Karlsruhe Institute of Technology

Institute for Applied Materials

Results of bundle tests on air ingress

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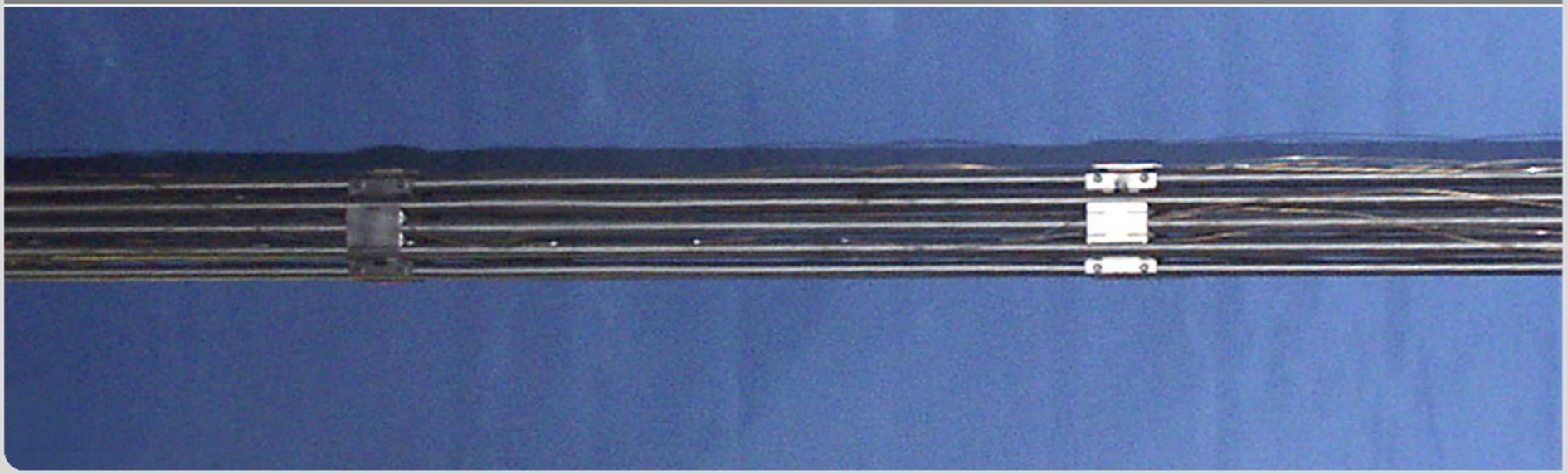
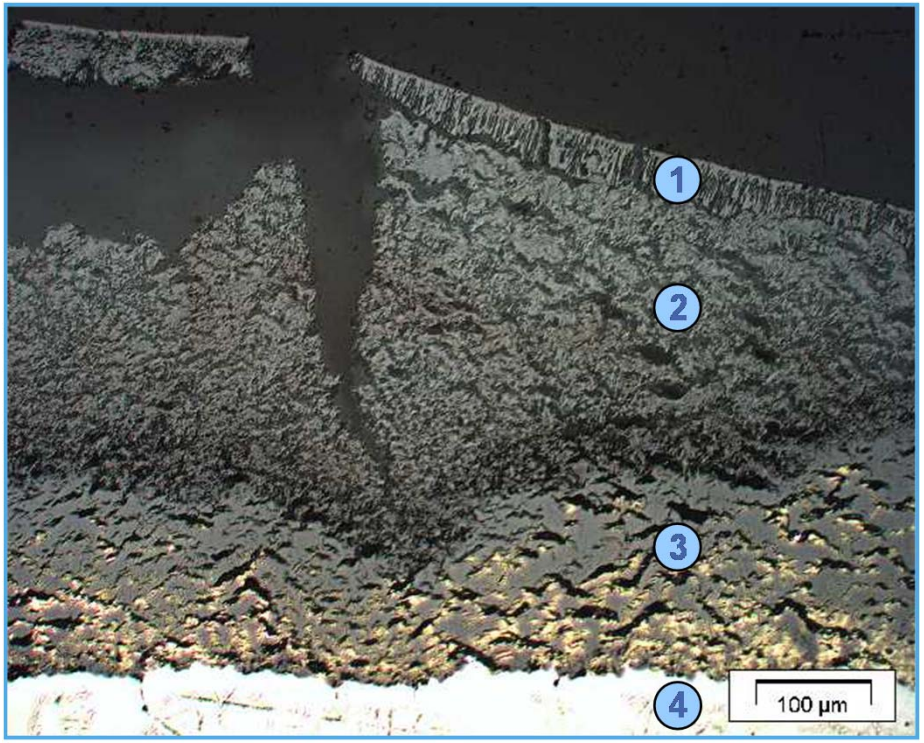
**IBRAE Moscow

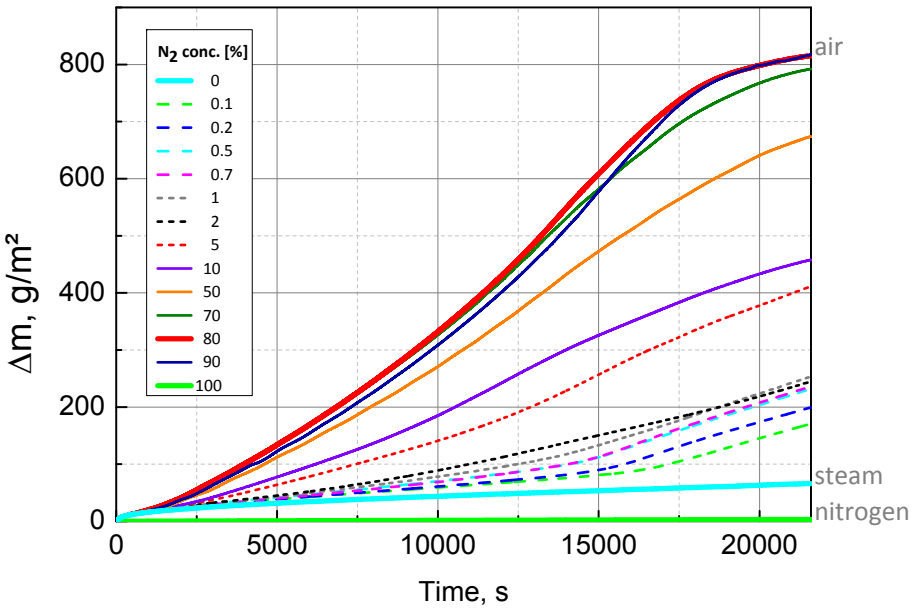
Institute for Applied Materials; Program NUKLEAR



Main results of single effect tests on air ingress

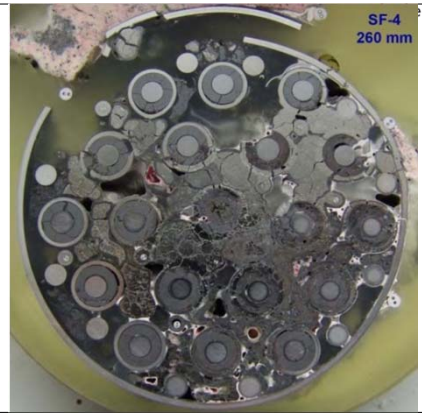


Typical cross-section through an oxide scale after oxidation of Zry-4 in air at 1000°C:
1 – initially formed dense oxide ZrO_2,
2 – porous oxide after oxidation of ZrN,
3 – ZrO_2/ZrN mixture,
4 – α-Zr(O).

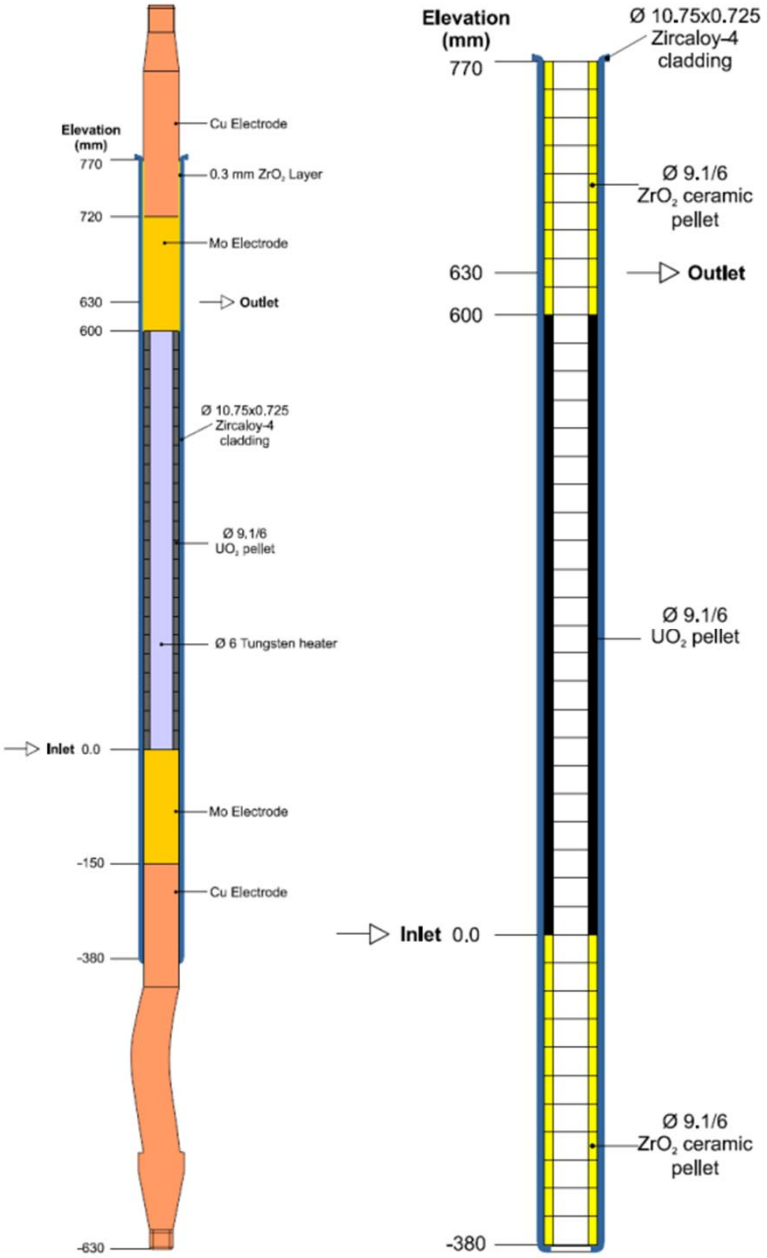


Mass gain versus time of oxidation of Zircaloy-4 at 800°C in steam-nitrogen mixtures.

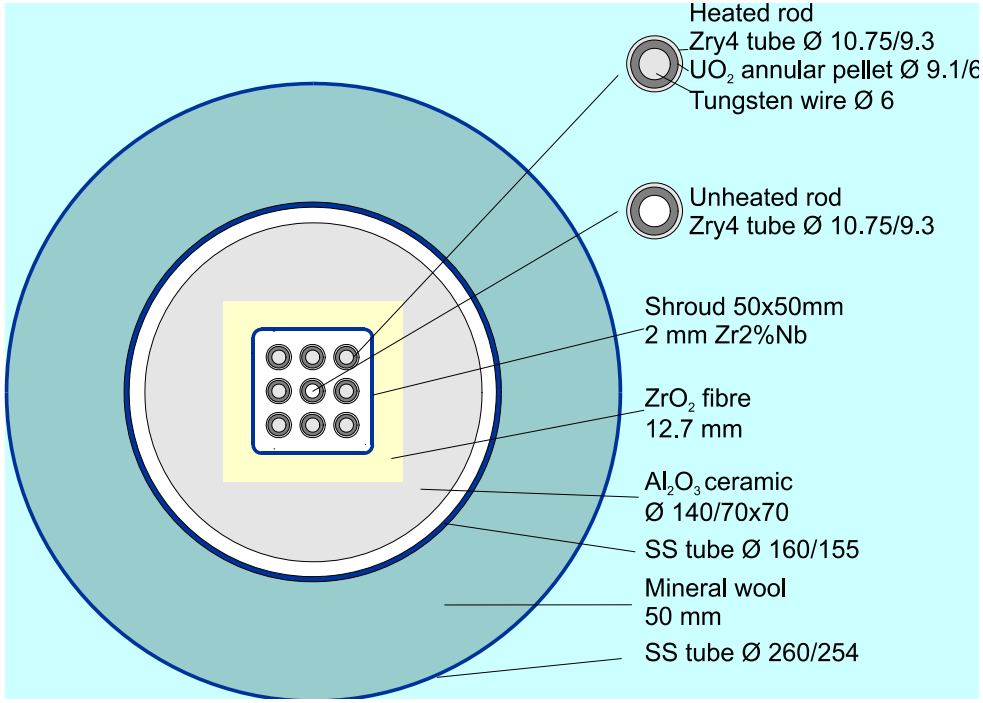
Overview of bundle air ingress experiments

280 mm  	 *260 mm*
CODEX AIT-1, AIT-2 (Zry-4) performed 1999 at AEKI/Budapest: small bundles with 9 rods	PARAMETER-SF4 (E110 claddings) performed 2009 at LUCH/Podolsk: very high temperatures on reflood initiation with following escalation (bundle melting)
635 mm 	*430 mm* 
QUENCH-10 (Zry-4 claddings) performed 2004 at KIT/Karlsruhe: strong pre-oxidised bundle	QUENCH-16 (Zry-4 claddings) performed 2011 at KIT/Karlsruhe: moderate pre-oxidised bundle

CODEX bundle

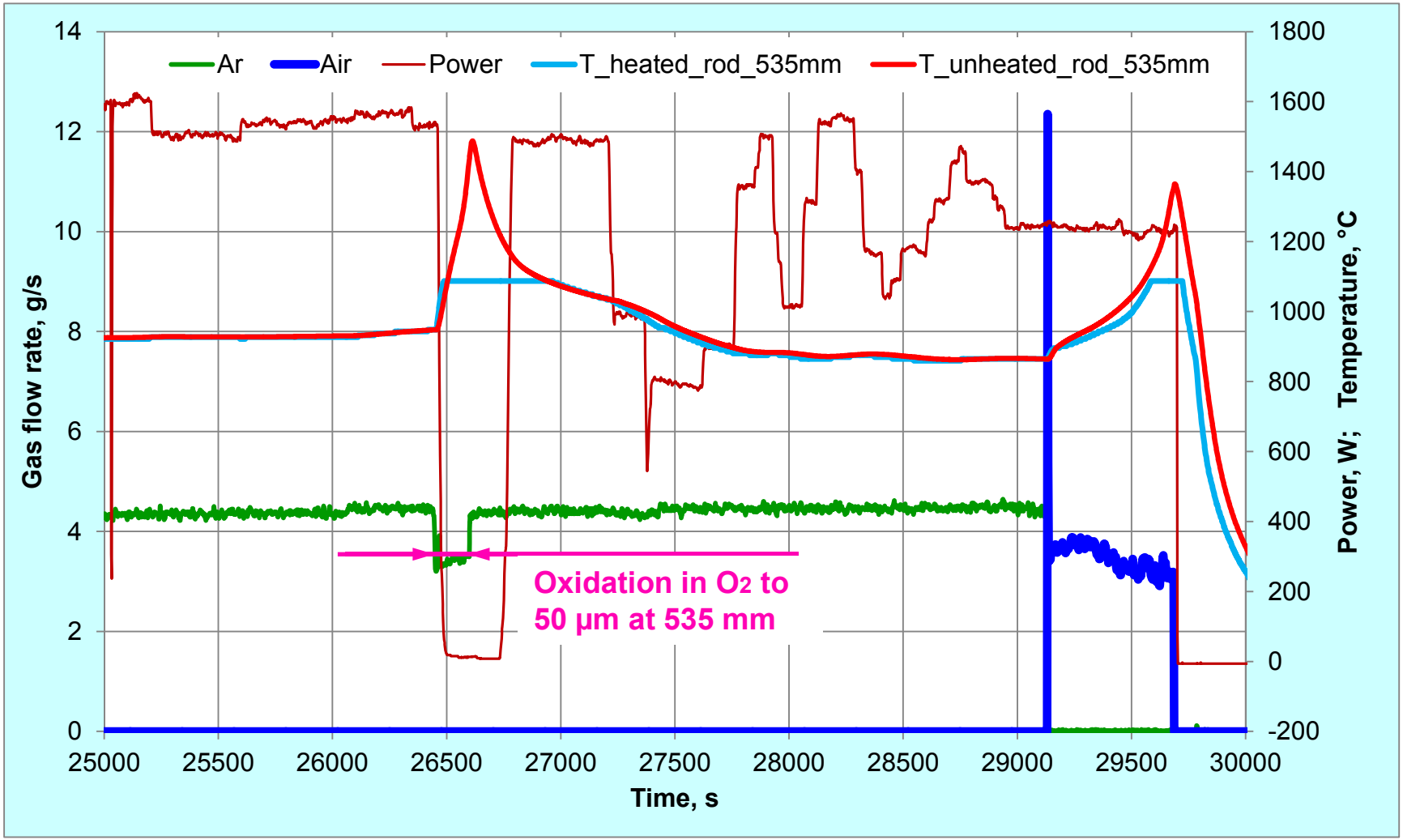


heated rod unheated rod

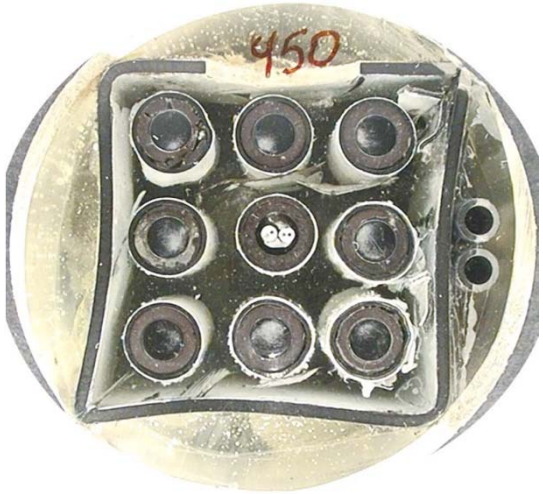
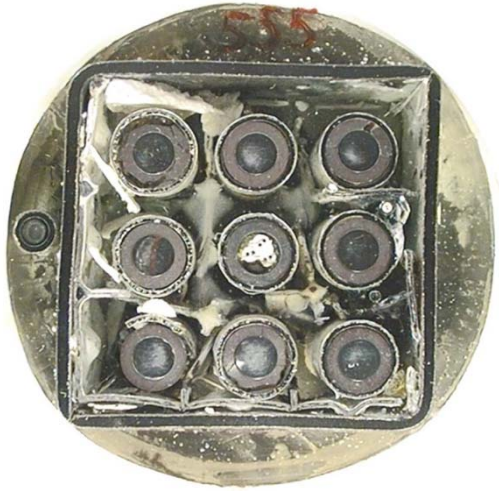


2 grid spacers (Zry-4): at -15 mm and at +535mm

CODEX AIT-1 test performance



CODEX-AIT1: cross-sections

		
50 mm: no nitrides	150 mm: no nitrides	300 mm: no nitrides
		
450 mm: nitrides	535 mm: nitrides	555 mm: nitrides

CODEX-AIT1 (9 rods, heated 600 mm, pre-ox. 40 µm): cladding structures at hot elevations with T (535 mm) ≈ 900°C – 1300 °C during air ingress (570 s)

