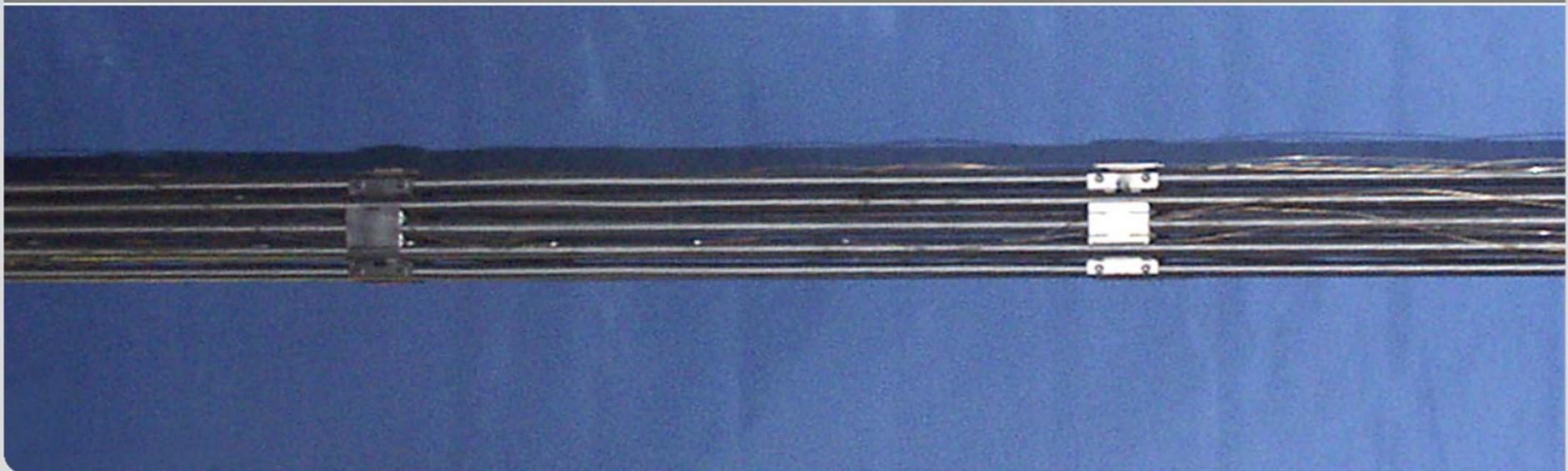


## Post-test results of the QUENCH-16 bundle test on air ingress: complex cladding oxidation during reflood and combined hydrogen

J. Stuckert, M. Steinbrück

*QWS18, Karlsruhe 2012*

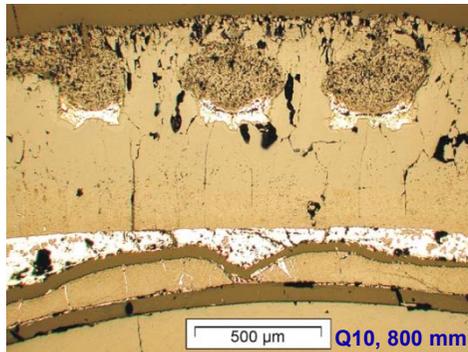
Institute for Applied Materials; Program NUKLEAR



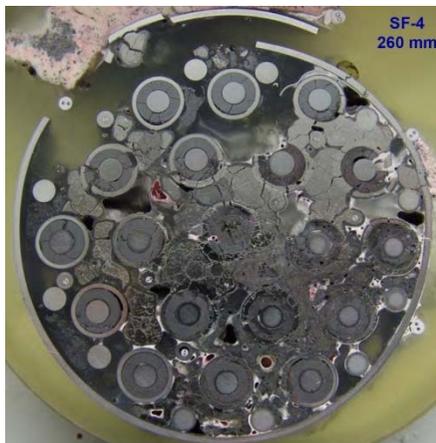
## Previous bundle air ingress experiments



- **CODEX AIT-1, AIT-2 (Zry-4) performed 1999 at AEKI/Budapest: *small bundles with 9 rods***



- **QUENCH-10 (Zry-4 claddings) performed 2004 at KIT/Karlsruhe: *strong pre-oxidised bundle***



- **PARAMETER-SF4 (E110 claddings) performed 2009 at LUCH/Podolsk: *very high temperatures on reflood initiation with following escalation (bundle melting)***

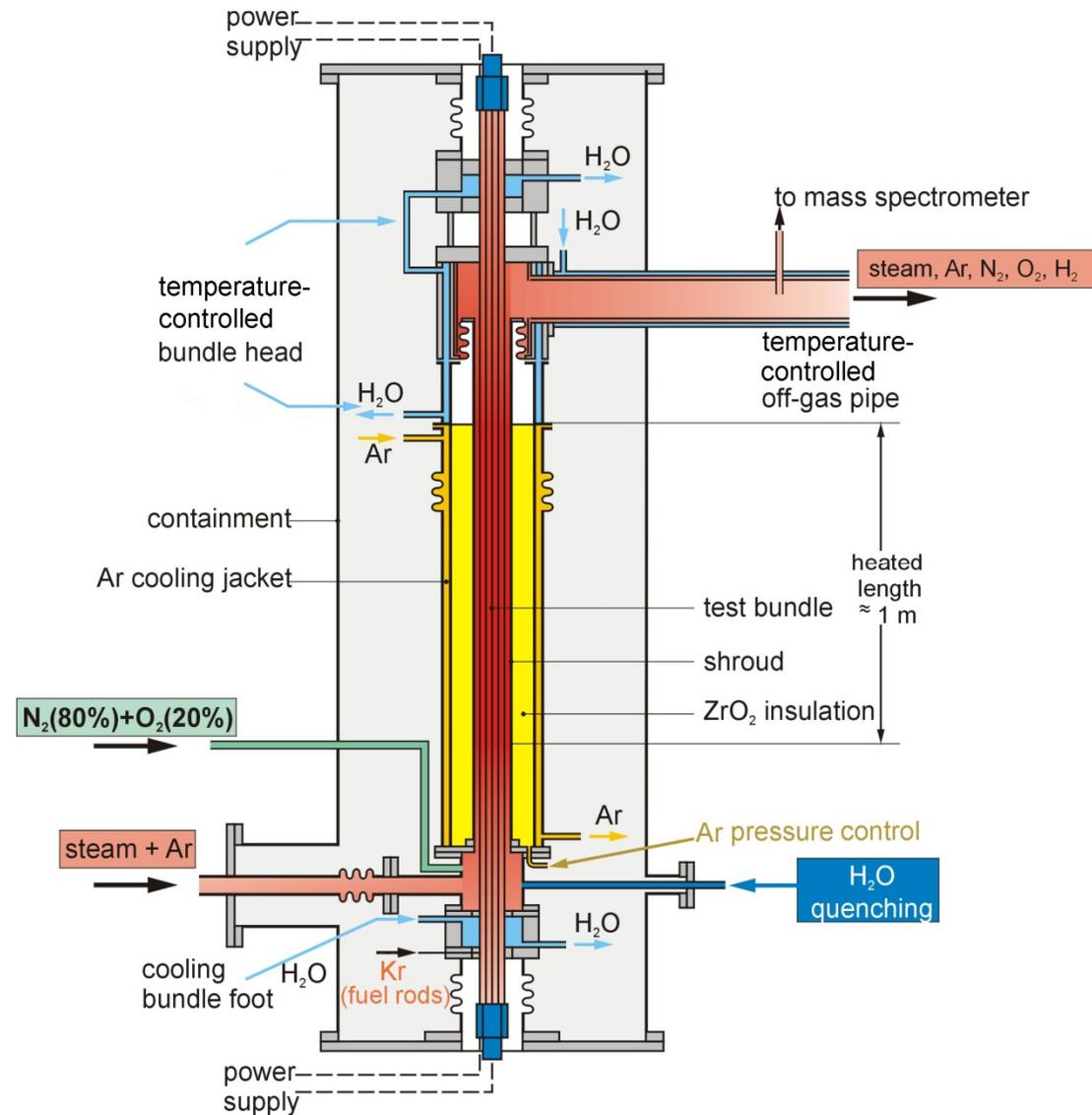
## Objectives of the QUENCH-16 test

- **air oxidation after rather moderate pre-oxidation in steam;**
- **slow oxidation and nitriding of zirconium in high temperature air and transition to rapid oxidation and temperature excursion;**
- **role of nitrogen under oxygen-starved conditions;**
- **formation of oxide and nitride layers on the surface of Zr;**
- **release of hydrogen from oxidised zirconium during air ingress scenario;**
- **reflooding of oxidised and nitrated bundle by water initiated at temperatures well below the melting point of the cladding, release of nitrogen.**

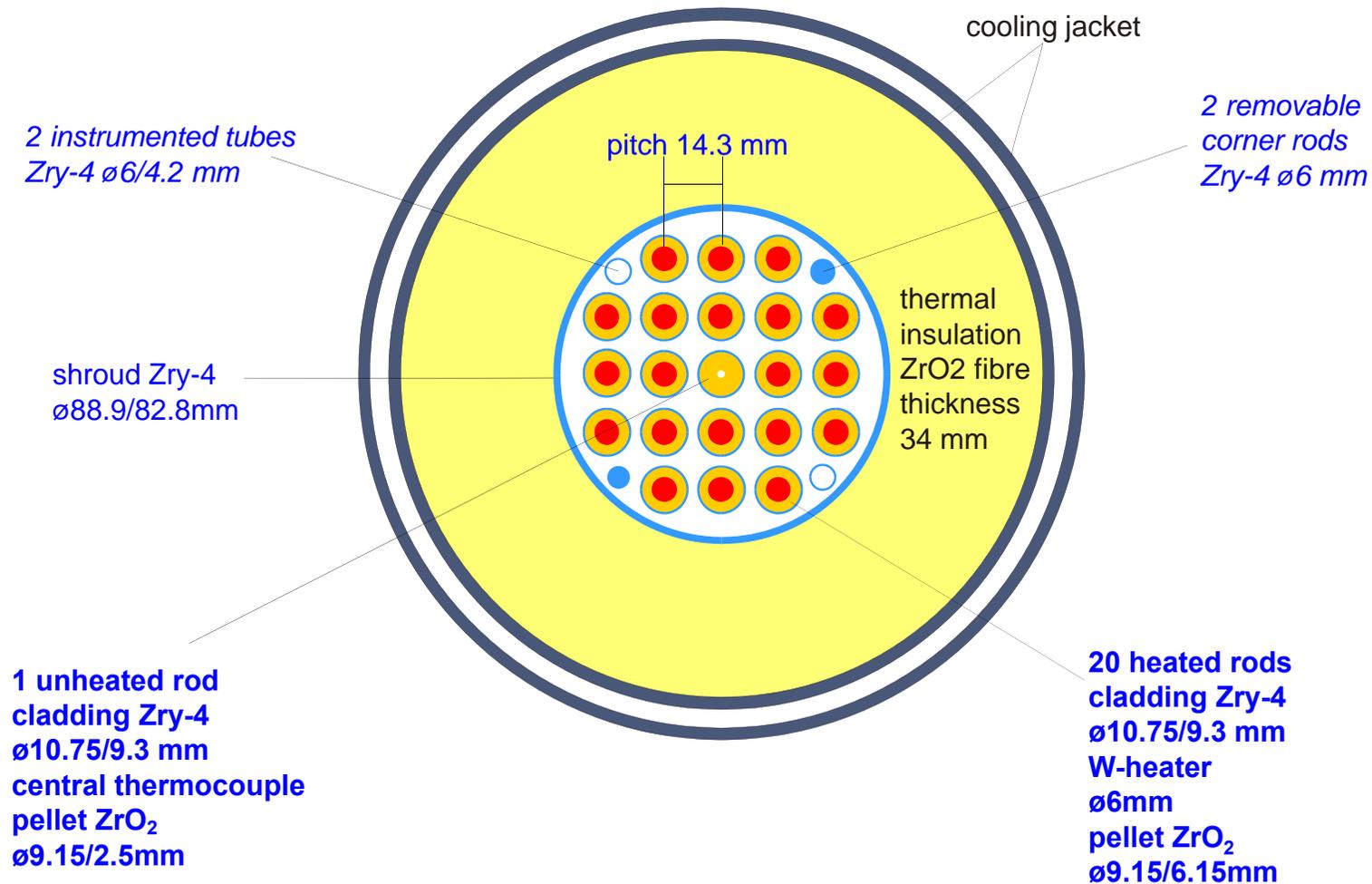
# QUENCH facility

## QUENCH-16 facility features:

- 1) controllable synthetic air input;
- 2) Krypton filling of rods;
- 3) temperature control for off-gas pipe (to avoid the steam condensation)
- 4) control of pressure in space between shroud and jacket

