Separate-effects tests on air ingress in the framework of SFP and KIT activities

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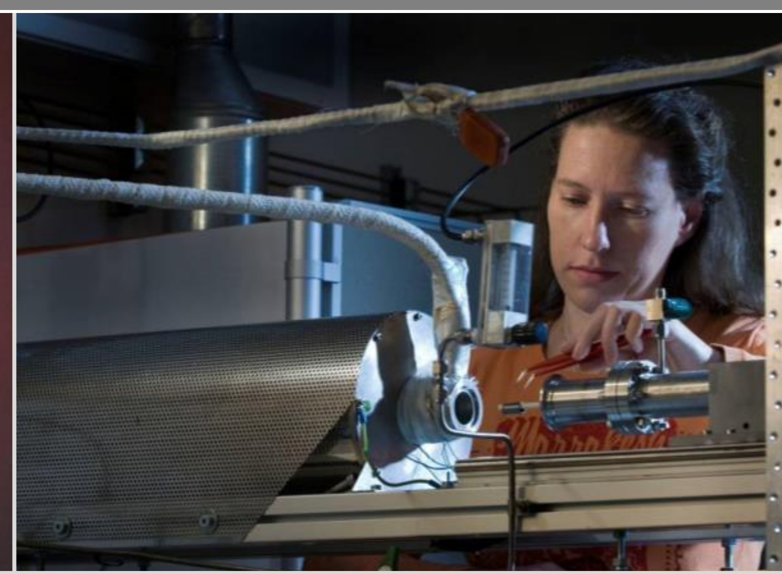
SFP Project Seminar 2013, OECD Conference Center, Paris, France, 22-23 October 2013

Institute for Applied Materials IAM-AWP & Program NUKLEAR



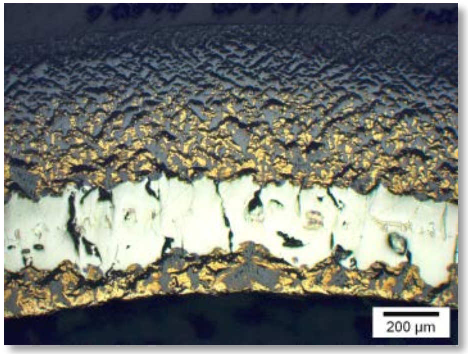


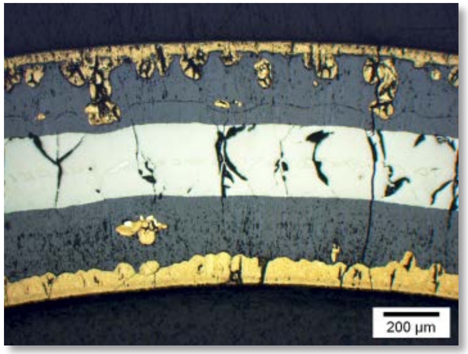
Outline

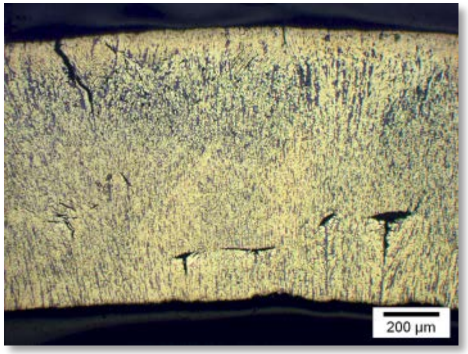
- Some words about air oxidation, especially the role of nitrogen

SFP related work

- Comparison of high-temperature oxidation of Zircaloy-2 and Zircaloy-4
- Experimental pre- and post-test simulation of oxidation during SFP phases I&II (pre-ignition and ignition)

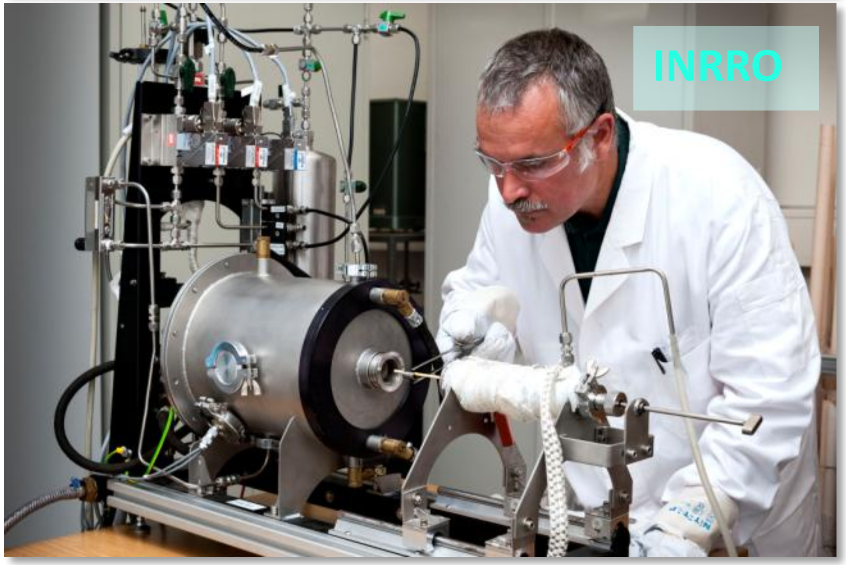






Experimental

- Most tests were conducted in a NETZSCH STA409 coupled with gas supply 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™)
- Atmospheres:
  steam, oxygen, air, nitrogen, mixtures of these
- Mostly isothermal tests, some transient experiments

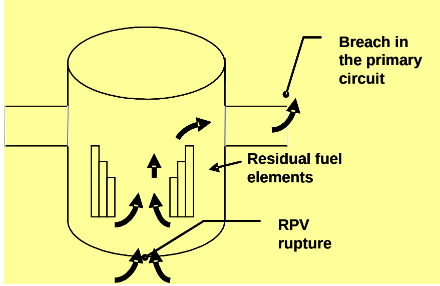


Oxidation in atmospheres containing nitrogen

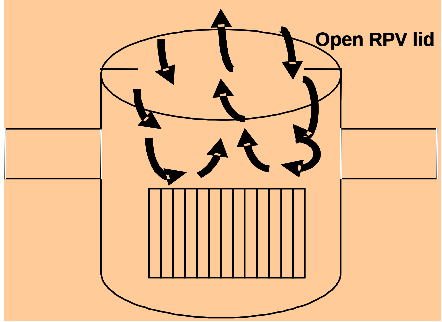
- Air ingress reactor core, spent fuel pond, or transportation cask
- Nitrogen in BWR containments (inertization) and ECCS pressurizers
- Prototypically following steam oxidation and mixed with steam