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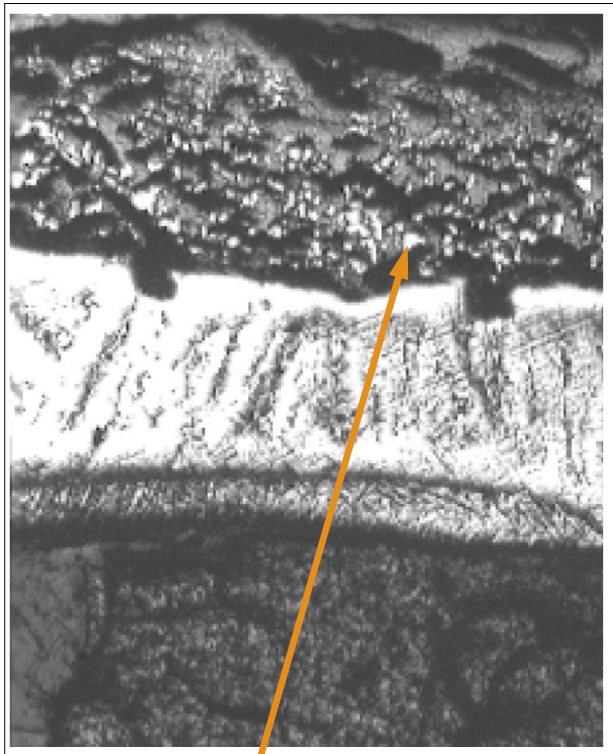	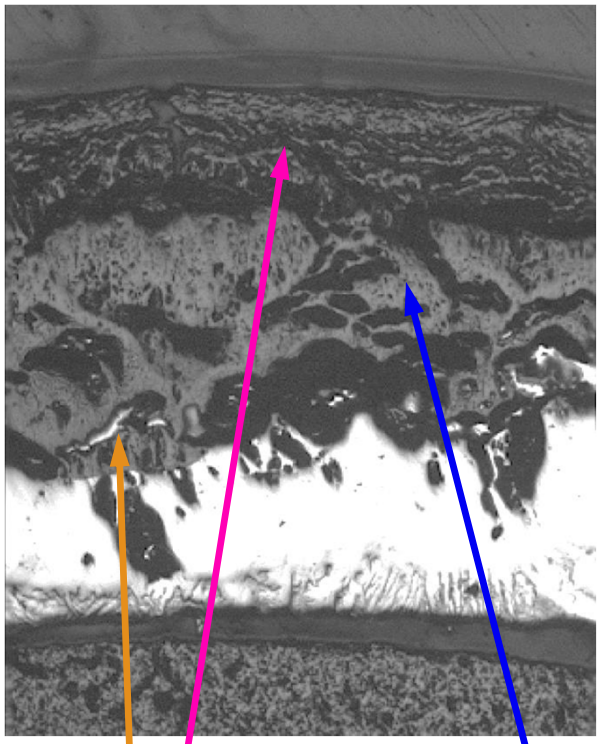	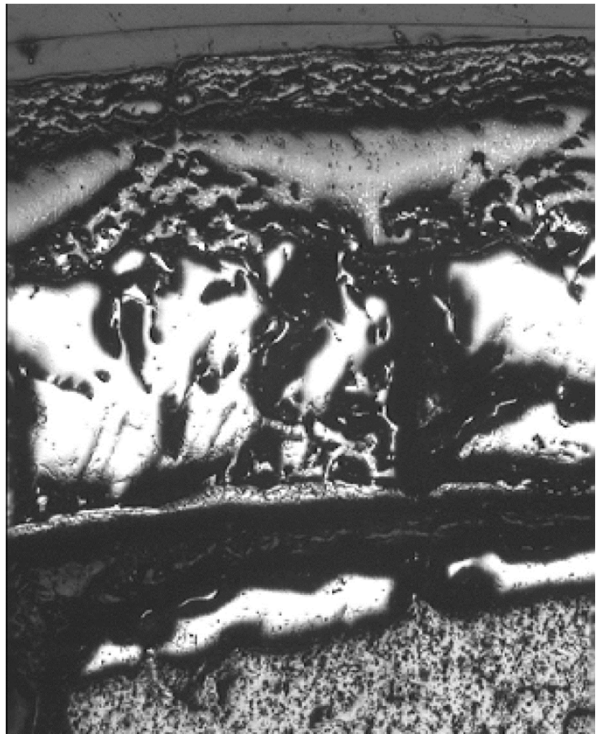
450 mm: **nitrides** inside oxide layer	535 mm: 1) **porous** outer oxide layer (formed during preoxidation in oxygen); 2) **dense** oxide layer (formed during air ingress); 3) single **nitrides** at boundary oxide-metal.	555 mm: similar to 535 mm

Practically total consumption of nitrogen below 500 mm

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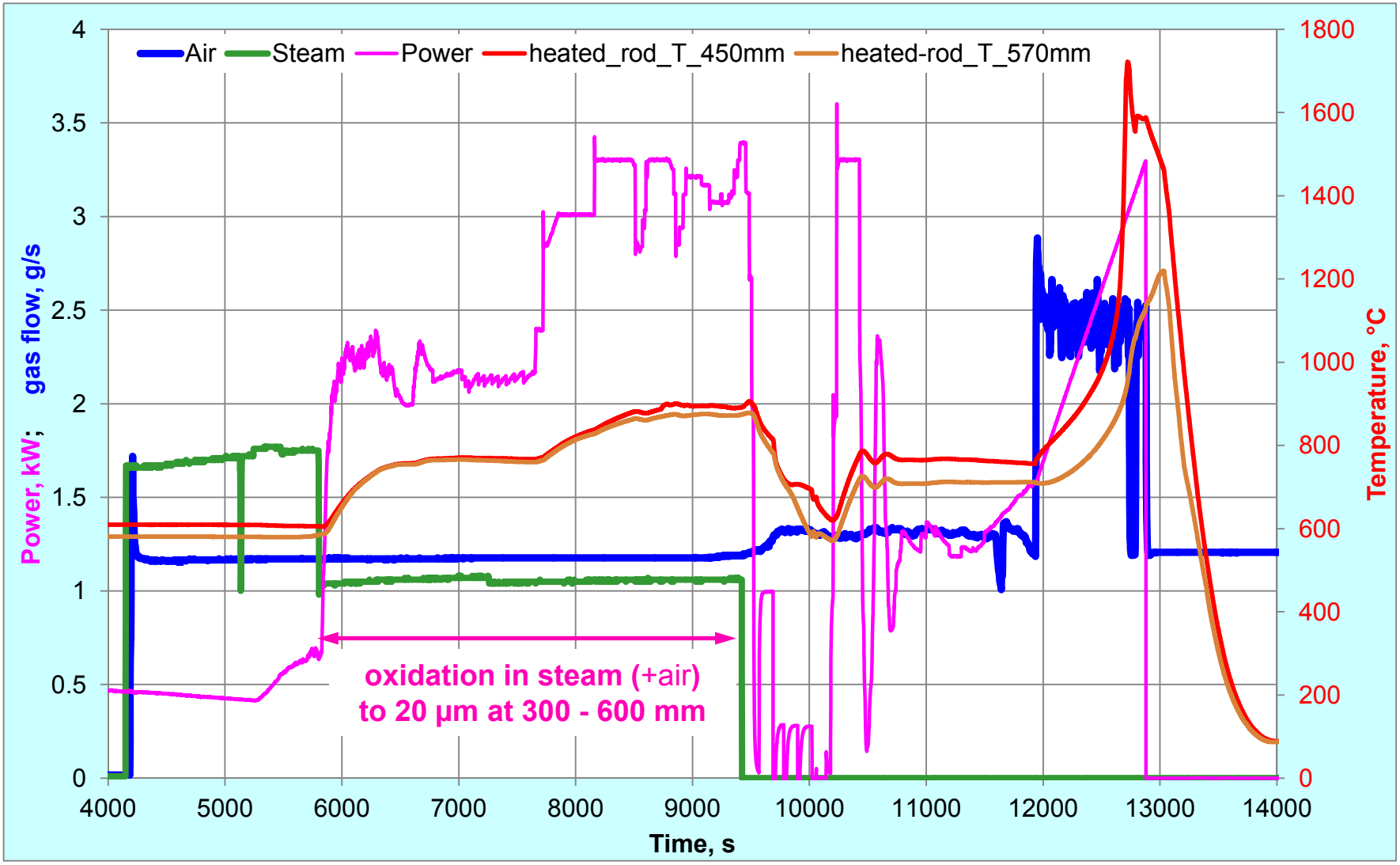
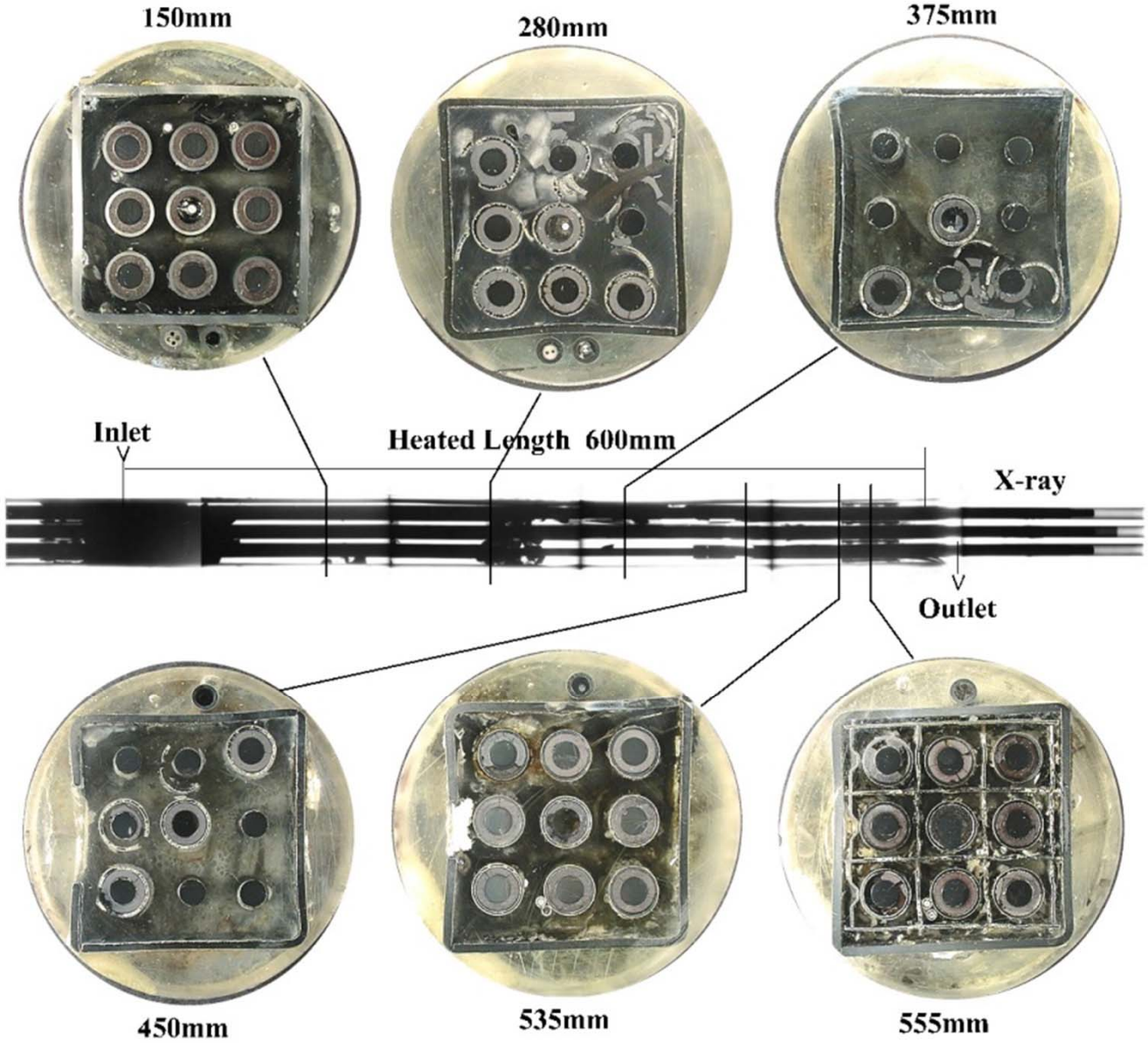
CODEX AIT-2 test performance



CODEX-AIT2: cross-sections

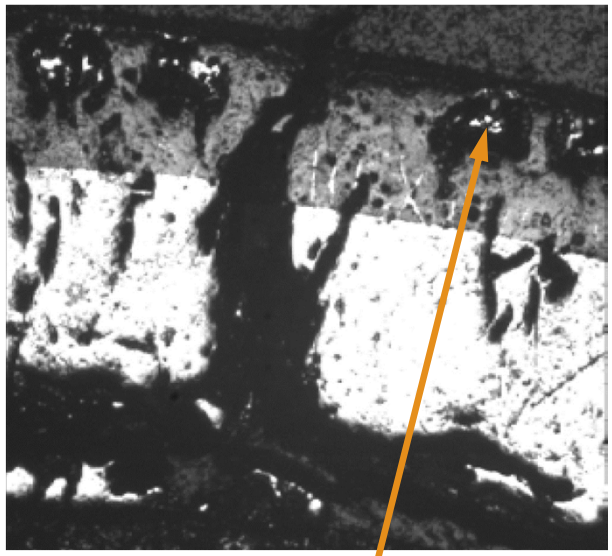
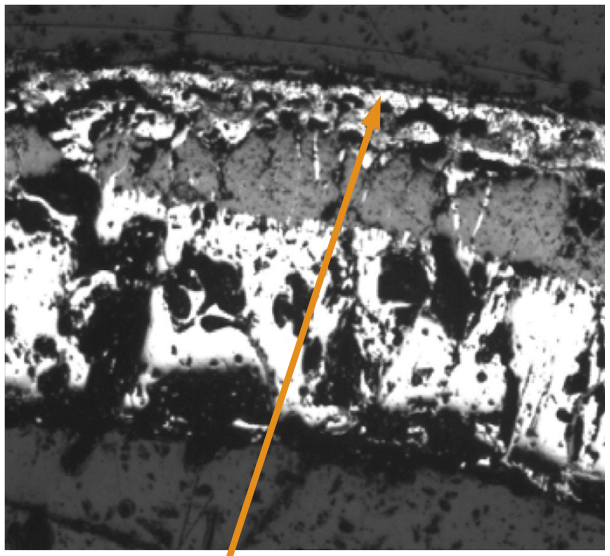
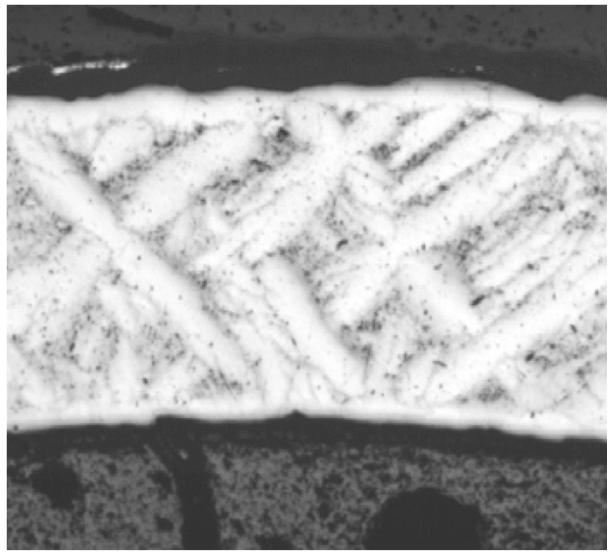


CODEX-AIT2

(9 rods, heated 600 mm, pre-ox. 35 µm):

cladding structures at hot elevations

with T (450 mm) ≈ 900°C – 1600 °C during air ingress (570 s)

		
280 mm: single **nitrides** inside “pockets” of upper part of oxide layer	375 mm: **nitrides** inside upper part of oxide layer	555 mm: few oxidised cladding (**steam and air starvation**)

CODEX-AIT SUMMARY

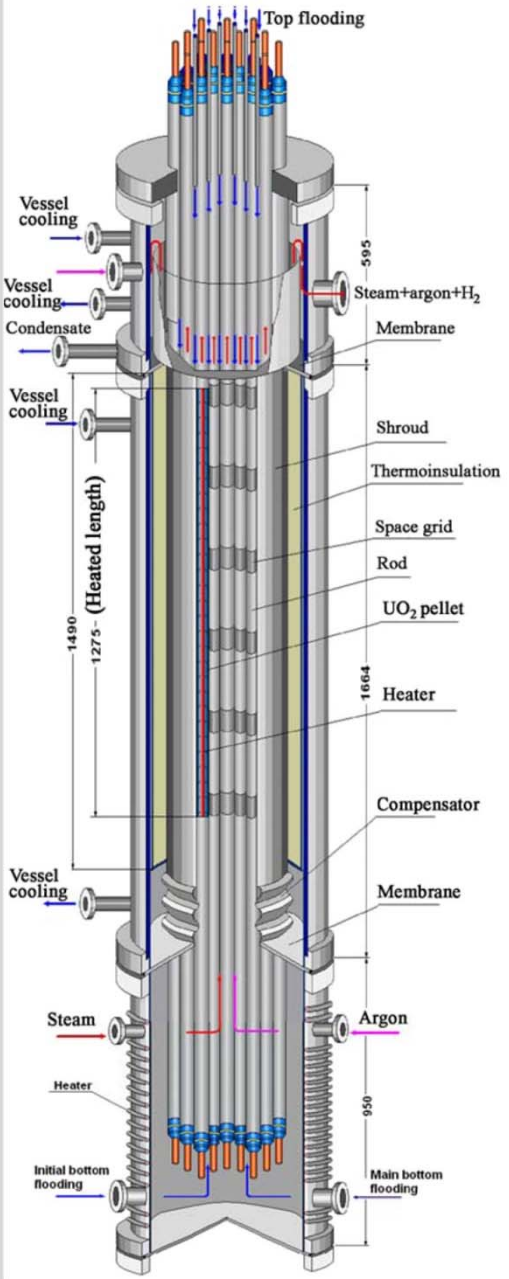
- air flow rate during air ingress: 4 g/s for AIT1, 2.5 g/s for AIT2 (1.2 g/s during preoxidation);

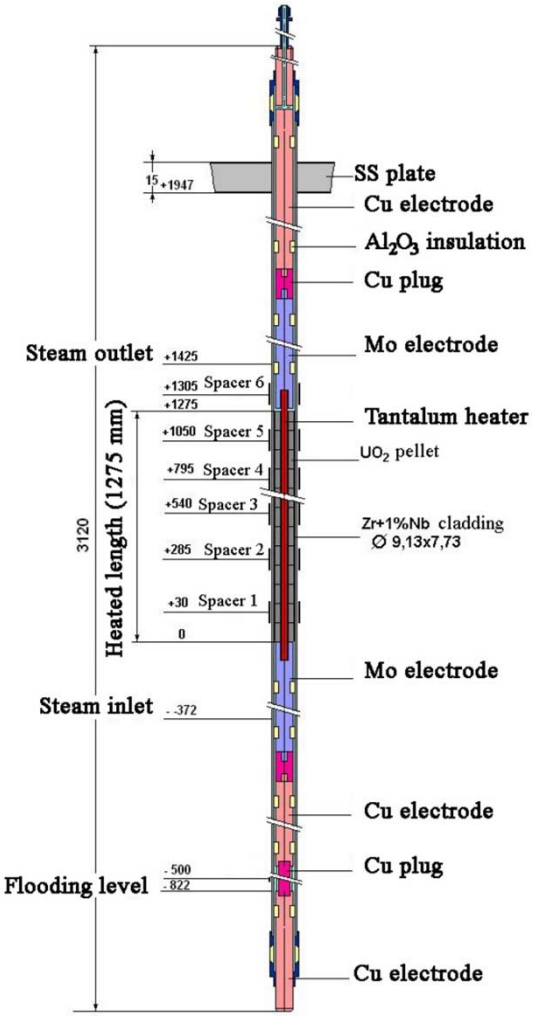
- air injection at temperatures: for AIT1 T_{max}(535 mm) = 900 – 1200 °C growing during 500 s; for AIT2 T_{max}(450 mm) = 800 – 1200°C growing during 1000 s;

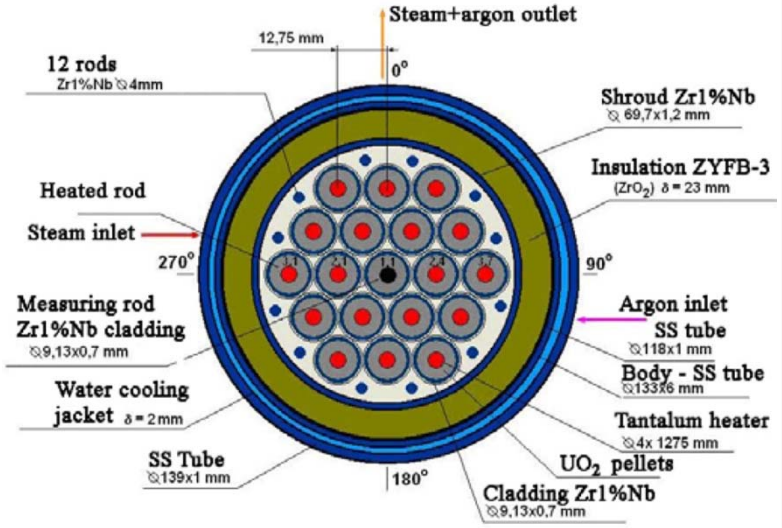
- *thin* initial oxide layer before air ingress: 50 µm for AIT1, 20 µm for AIT2;

- formation of nitrides at 300 – 500 mm inside the oxide layer.