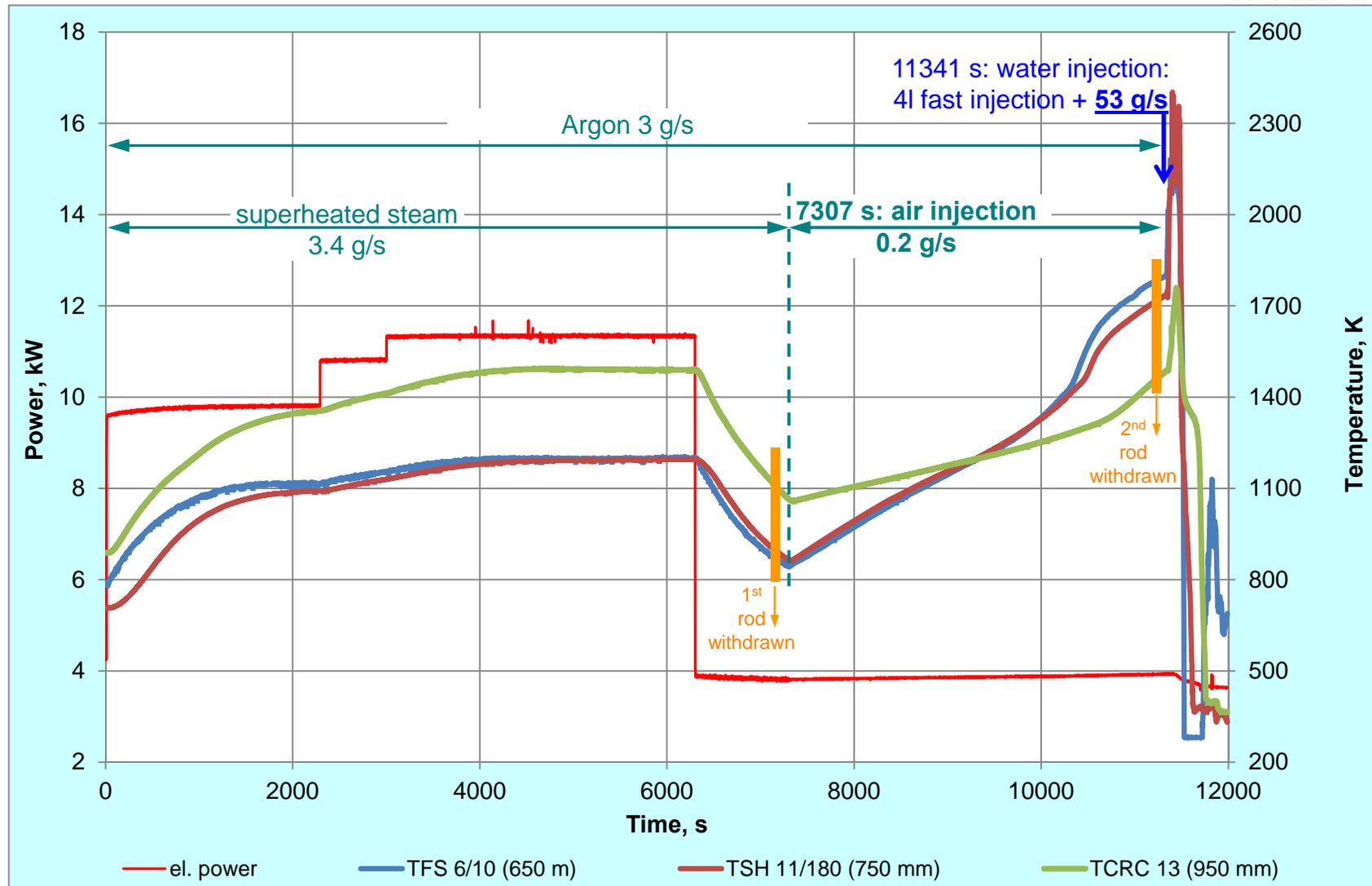


## Cross section of the PWR test column

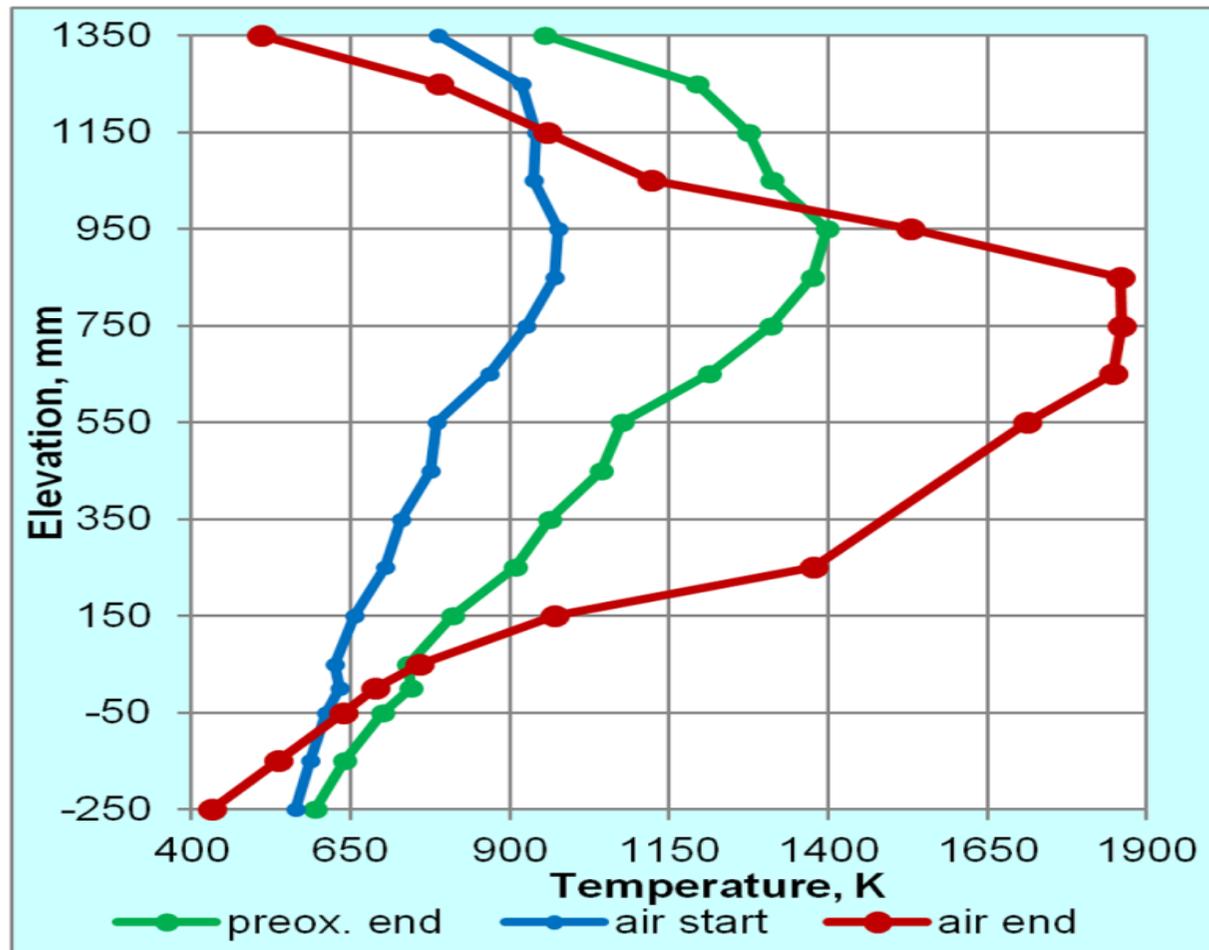


# QUENCH-16 test progression

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

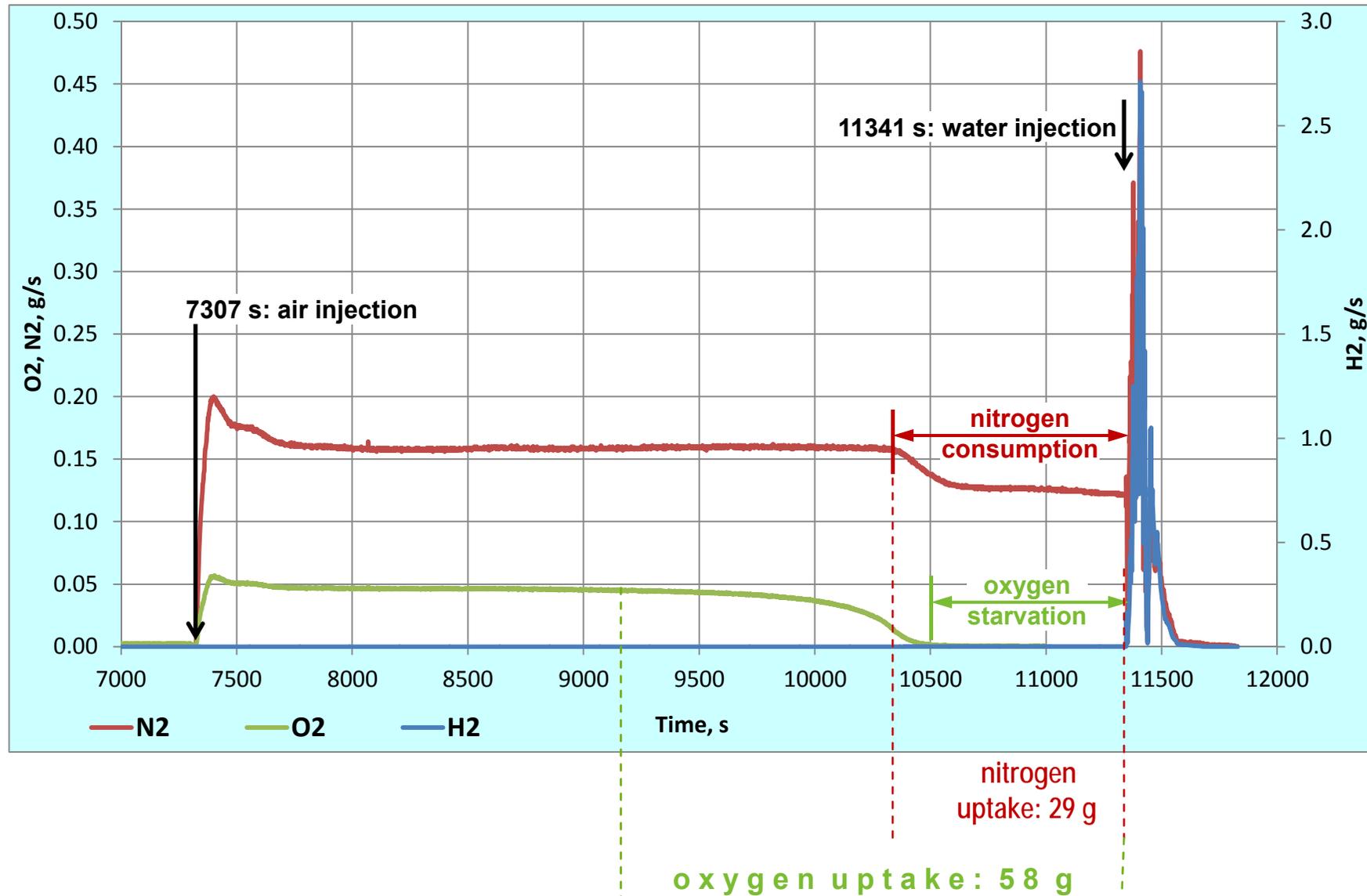


## Axial temperature distributions for different test phases

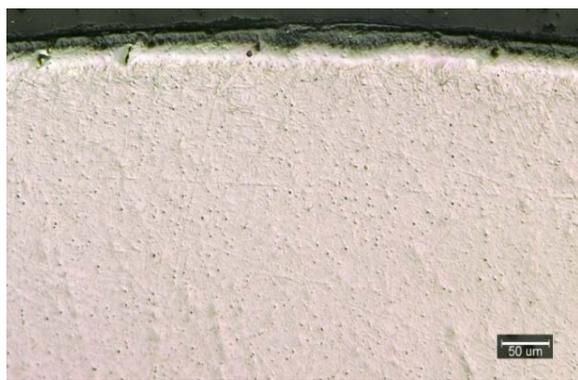


**strong growth of temperatures at elevations 250 – 950 mm during the air ingress phase**

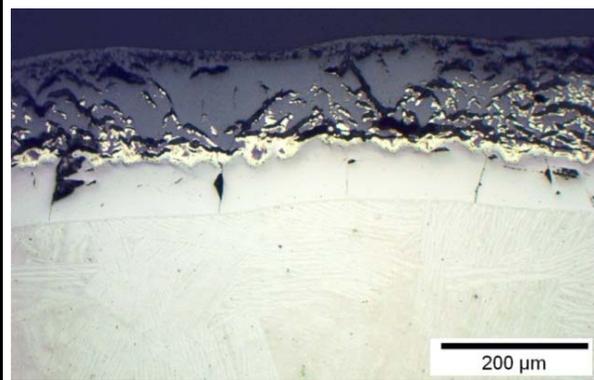
