Karlsruhe Institute of Technology

Institute for Applied Materials

Zry-4 oxidation in mixed oxygen-nitrogen atmospheres

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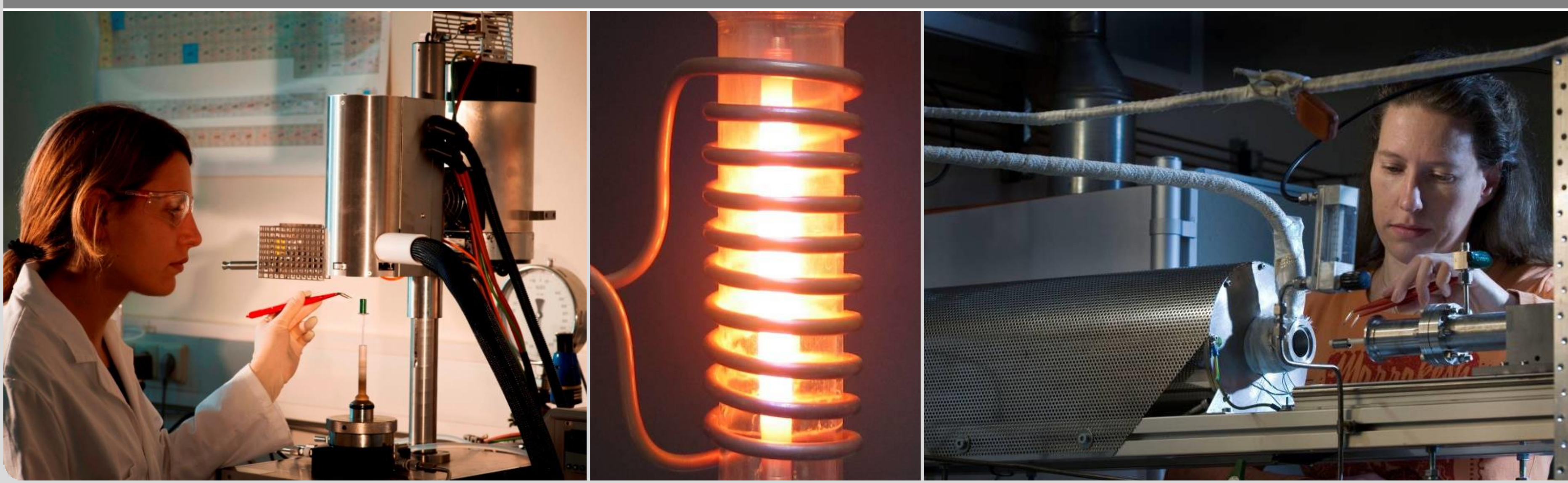
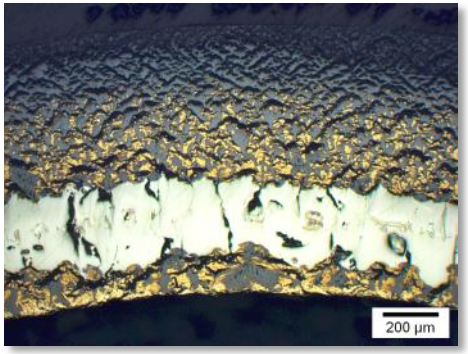
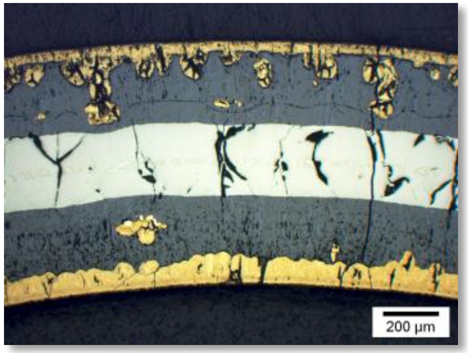
Institute for Applied Materials IAM-AWP & Program NUKLEAR

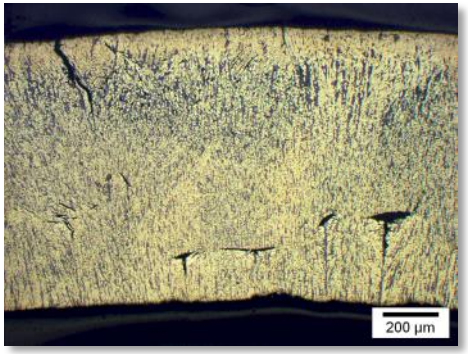


Motivation

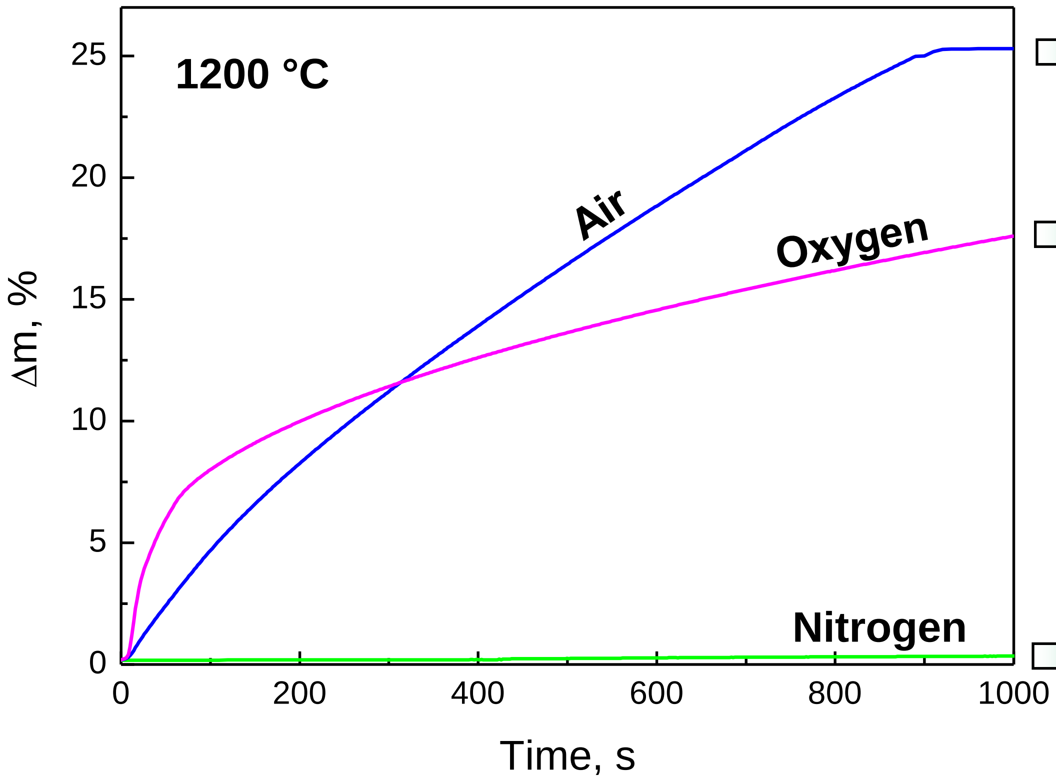
- Air ingress and Zr oxidation in atmospheres containing nitrogen is of actual interest in many countries
  - OECD SFP project indicated a strong need for more experiments
  - PhD thesis EdF and PSI just started
- Air oxidation of Zr alloys is very complex
- During air oxidation, the oxygen/nitrogen ratio changes due to preferred consumption of oxygen
- Which range of composition is affected by the mutual interaction of oxide and nitride formation?
- Experiments in oxygen-nitrogen model mixtures can be used for modeling purposes