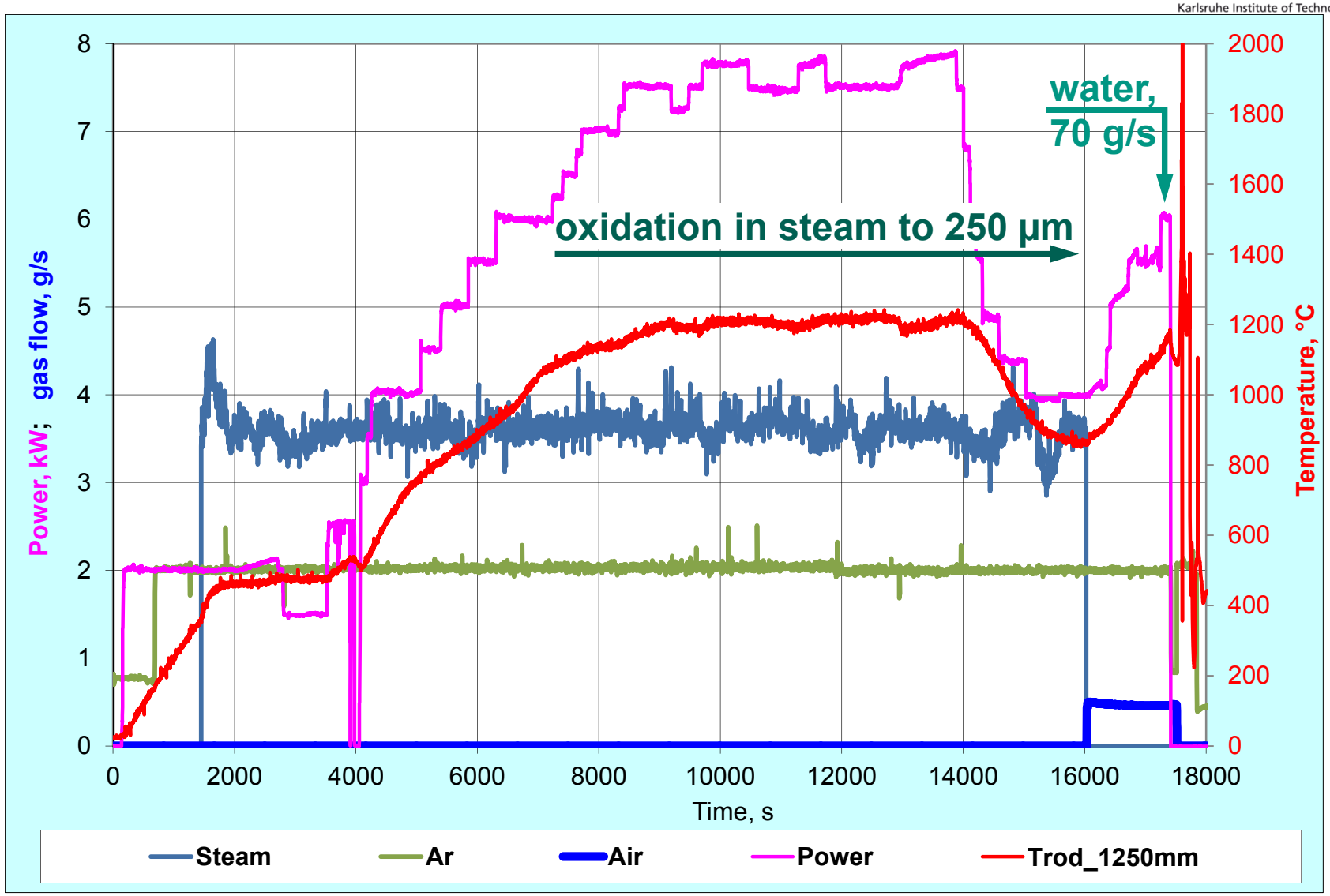
PARAMETER bundle



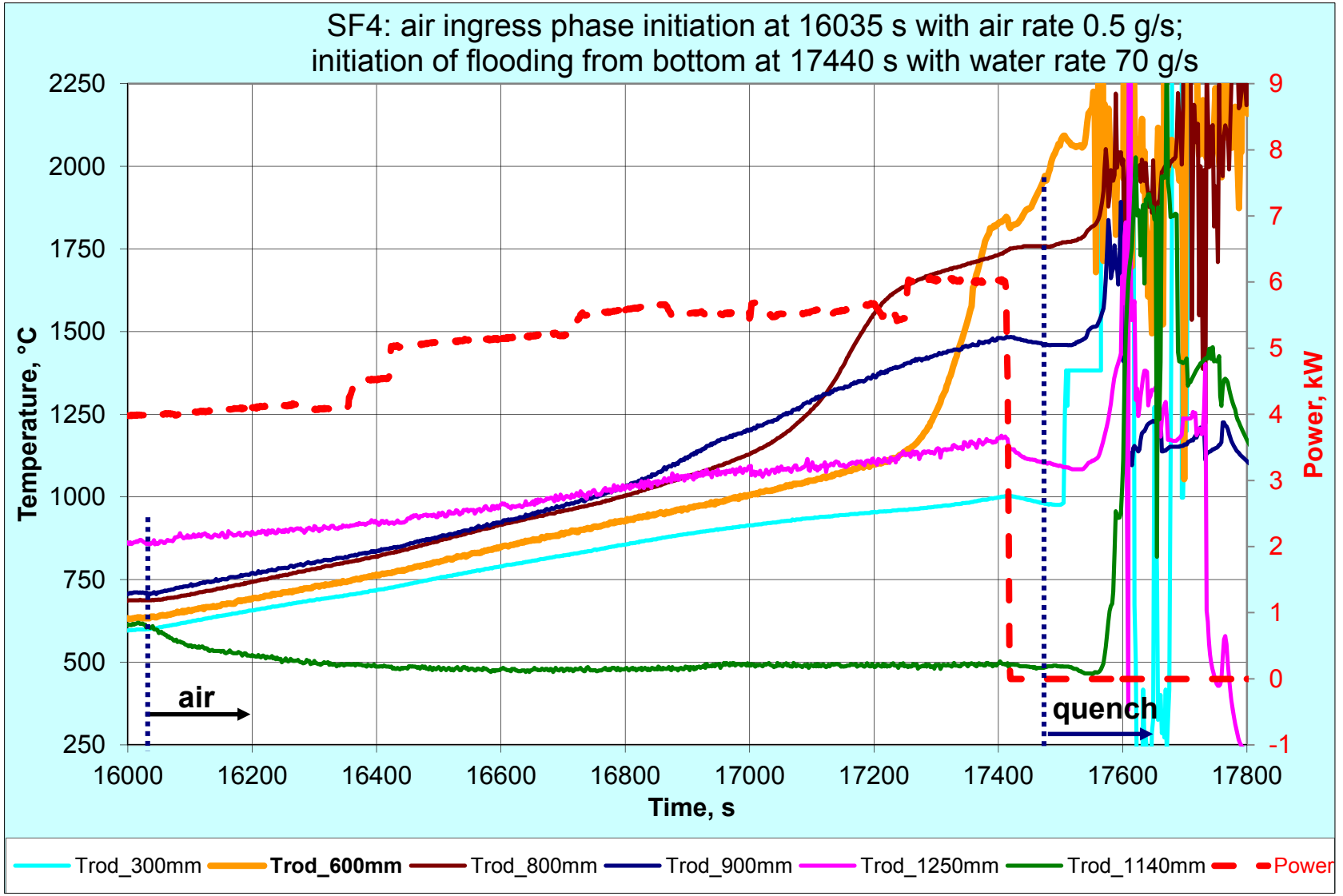




PARAMETER SF-4 test performance



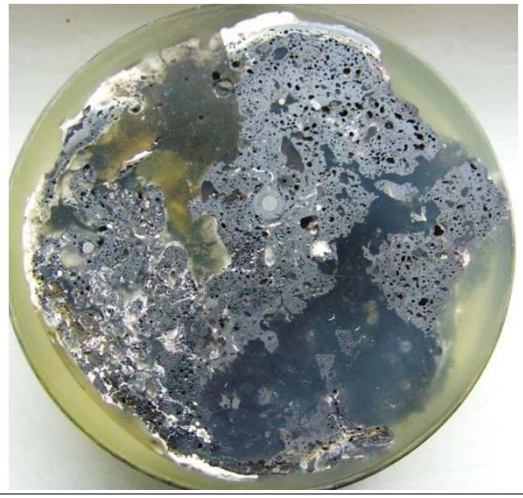
SF-4: temperature escalations during air ingress and after reflood initiation



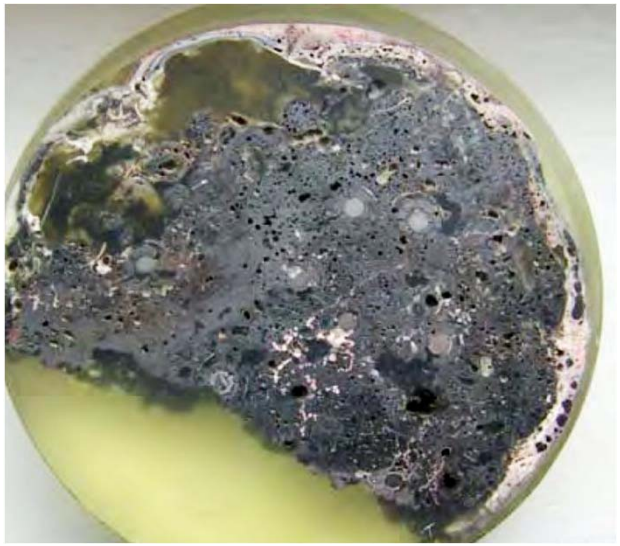
SF4: cross-sections

130 mm: intact rods, small melt pools

260 mm: rods partially dissolved by relocated melt



300 mm: melt

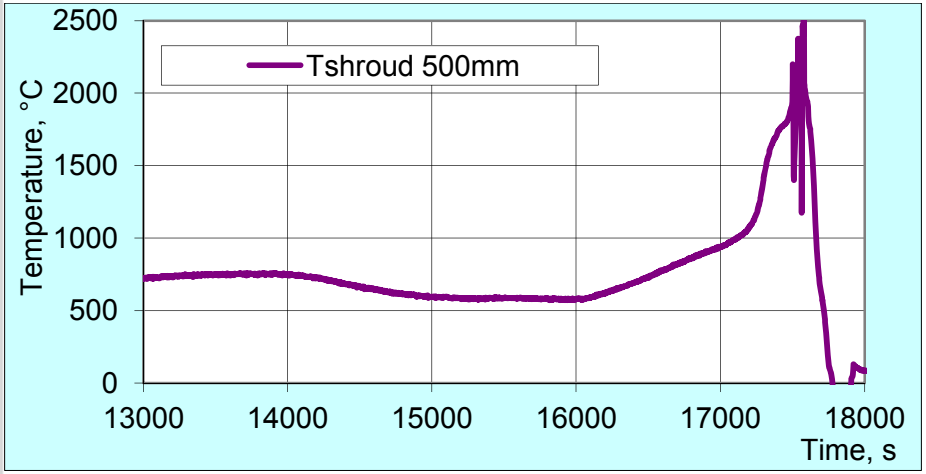


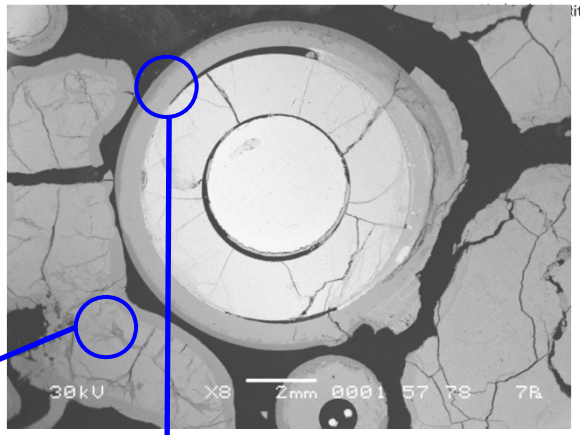
380 mm: melt

600 mm: melt

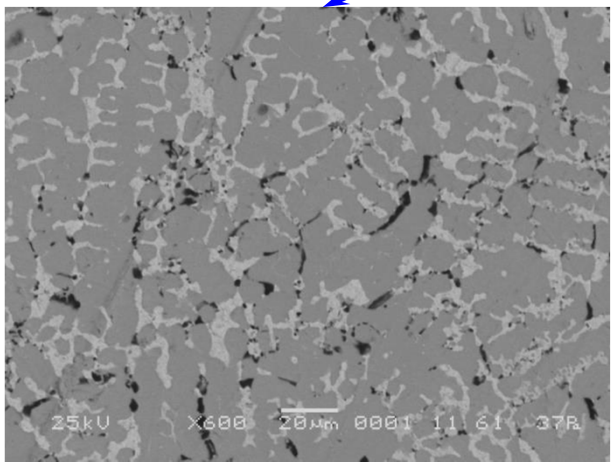
1200 mm: absence of melted claddings

SF4 cladding structure at 260 mm (Tmax)

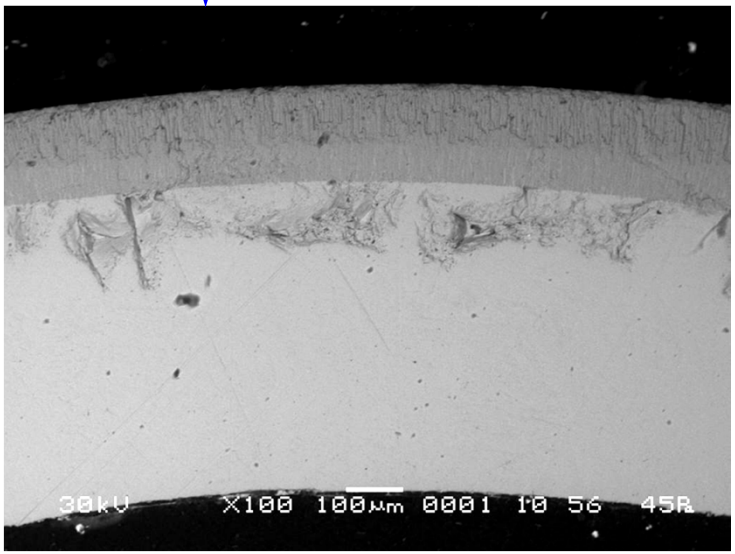




Rod 2.2



oxidised relocated melt



homogeneous ZrO_2 : 200 µm;
no nitrides

PARAMETER SF-4 test (19 rods, heated 1275 mm, pre-ox 250 µm)
Temperature transient during air ingress (1476 s): T=1173-2110 K

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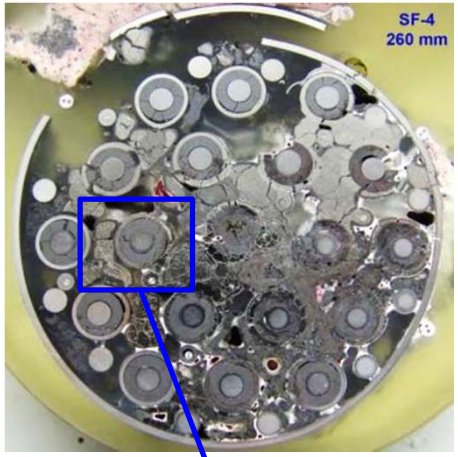
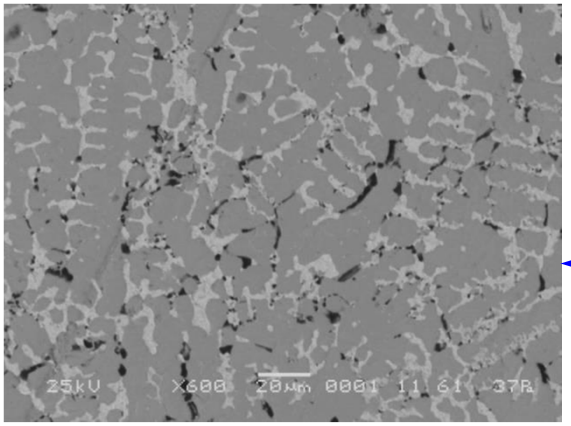
130 mm: intact bundle

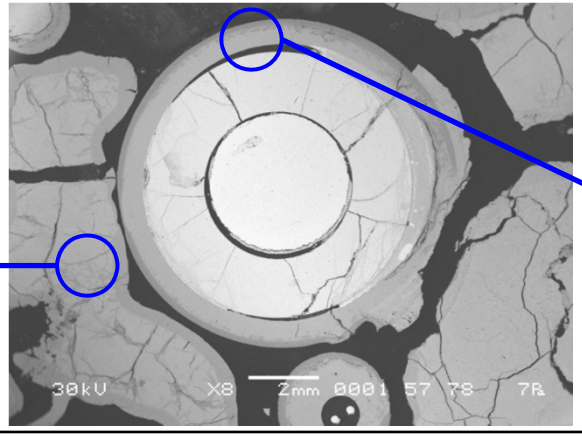


260 mm: melt

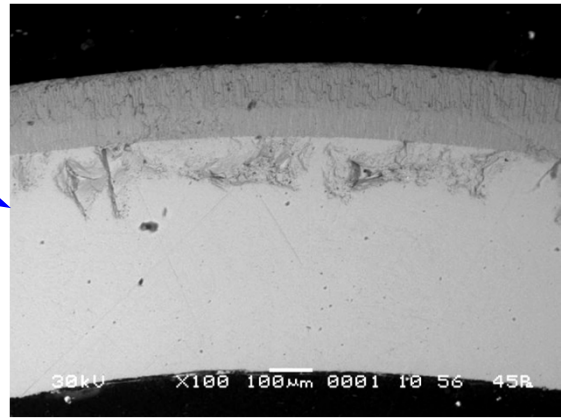
1200 mm: melt; *nitrides dissolved by melt*