- 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

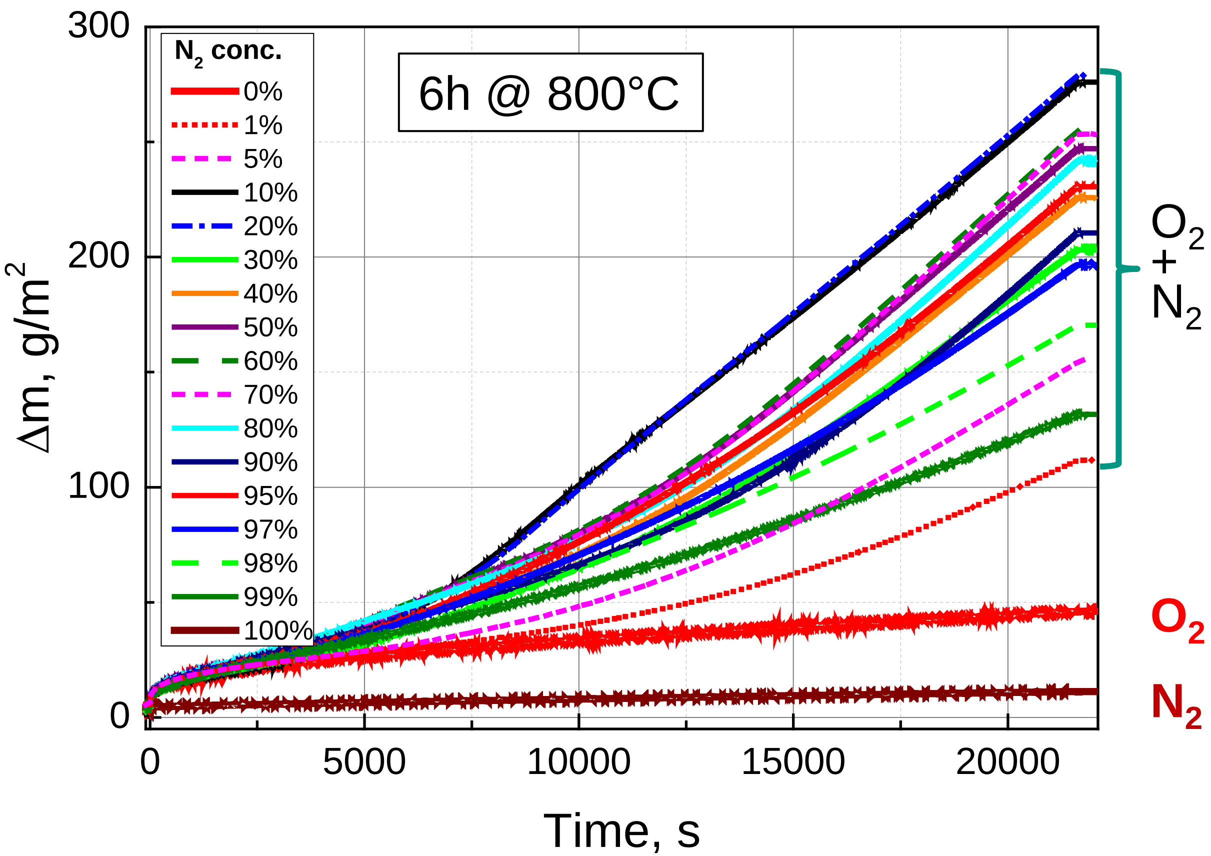


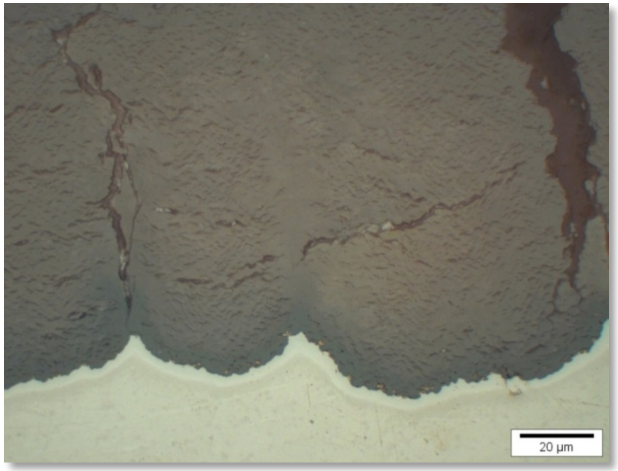
Mid loop operation



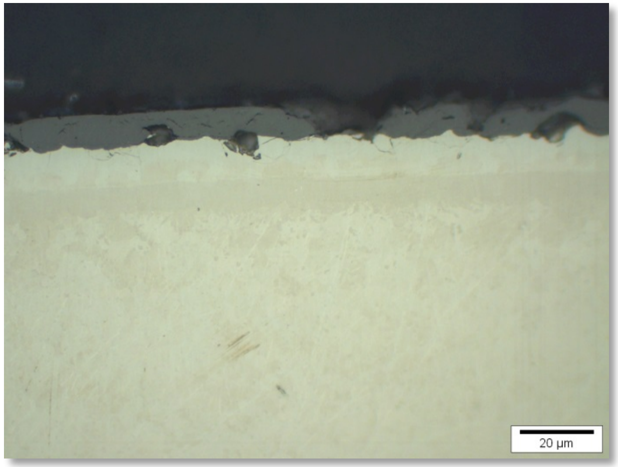
Spent fuel storage pool accident

Reaction of Zircaloy-4 in N_2-O_2 mixtures





10% N_2



0% N_2

- Strong effect of nitrogen on oxidation kinetics of Zry-4 in N_2-O_2 mixtures over a wide range of composition

Consequences of air ingress for cladding

1 hour at 1200°C in steam

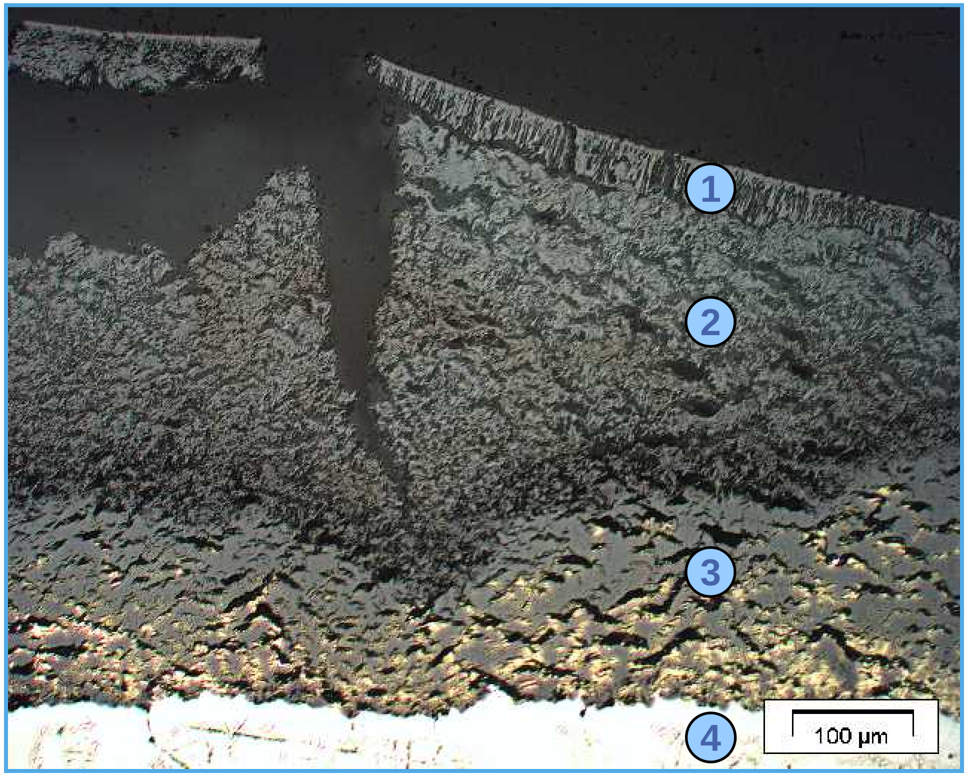
1 hour at 1200°C in air

→ Loss of barrier effect of cladding

Mechanism of air oxidation

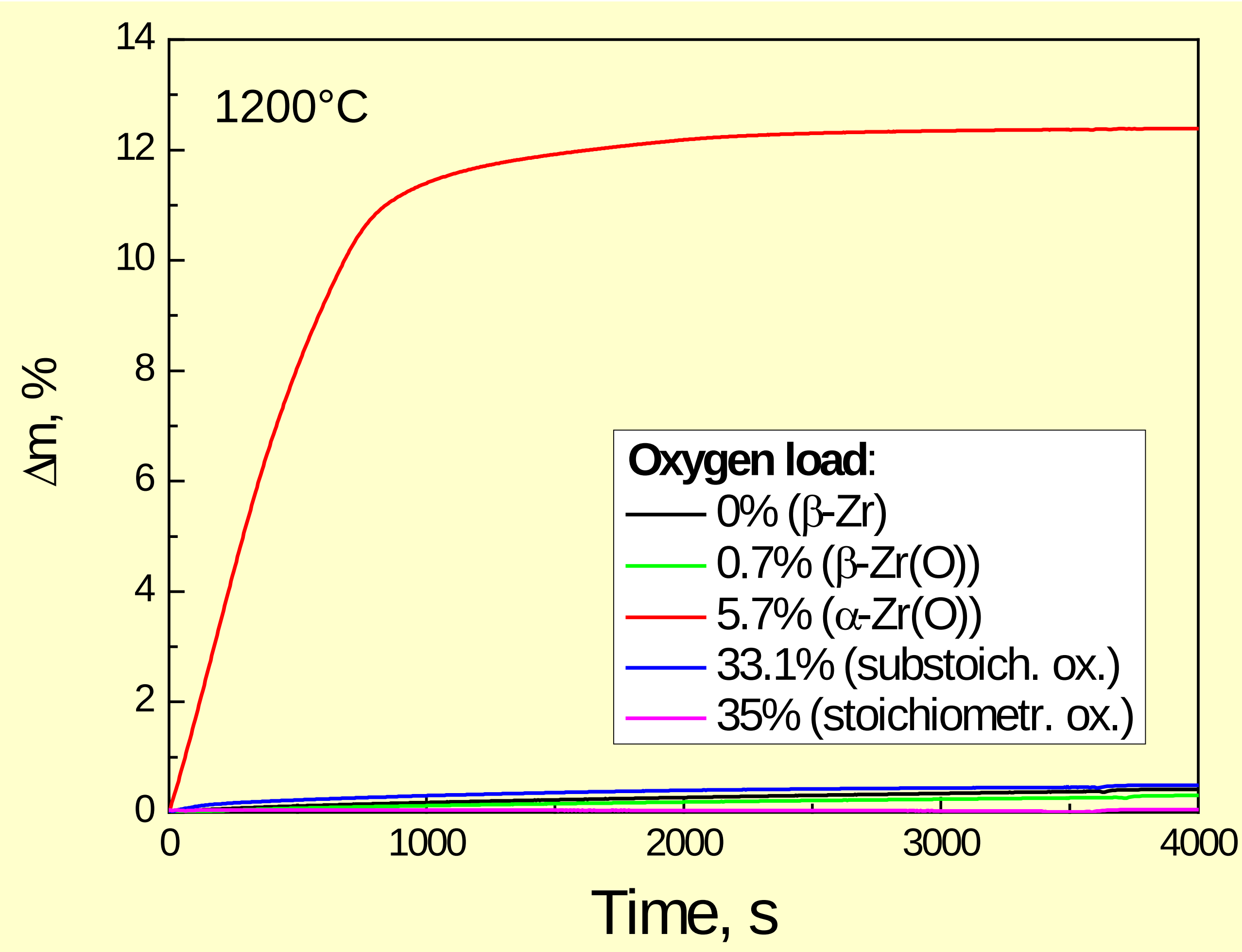
- Diffusion of air through imperfections in the oxide scale to the metal/oxide interface
- Consumption of oxygen
- Remaining nitrogen reacts with zirconium and forms ZrN
- ZrN is re-oxidized by fresh air with progressing reaction associated with a volume increase by 48%

➡ 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)