Oxidation of Zr alloys in N_2, O_2 and air



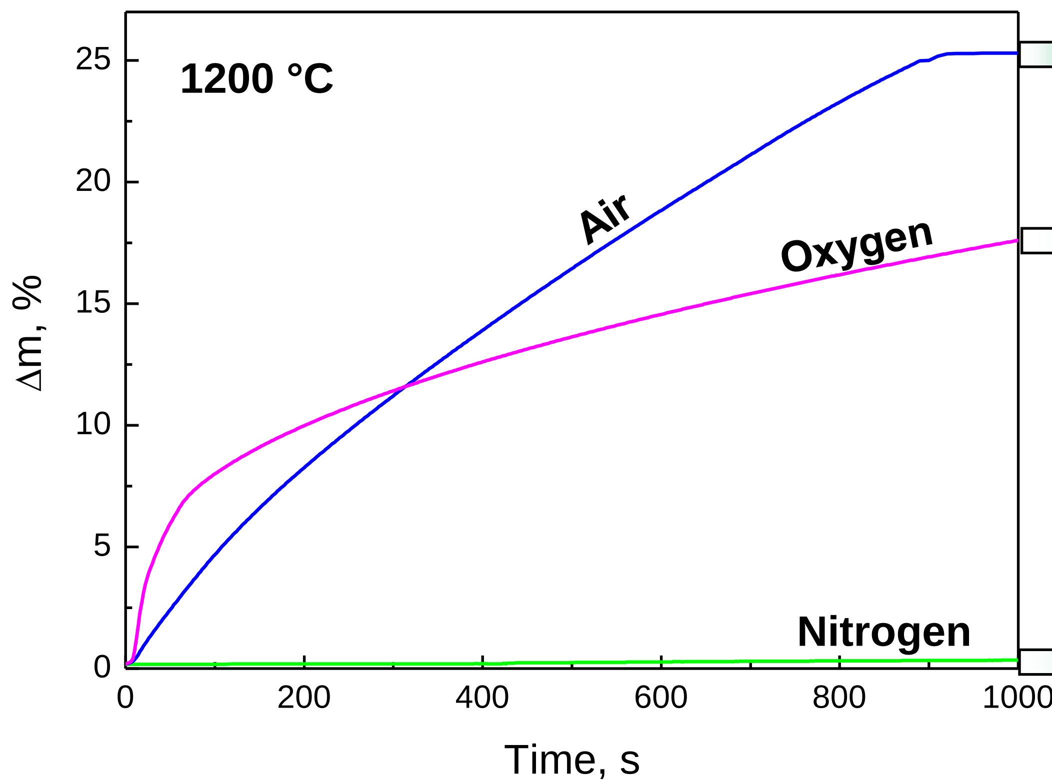
~ Linear oxidation kinetics

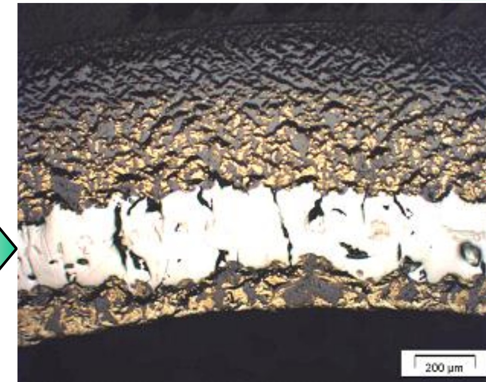
Parabolic oxidation kinetics

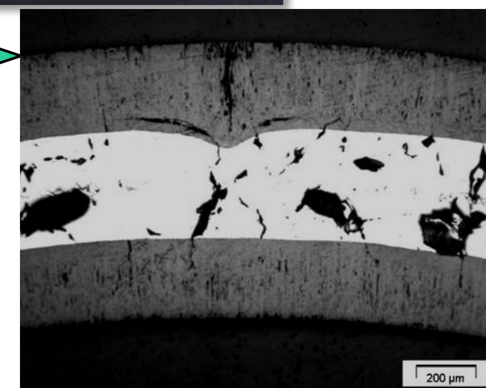
Parabolic reaction kinetics

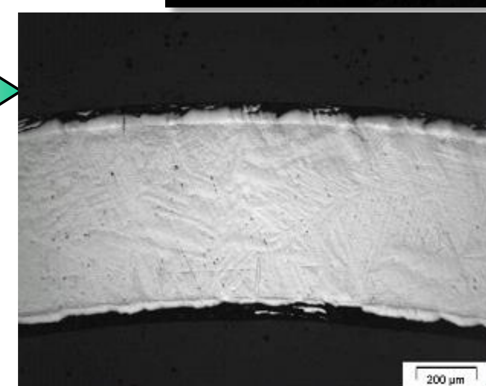
Oxidation rate in air is much higher than in oxygen or steam

Oxidation of Zr alloys in N_2, O_2 and air









Experimental setup

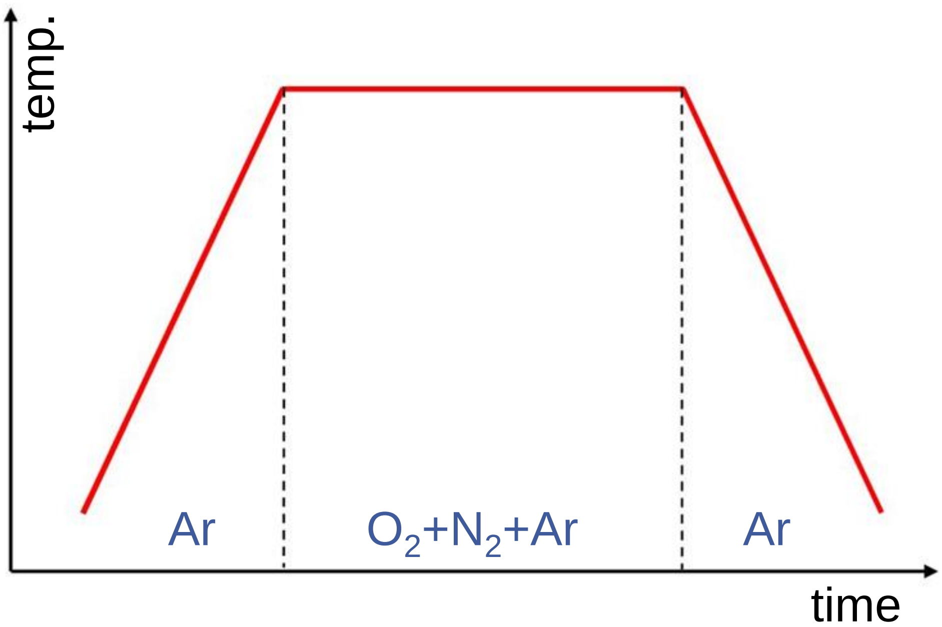
Thermal balance (STA-409)