oxidised relocated melt



260 mm: melt



homogeneous ZrO2 : 200 µm;
no nitrides

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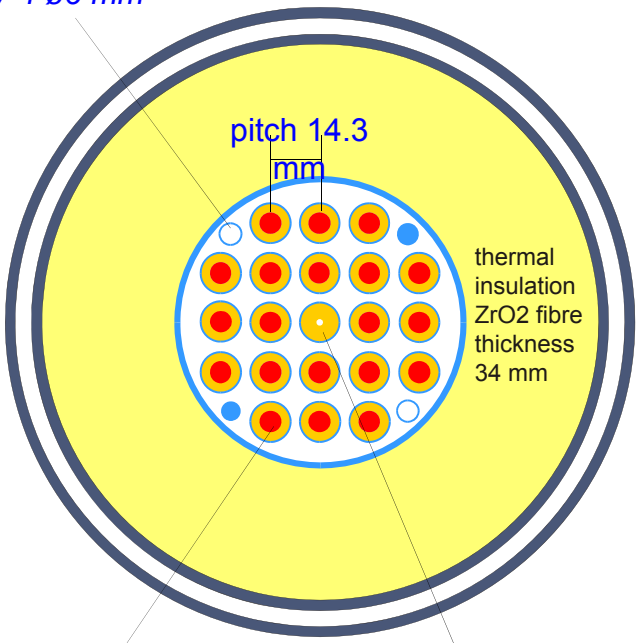
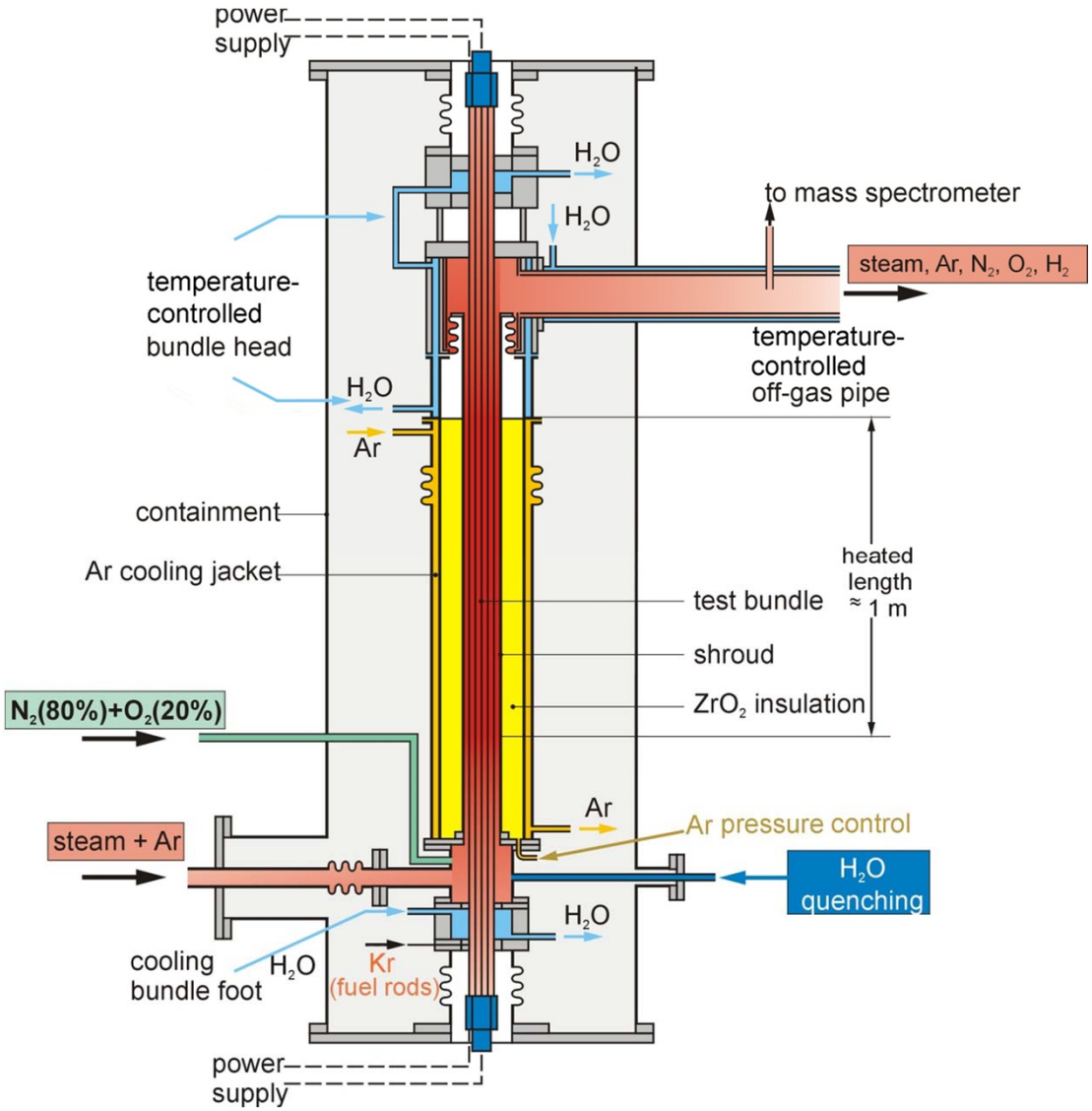
PARAMETER-SF4 SUMMARY

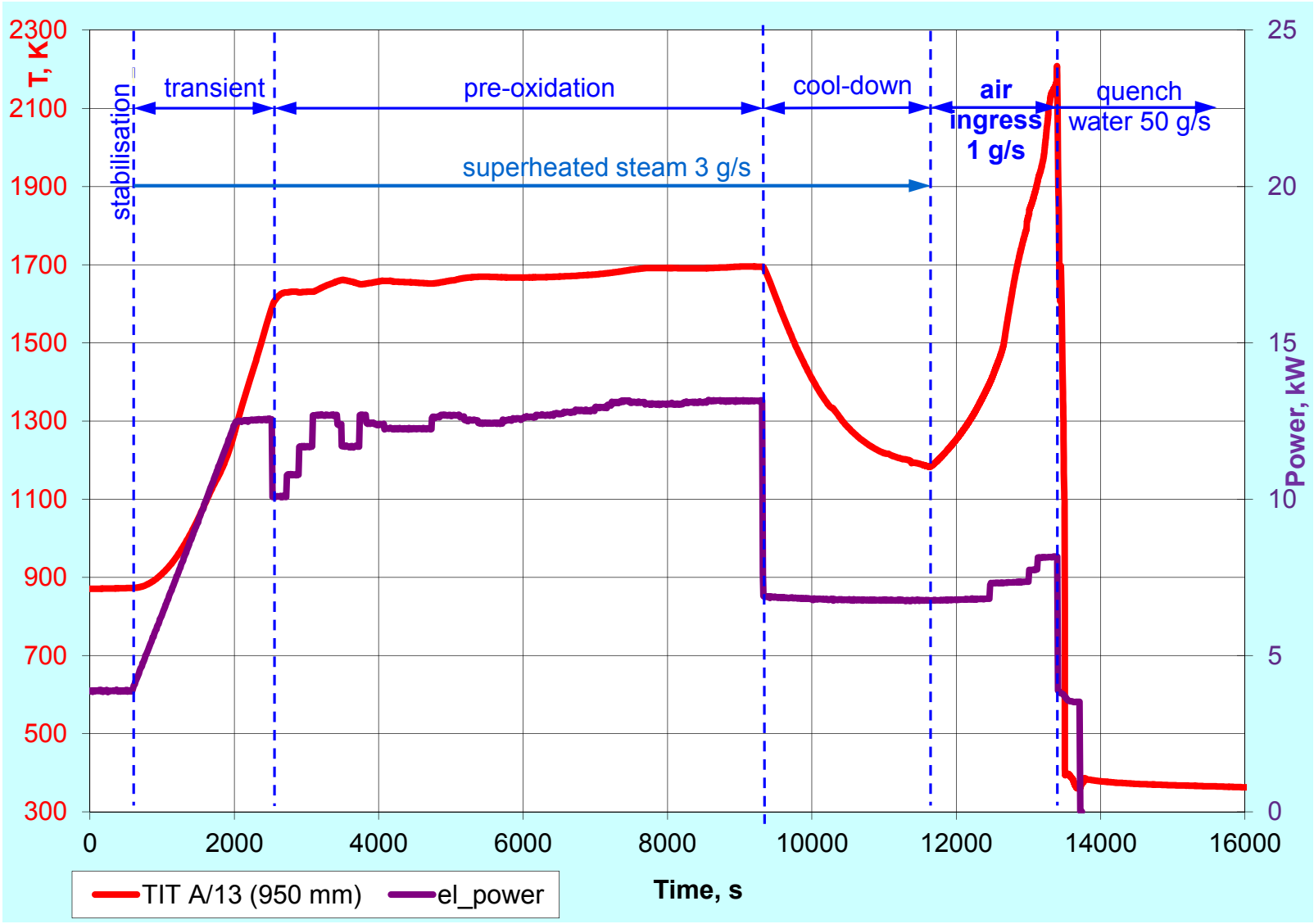
- low air flow rate during air ingress: 0.5 g/s
- air injection at relative *low* temperatures: 850°C at hottest elevation 1250 mm;
- *moderate* initial oxide layer before air ingress: 250 µm at hottest elevation 1250 mm; 30 µm at 250 mm;
- temperature escalation on the end of air ingress up to melting of claddings;
- no noticeable nitride formation.

QUENCH facility

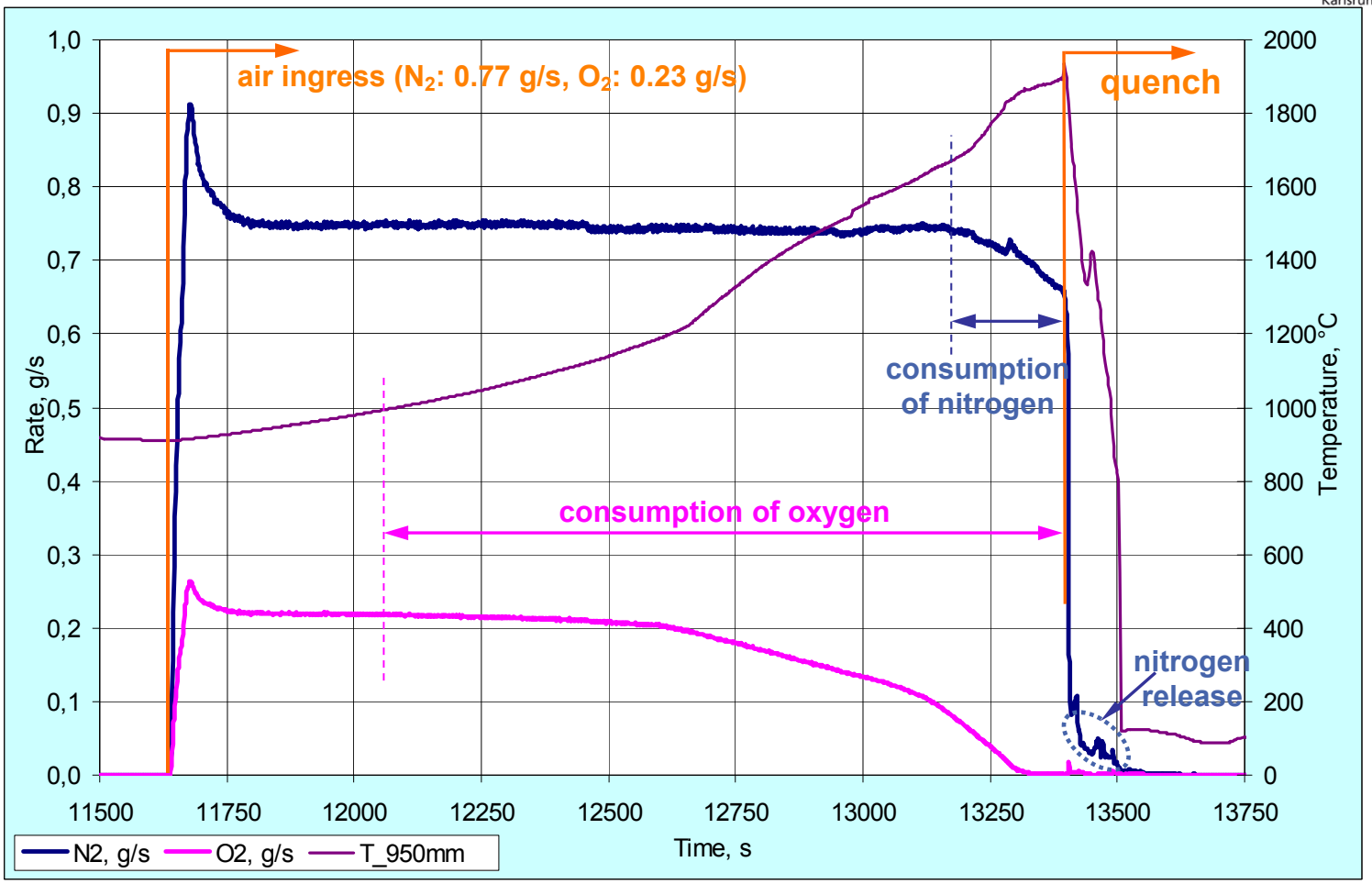




QUENCH-10 test performance



QUENCH-10: Mass spectrometer measurement of N_2 and O_2 after air ingress



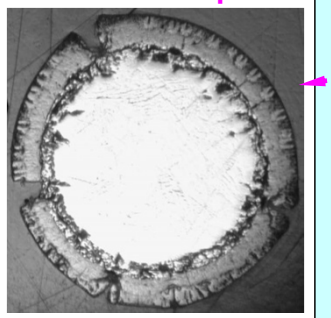
Oxygen : injected 302 g, consumed 83.5 g

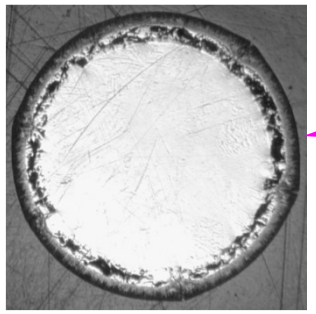
Nitrogen: injected 1312 g, consumed 8 g, re-oxidised (quench) **3.5 g** ($2ZrN + 4H_2O = 2ZrO_2 + \mathbf{4H_2} + \mathbf{N_2}$)

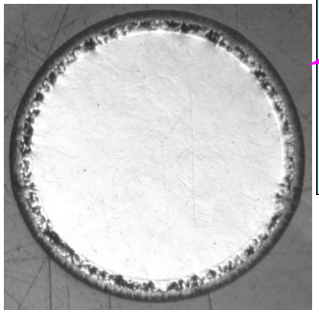
Hydrogen (quench): 5 g, thereof **1 g** from nitride re-oxidation

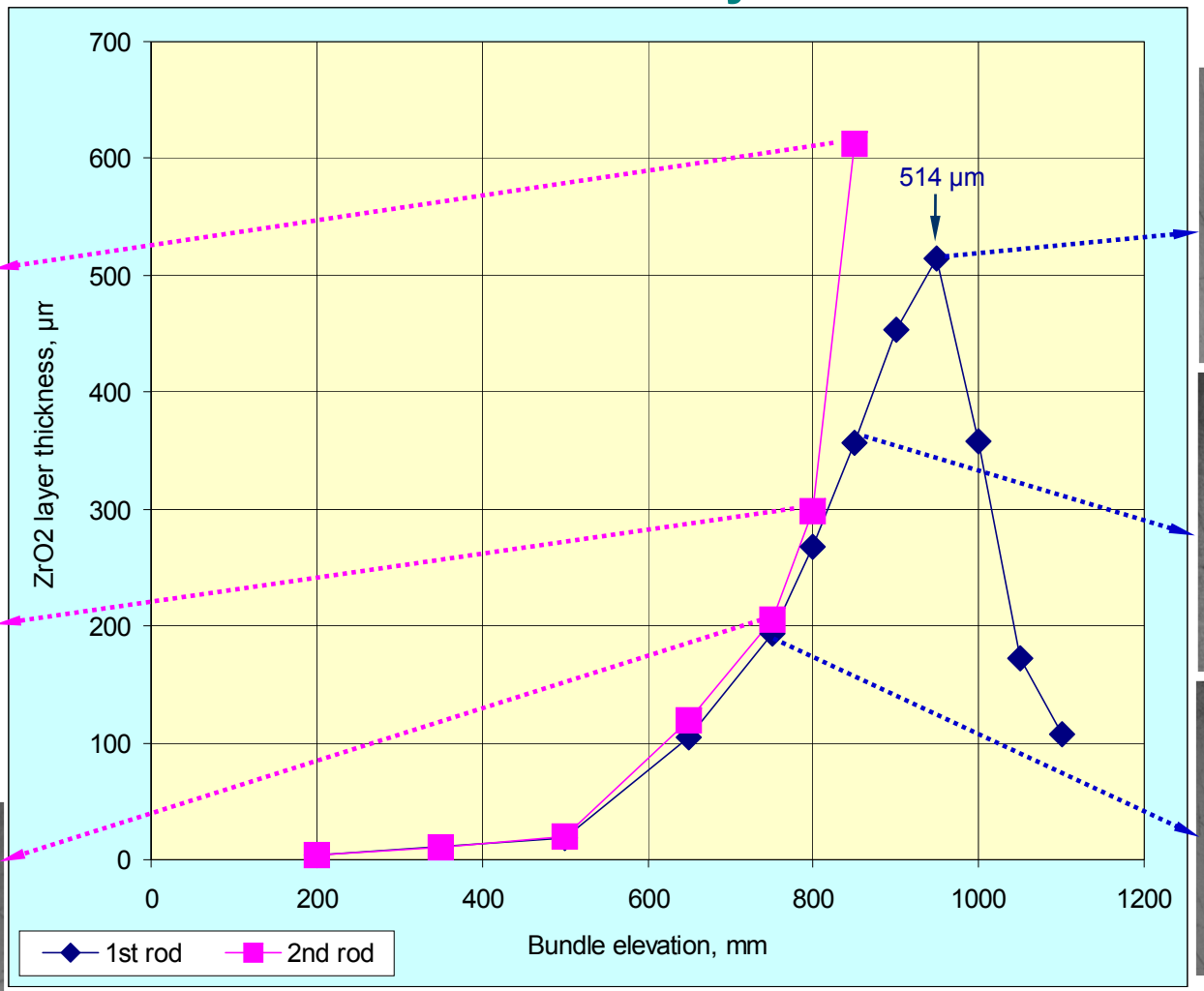
QUENCH-10: Withdrawn corner rods: axial distribution of oxide layer thickness

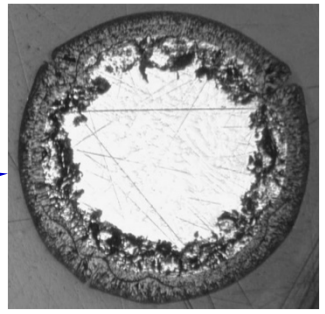
2nd rod:
before flooding
max 600 µm

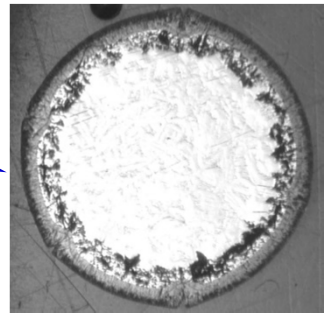


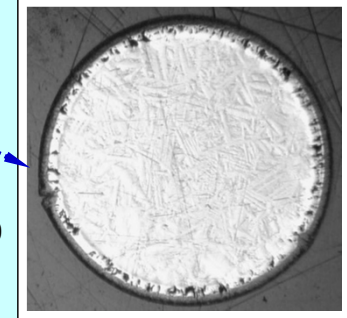






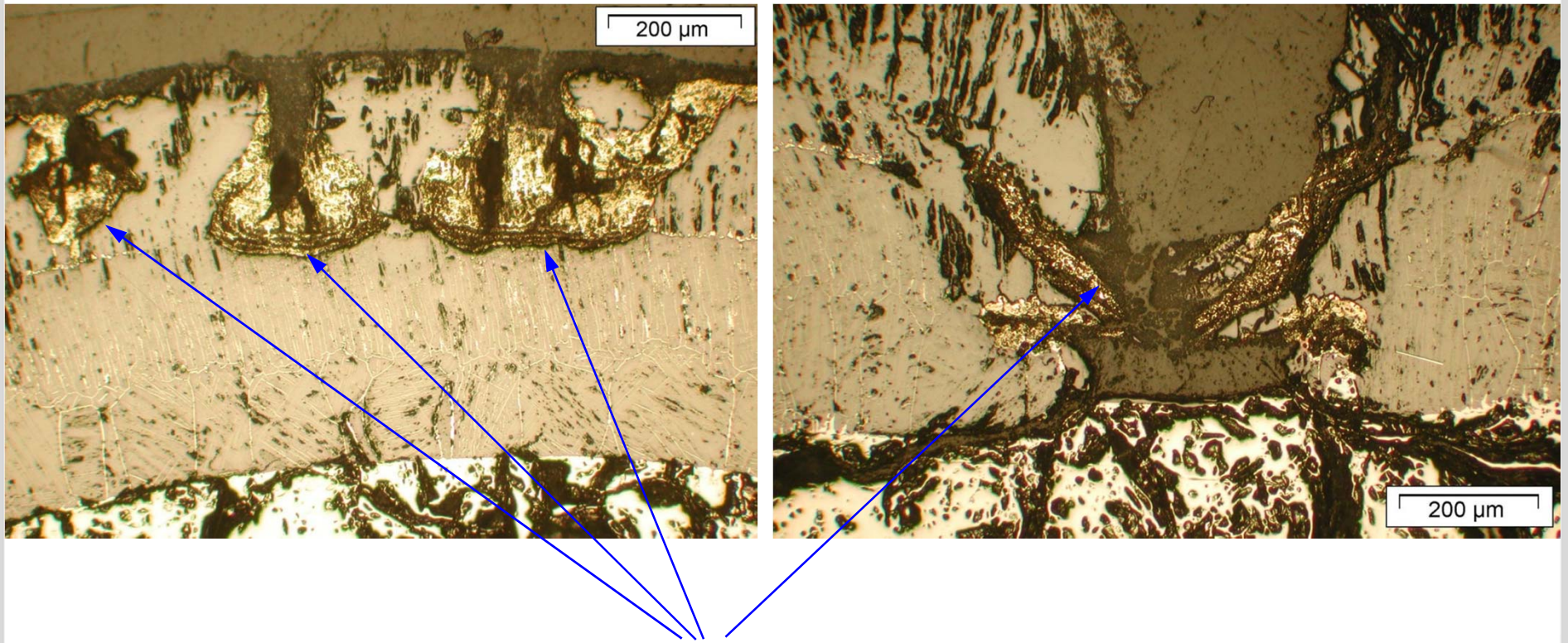






1st rod:
before air ingress
max 500 µm

QUENCH-10: Nitride formation on the end of the air ingress phase (withdrawn Zry-4 corner rod)