# Consumption of nitrogen and oxygen during air ingress phase: data of mass spectrometer



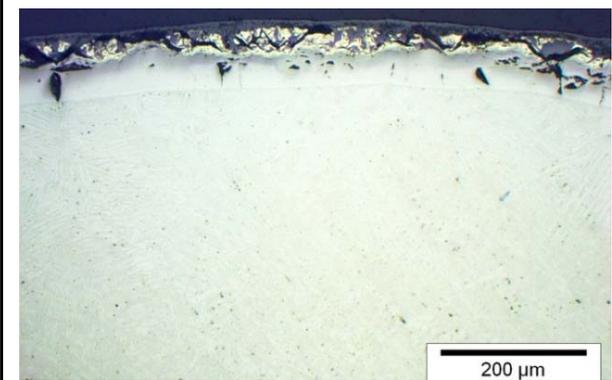
# Corner rod D withdrawn from the bundle on the end of the air ingress phase: nitride formation between 300 and 900 mm



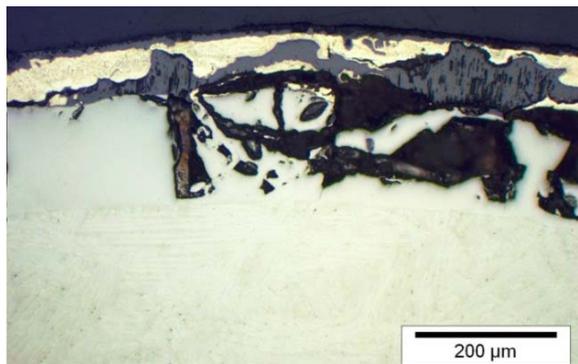
250 mm (1070°C): no nitrides



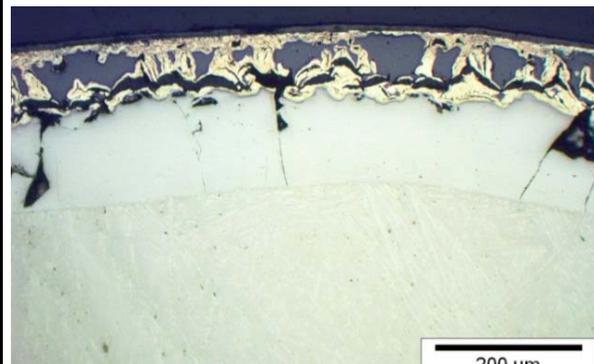
450 mm (1530°C): strong corrosion; nitrides



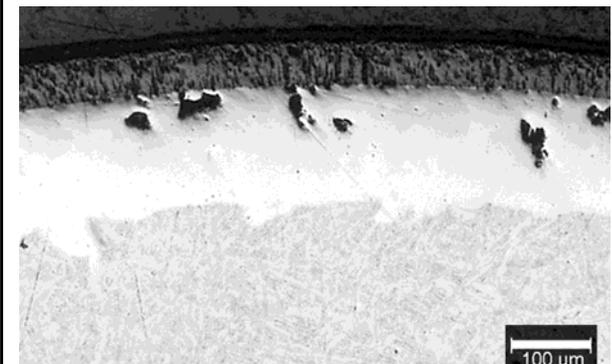
650 mm (1400°C): moderate corrosion; nitrides