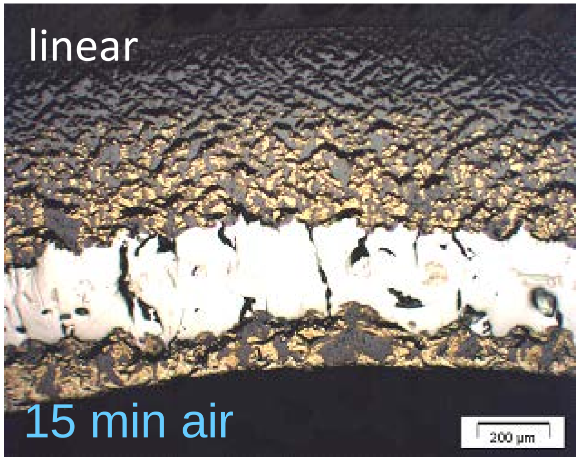
Reaction of ZrO_x with nitrogen

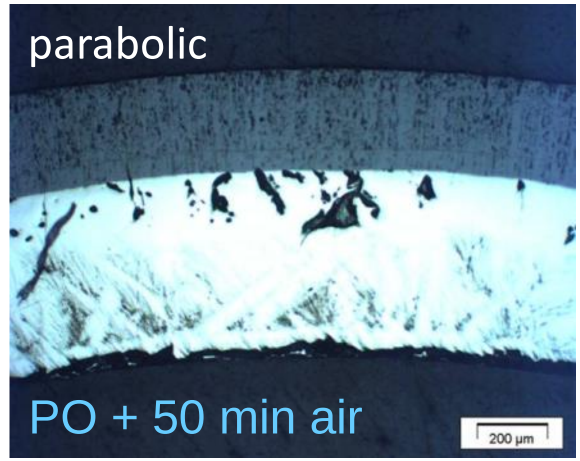


- Fast reaction of α-Zr(O) with nitrogen with linear kinetics

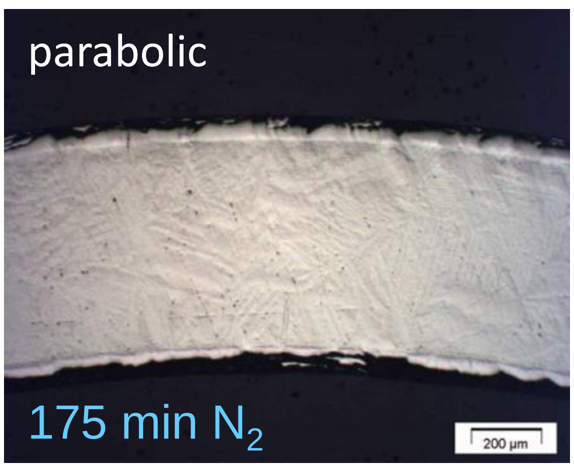
Influence of pre-oxidation (PO) in steam on subsequent reaction in air and nitrogen

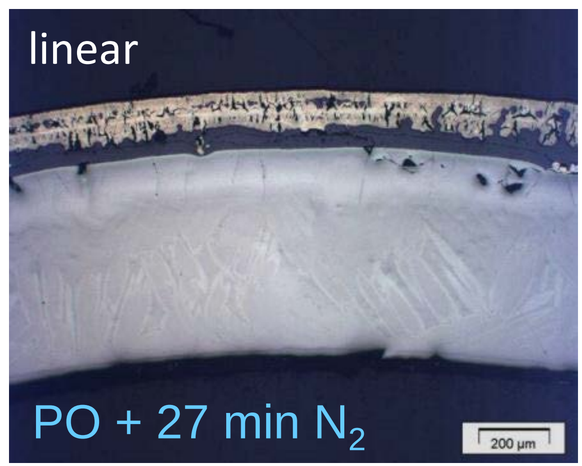
Example: Zry-4, 1200°C





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 in mixed steam-air atmospheres

Zry-4, 1 hour at 1200°C

H_2O

0.7 H_2O
0.3 air

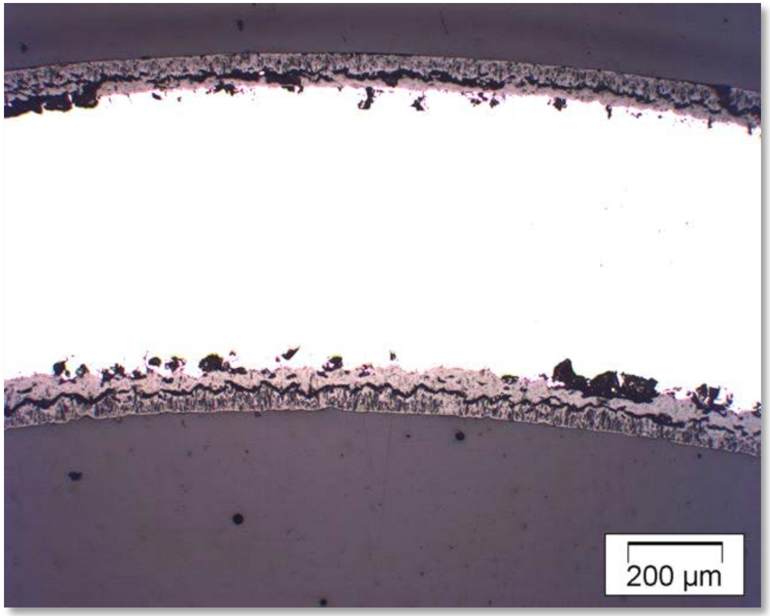
0.3 H_2O
0.7 air

0.1 H_2O
0.9 air

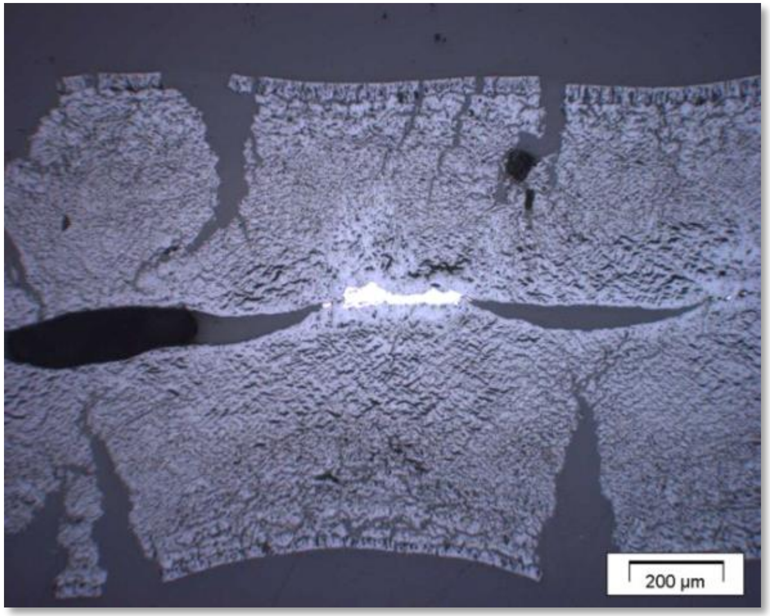
- Increasing degradation with raising content of air in the mixture

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

SFP related activities

- Proof of the similarity of high-temperature oxidation and mechanical properties of Zircaloy-2 (BWR) and Zircaloy-4 (PWR)
- Investigation of the influence of the swage-down process during manufacturing of the Zircaloy-2 heater rods
- Simulation of pre-ignition and ignition phases of SFP I&II
- Report distributed Nov 2010

Composition of Zircaloy-2 and Zircaloy-4

KIT Karlsruhe Institute of Technology

ATI Wah Chang Allegheny Technologies

TECHNICAL DATA SHEET

COMPOSITION (WEIGHT PERCENT)

Name	Zircaloy-2	Zircaloy-4
UNS Grade	R60802	R60804
Tin	1.20-1.70	1.20-1.70
Iron	0.07-0.20	0.18-0.24
Chromium	0.05-0.15	0.07-0.13
Nickel	0.03-0.08	---
Niobium	---	---
Oxygen	Per P.O.	Per P.O.
Iron + Chromium + Nickel	0.18-0.38	---
Iron + Chromium	---	0.28-0.37

MAXIMUM IMPURITIES, WEIGHT %

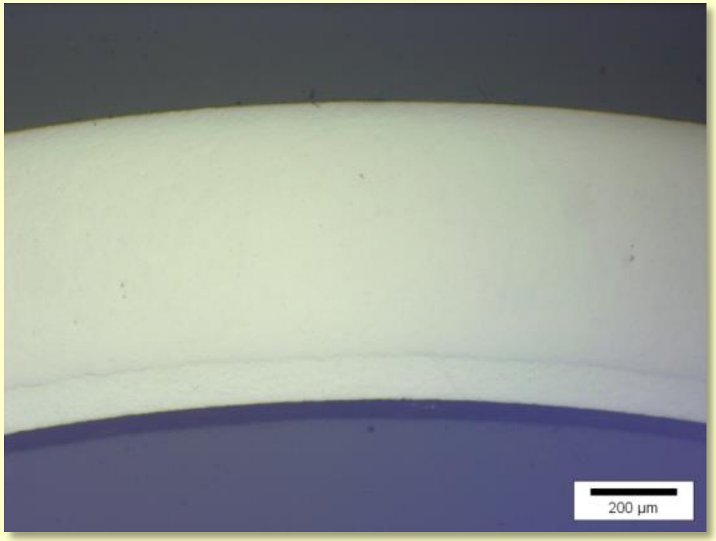
Name	Zircaloy-2	Zircaloy-4
Aluminum	0.0075	0.0075
Boron	0.00005	0.00005
Cadmium	0.00005	0.00005
Carbon	0.027	0.027
Chromium	---	---
Cobalt	0.0020	0.0020
Copper	0.0050	0.0050
Hafnium	0.010	0.010
Hydrogen	0.0025	0.0025
Iron	---	---
Magnesium	0.0020	0.0020
Manganese	0.0050	0.0050
Molybdenum	0.0050	0.0050
Nickel	---	0.0070
Nitrogen	0.0080	0.0080
Phosphorus	---	---
Silicon	0.0120	0.0120
Tin	---	---
Tungsten	0.010	0.010
Titanium	0.0050	0.0050
Uranium (total)	0.00035	0.00035