Nitride formation under oxygen starvation conditions
at the elevation 850 mm

QUENCH-10: cross-sections

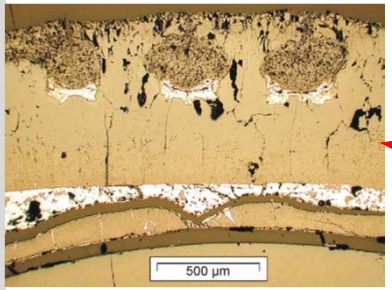
650 mm: relocated debris

750 mm: oxidised claddings

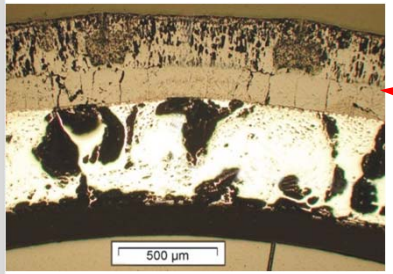
850 mm: debris

950 mm: absence of claddings

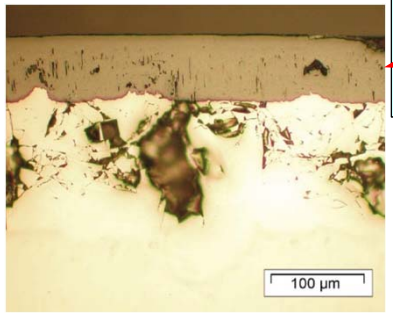
QUENCH-10: Axial change of oxide layer structure and residual nitrides after reflood



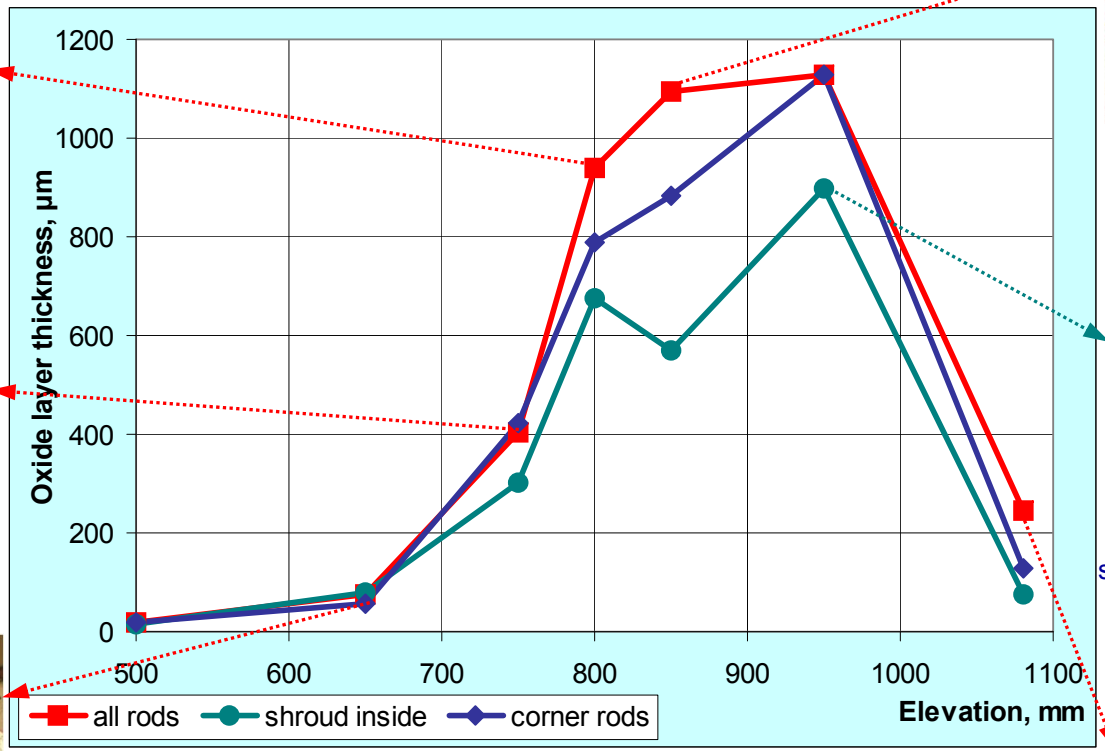
clad. 800 mm: residual nitrides at bottom of fragile regions

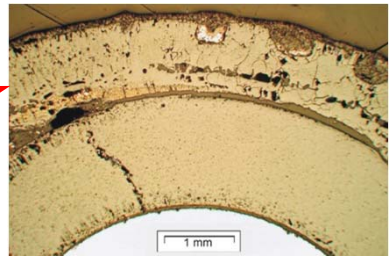


clad. 750 mm: fragile regions

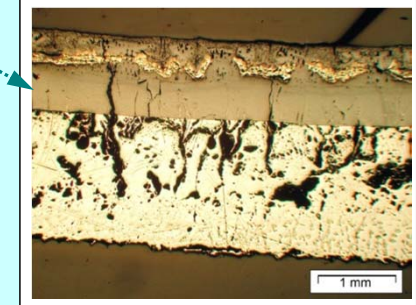


clad. 650 mm: regular oxide layer

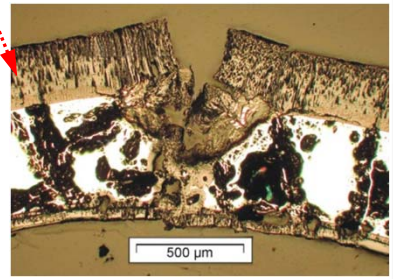




clad. 850 mm: residual nitrides at bottom of fragile regions

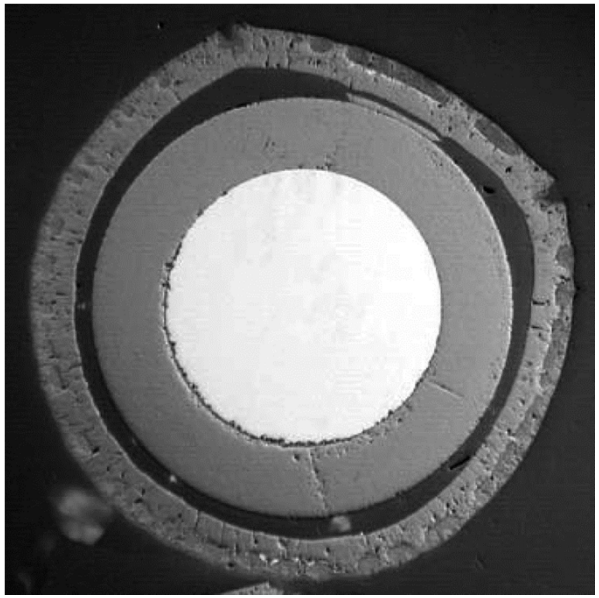
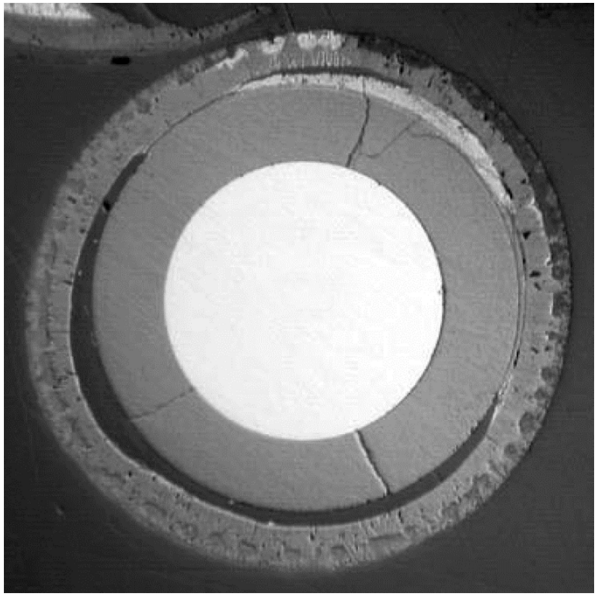
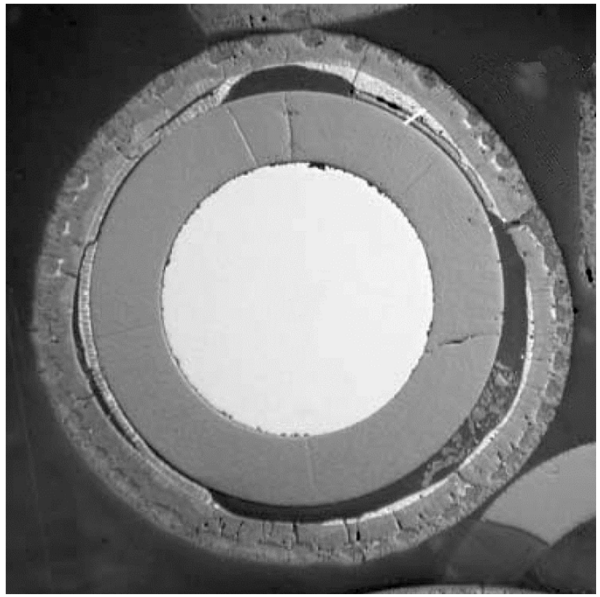


shroud 950 mm: residual nitrides at bottom of fragile surface layer



clad. 1080 mm: nitrides at scale wedge crack

QUENCH-10: formation of porous “pockets” at outer surface of thick oxide due to re-oxidation of nitrides

		
rod 3, 800 mm	rod 15, 800 mm	rod 20, 800 mm

QUENCH-10 SUMMARY

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- Pre-oxidation in superheated steam during 6800 s at ~1700 K to a max oxide of 514 µm;

- An intermediate cooling to 1183 K prior to air ingress;

- Air ingress: of 1 g/s (0.22 g/s O_2) during ~30 min; 28 % (84 g) of the oxygen were consumed;

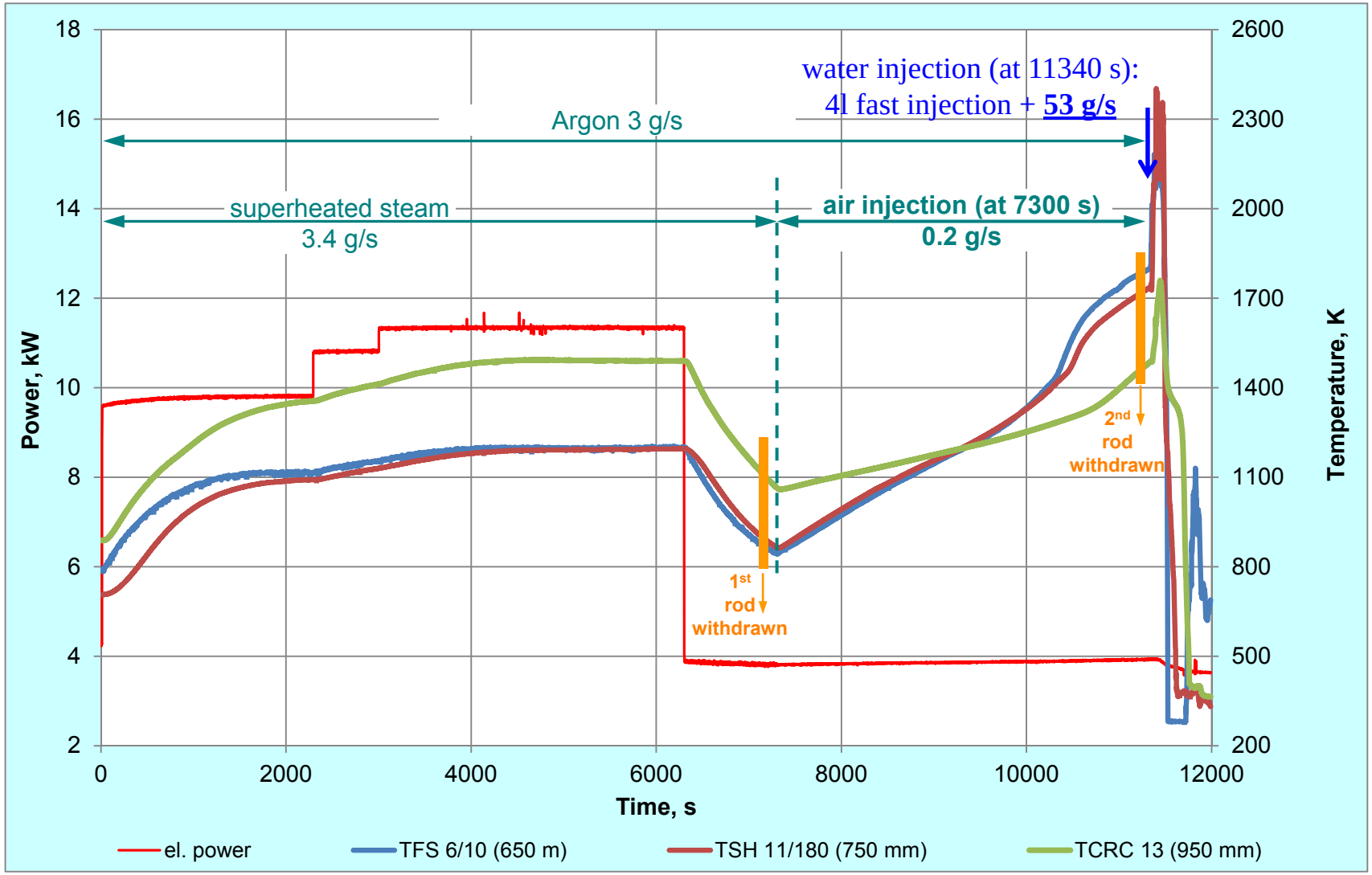
- Duration of oxygen starvation conditions about 80 s; nitrogen consumption (8 g from injected 1300 g); formation of zirconium nitrides inside the oxide layer at elevations 750-900 mm;

- Quench: nitride re-oxidation, release of about 44 % (3.5 g) of the nitrogen that was taken up during air ingress; hydrogen release 1 g due to nitride re-oxidation;

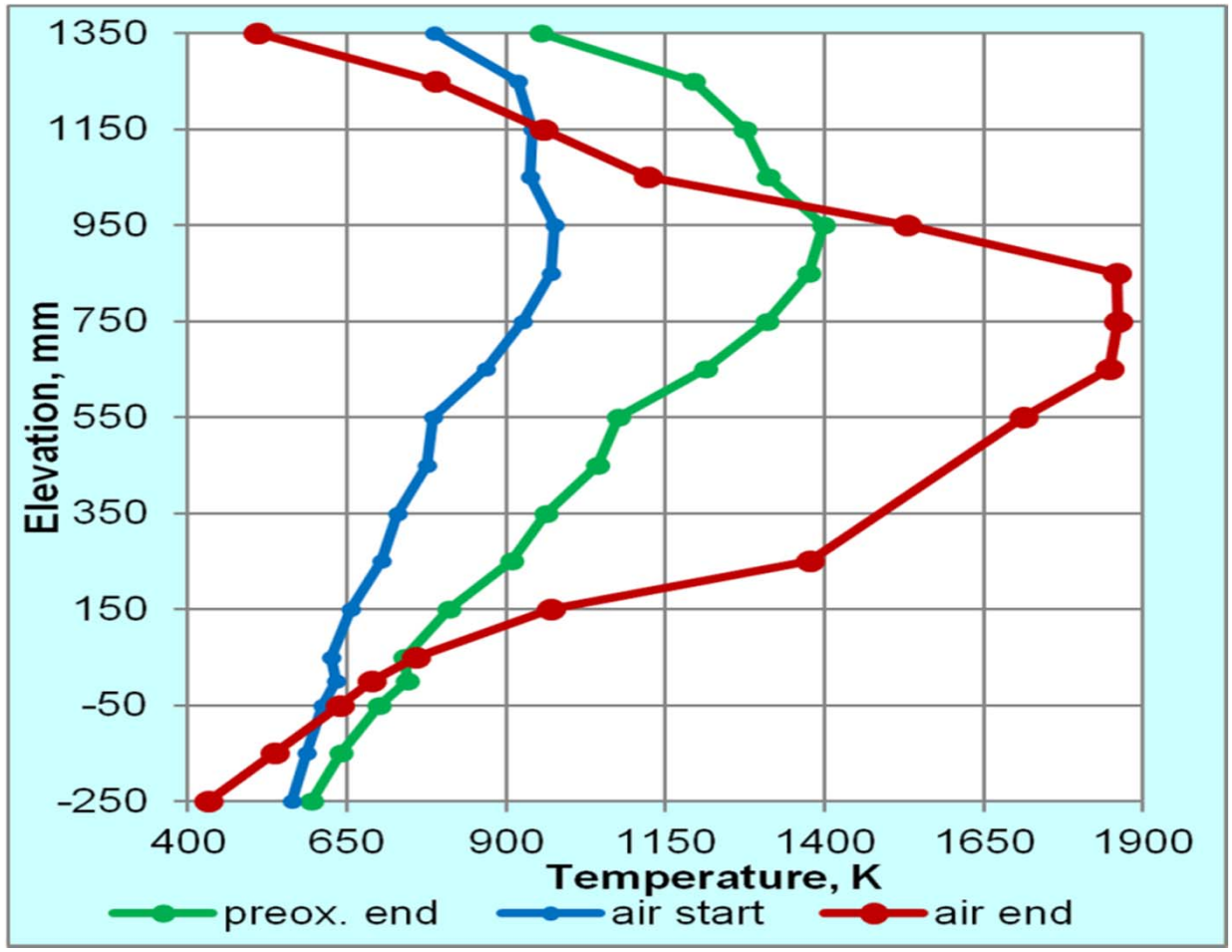
- Formation of porous “pockets” inside oxide as result of re-oxidation of zirconium nitrides during reflood; hydrogen release 4 g due to clad metal oxidation under outer oxide scale.