750 mm (1460°C): strong corrosion; nitrides

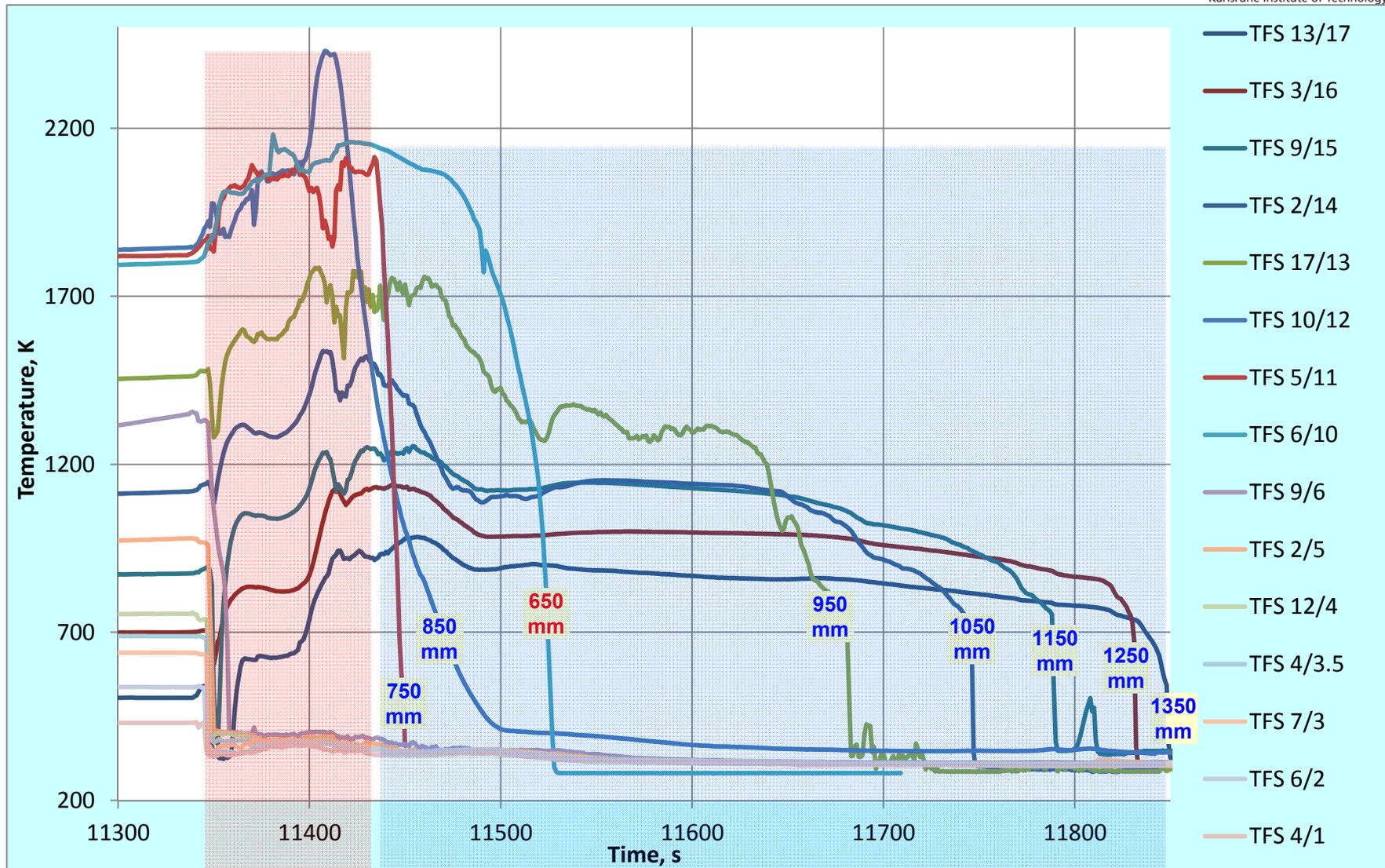


850 mm (1570°C): strong corrosion; nitrides



950 mm: no nitrides

# Temperature escalation (above Zr melting point) and cooldown during reflow



Durations: **escalation 100 s**

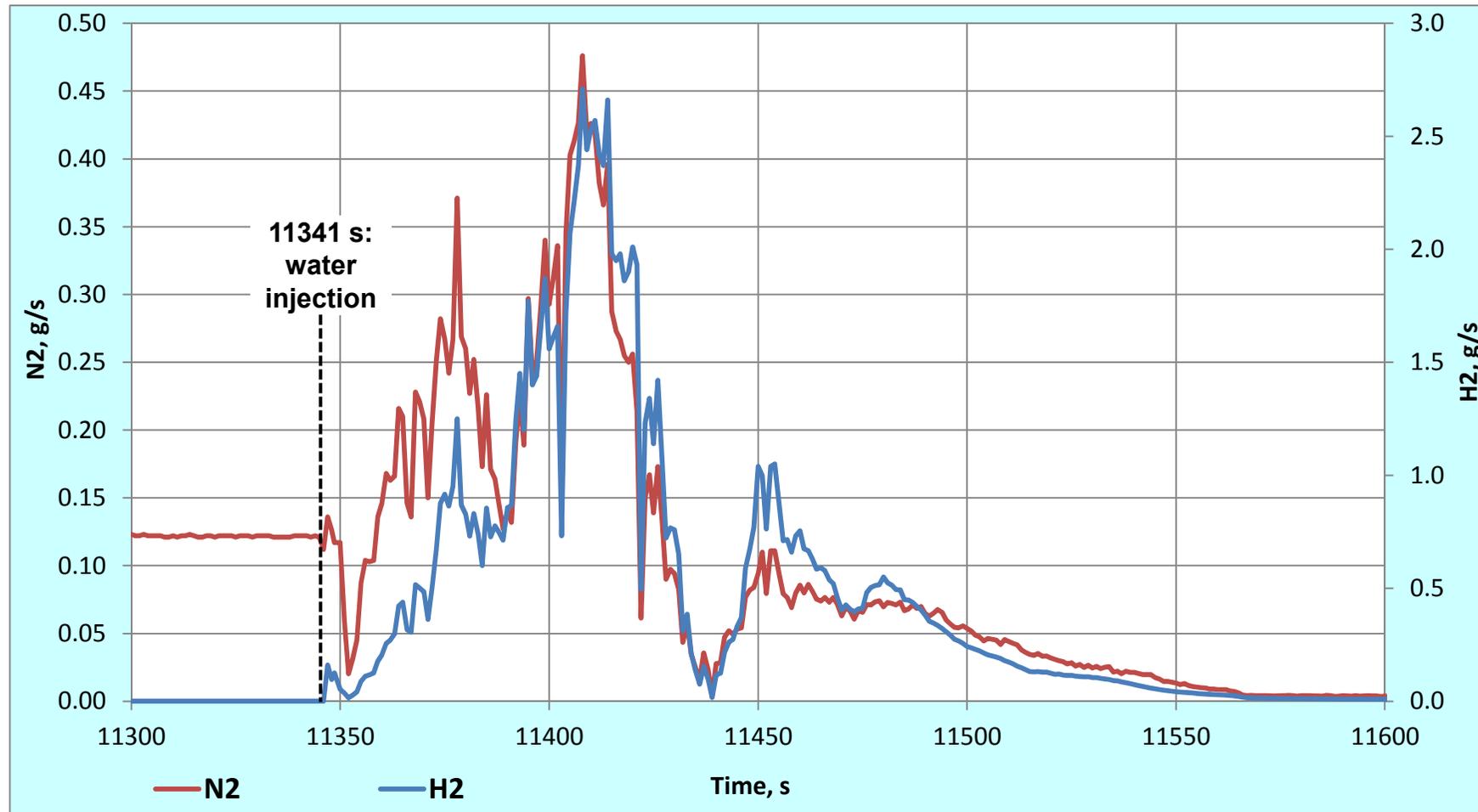
**cooldown 400 s**

# Post-test visual investigations by endoscope introduced at the position of the corner rod B: side view

		
<p><b>350 mm: frozen metallic melt relocated from upper elevations</b></p>	<p><b>420 mm: oxide shells of melt droplets and rivulets</b></p>	<p><b>600 mm: intensive cladding damaging</b></p>
		
<p><b>835 mm: spalling of outer scale of oxide layer</b></p>	<p><b>880 mm: not damaged outer scale of oxide layer</b></p>	<p><b>1050 mm: dark oxide of claddings, intact Grid Spacer #4</b></p>

# Release of hydrogen and nitrogen during quench phase

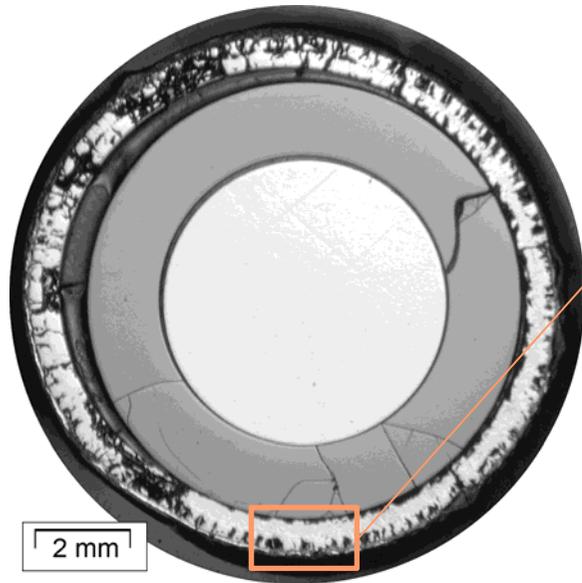
/data of mass spectrometer/



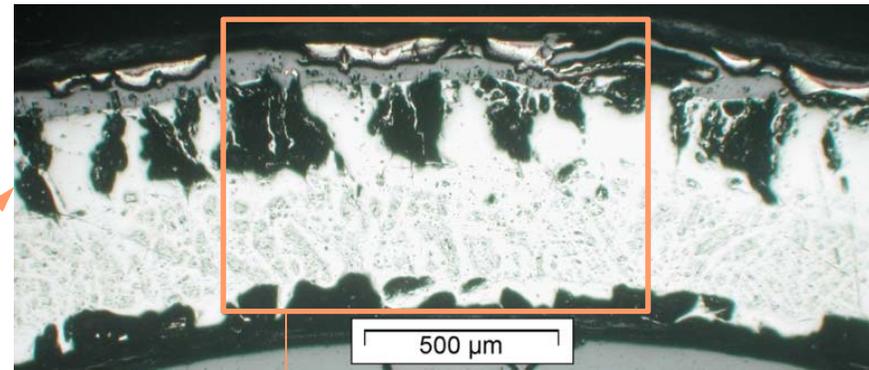
**hydrogen release: 128 g.** 3 main sources: 1) re-oxidation of Zr-nitrides;  
2) secondary oxidation of cladding; 3) melt oxidation

**nitrogen release during re-oxidation of nitrides: 24 g (from consumed 29 g) -> correspond 7 g hydrogen**

# Nitride re-oxidation during quench at elevation 350 mm

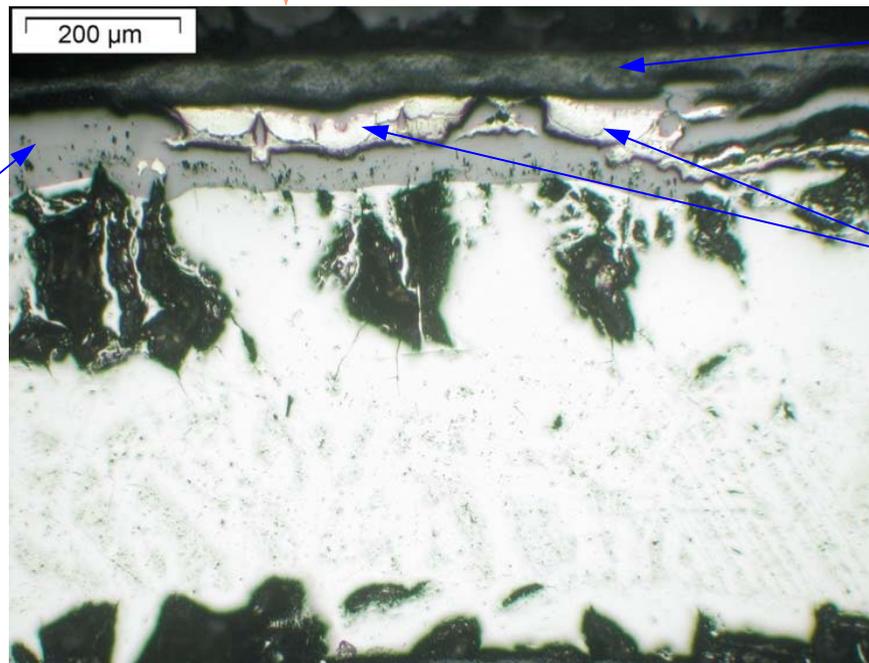


rod #5



α-Zr

prior β-Zr

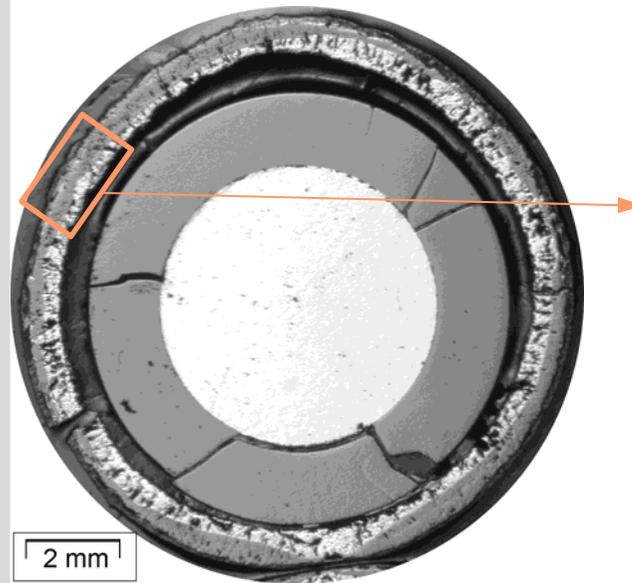


porous oxide scale  
(re-oxidised during  
quench)

Zr-nitrides

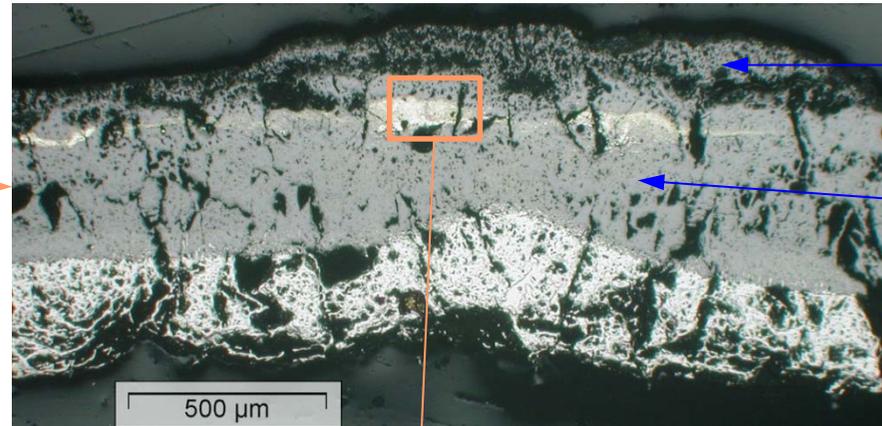
dense inner oxide  
(grown during  
quench phase)