→ Very similar composition of both alloys

Specimens

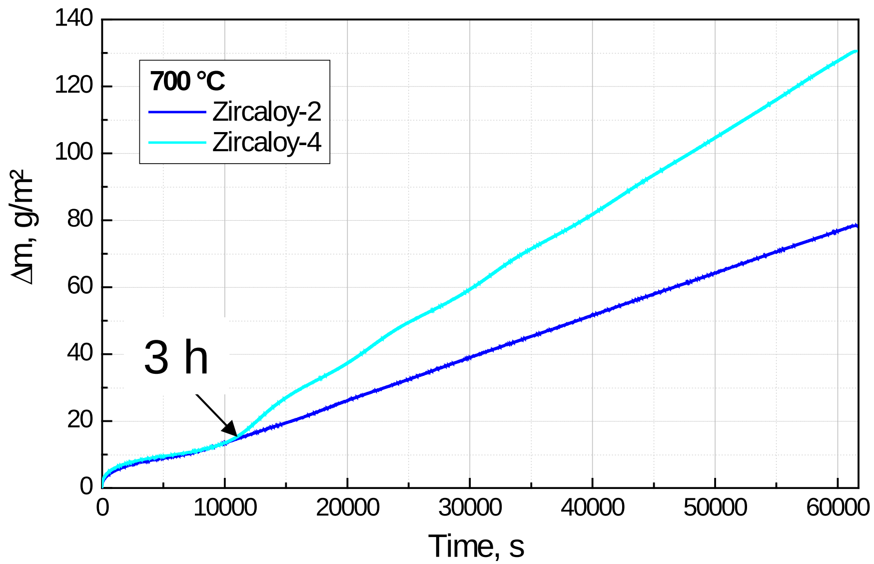
As-received Zry-2 and prototype heater rods

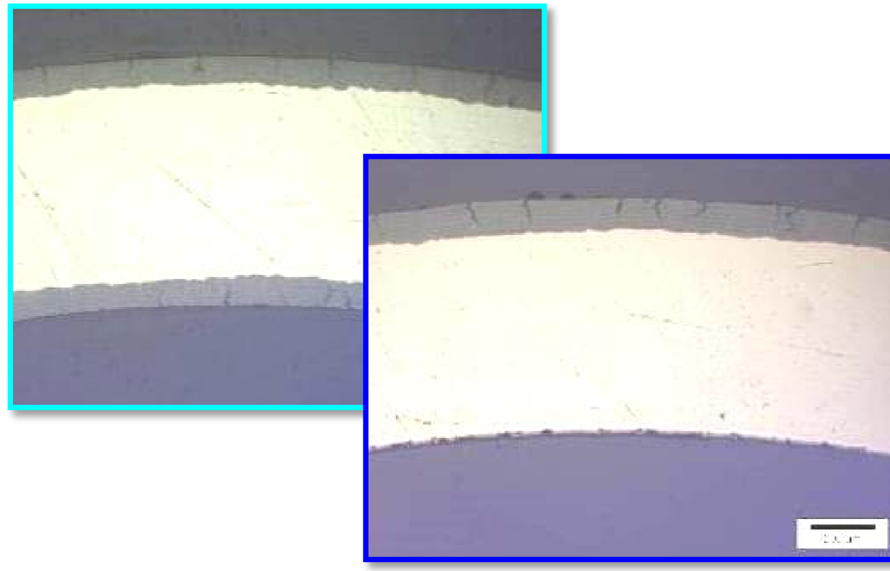
2-cm cladding segment for TG tests



Cross-section of as-received Zry-2 with 100 µm inner Zr liner

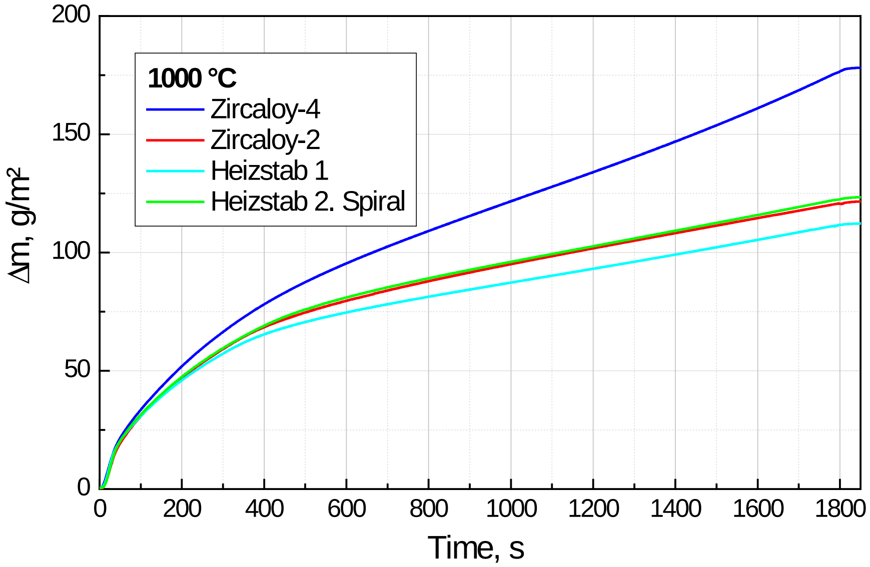
Oxidation in air of as-received claddings

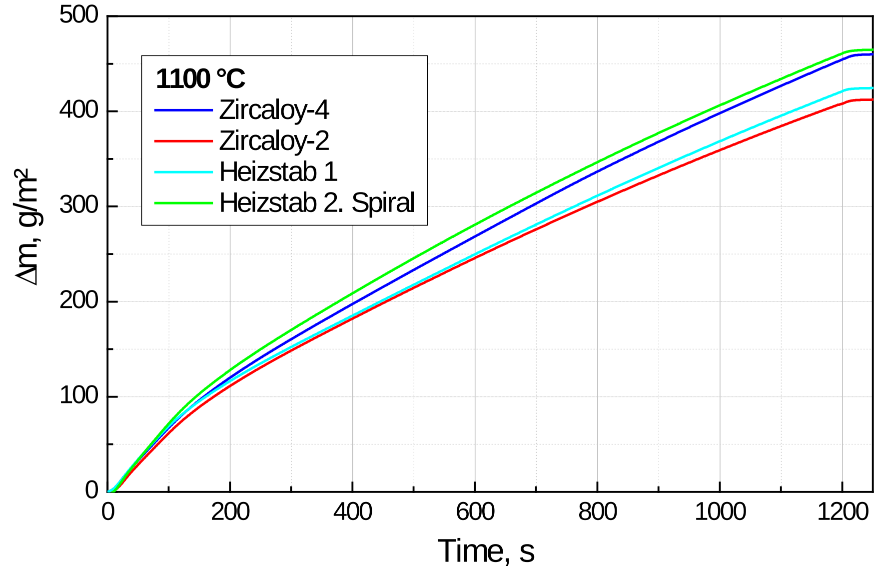




- Positive effect of inner Zr layer (but no effect in SFP tests)
- Comparable external oxidation
- Breakaway after ca. 3 hours

Oxidation of heater rods

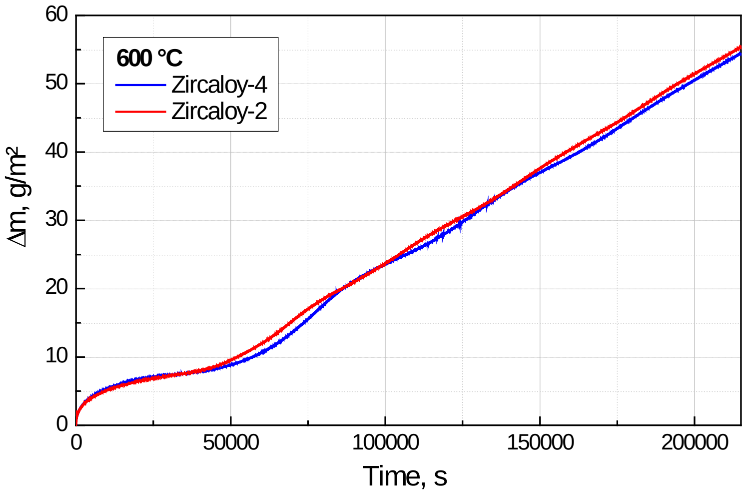


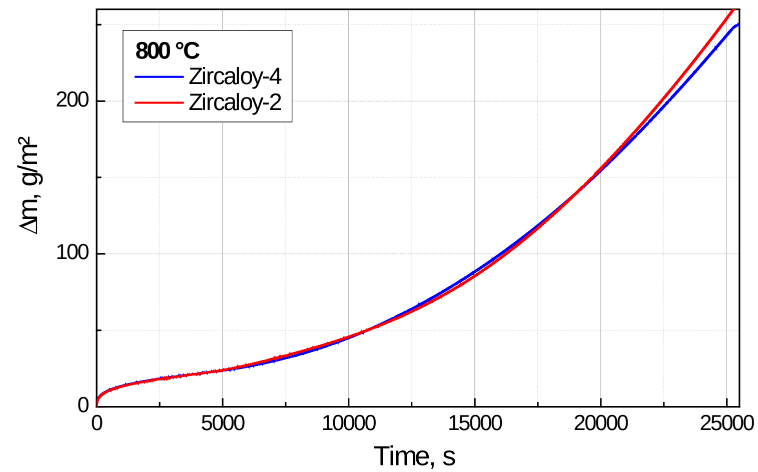


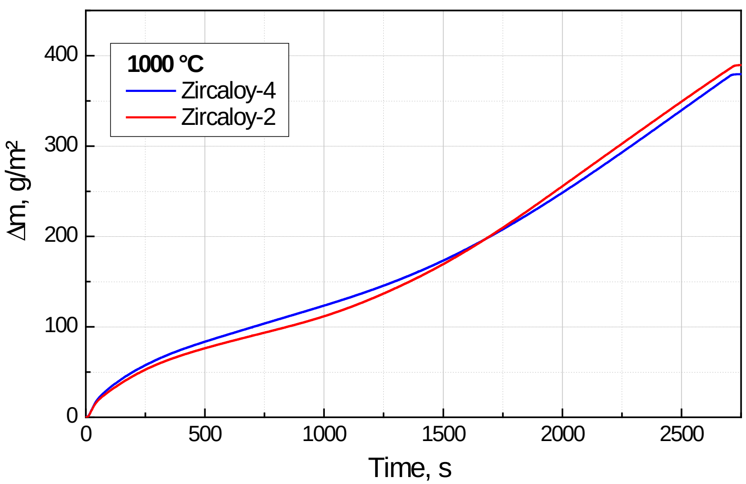
- No effect of swage-down process on oxidation behavior of Zircaloy-2

