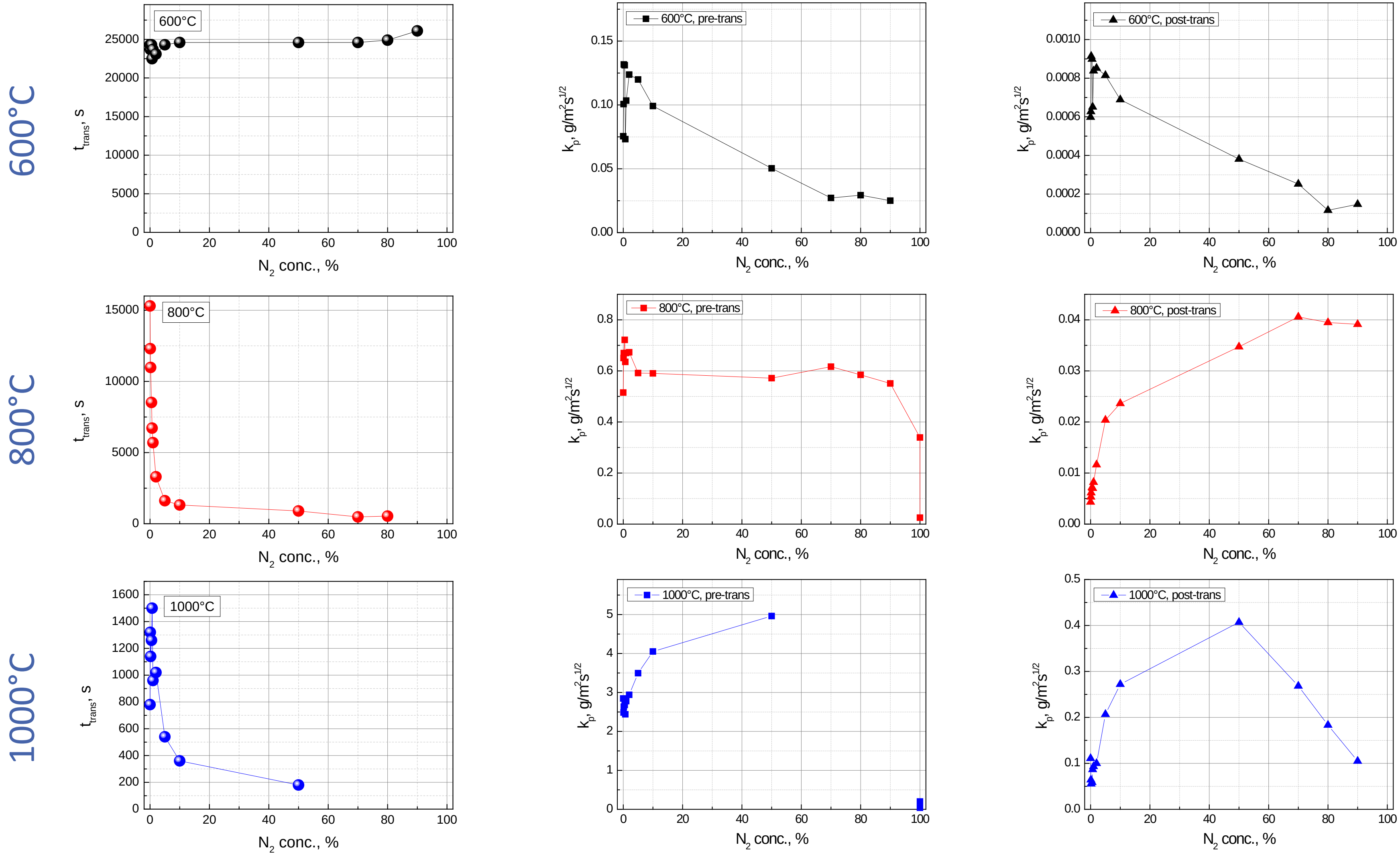
1 h, 1000°C, 80/20 N_2/O_2



1 h, 1000°C, 80/20 N_2/H_2O

Transition times and rate constants

Transition times | Parabolic rate const. | Linear rate const.



Summary

- The strong effect of nitrogen on the oxidation kinetics of zirconium alloys above 600°C was confirmed in these tests.
- Already very low concentrations of nitrogen (in steam) as well as of steam (in nitrogen) significantly affect reaction kinetics.
- Nitrogen reduces transition time from protective to non-protective oxide scale (breakaway) at 800 and 1000°C.
- Nitrogen seems to influence also the pre-transition reaction kinetics at higher temperatures.
- The formation of zirconium nitride, ZrN, and its re-oxidation is the main reason for the strongly porous oxide scales after transition and the much faster kinetics.
- Results are safety relevant, and they should be taken into account for experimental work on HT oxidation of Zr alloys.