# Nitride re-oxidation and secondary cladding oxidation during quench at elevation 450 mm



2 mm

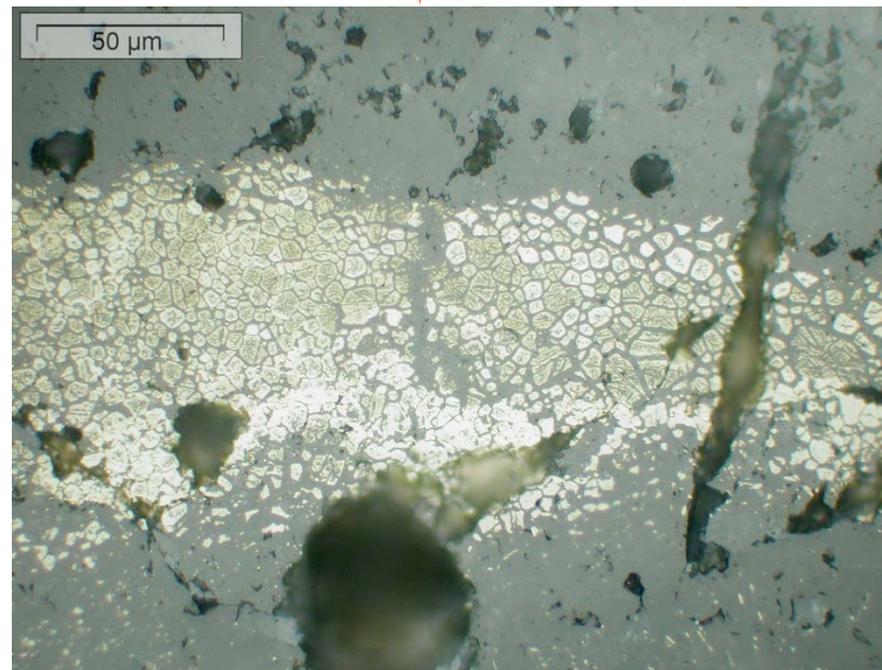
rod #4



porous oxide scale  
(re-oxidised during  
quench)

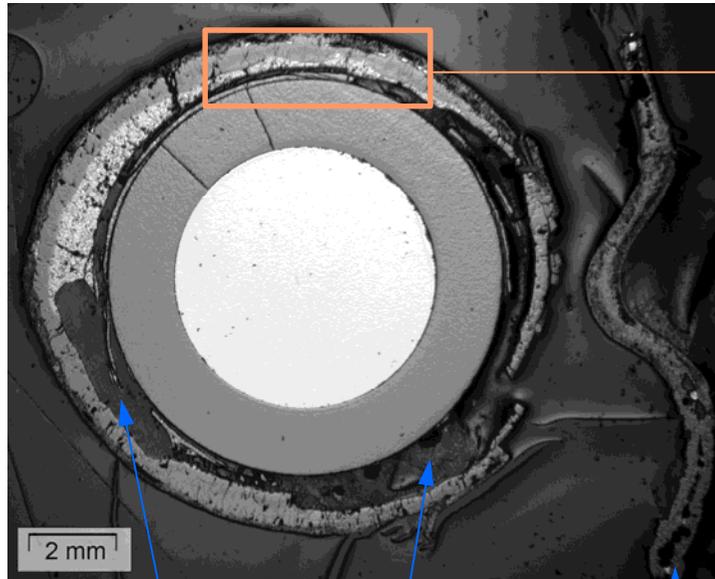
secondary  
dense inner oxide  
(grown during  
quench phase)

$\alpha$ -Zr(O)



residual  
Zr-nitrides

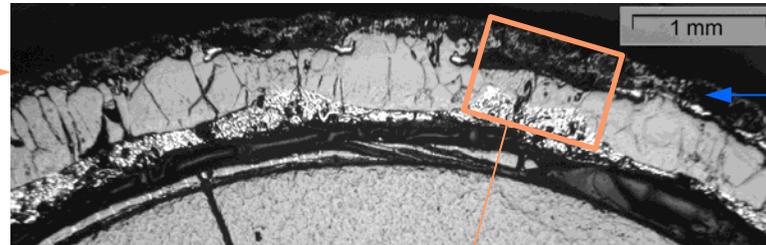
## Secondary oxidation and melting at elevation 550 mm



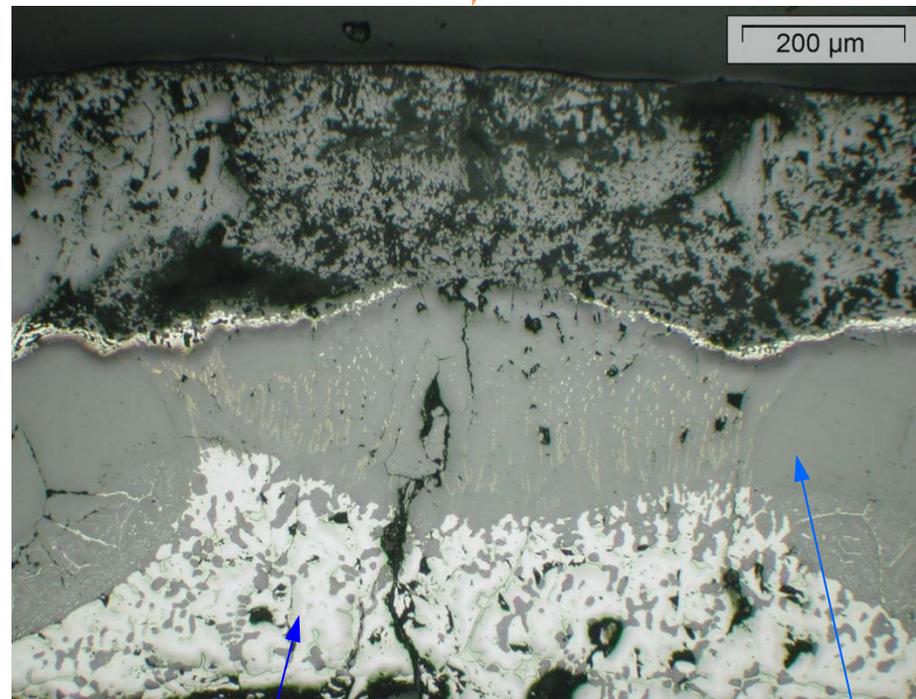
rod #9

voids from downwards relocated melt

completely oxidised Zry grid spacer



porous outer oxide scale



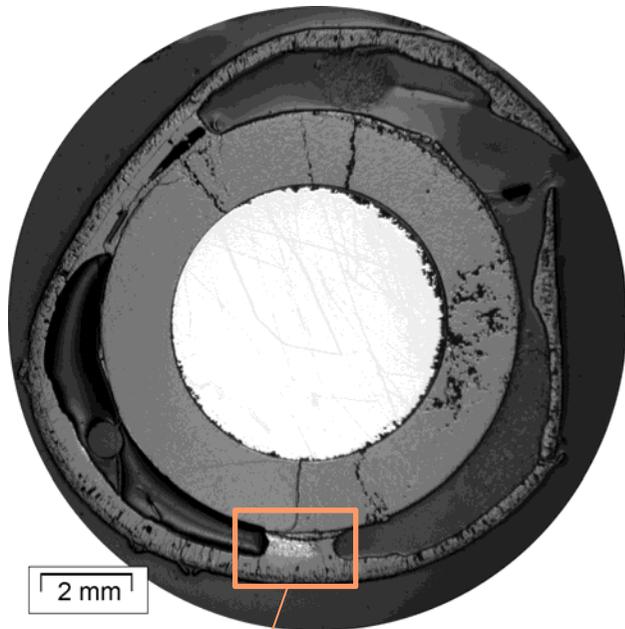
frozen partially oxidised melt

Zr-nitrides

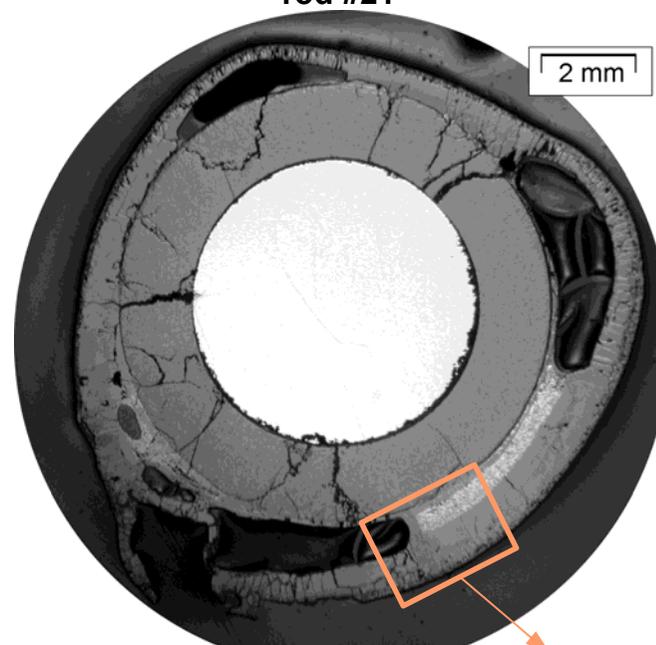
secondary dense inner oxide (grown during quench phase)

# Intensive metal formation at elevation 650 mm

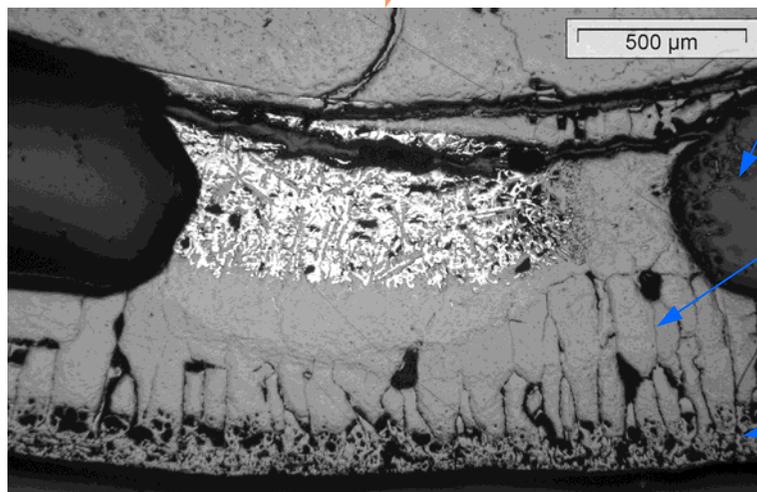
rod #9



rod #21



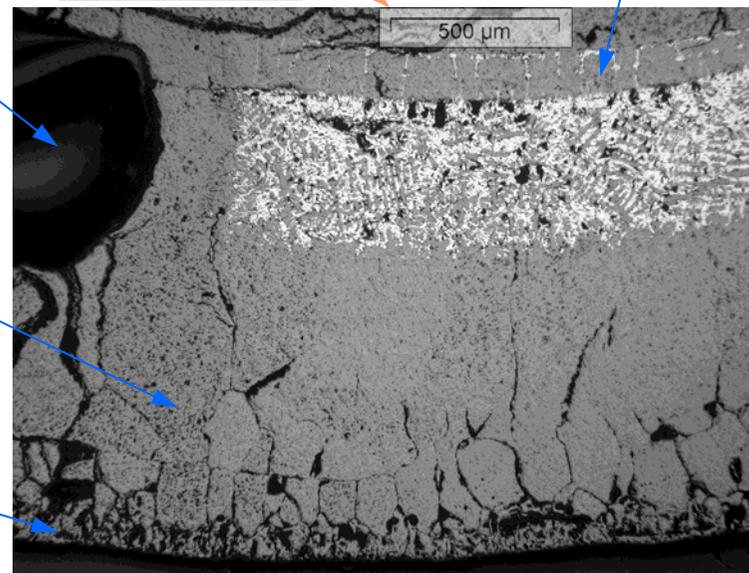
internal  
ZrO<sub>2</sub>



voids  
from  
relocated  
melt

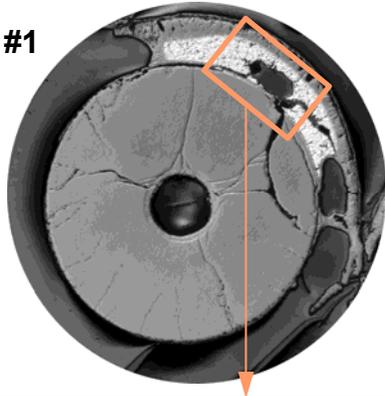
secondary  
dense inner  
oxide  
(grown during  
quench phase)