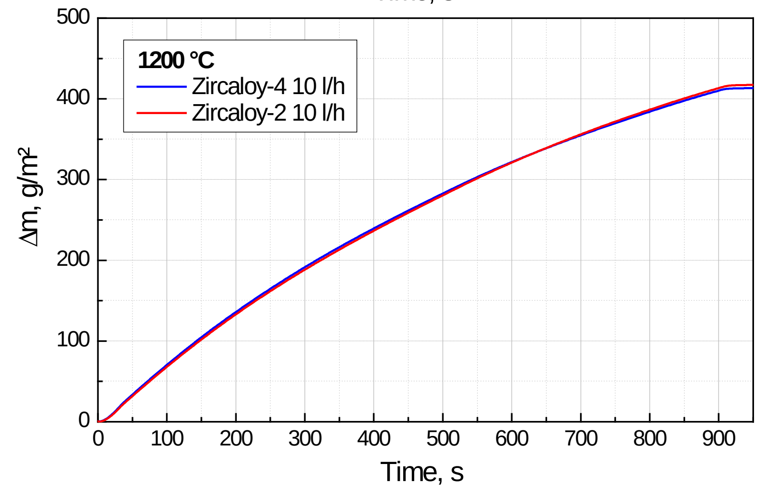
Oxidation of reamed claddings

Mass gain during isothermal oxidation in air



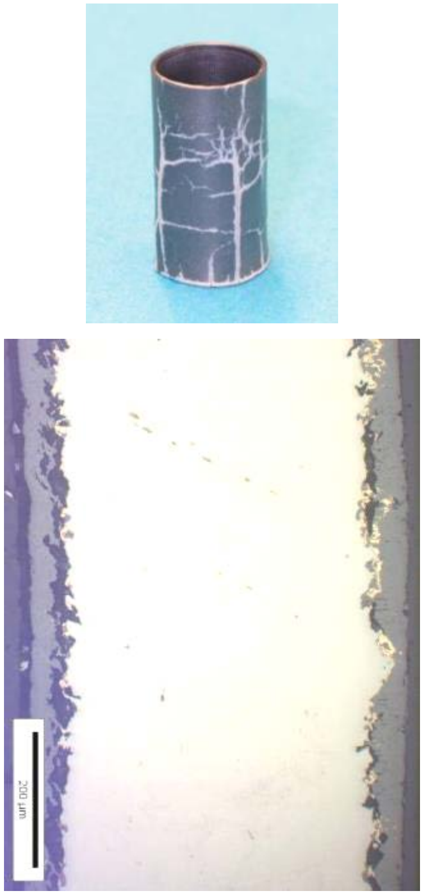




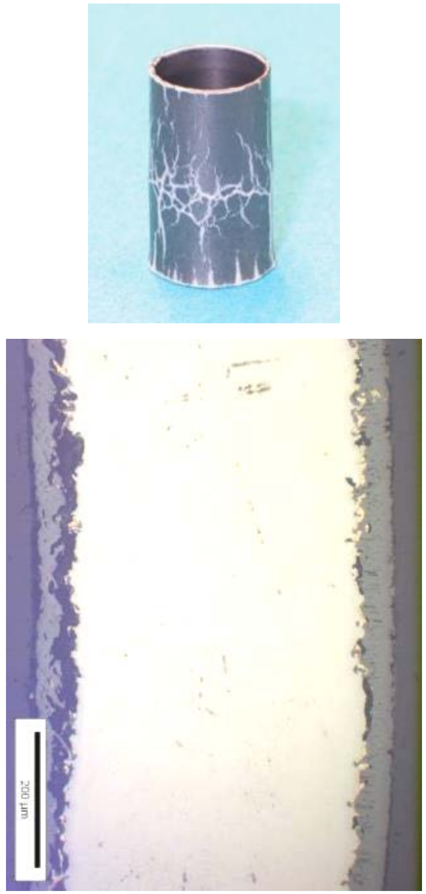


- Identical oxidation of Zry-2 and Zry-4 in air between 600 and 1400°C

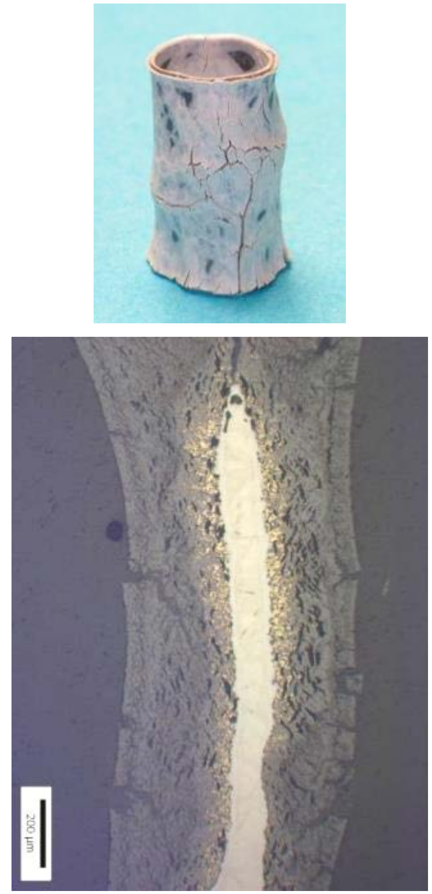
Oxidation of Zry-4 and Zry-2 claddings
Post-test examinations (Example from 1100°C tests)