Mass spectrometer

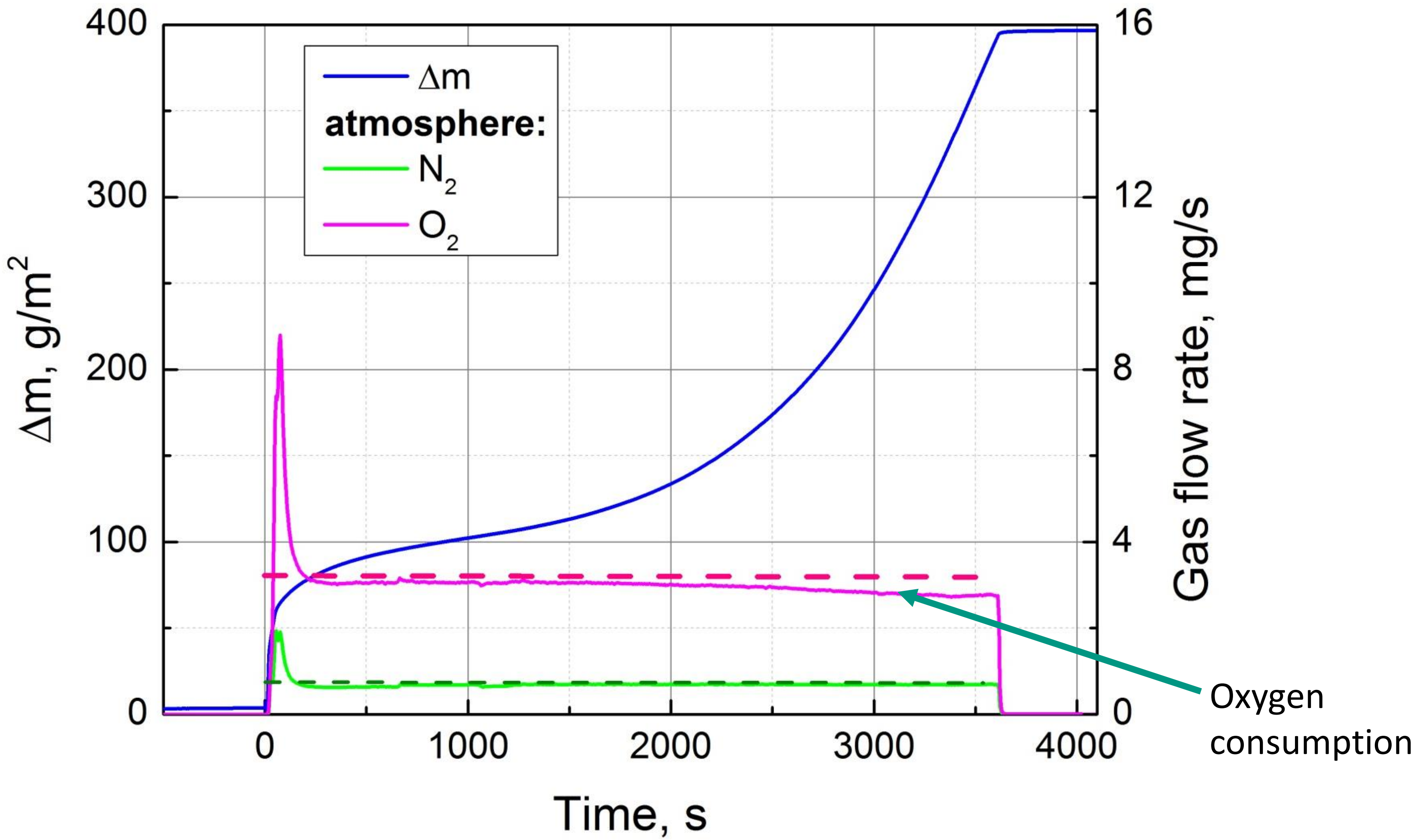
MFCs

Samples and test matrix

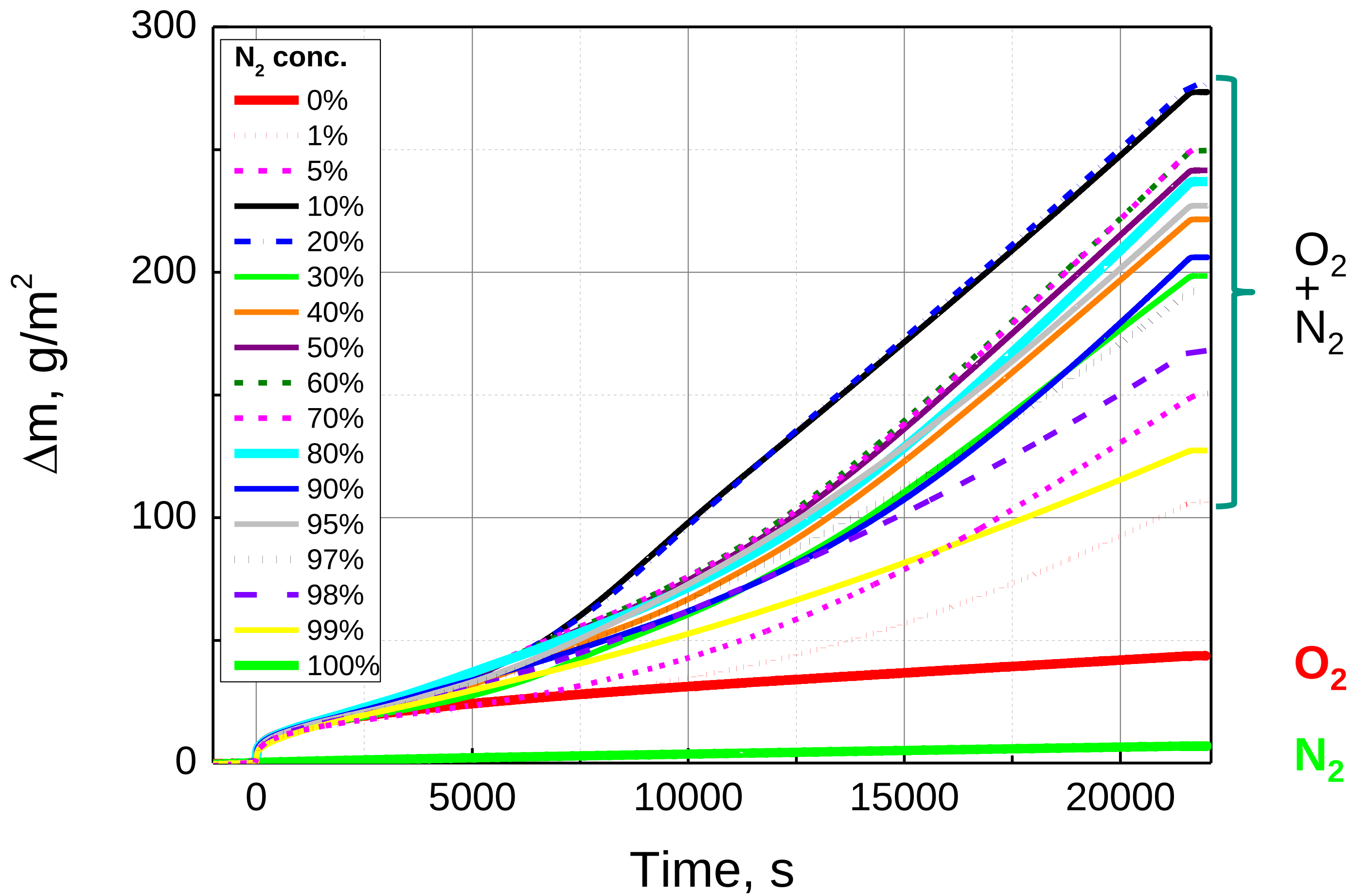
- 2 cm cladding tube segments made of Zircaloy-4
- Isothermal tests
- Temperatures and times:
  6 h @ 800°C
  1 h @ 1000°C
  15 min @ 1200°C
- Atmospheres:
  0-100% nitrogen incl. 1 and 99%
- Flow rates:
  10 l/h O_2+N_2, 3 l/h Ar



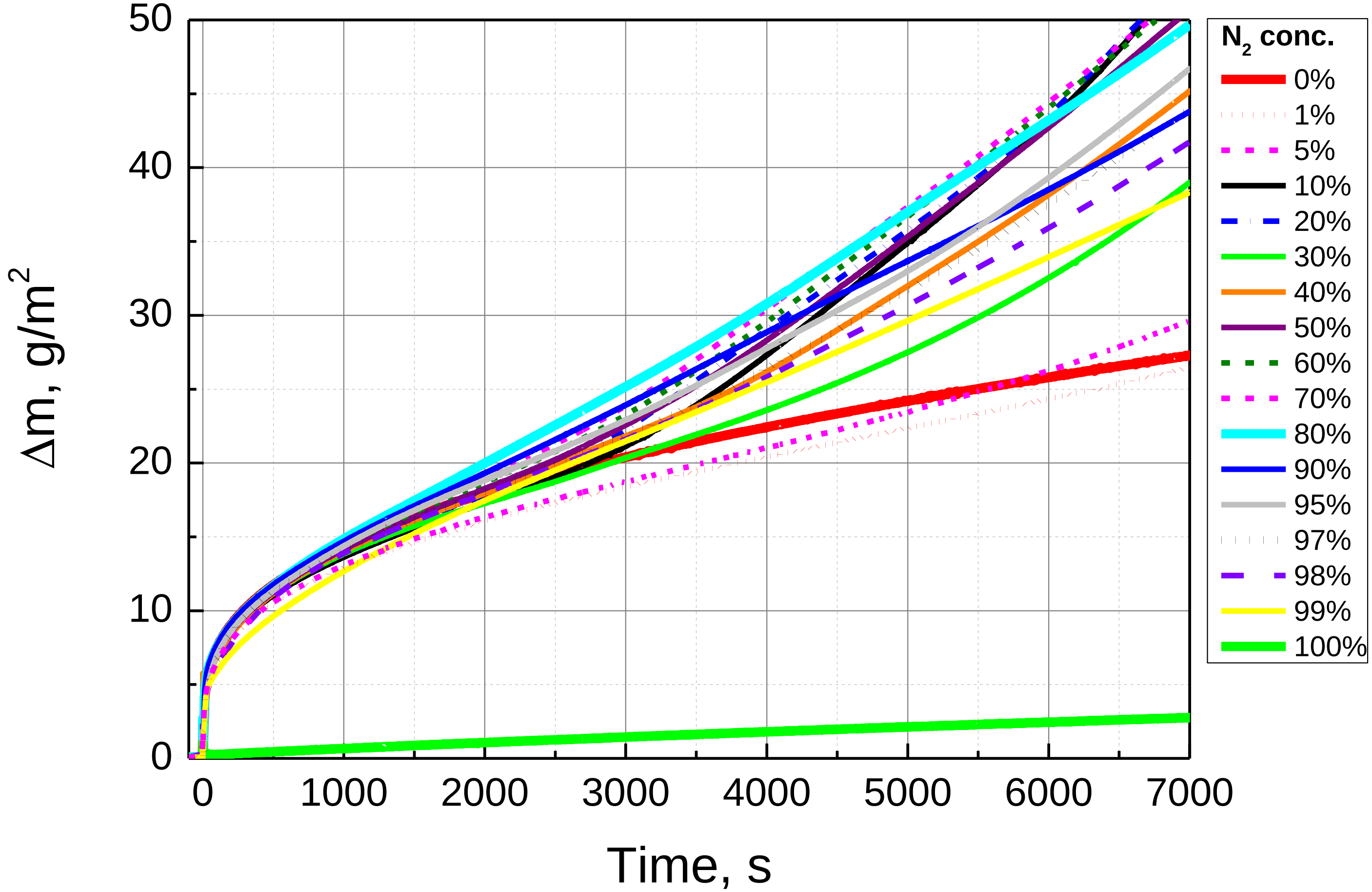
Test conduct; example 1000°C, 80% O_2 + 20% N_2