porous re-  
oxidised  
scale

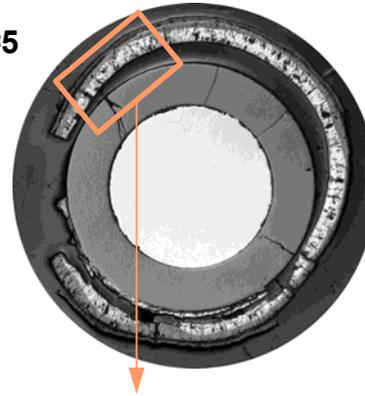


# Spalling of re-oxidised scales from secondary oxide at 750 mm

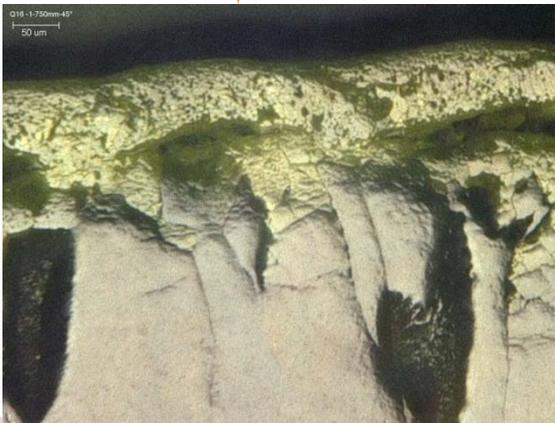
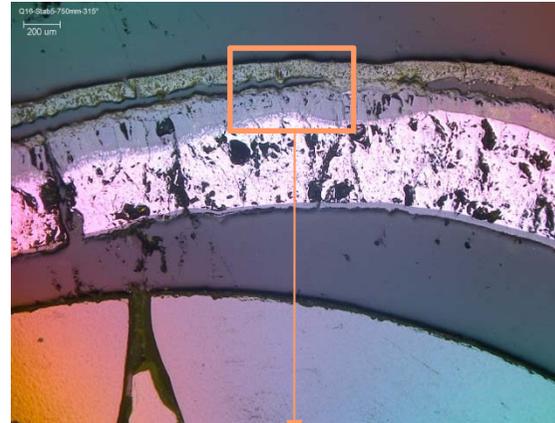
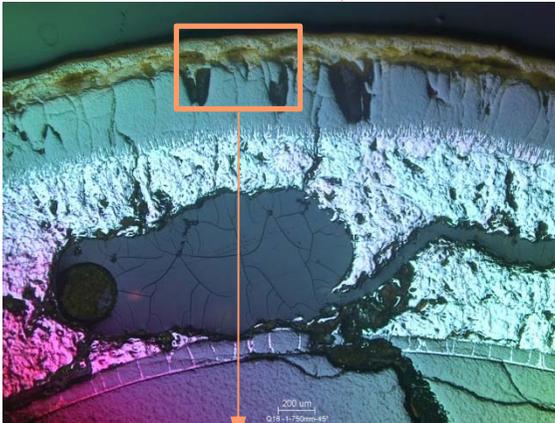
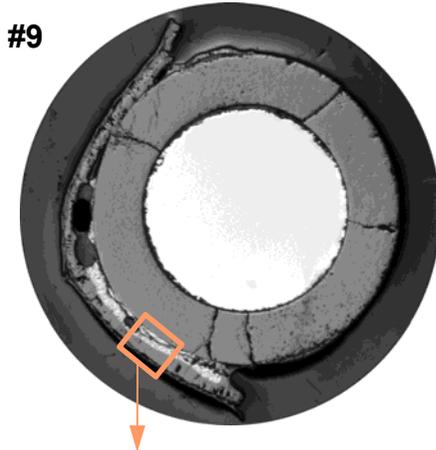
rod #1



rod #5



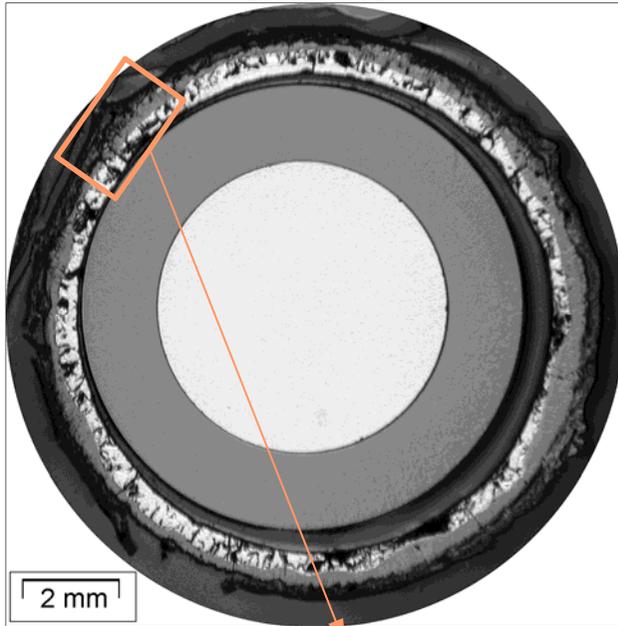
rod #9



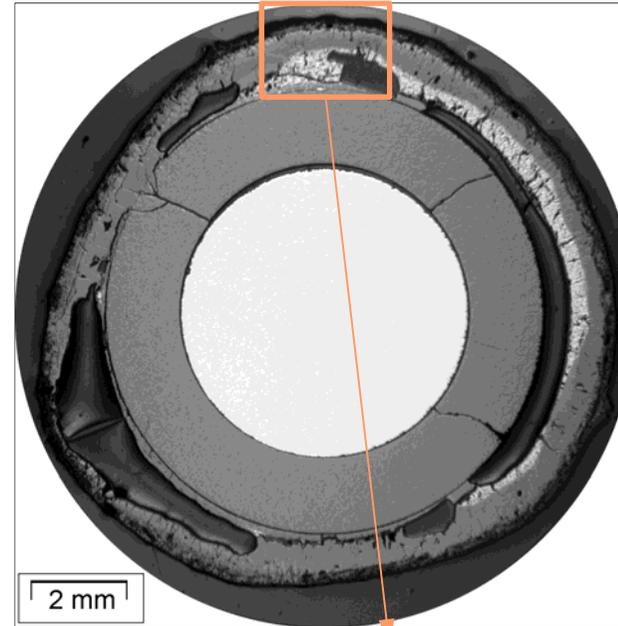
prior nitrated scale  
re-oxidised during quench  
and spalled from  
inner ZrO<sub>2</sub> layer growing during  
quench

# Re-oxidation of nitrided scales and metal melting at elevation 850 mm

rod #6



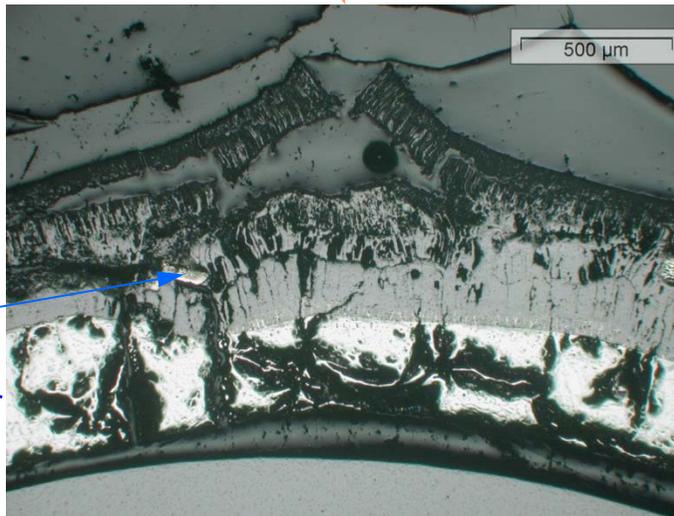
rod #18



porous scale  
(re-oxidised during  
quench)