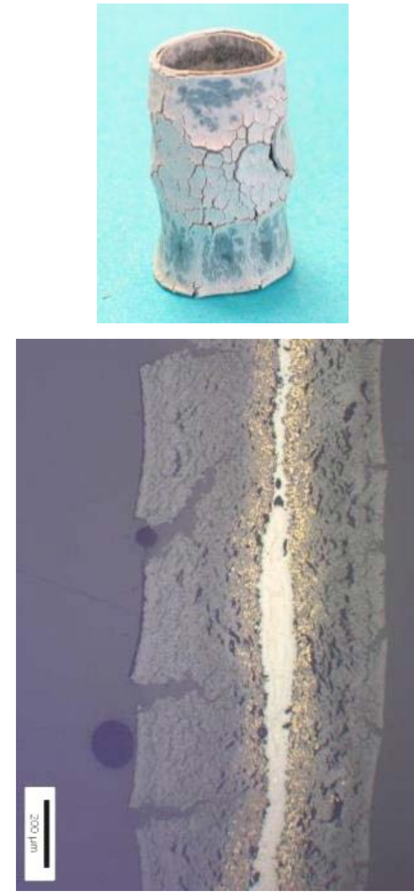
Zry-4, 15 min



Zry-2, 15 min



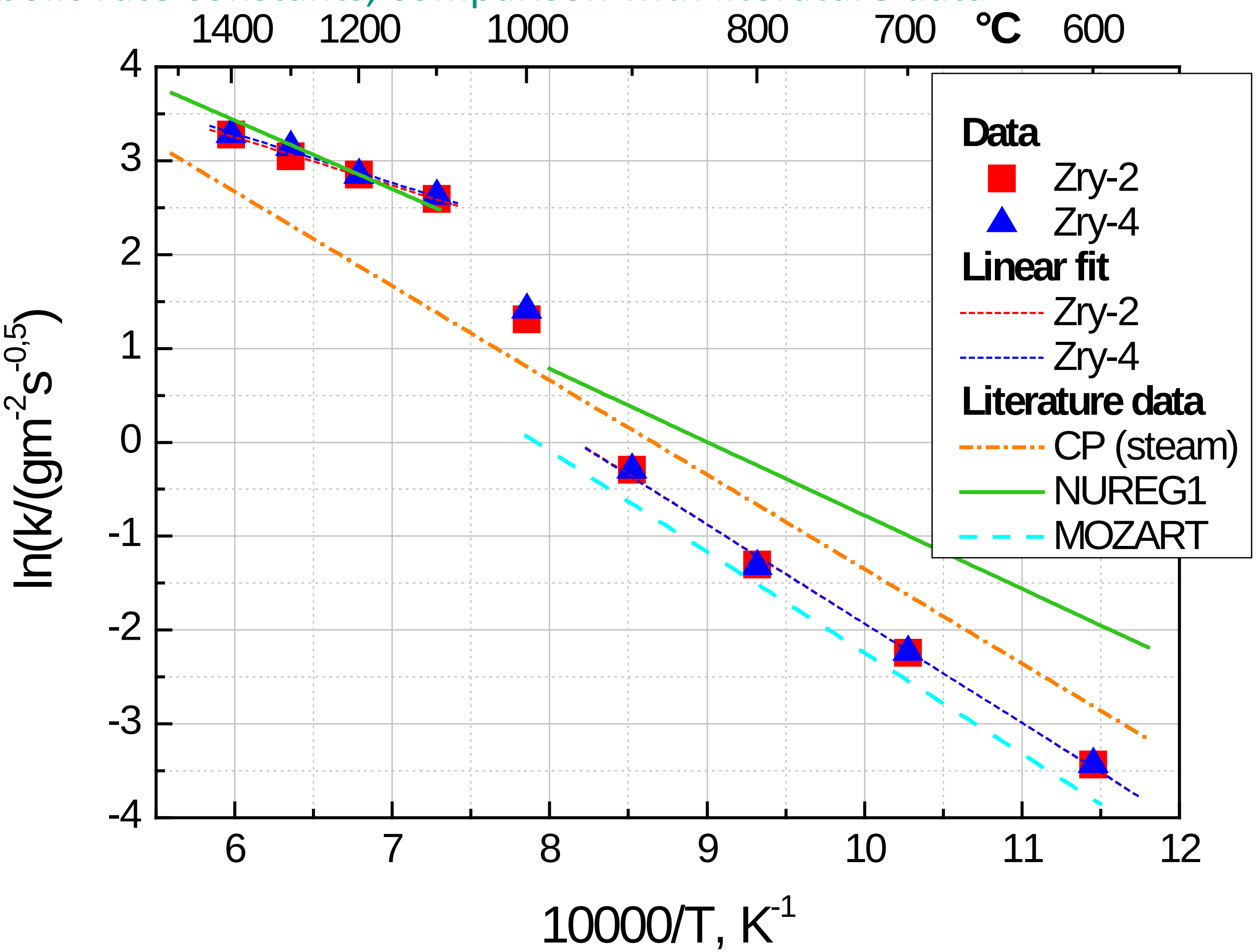
Zry-4, 45 min



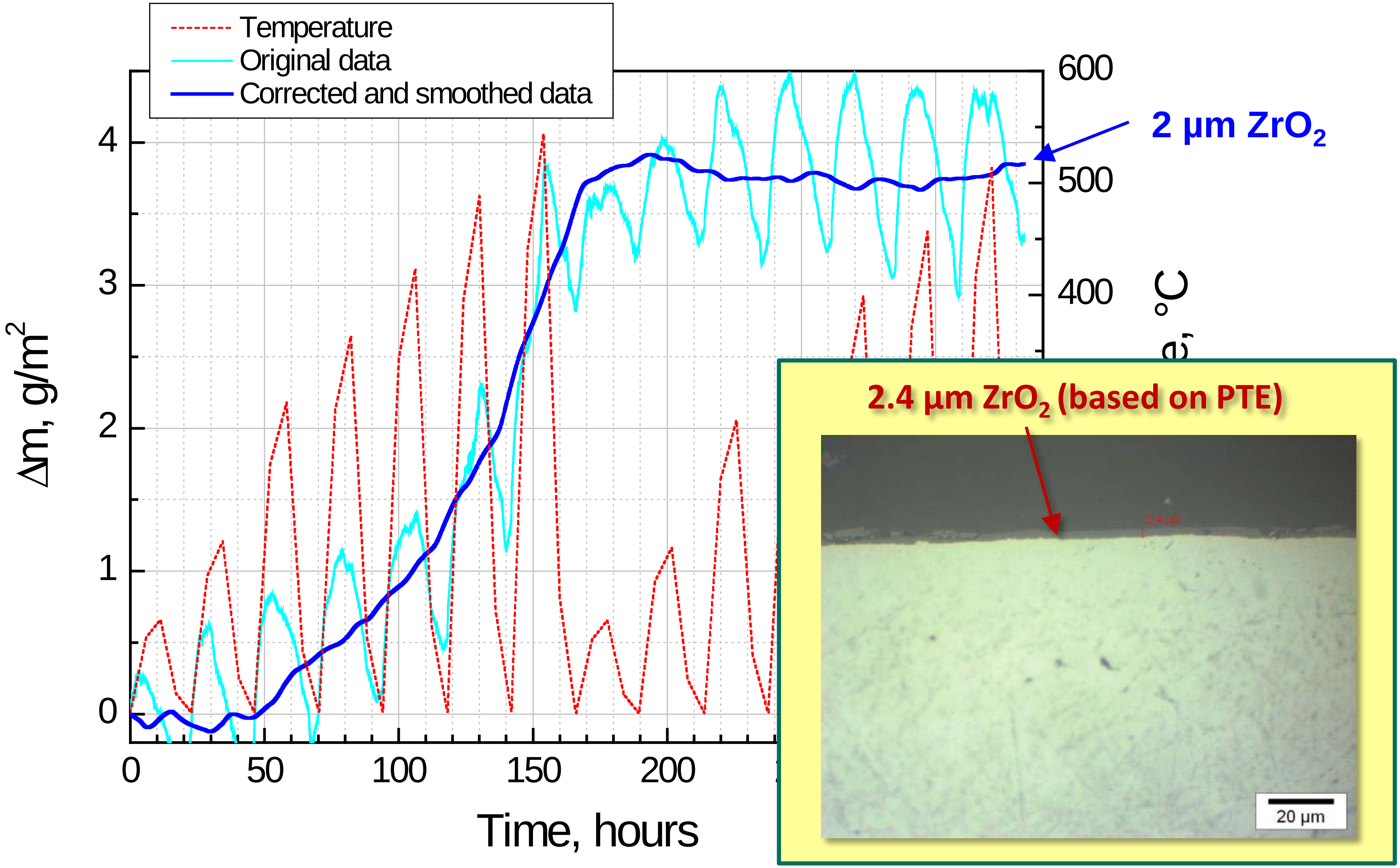
Zry-2, 45 min

Oxidation of zirconium alloy claddings

Parabolic rate constants, comparison with literature data

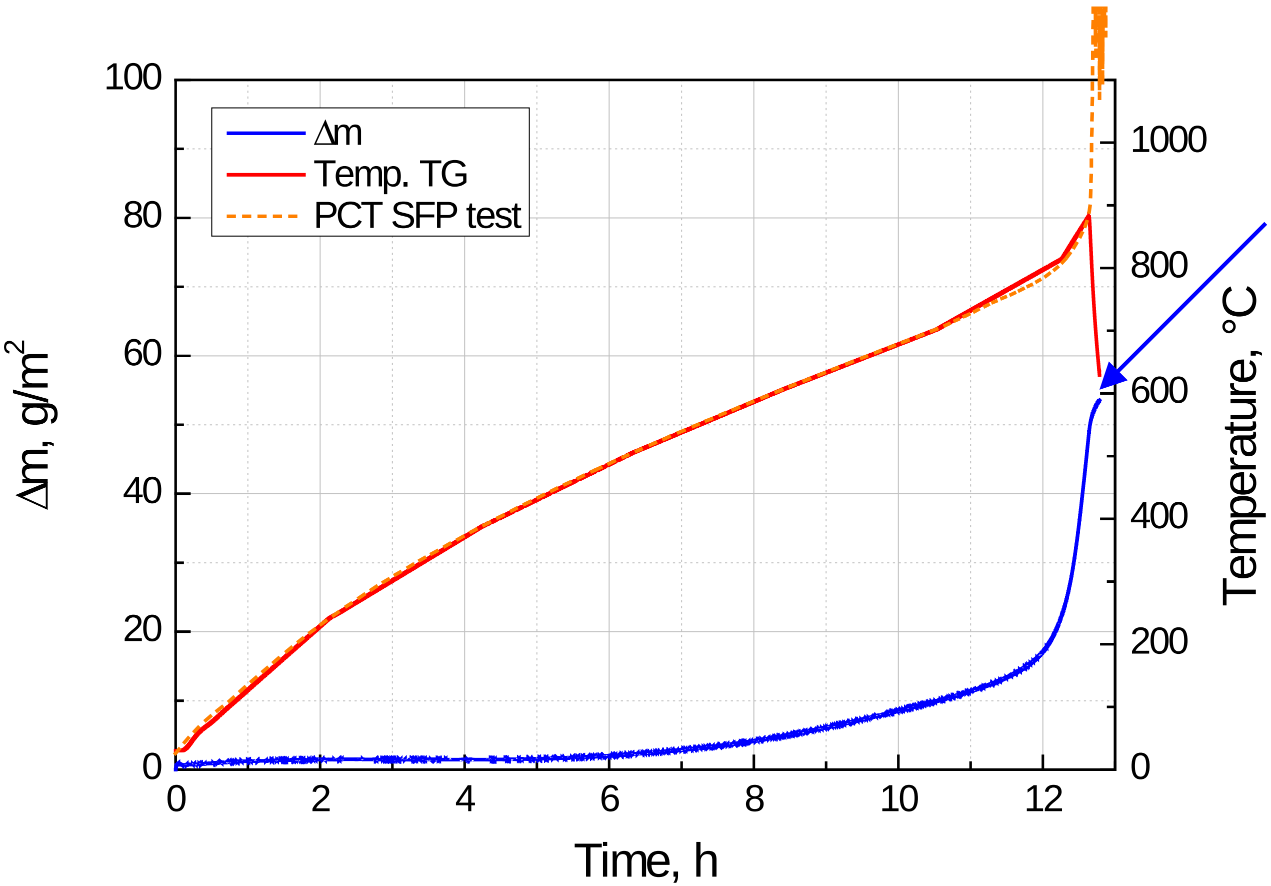


Simulation of SFP phase I pre-ignition tests

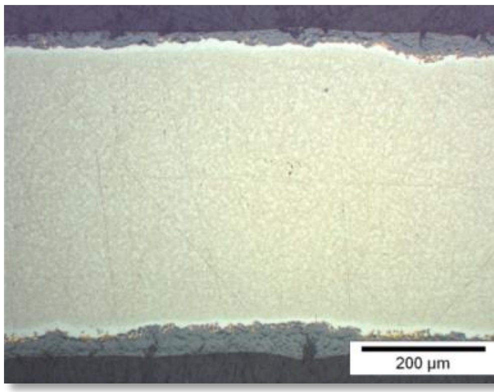


Simulation of SFP phase I ignition test

Karlsruhe Institute of Technology

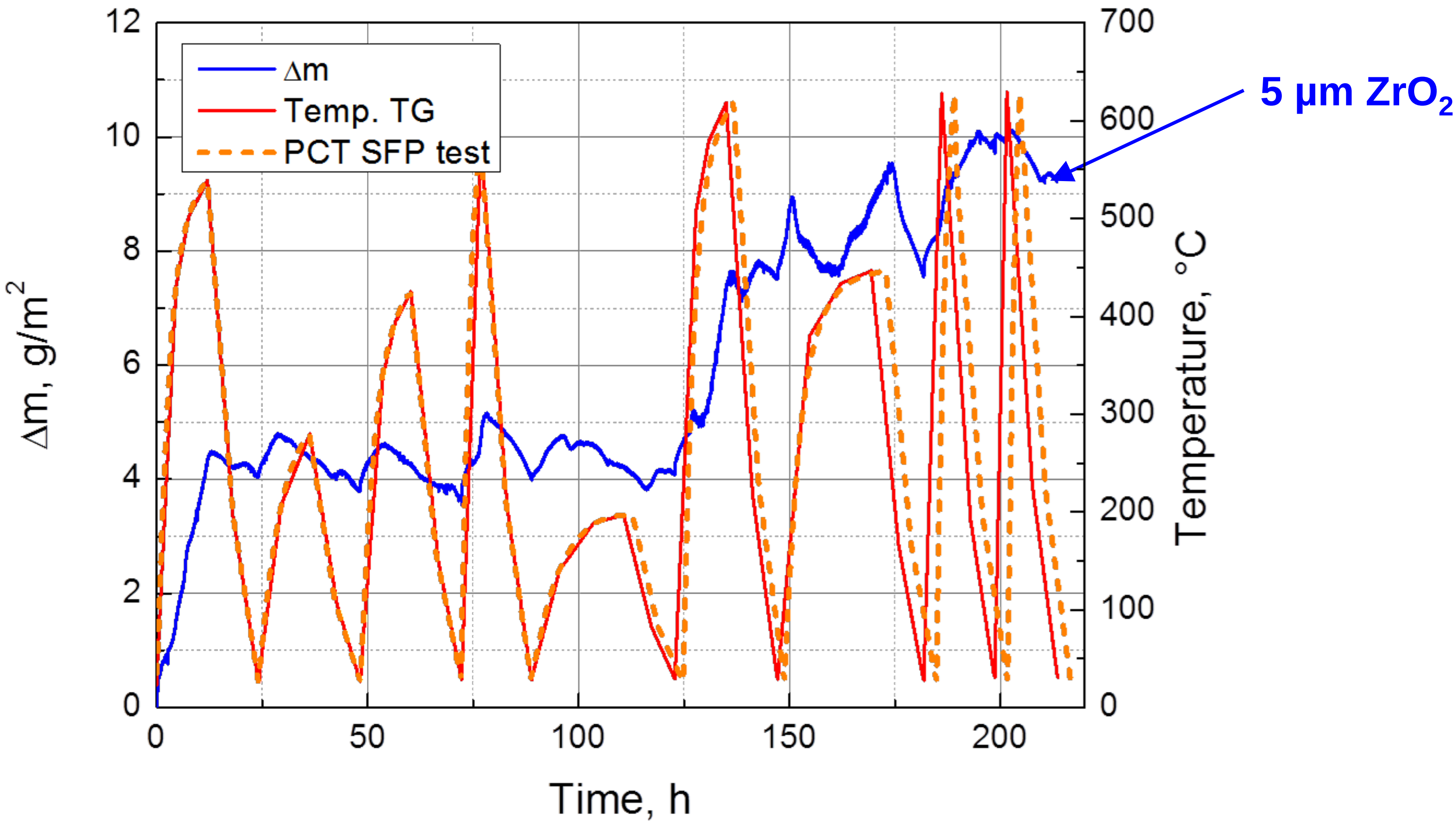


30 µm ZrO_2



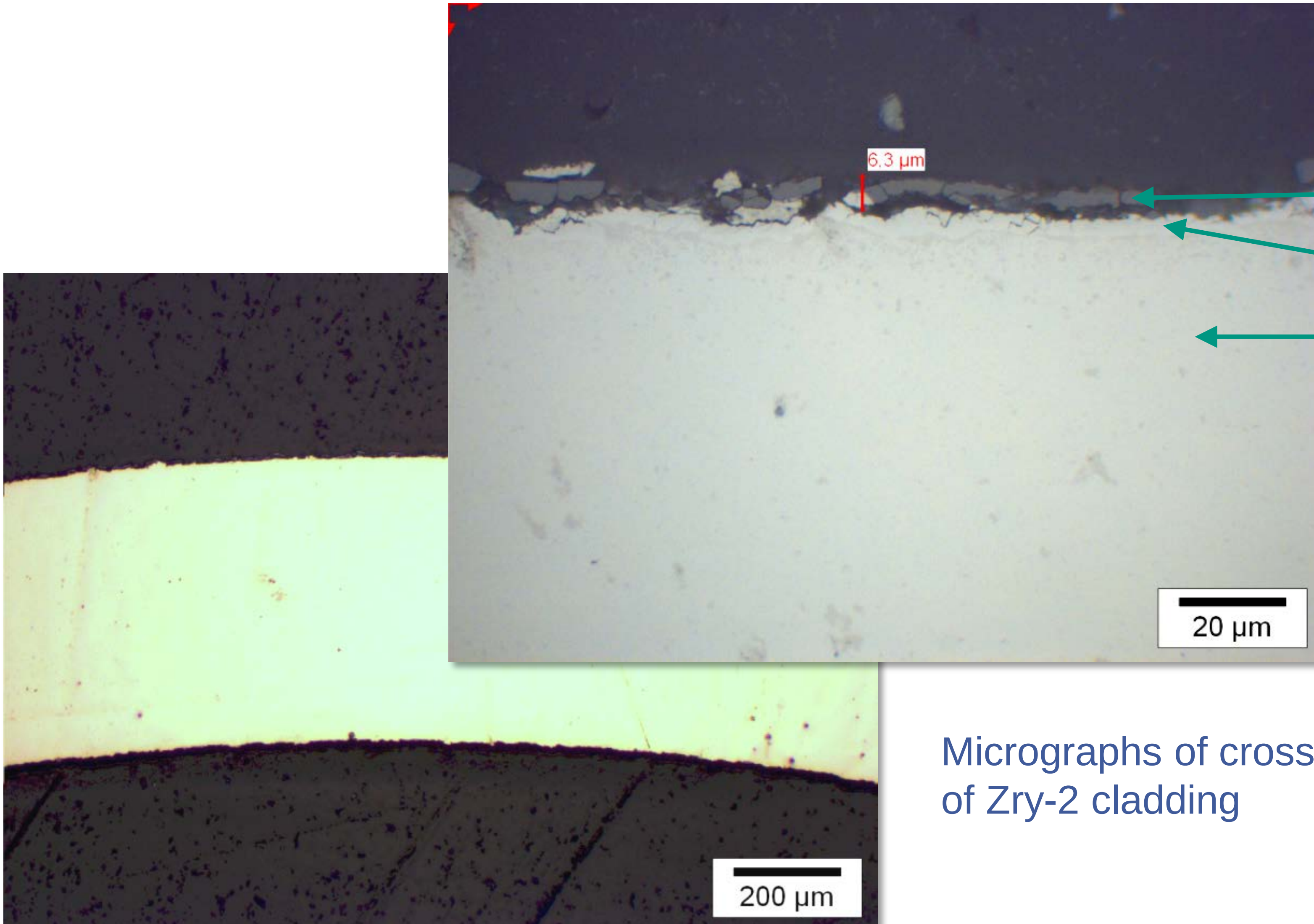
20-50 µm ZrO_2

Simulation of SFP phase II pre-tests; TG