QUENCH-16 test progression

test performed on 27.07.2011 at KIT/IAM
according to pre-test calculations from PSI, GRS, EdF

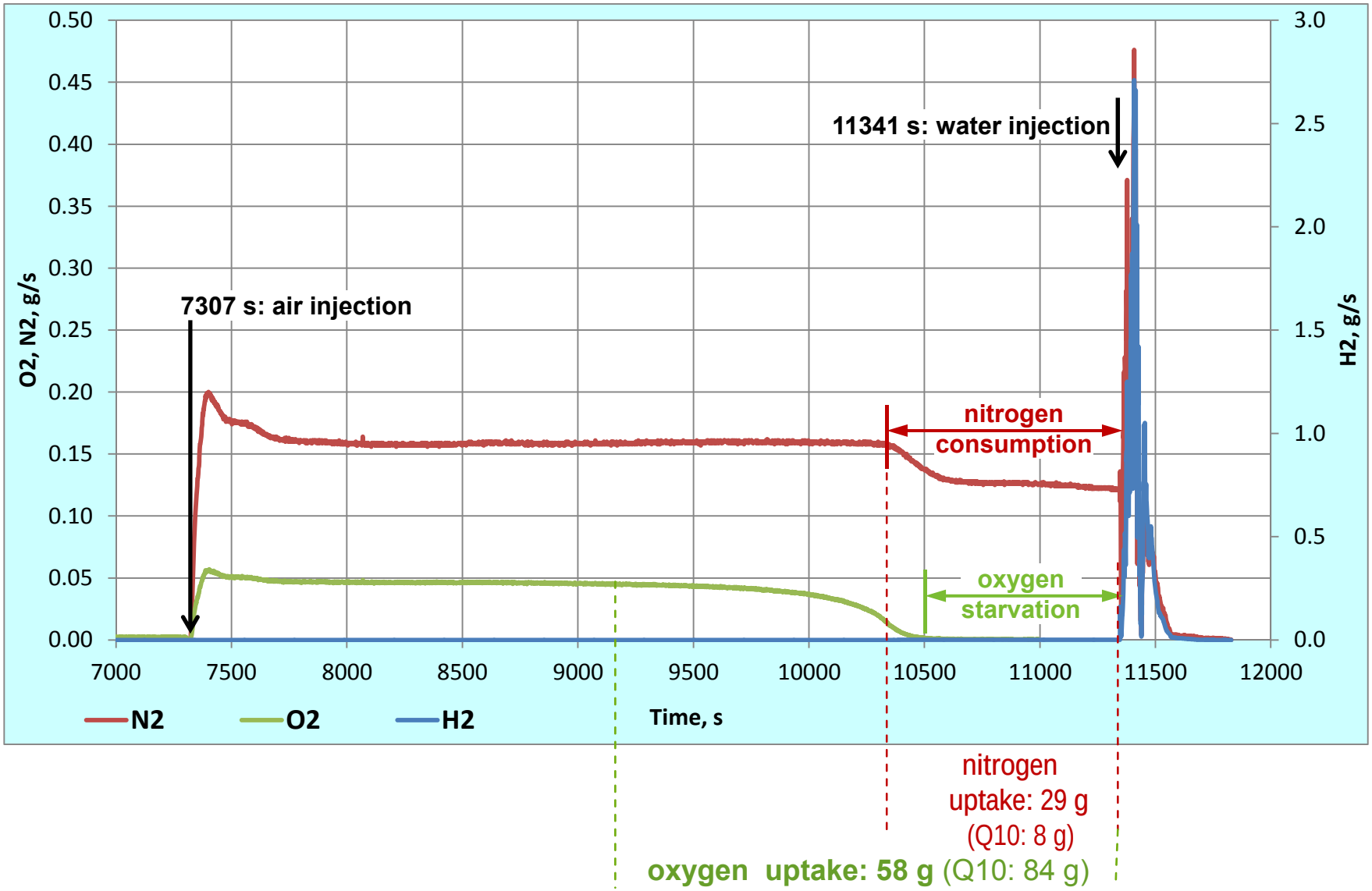


QUENCH-16: Axial temperature distributions for different test phases



strong growth of temperatures at elevations 250 – 950 mm during the air ingress phase

QUENCH-16: Consumption of nitrogen and oxygen during air ingress phase, data of mass spectrometer



QUENCH-16: Corner rod D withdrawn from the bundle on the end of the air ingress phase; nitride formation between 300 and 900 mm

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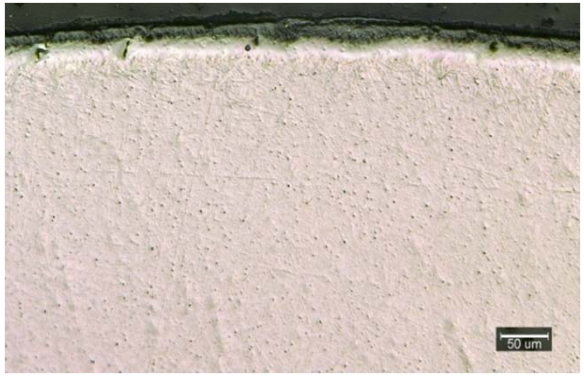
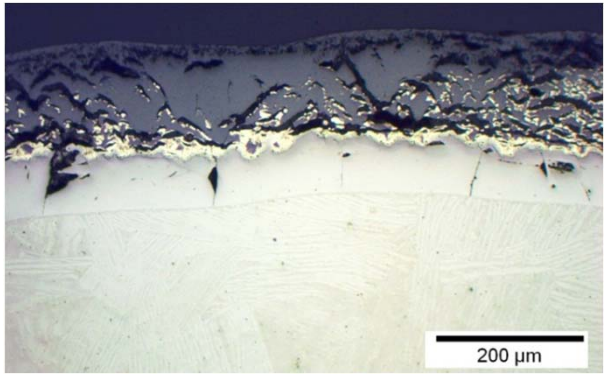
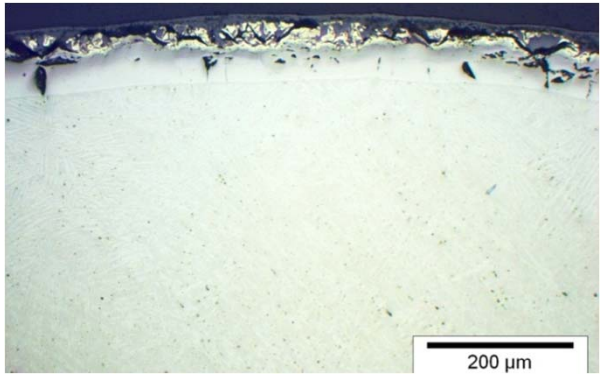
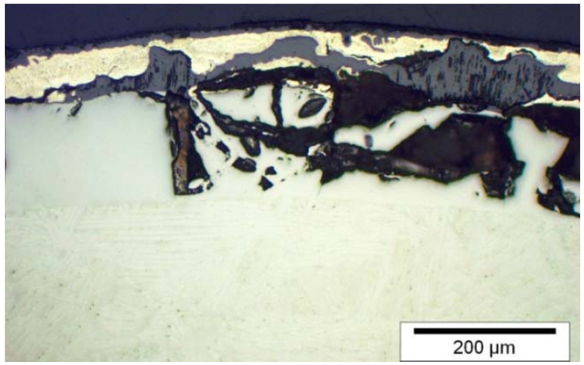
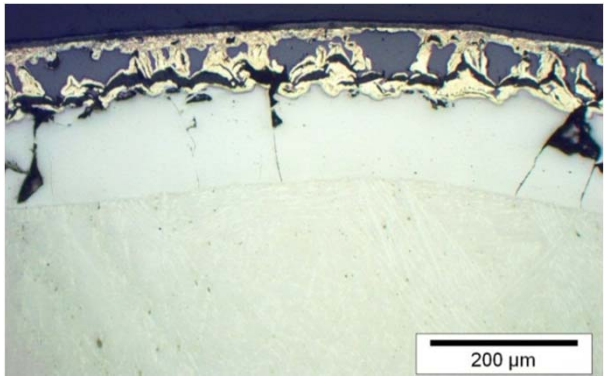
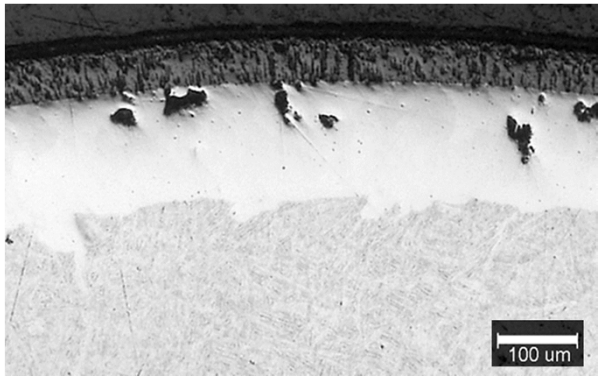
		
250 mm (1070°C): no nitrides	450 mm (1530°C): strong corrosion; nitrides	650 mm (1400°C): moderate corrosion; nitrides
		
750 mm (1460°C): strong corrosion; nitrides	850 mm (1570°C): strong corrosion; nitrides	950 mm: no nitrides

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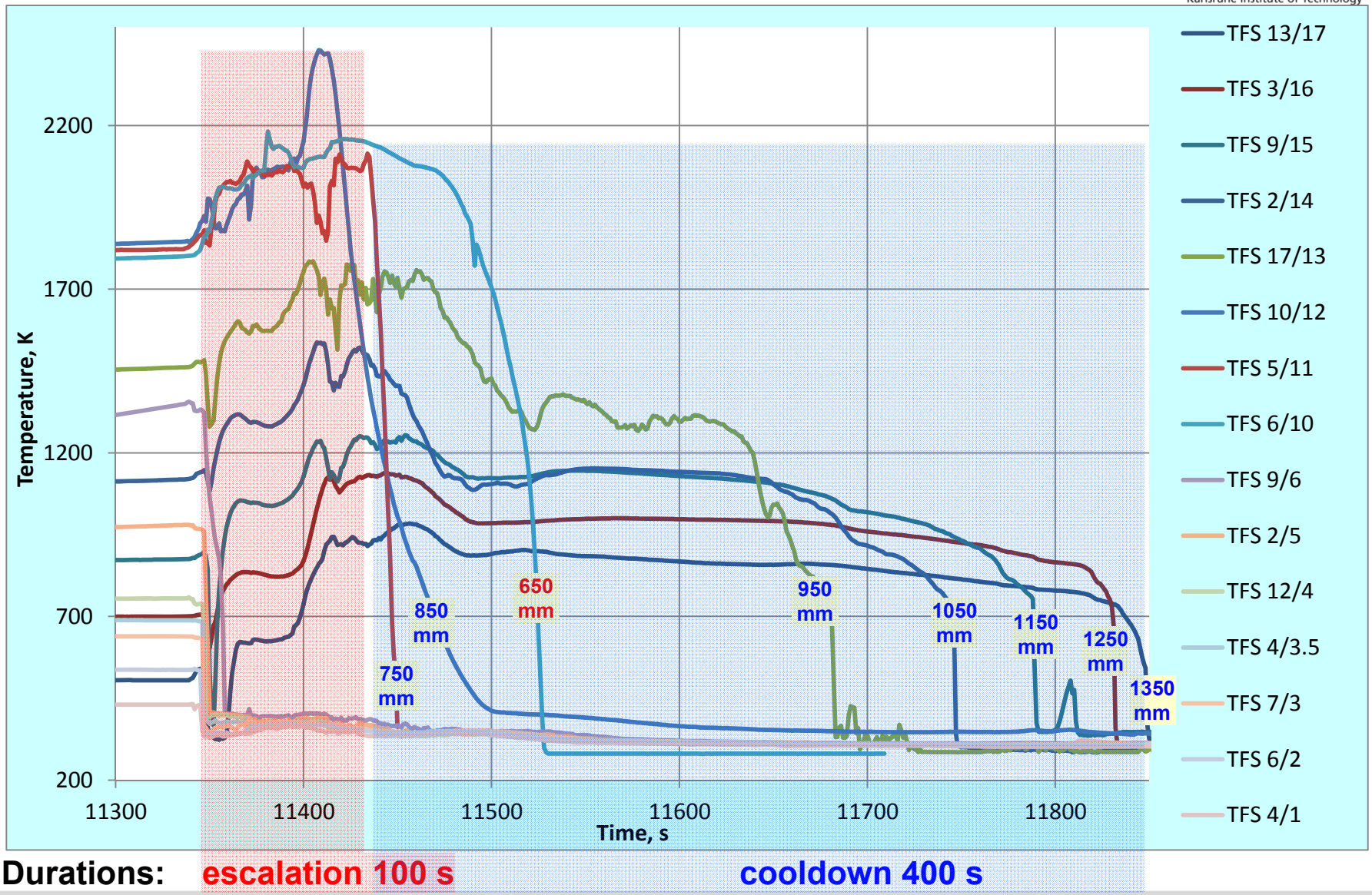
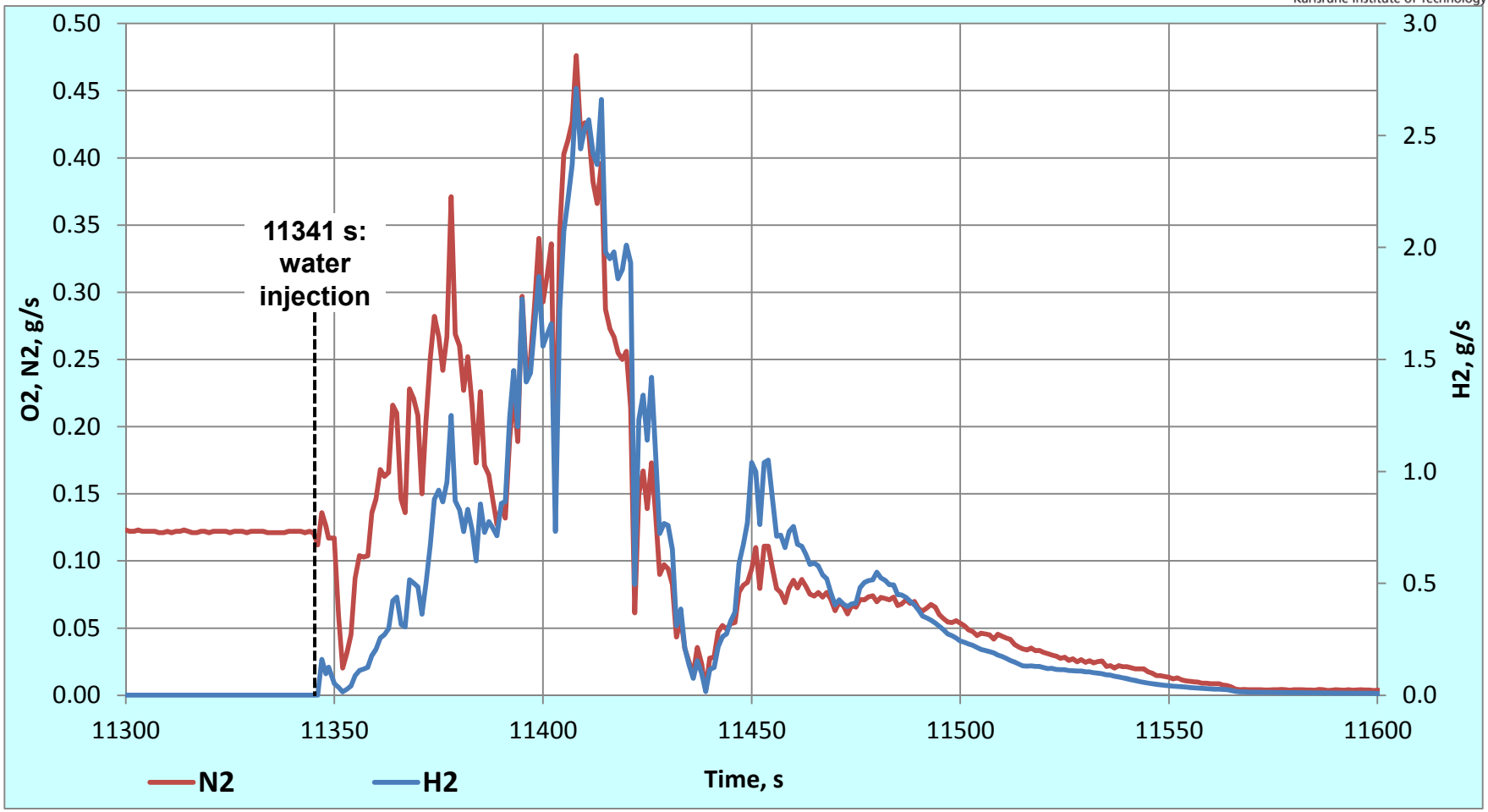
QUENCH-16: Temperature escalation (above Zr melting point) and cooldown during reflood



Durations: escalation 100 s cooldown 400 s

QUENCH-16: Release of hydrogen and nitrogen during quench phase

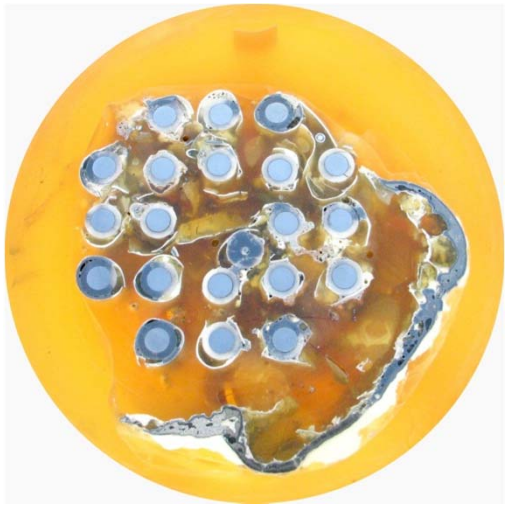
/data of mass spectrometer/



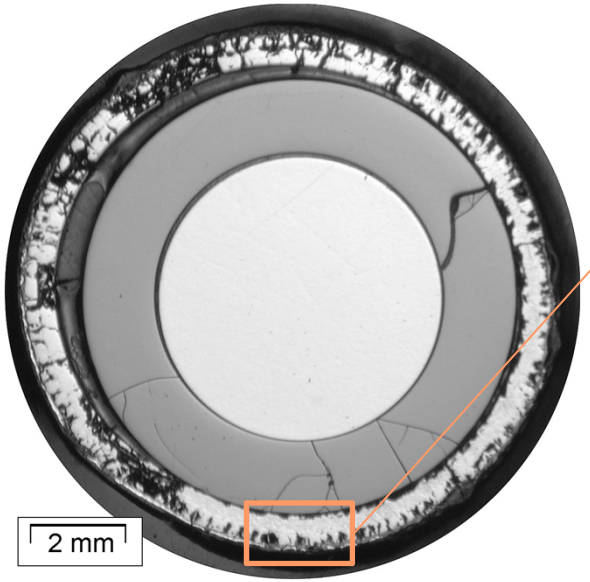
nitrogen release during re-oxidation of nitrides: 24 g (from consumed 29 g): $2ZrN + 4H_2O = 2ZrO_2 + 4H_2 + N_2$

hydrogen release: 128 g. 3 main sources: 1) re-oxidation of Zr-nitrides (**7 g**);
2) secondary oxidation of cladding (**96 g**);
3) melt oxidation (**25 g**).