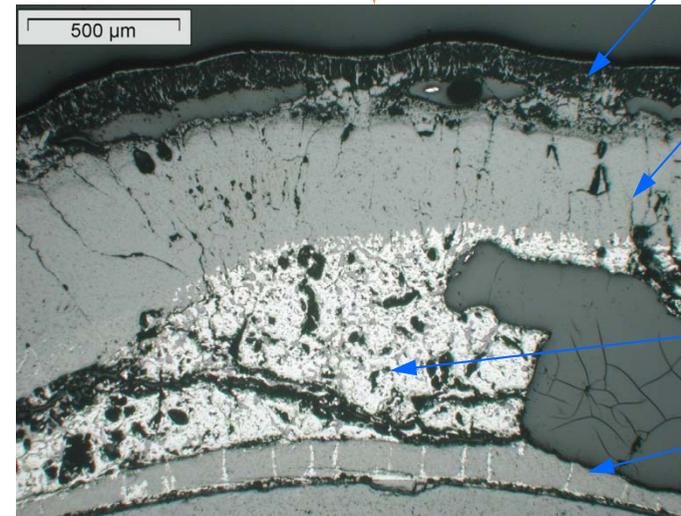
Zr-nitrides

α-Zr



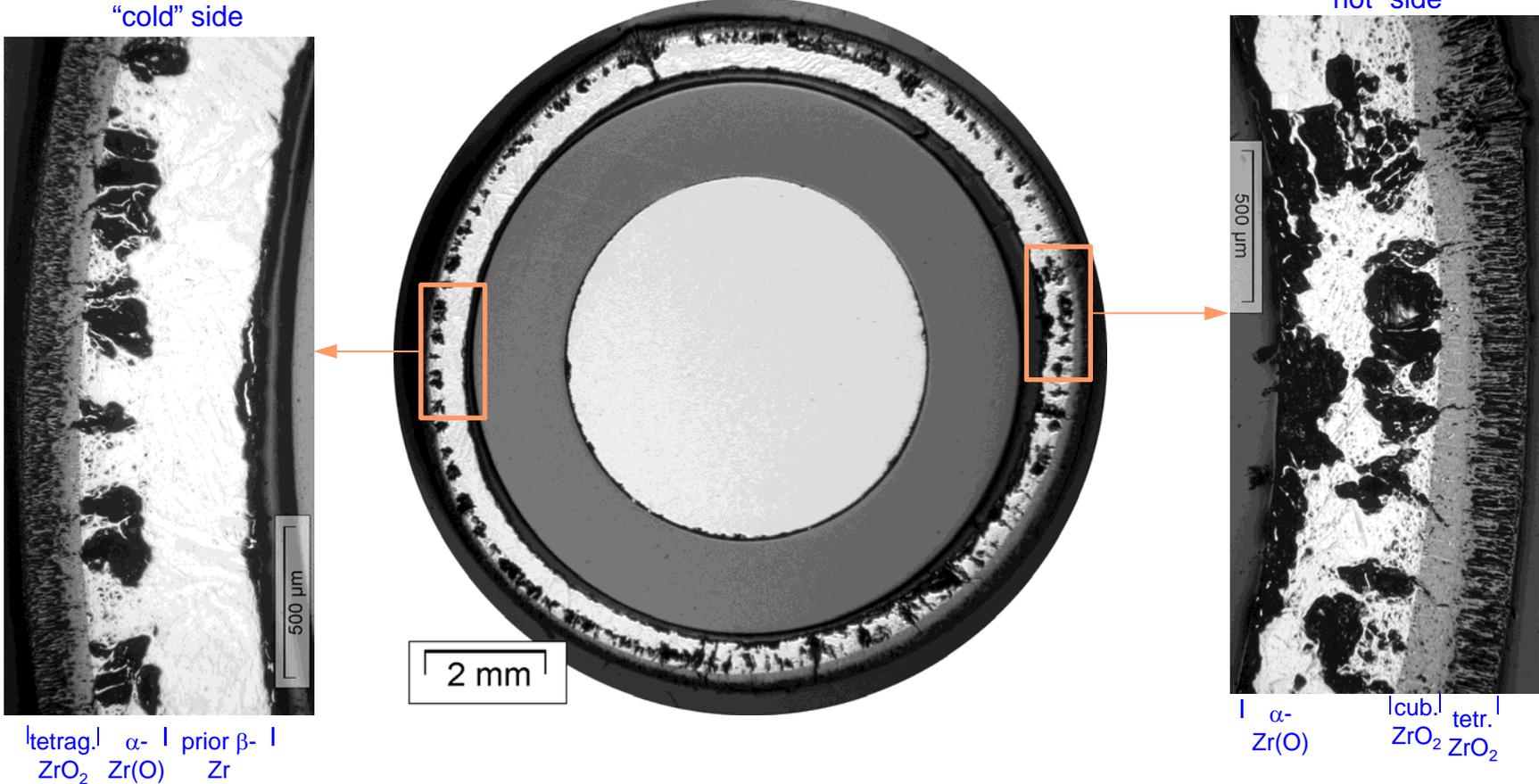
secondary  
dense inner  
oxide  
(grown during  
quench phase)

frozen  
partially  
oxidised  
melt  
internal  
oxide  
layer



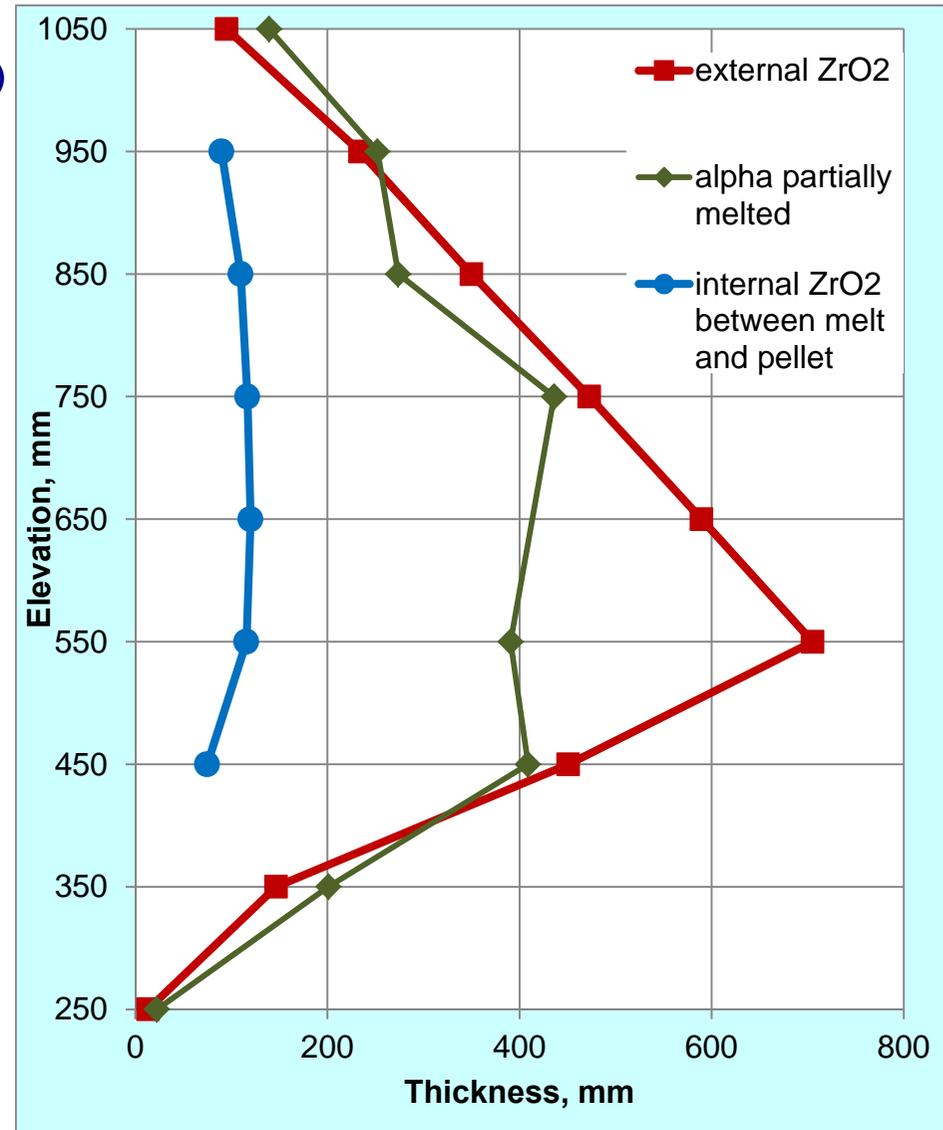
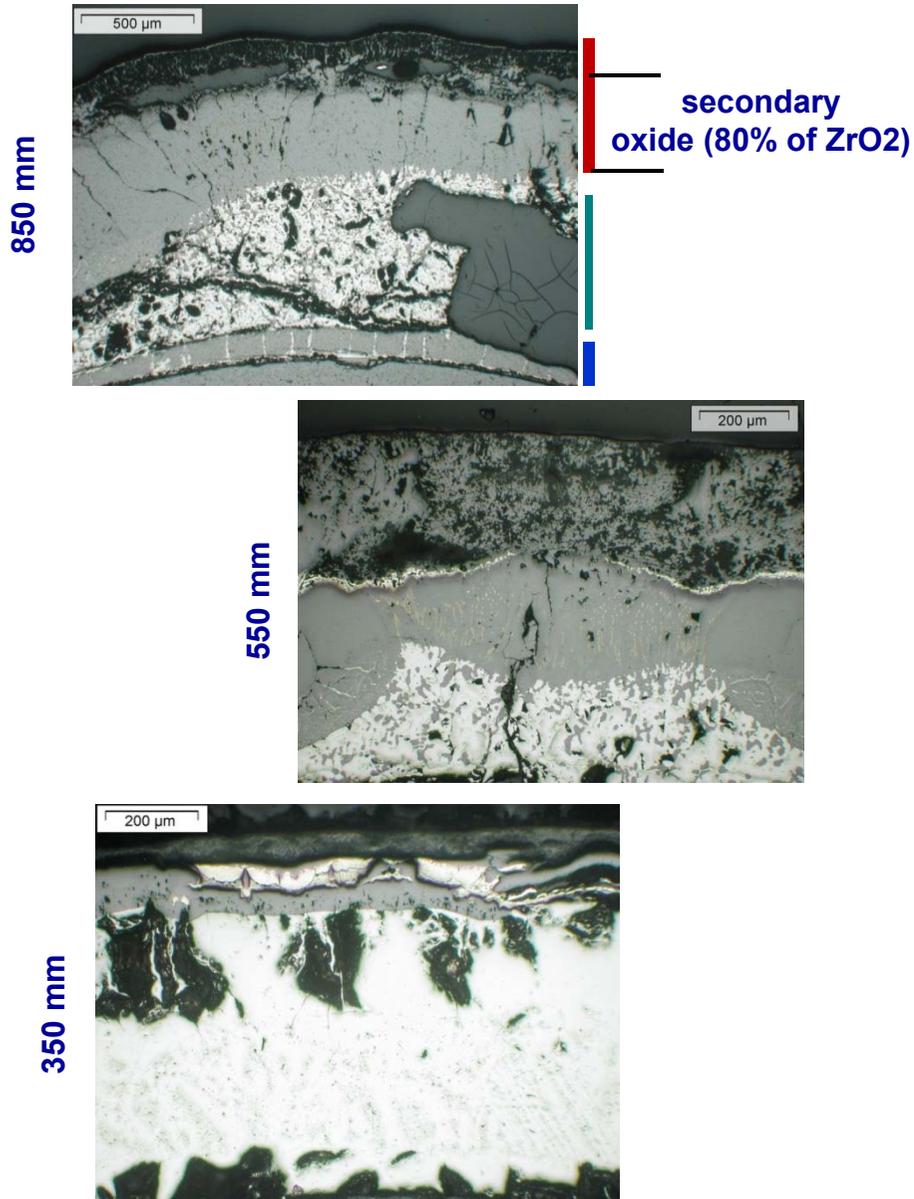
# Elevation 950 mm: no nitrides, no melt formation

rod #8



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

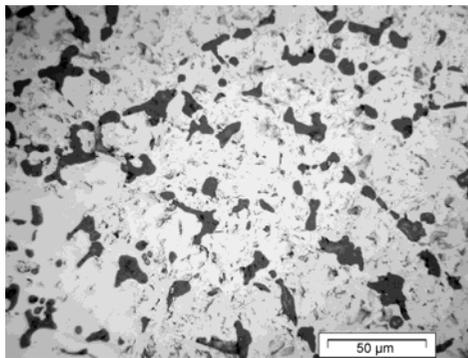
# Axial distribution of cladding oxidation rate