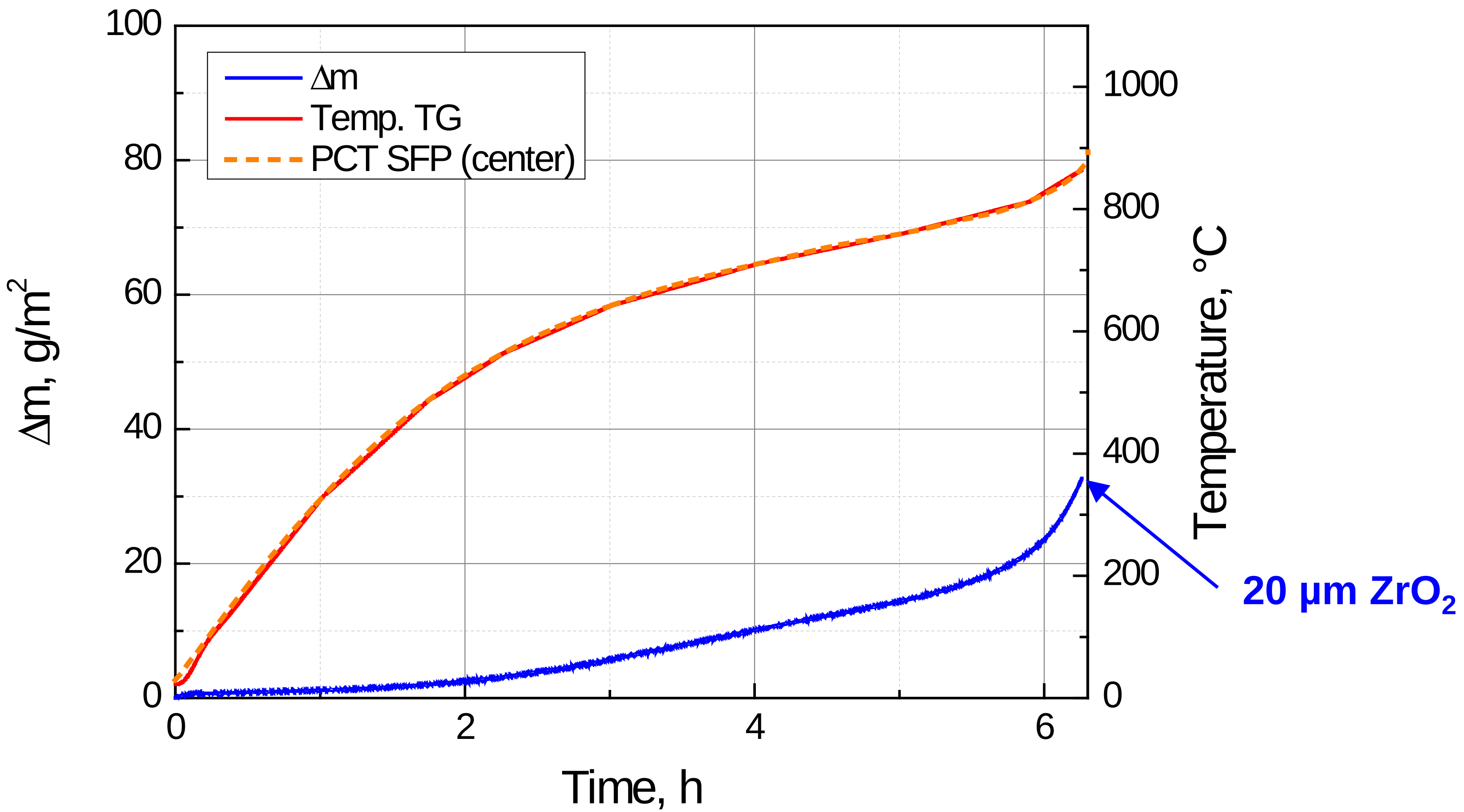
SFP max. center temperature, test temperature and resulting mass gain

Simulation of SFP phase II pre-tests; micrographs



Micrographs of cross section of Zry-2 cladding

Simulation of SFP phase II ignition test; TG



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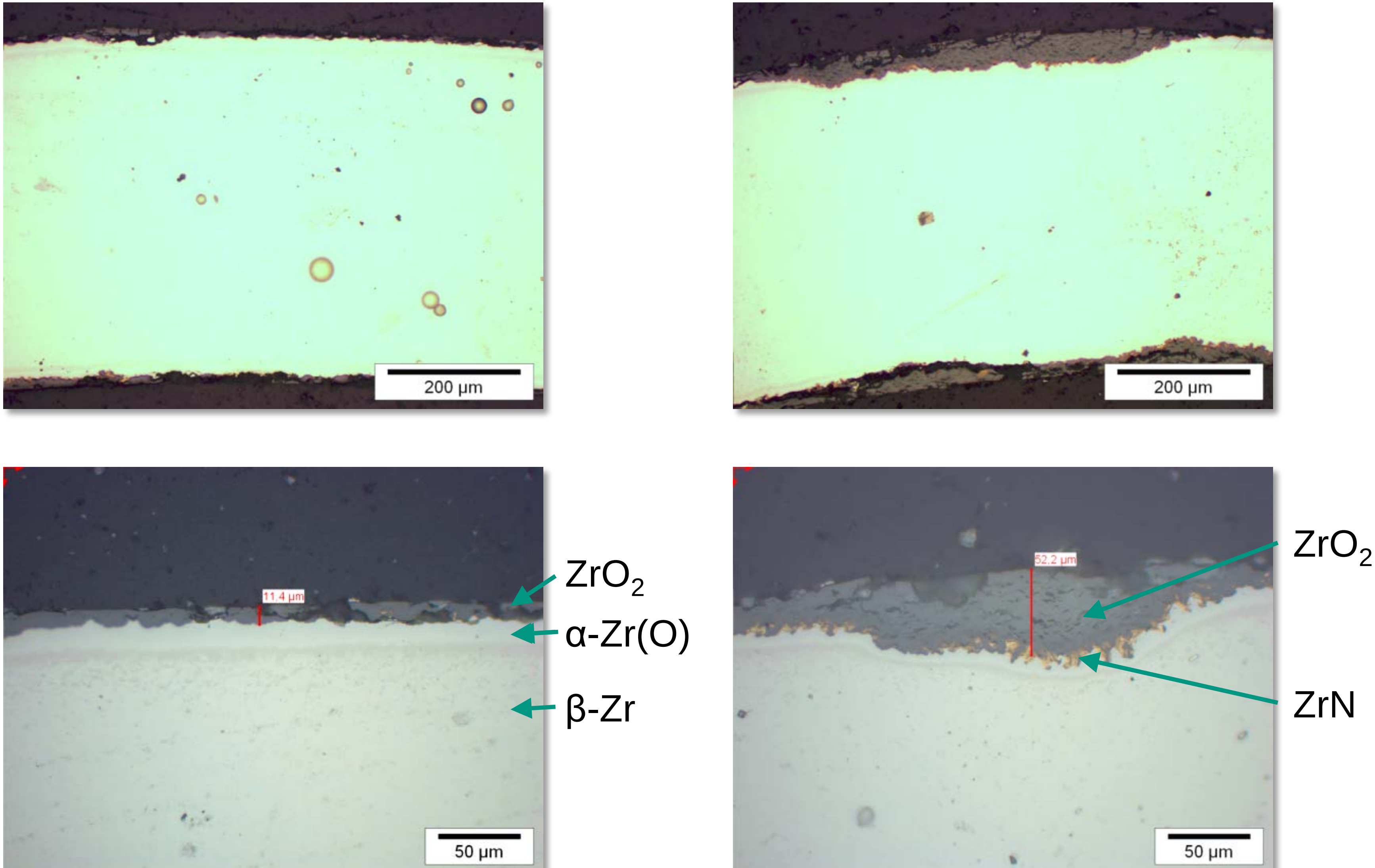

Conclusions

- Nitrogen strongly affects oxidation kinetics by the (temporary) formation of ZrN
- Very similar oxidation behavior of the two alloys Zircaloy-2 and Zircaloy-4 and hence no concern regarding use of Zircaloy-2 for PWR tests
- No effect of swage-down process on oxidation