Karlsruhe Institute of Technology

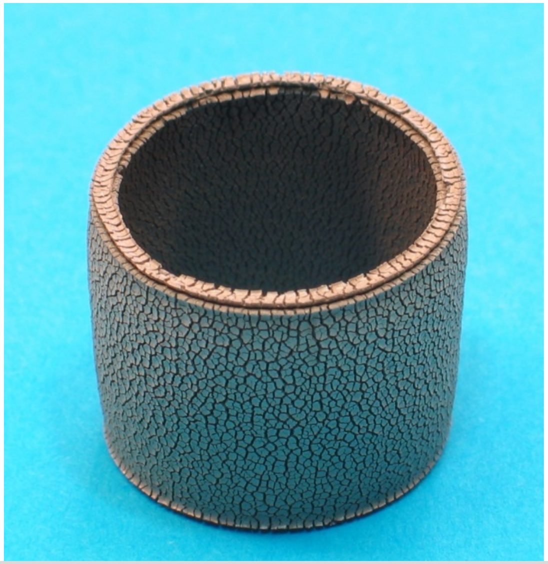
Institute for Applied Materials

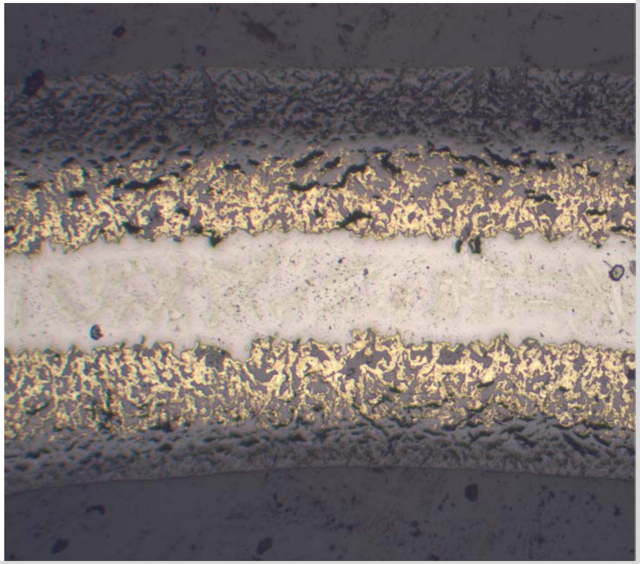
Zry-4 oxidation in mixed steam-nitrogen atmospheres