TG results at 800°C

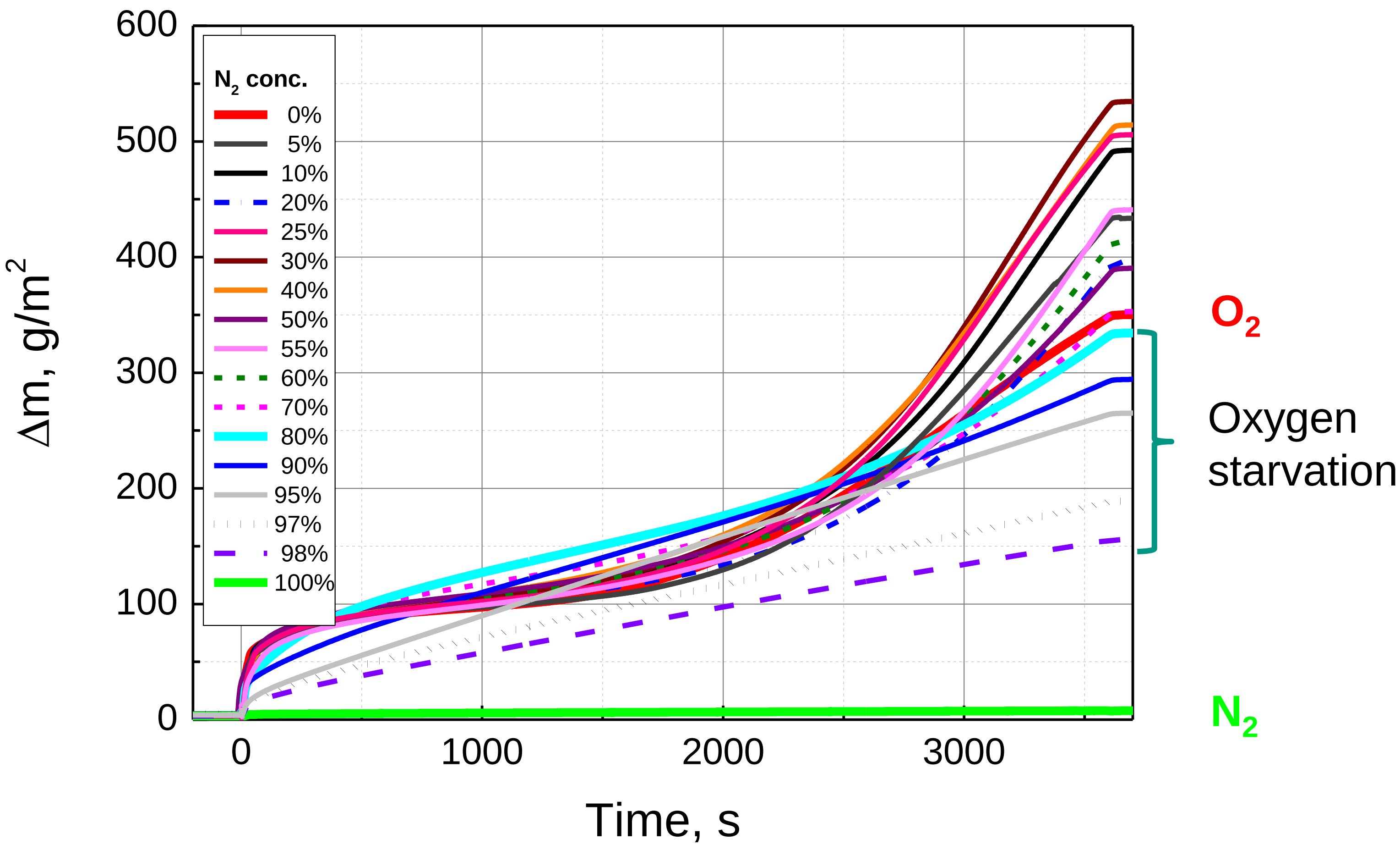


TG results at 800°C (initial phase)

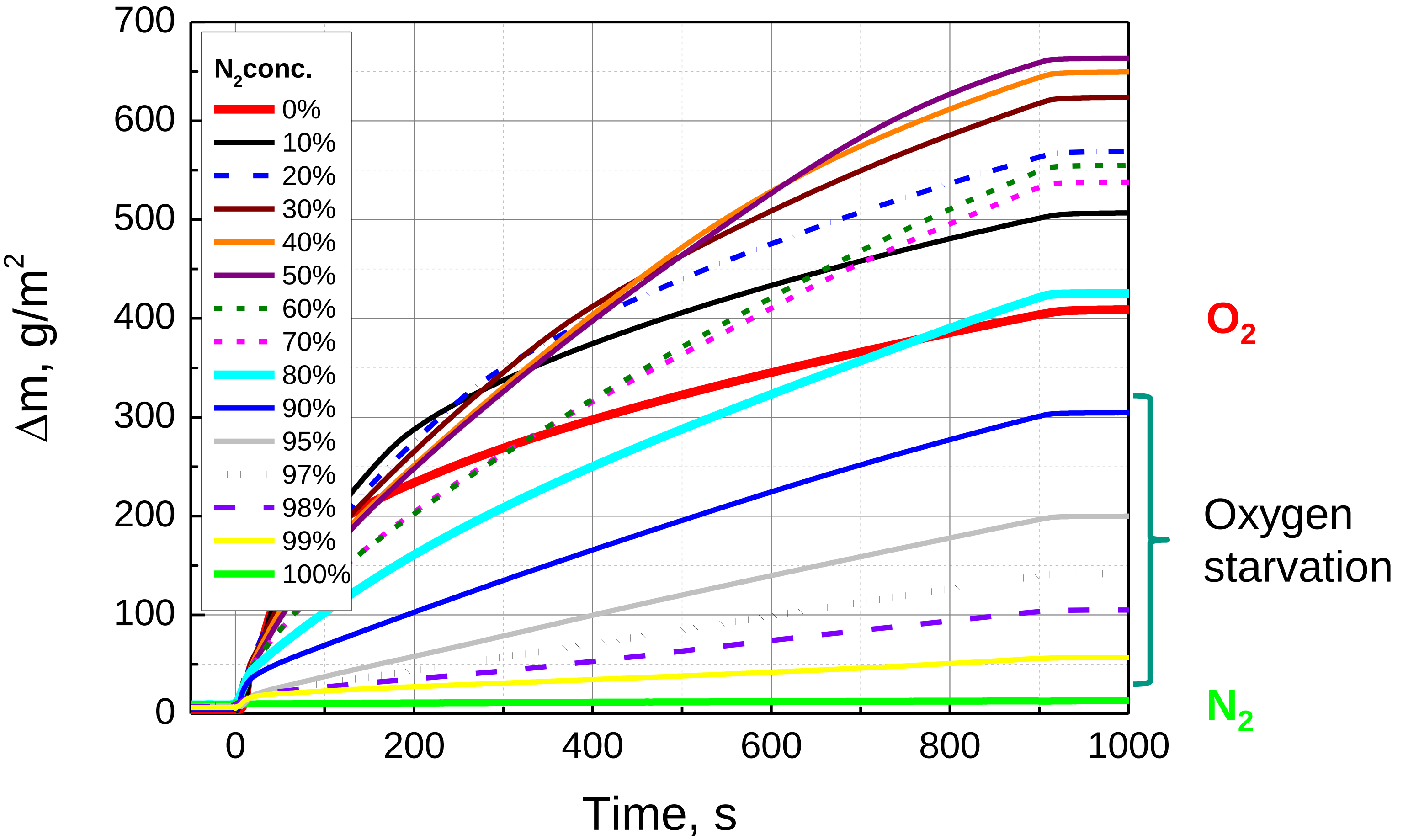


- Deviation from (sub-)parabolic kinetics after ca. 30 min (after 7 hours in pure oxygen)