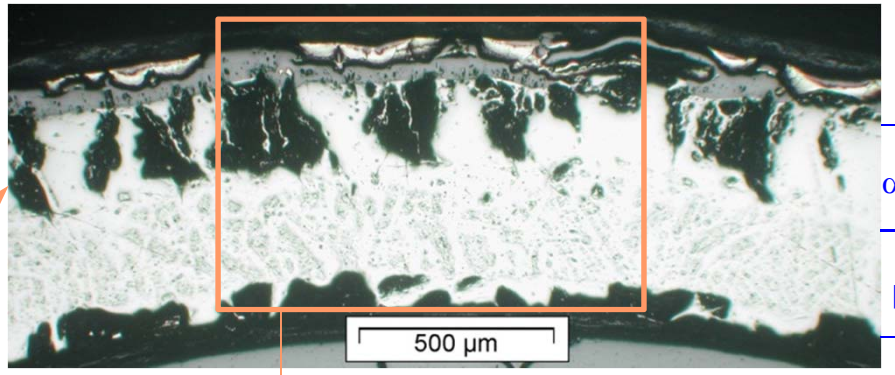
QUENCH-16: Bundle cross sections

		
350 mm: metallic and oxidised **melt pools**	450 mm: mostly oxidised **melt pools**	550 mm: downwards **relocated cladding metal**
		
650 mm: downwards **relocated cladding metal**	750 mm: downwards **relocated cladding metal**	850 mm: outer oxide layer not failed

QUENCH-16: Nitride re-oxidation during quench at elevation 350 mm

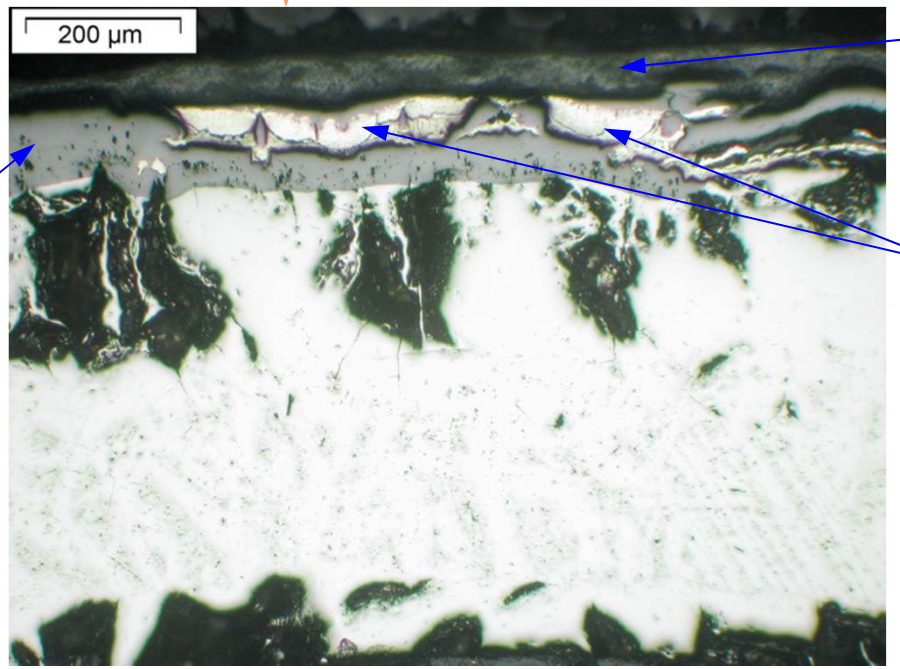


rod #5



α-Zr

prior β-Zr

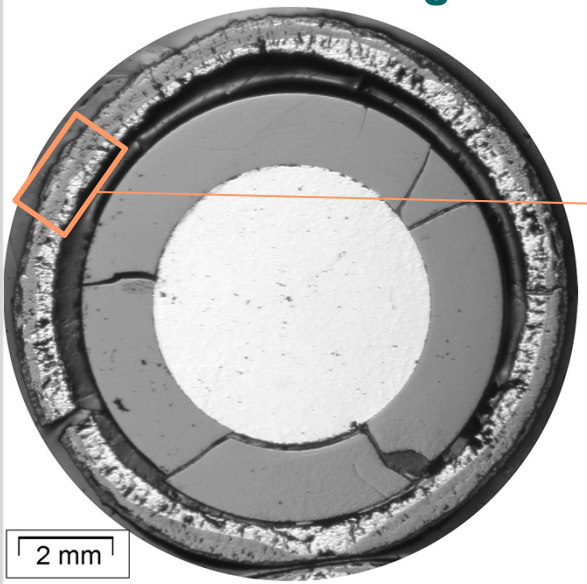


porous oxide scale (re-oxidised during quench)

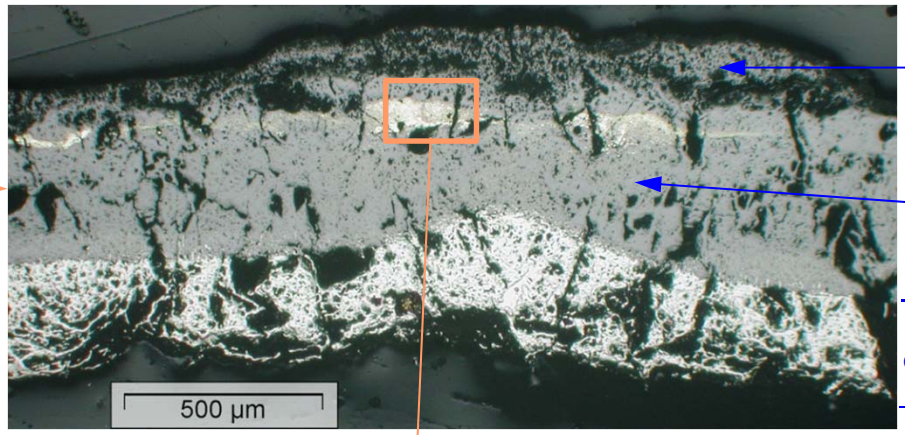
Zr-nitrides

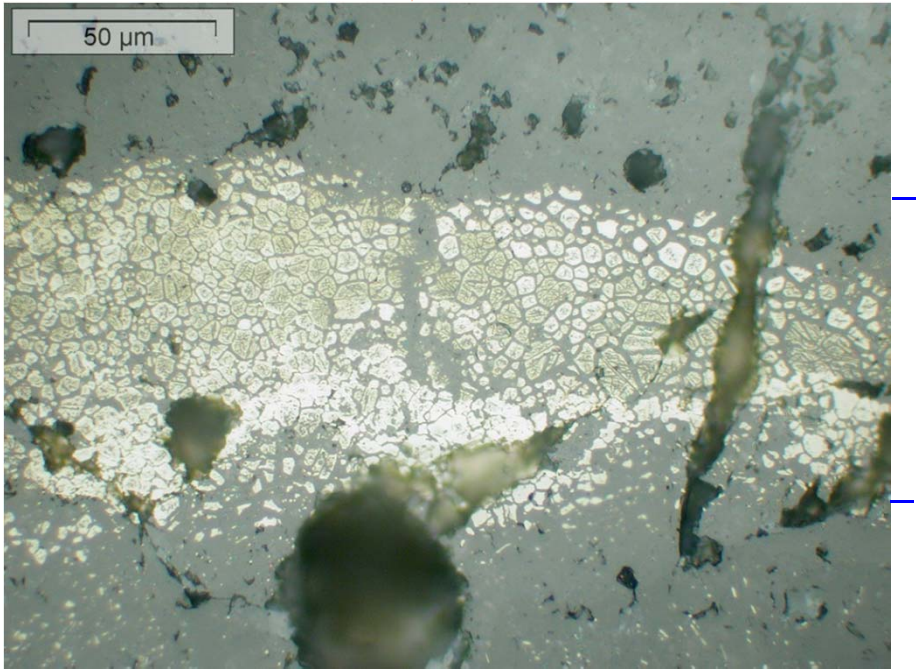
dense inner oxide (grown during quench phase)

QUENCH-16: Nitride re-oxidation and secondary cladding oxidation during quench at elevation 450 mm



rod #4





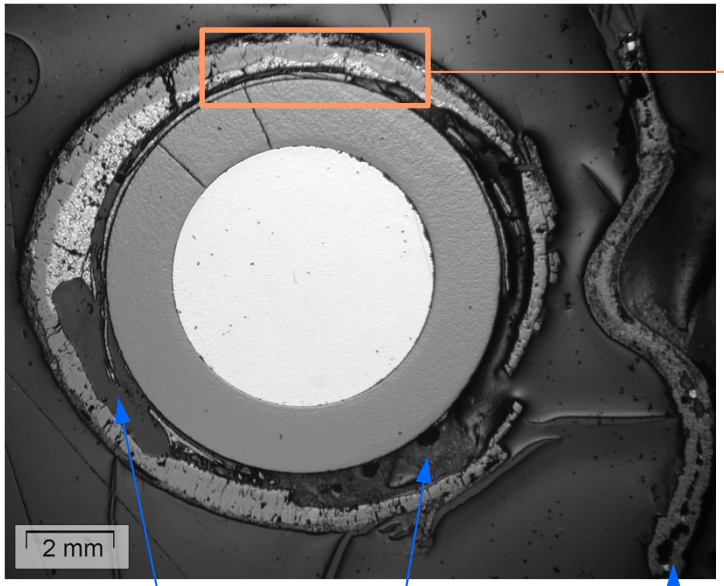
porous oxide scale (re-oxidised during quench)

secondary dense inner oxide (grown during quench phase)

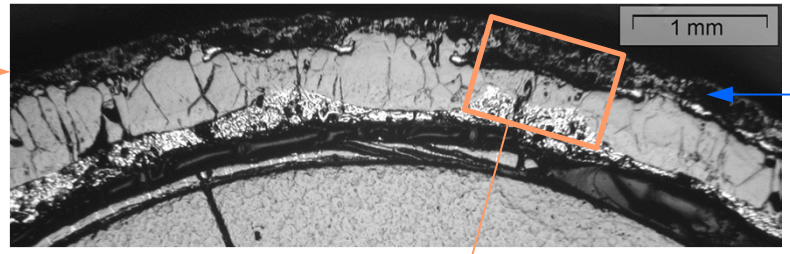
α-Zr(O)

residual Zr-nitrides

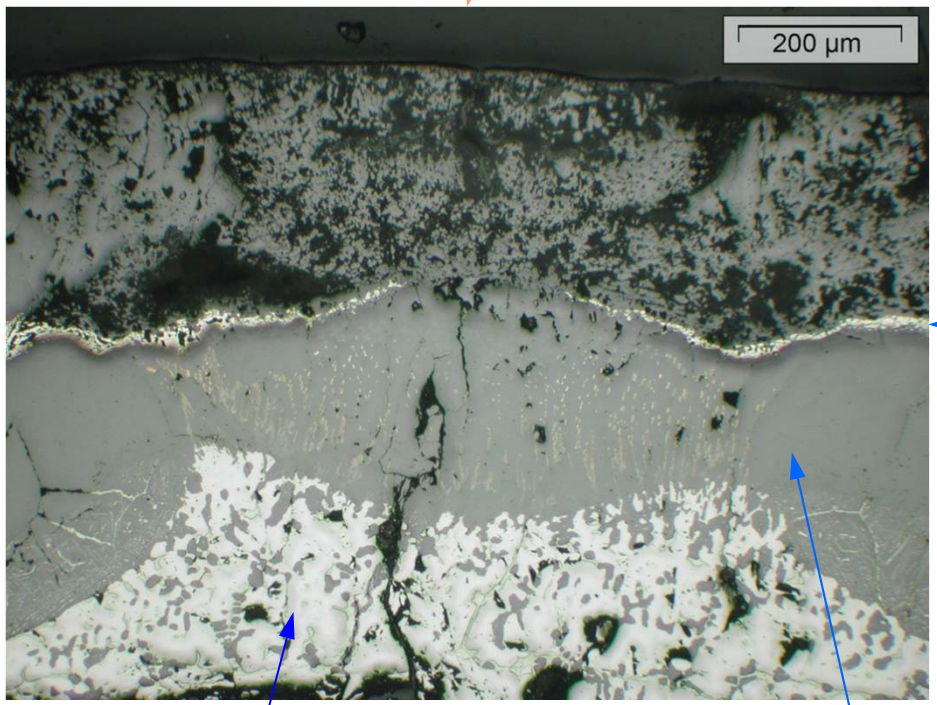
QUENCH-16: Secondary oxidation and melting at elevation 550 mm



rod #9



porous outer oxide scale



completely oxidised Zry grid spacer

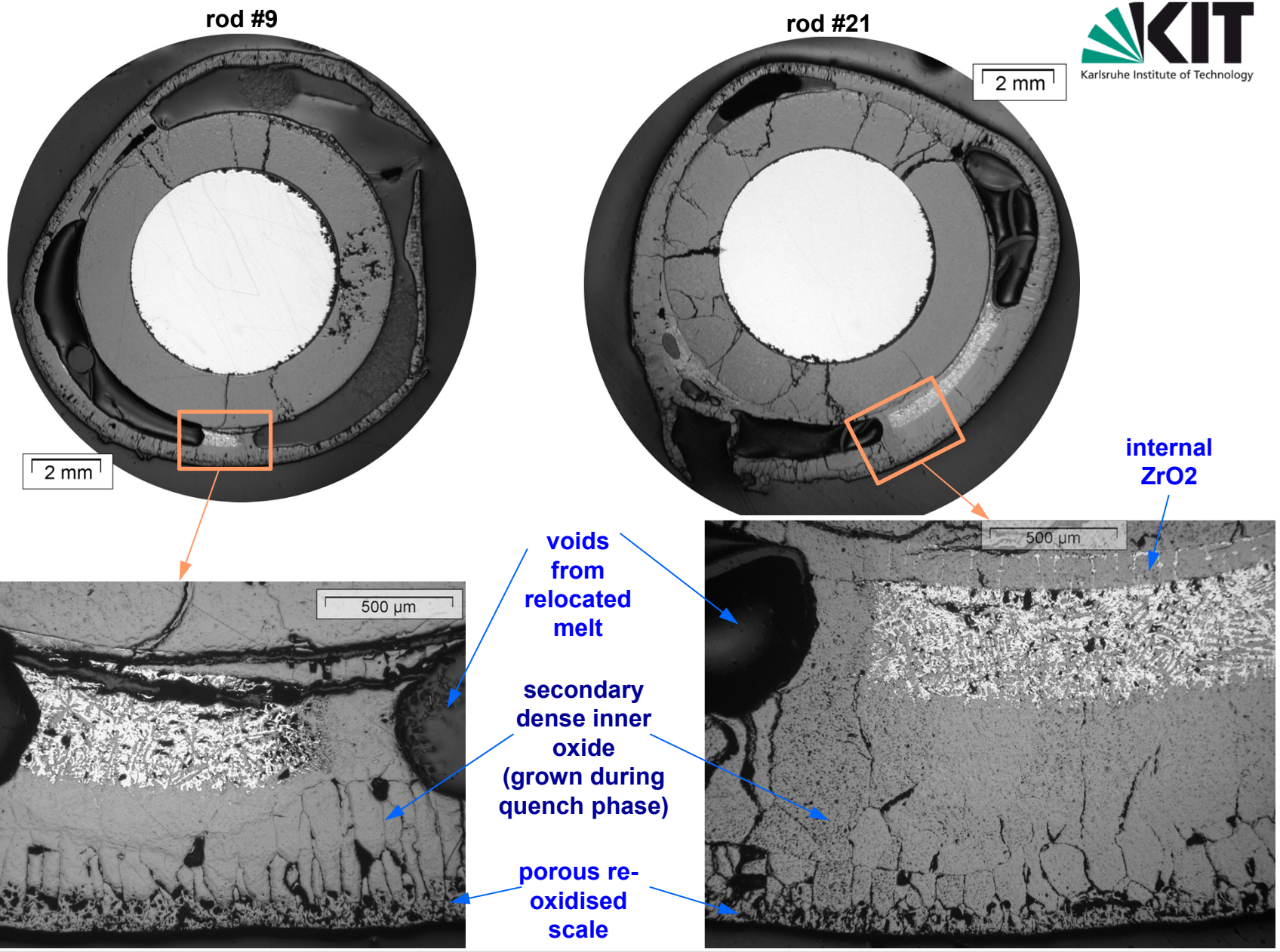
voids from downwards relocated melt

Zr-nitrides

frozen partially oxidised melt

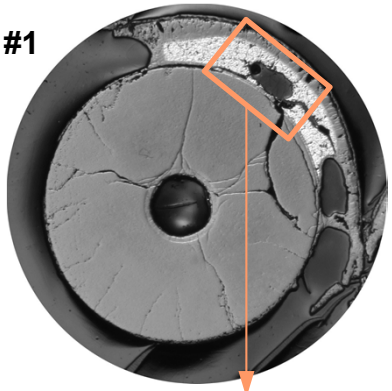
secondary dense inner oxide (grown during quench phase)

QUENCH-16: Intensive melt formation at elevation 650 mm

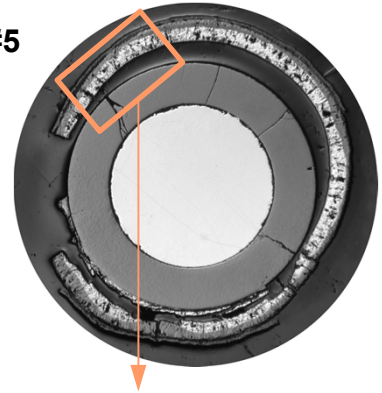


QUENCH-16: Spalling of re-oxidised scales from secondary oxide at 750 mm

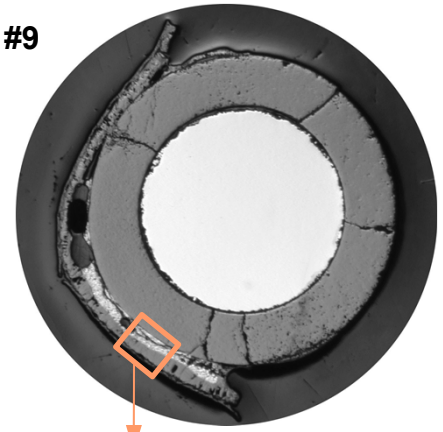
rod #1

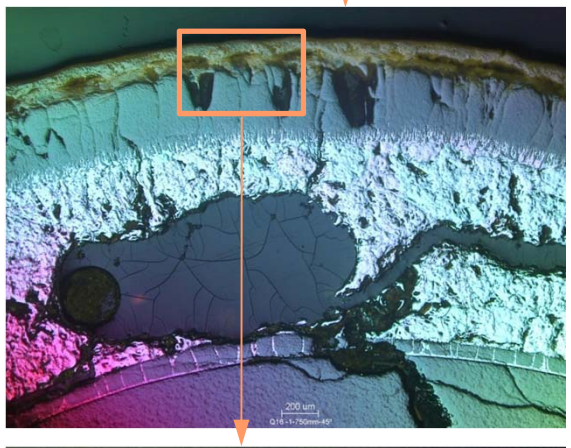


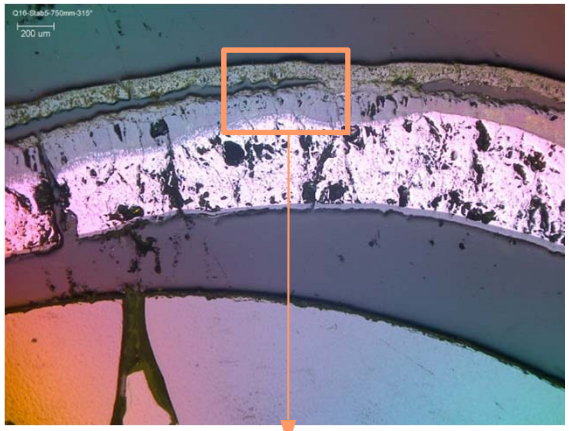
rod #5

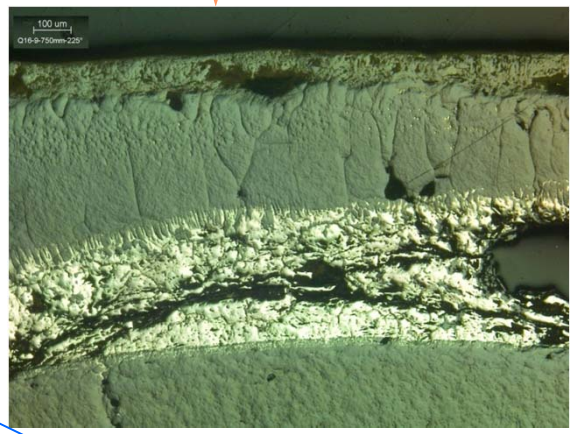


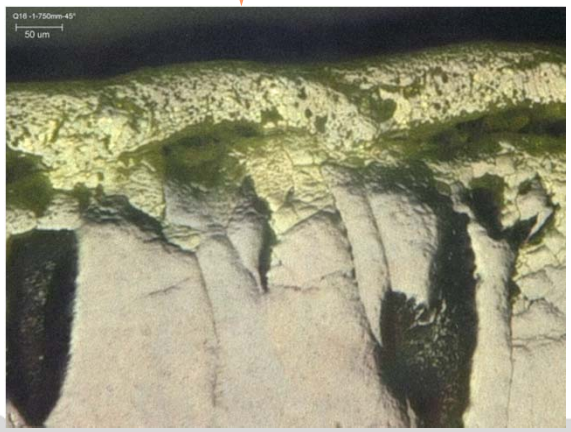
rod #9











prior nitrided scale re-oxidised during quench and spalled from inner ZrO_2 layer growing during quench