- Only very low oxidation (2 and 5 µm, respectively) of cladding during pre-ignition tests
- During main tests about 20-30 µm ZrO_2/ZrN were formed in the center bundle before ignition started

Finally…

- The financial support of this work by the SFP program is acknowledged

- Next QUENCH Workshop:
  - Nov 19-21, 2013
  - KIT, Karlsruhe, Germany
  - quench.forschung.kit.edu

Thank you for your attention!

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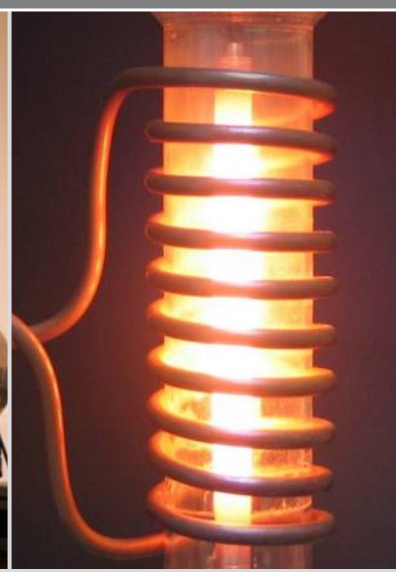
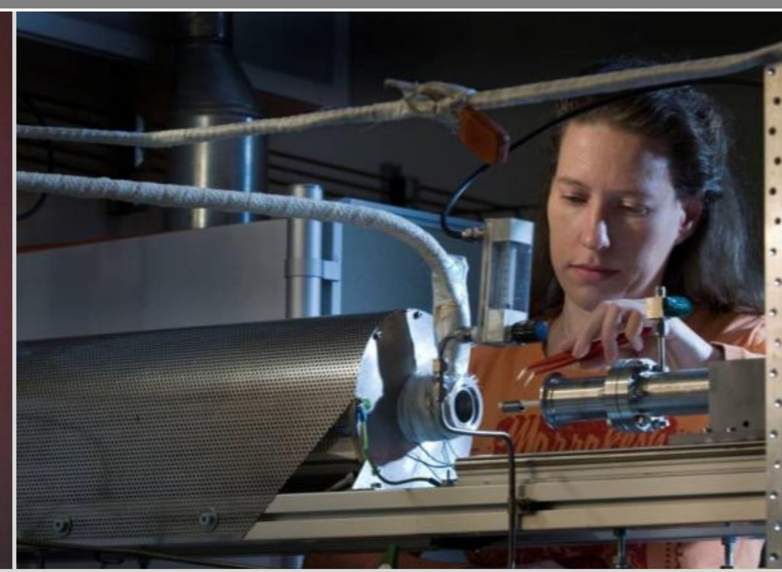
SFP Project Seminar 2013, OECD Conference Center, Paris, France, 22-23 October 2013

Institute for Applied Materials IAM-AWP & Program NUKLEAR

Phase diagram Zr - O