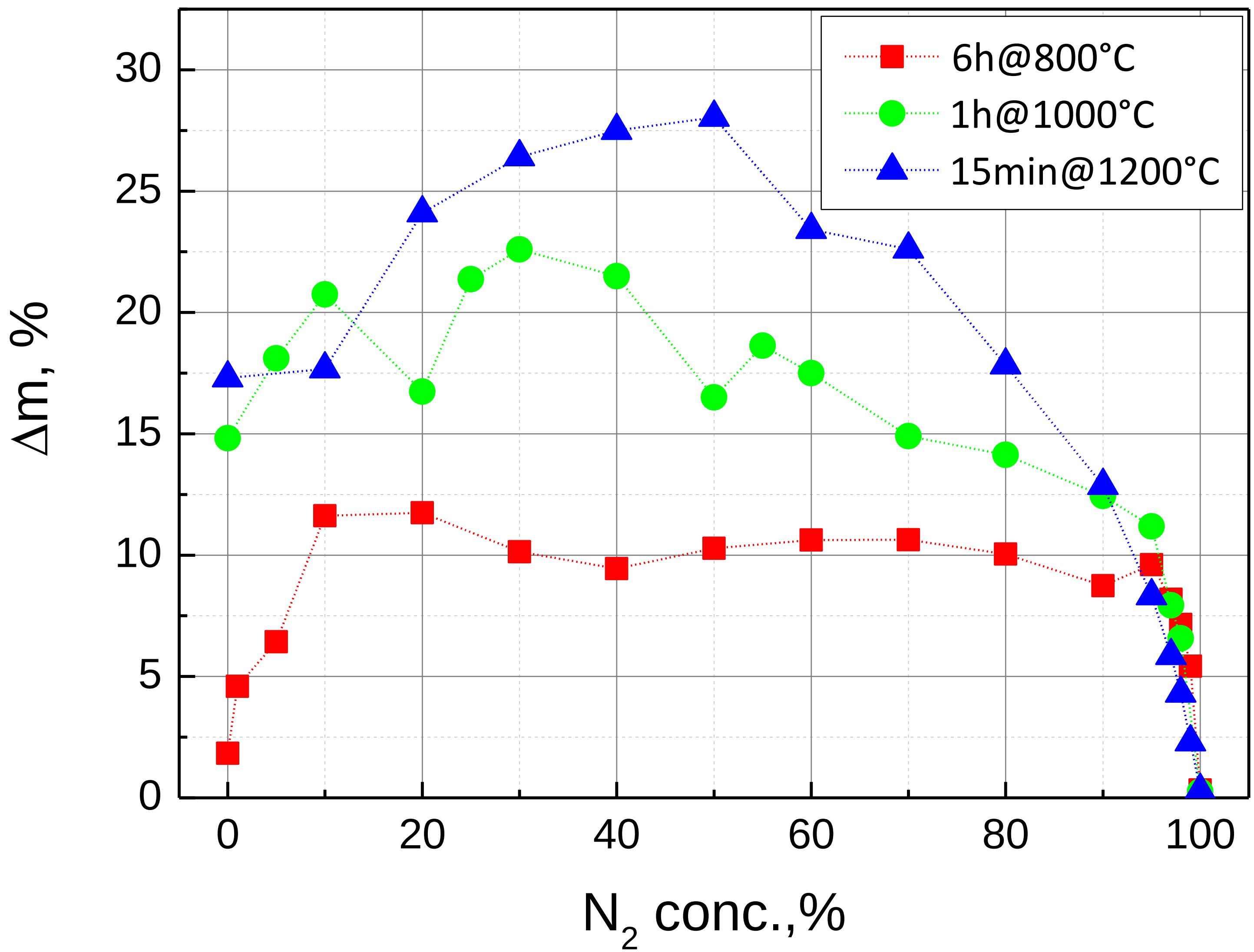
TG results at 1000°C



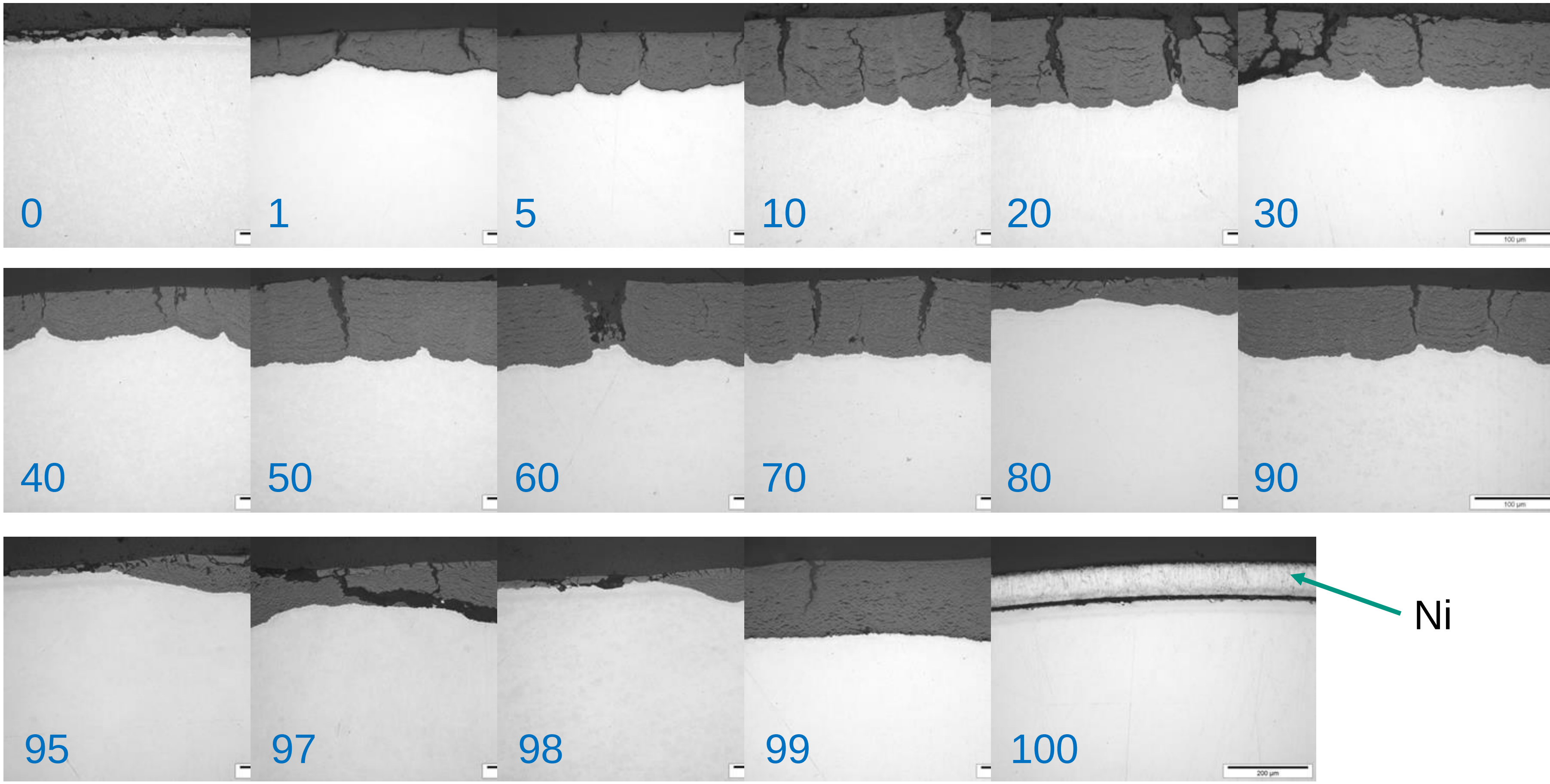
TG results at 1200°C



TG results summary

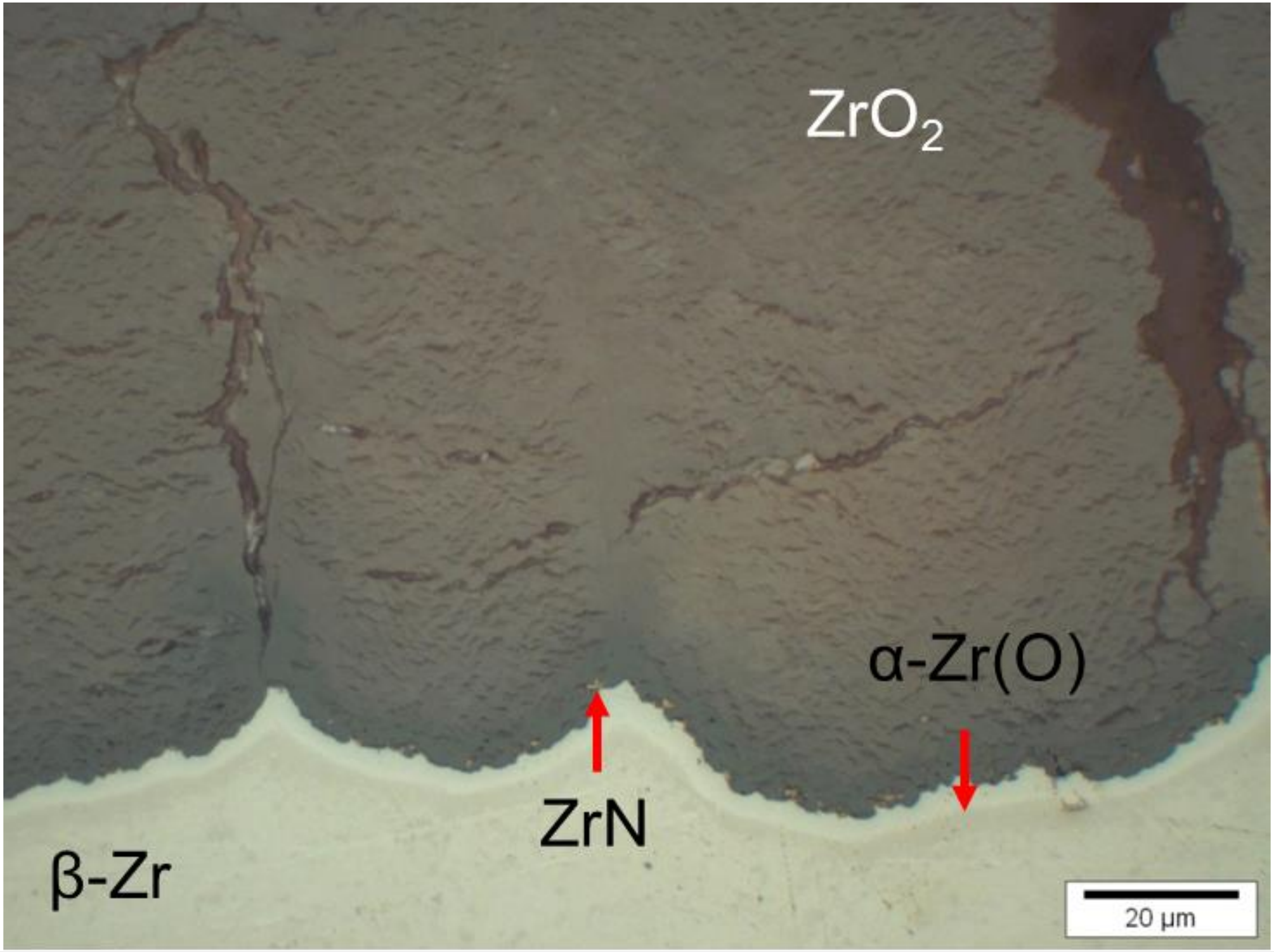


Micrographs of 800°C samples

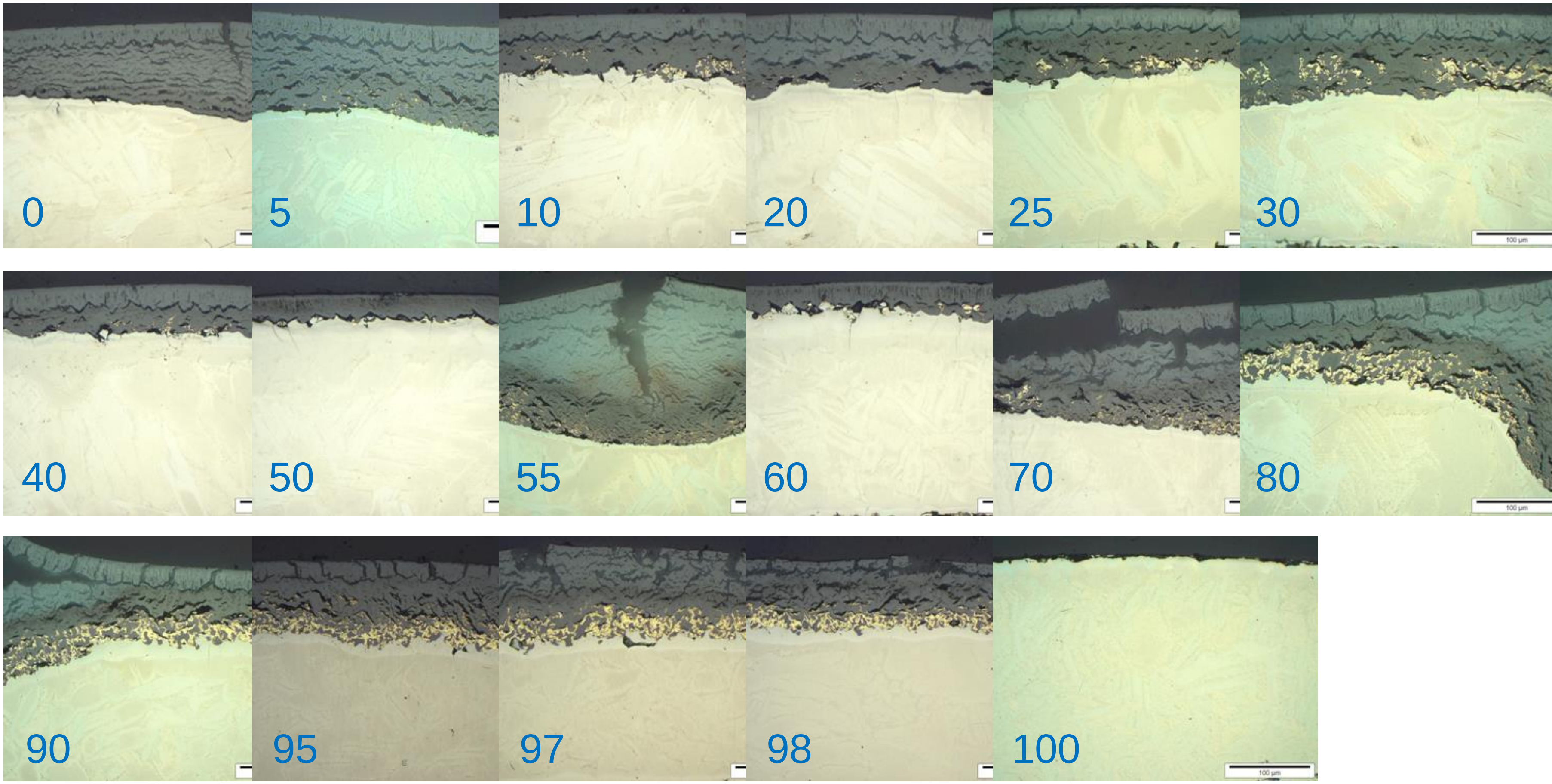


N_2 content in the mixture

Micrograph: 800°C, 10% nitrogen

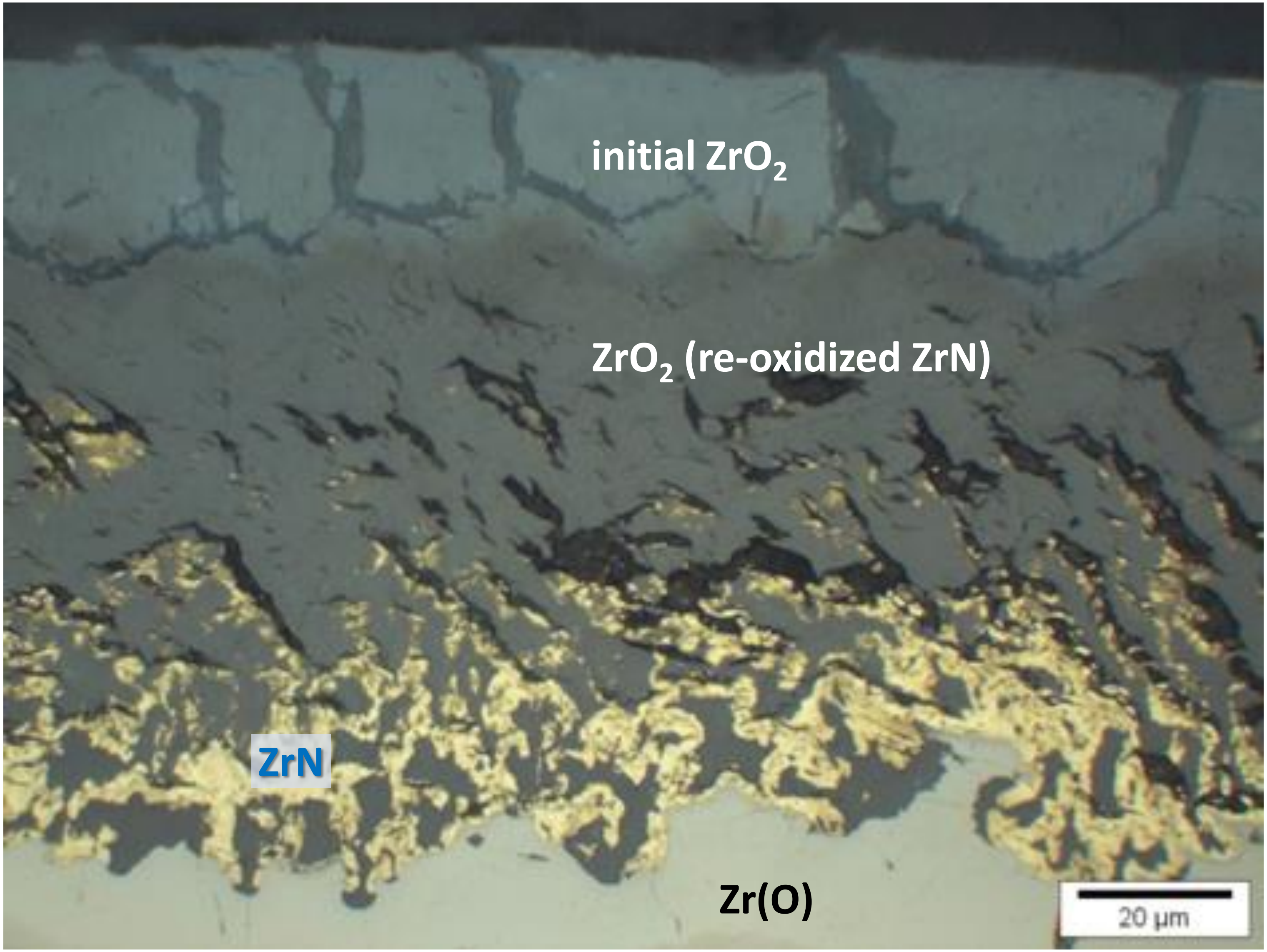