M. Steinbrück, F. Oliveira da Silva, H.J. Seifert

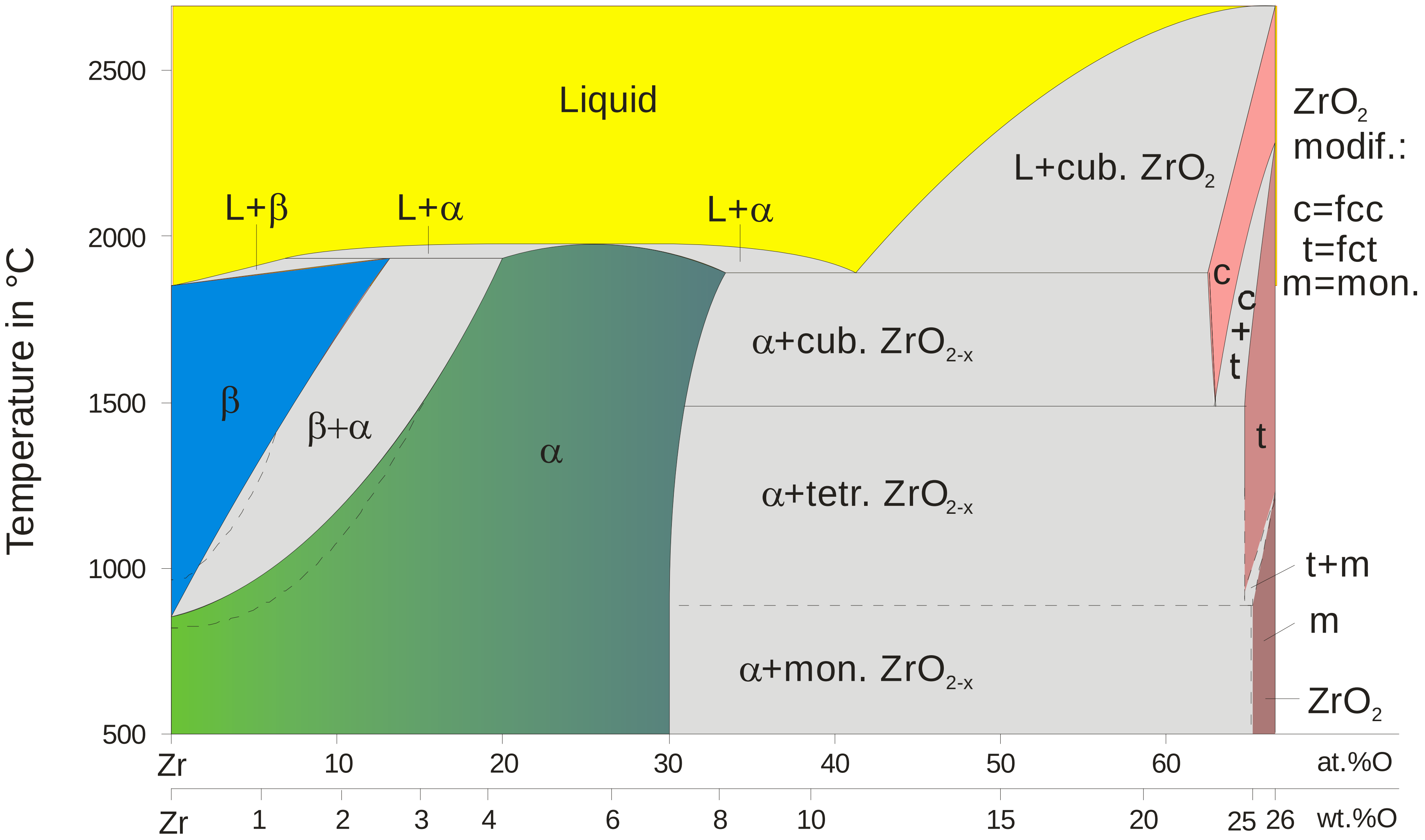
NuMat 2014*: The Nuclear Materials Conference, 27-30 October 2014, Clearwater Beach, Florida, USA*