QUENCH-16: Re-oxidation of nitrided scales and metal melting at elevation 850 mm

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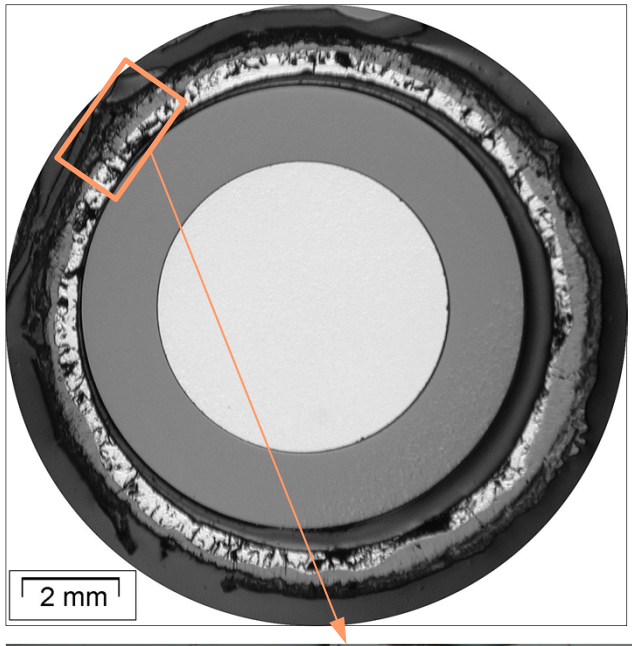
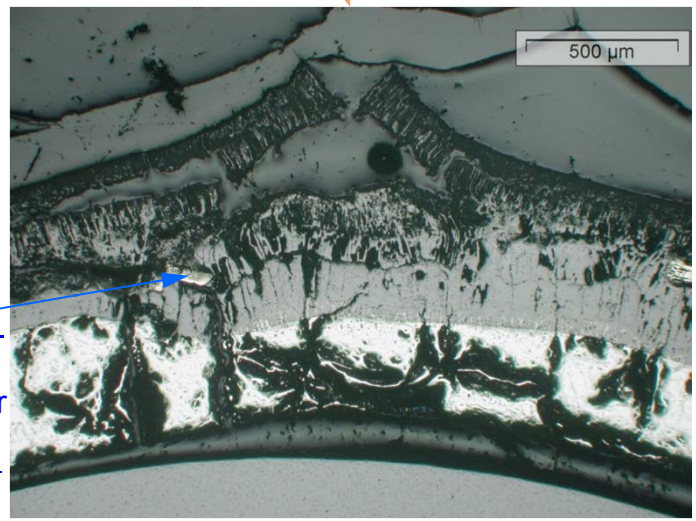
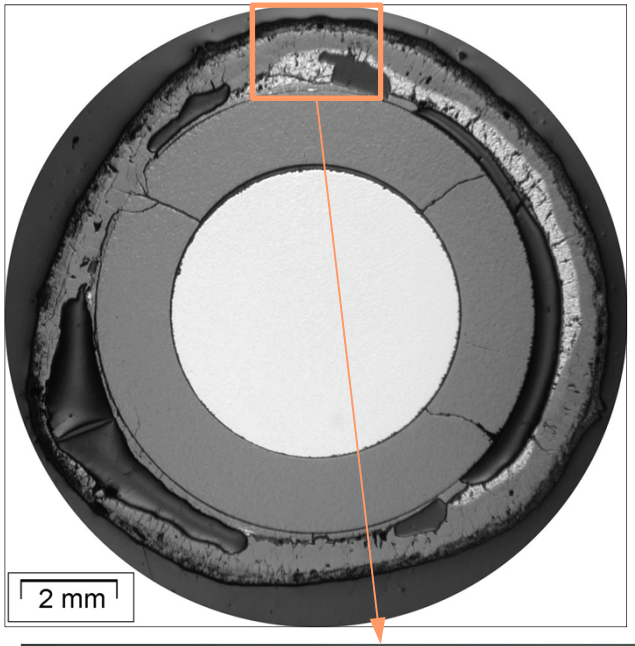
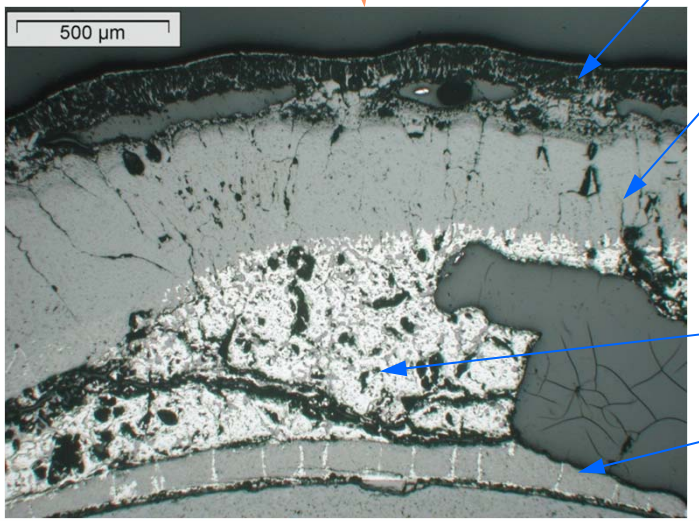
rod #6





rod #18





Zr-nitrides

α-Zr

porous scale (re-oxidised during quench)

secondary dense inner oxide (grown during quench phase)

frozen partially oxidised melt

internal oxide layer

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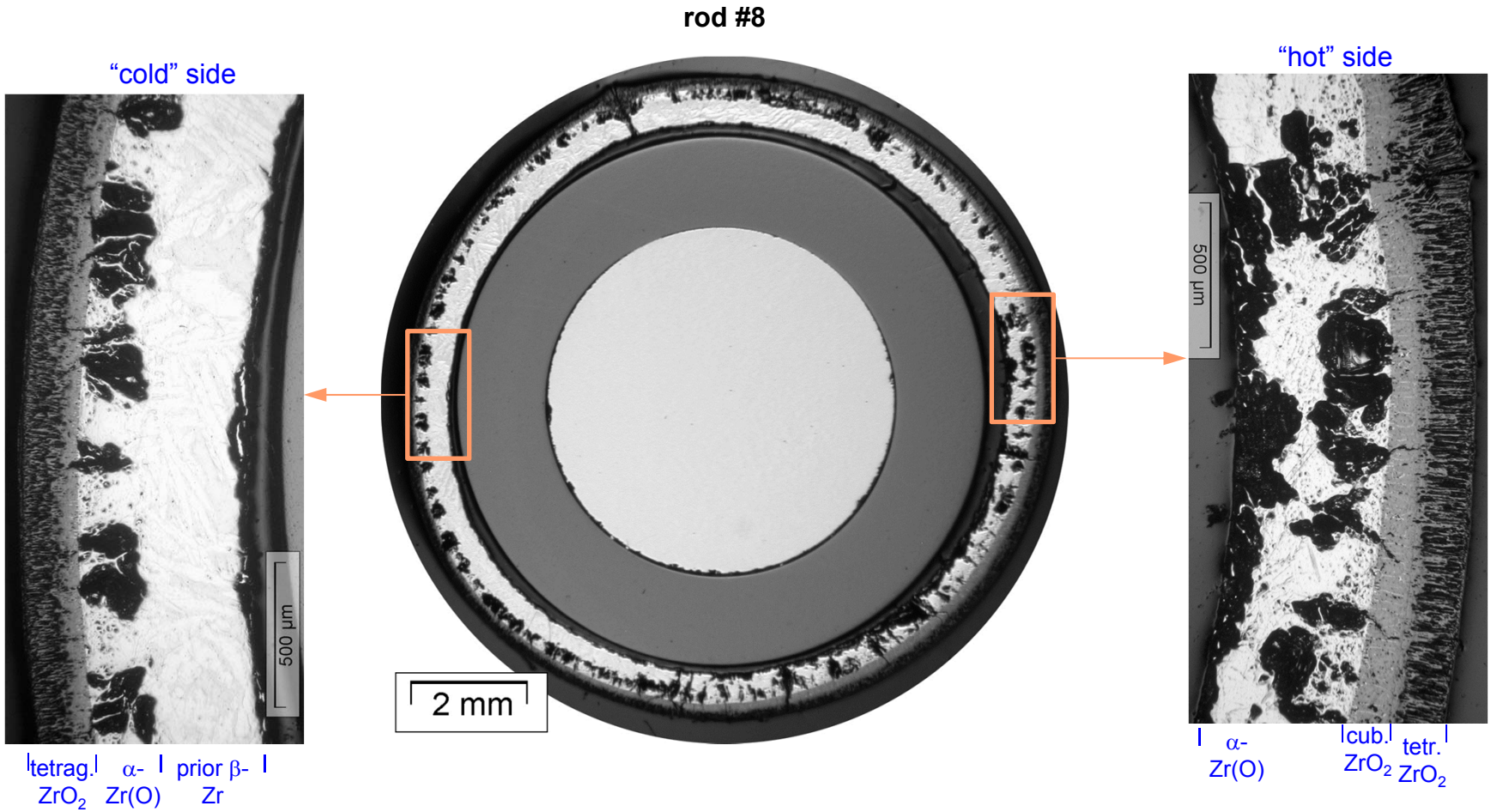
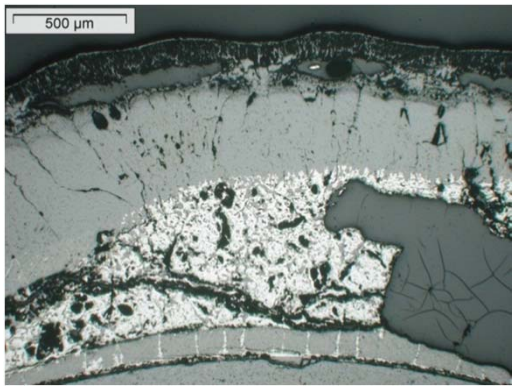
Elevation 950 mm: no nitrides, no melt formation



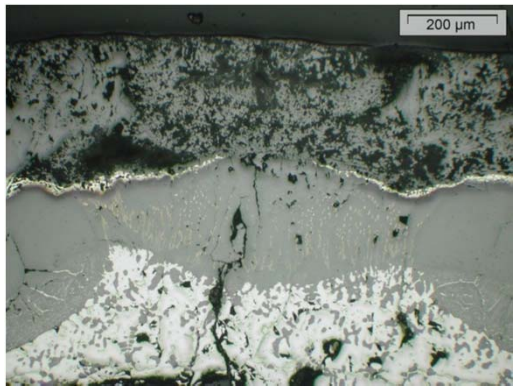
Relative thick oxide layer after pre-oxidation (~100 µm) and low temperatures during air ingress (<1500 K) prevented nitride formation at this elevation

QUENCH-16: Axial distribution of cladding oxidation rate

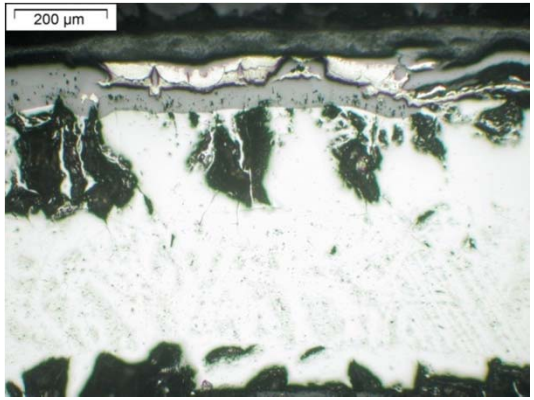


850 mm

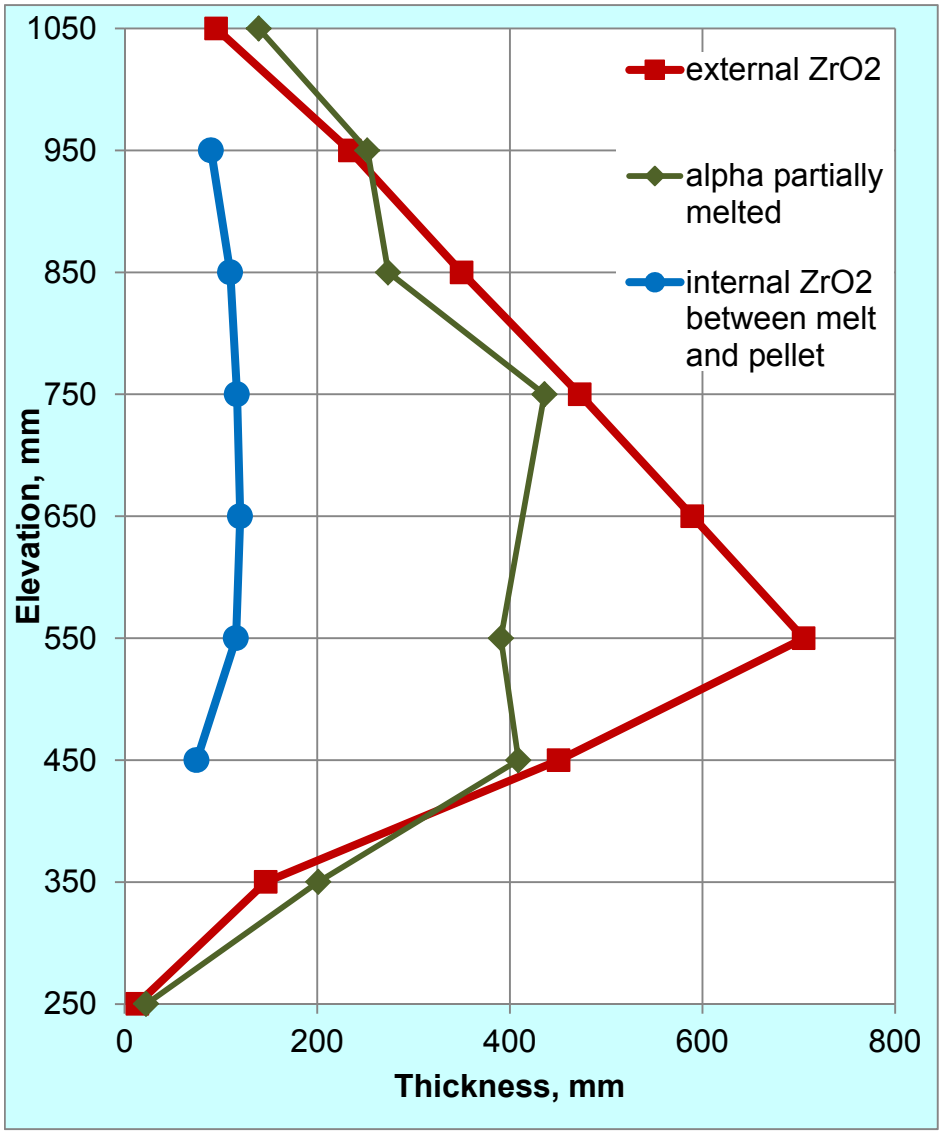
secondary oxide (80% of ZrO2)



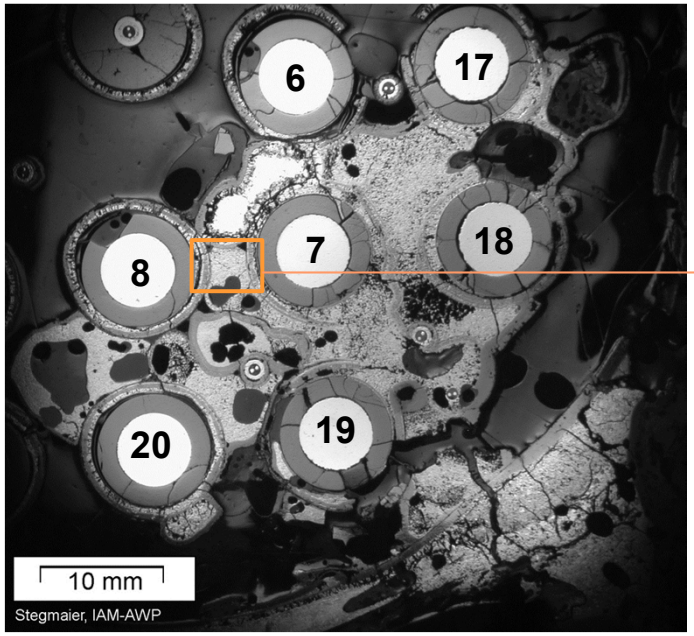
550 mm

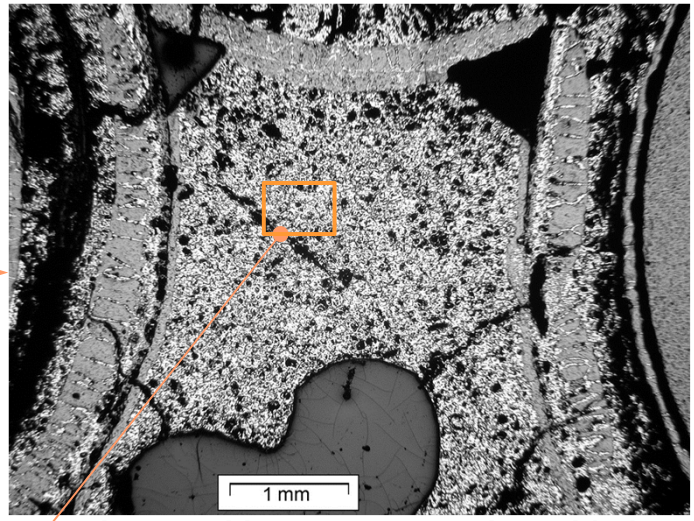


350 mm

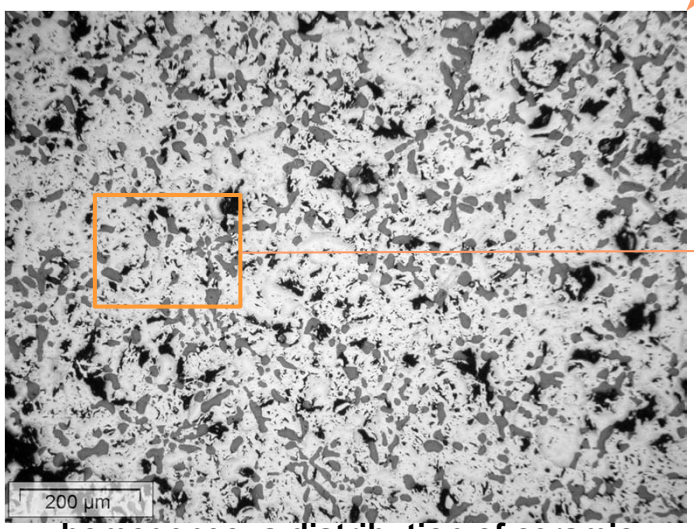


QUENCH-16. Frozen melt at elevation 450 mm: mostly oxidised melt

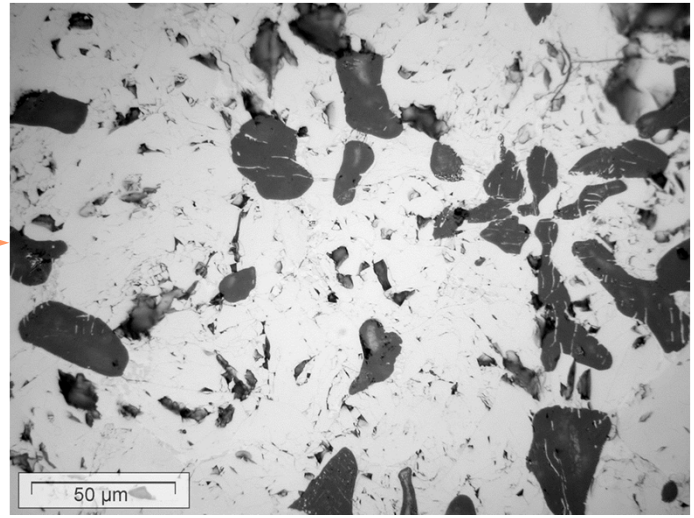




molten pool between two rods: oxidation at melt periphery and ceramic precipitates inside melt



homogeneous distribution of ceramic precipitates in the melt



precipitates part 28% → C_{oxygen} = 11.5 wt%

QUENCH-16 SUMMARY

- Three typical features of QUENCH-16: 1) moderate pre-oxidation to 135 µm of oxide layer (instead 500 µm for QUENCH-10), 2) a long period of oxygen starvation during the air ingress phase (800 s instead 80 s for QUENCH-10), and 3) reflood initiation at temperatures significantly below the melting point of the cladding (1700 K instead of 2200 K for QUENCH-10 and SF4).

- A partial consumption of nitrogen during the oxygen starvation caused the formation of *porous* zirconium nitrides inside the oxide layer at bundle elevations between 350 and 850 mm (QUENCH-10: between 750 and 850 mm).

- Immediate temperature escalations to 2420 K after reflood initiation were caused by massive steam penetration through the *porous* oxide/nitride scales and intensive reaction with nitrides and especially with metallic cladding. **7 g** hydrogen were release due to re-oxidation of nitrides.

- The main part of hydrogen production during reflood (**96 g**) was released due to secondary cladding oxidation by steam penetrated through the porous re-oxidized nitrides.

- Relocated melt was frozen between rods at elevations between 300 and 500 mm. The hydrogen release due to melt oxidation estimated as **25 g**.

Thank you for your attention

http://www.iam.kit.edu/wpt/english/471.php/
http://quench.forschung.kit.edu/