Micrographs of 1000°C samples

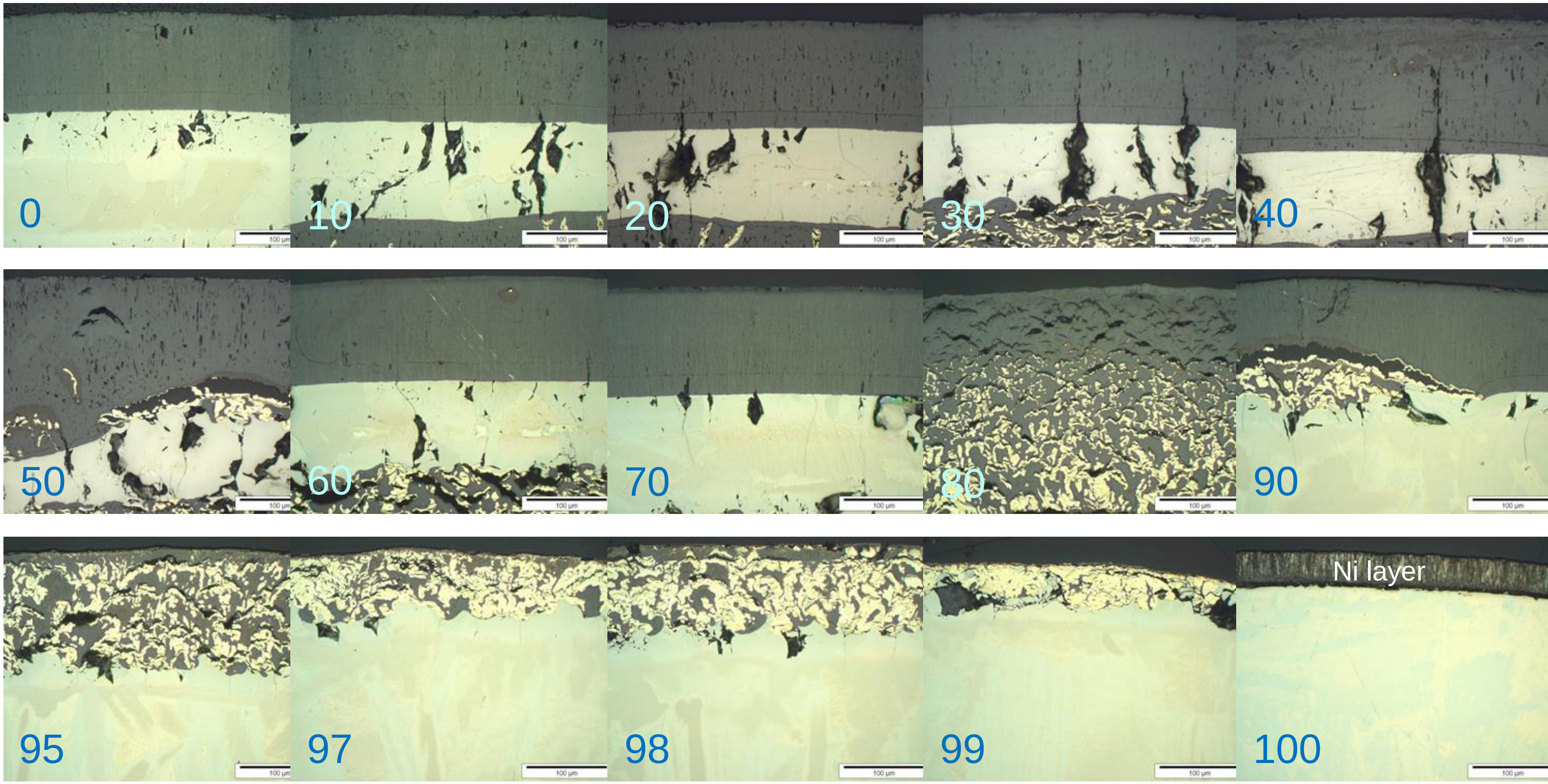


N_2 content in the mixture

Micrograph: 1000°C, 95% nitrogen

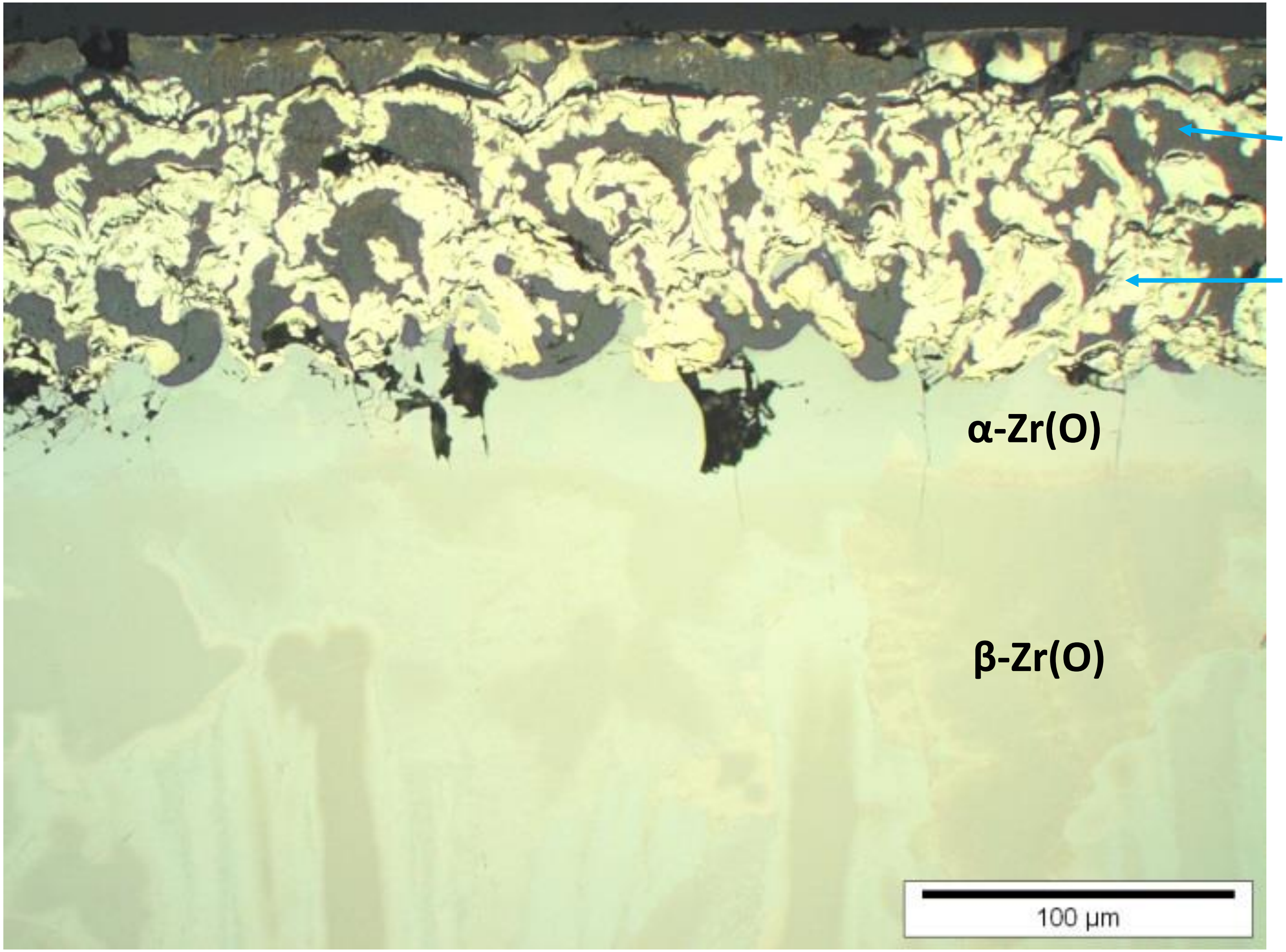


Micrographs of 1200°C samples

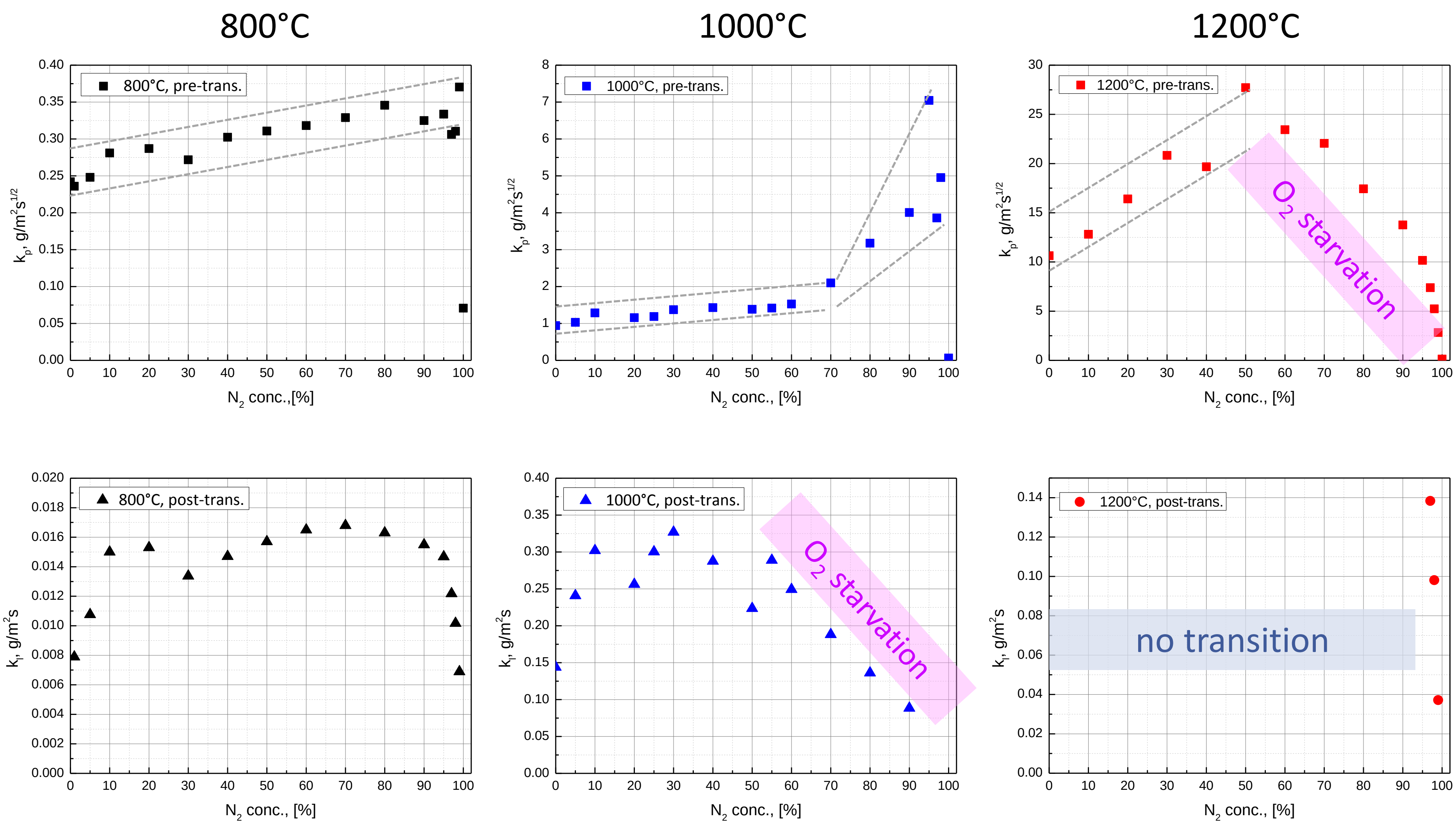


N_2 content in the mixture

Micrograph: 1200°C, 98% nitrogen



Parabolic (pre-trans.) and linear (post-trans.) rate constants



Summary

- The strong effect of nitrogen on the oxidation kinetics of zirconium alloys was confirmed in these tests
- Already very low concentrations of nitrogen (in oxygen) as well as of oxygen (in nitrogen) strongly affect reaction kinetics.
- Nitrogen strongly reduces transition time from protective to non-protective oxide scale (breakaway).
- The formation of zirconium nitride, ZrN, and its re-oxidation is the main reason for the strongly porous oxide scales after transition.
- Nitrogen seems to affect also the pre-transition reaction kinetics. This effect increases with temperature.

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