Institute for Applied Materials IAM-AWP & Program NUKLEAR

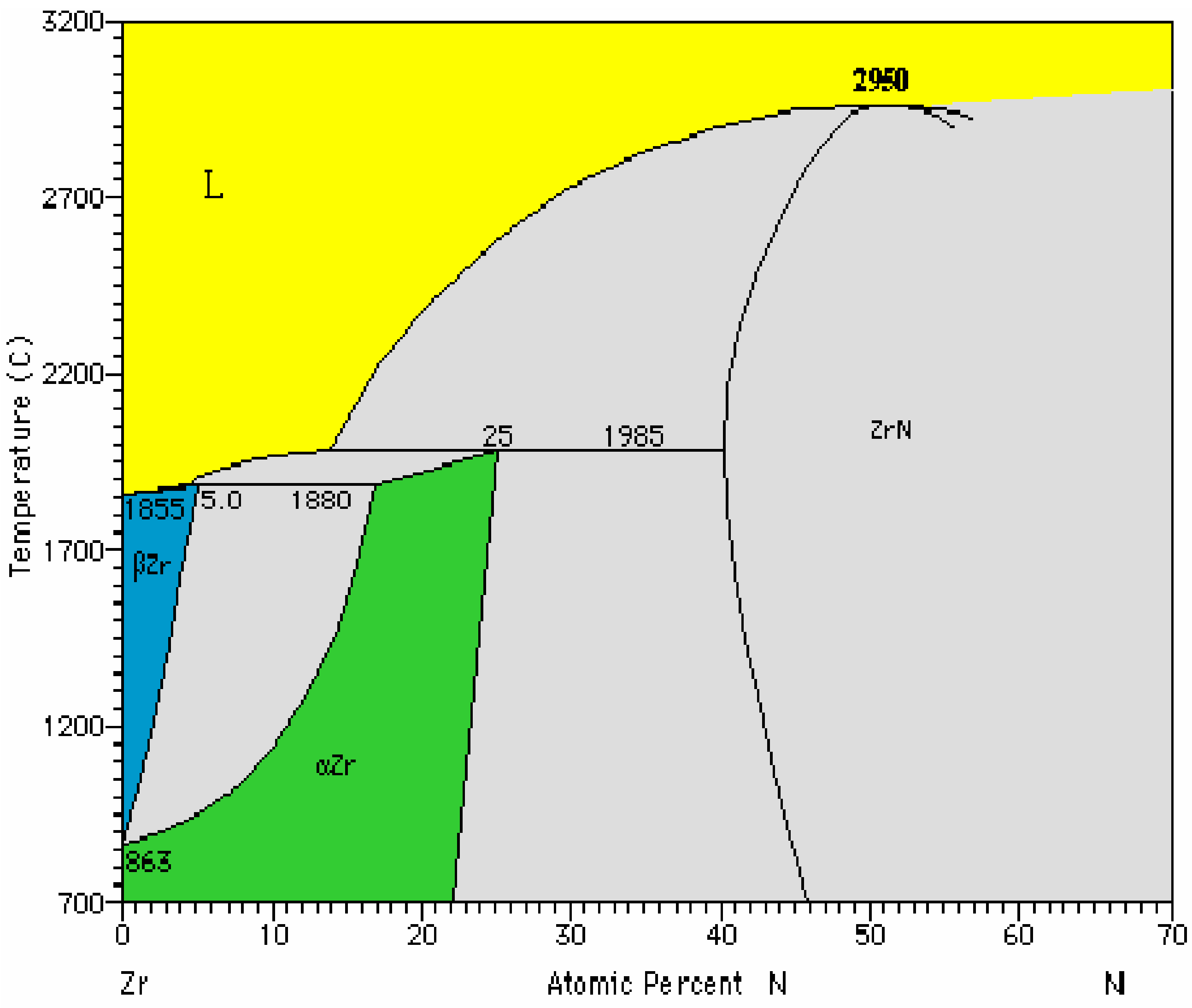




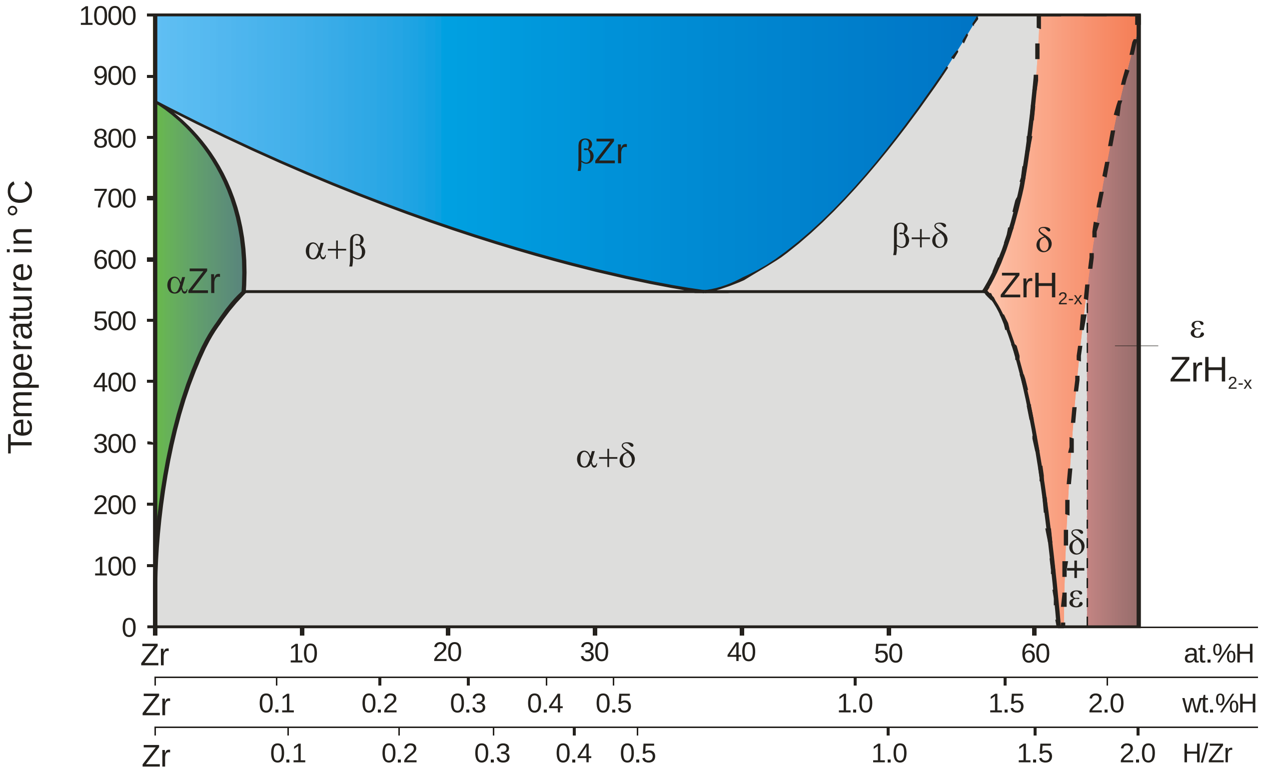
Phase diagram Zr - O



Phase diagram Zr-N



Phase diagram Zr - H



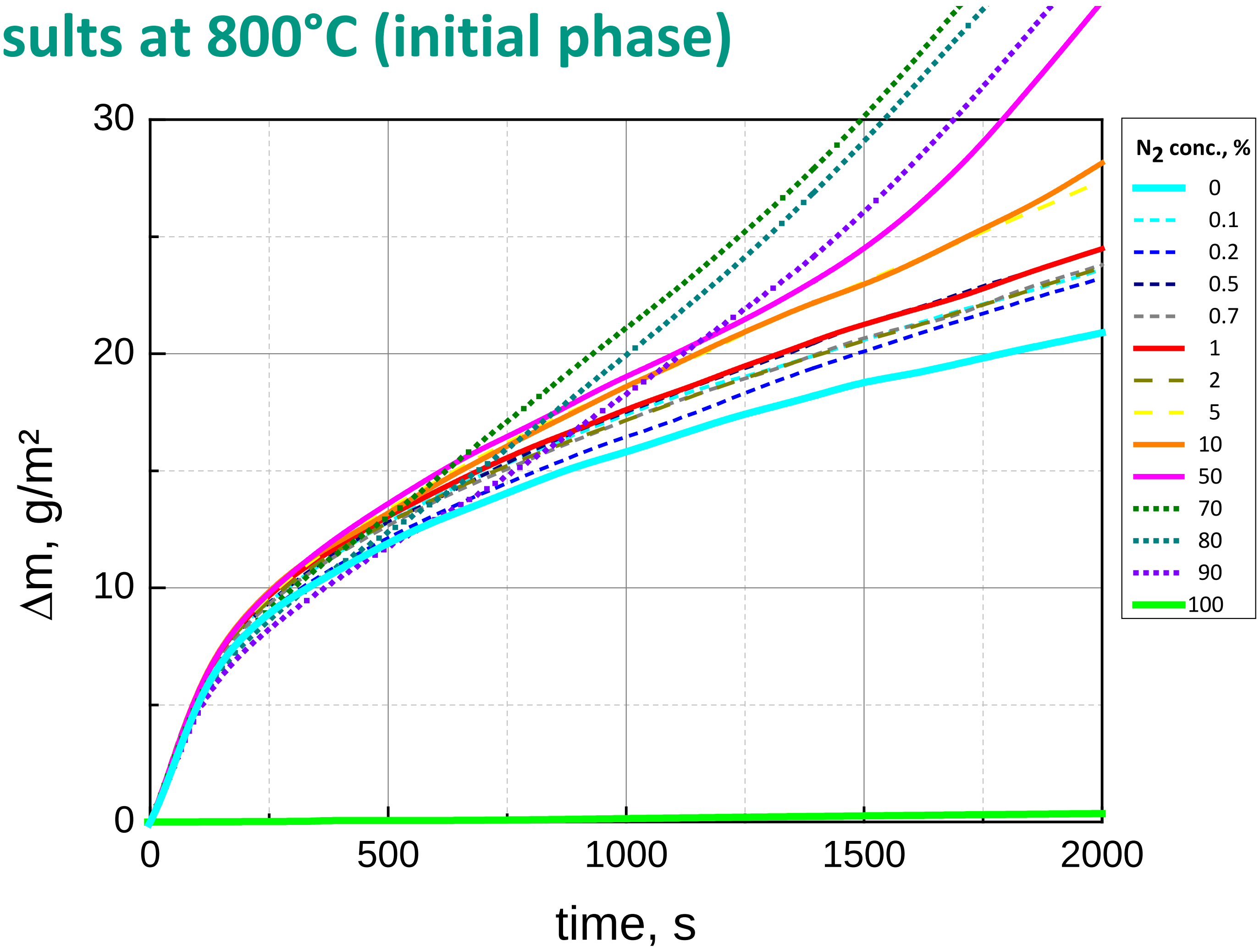
Sieverts' law:

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

with

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

TG results at 800°C (initial phase)



- Deviation from (sub-)parabolic kinetics after >700 s (after 7 hours in pure steam)