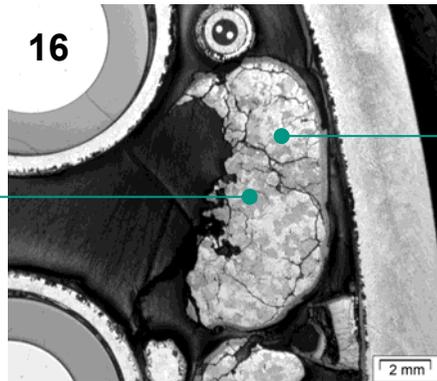
# Bundle cross sections: melt formation and relocation

		
<p>350 mm: metallic and oxidised <b>melt pools</b></p>	<p>450 mm: mostly oxidised <b>melt pools</b></p>	<p>550 mm: downwards <b>relocated cladding metal</b></p>
		
<p>650 mm: downwards <b>relocated cladding metal</b></p>	<p>750 mm: downwards <b>relocated cladding metal</b></p>	<p>850 mm: <b>outer oxide layer not failed</b></p>

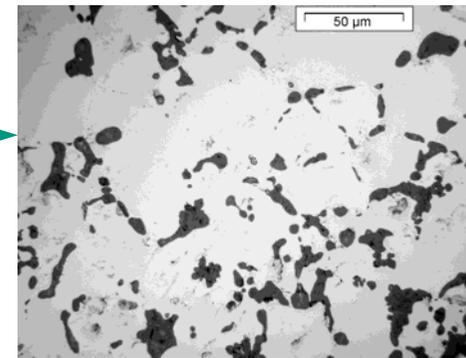
# Frozen melt at elevation 350 mm: not oxidised and oxidised melt



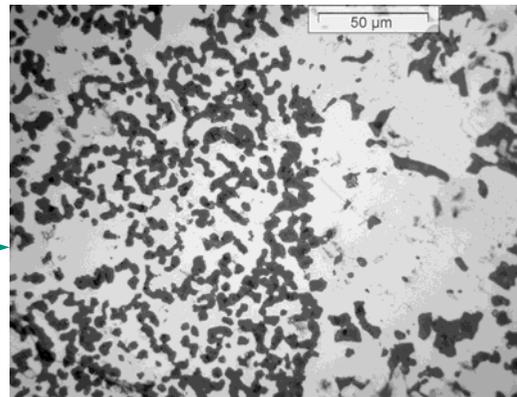
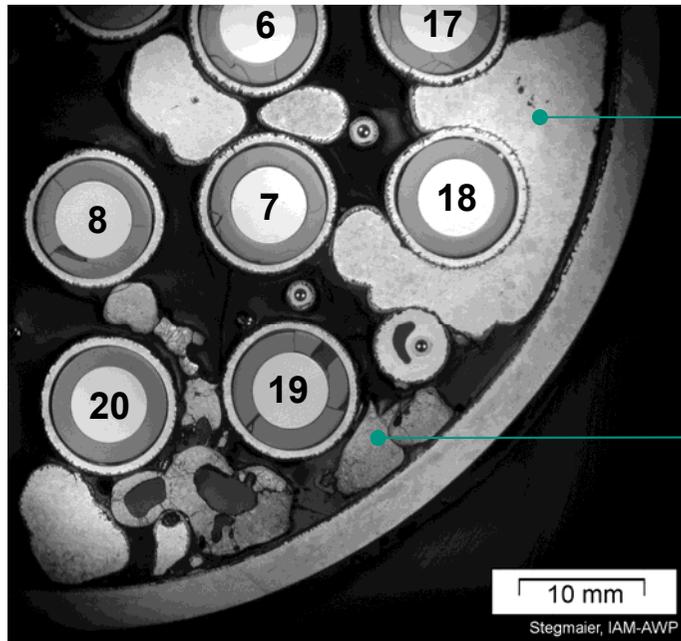
grey porous region;  
precipitates 10%



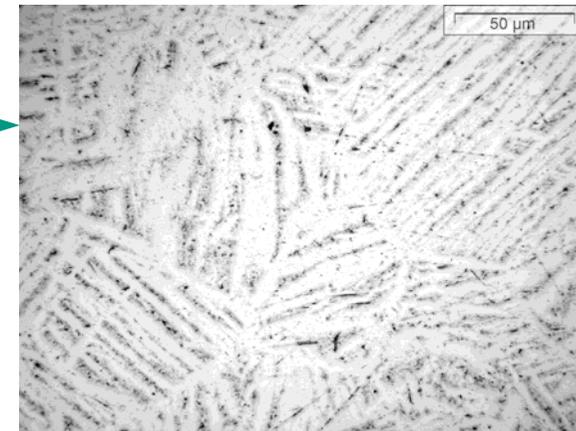
grey and light melt regions



light non porous region;  
precipitates 10% →  $C_O = 8 \text{ wt\%}$

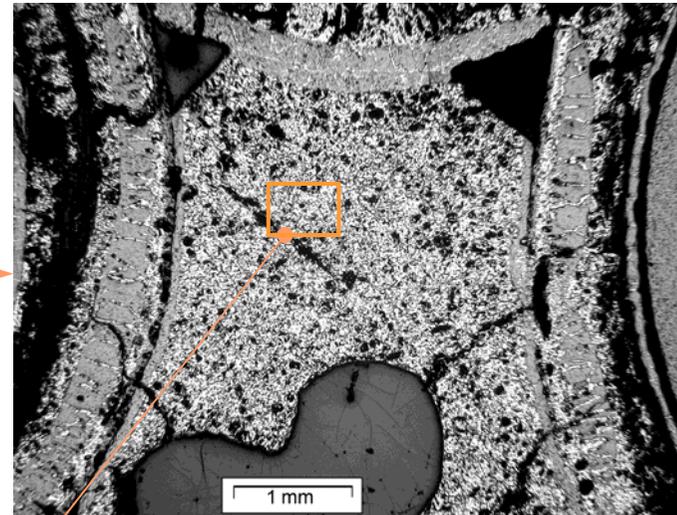
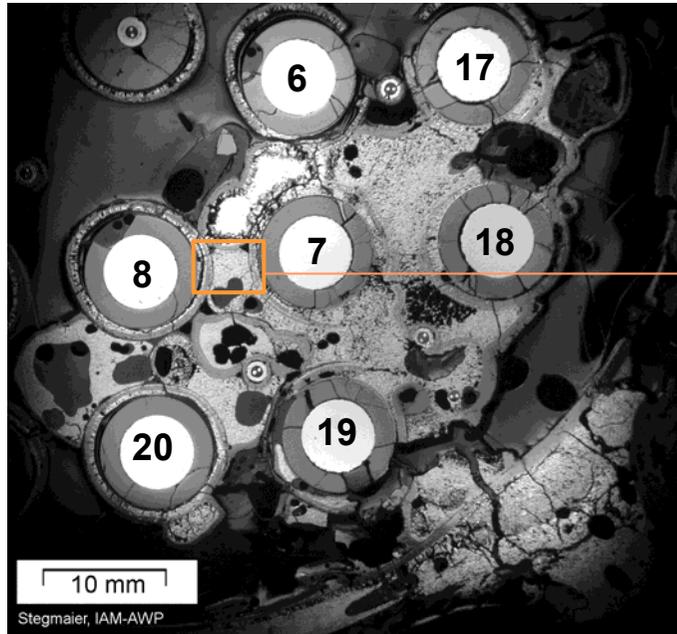


precipitates part 20% →  $C_O = 10 \text{ wt\%}$  [<http://bibliothek.fzk.de/zb/berichte/FZKA6383.pdf>]

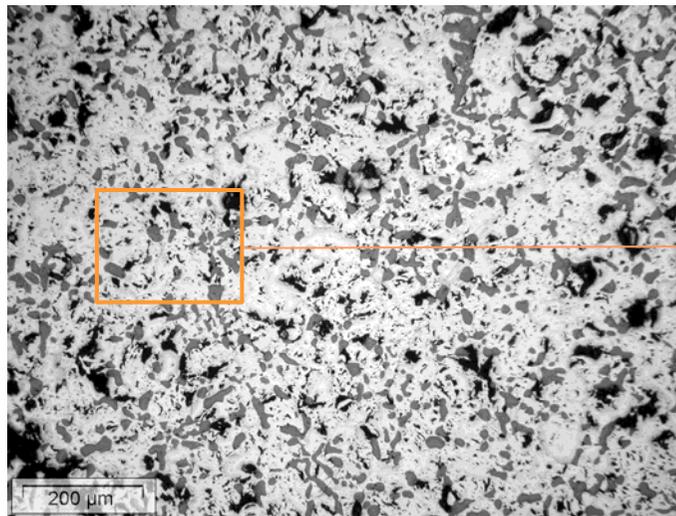


Widmanstätten pattern  
of frozen metallic melt

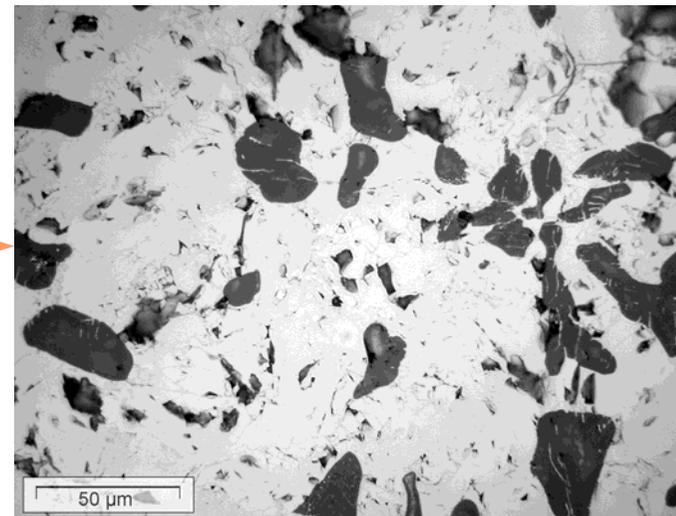
## Frozen melt at elevation 450 mm: mostly oxidised melt



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% →  $C_0 = 11.5 \text{ wt\%}$

## SUMMARY

- Three typical features of QUENCH-16: moderate pre-oxidation to 135  $\mu\text{m}$  of oxide layer (instead 500  $\mu\text{m}$  for QUENCH-10), a long period of oxygen starvation during the air ingress phase (800 s instead 80 s for QUENCH-10), and reflood initiation at temperatures significantly below the melting point of the cladding (1700 K instead of 2200 K for QUENCH-10).
- A partial consumption of nitrogen during the oxygen starvation, accompanied by acceleration of the temperature increase at mid bundle elevations, caused the formation of *porous* zirconium nitrides inside the oxide layer at bundle elevations between 350 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. The cooling phase to the final quench lasted ca. 500 s after achievement of peak temperature.
- 24 g nitrogen from 29 g, consumed during oxygen starvation period, were released during the quench phase. This quantity of released nitrogen corresponds to 7 g hydrogen developed during re-oxidation of nitrides.

## SUMMARY (cont.)

- Metal part of different rods at elevations between 450 and 950 mm was melted during reflood. Practically all melt formed at 650 mm was released into the space between rods and relocated to the lower positions. Melt at other elevations was partially kept between rods and pellets with formation of internal oxide layer adjacent to pellet.
- Relocated melt was frozen between rods at elevations between 300 and 500 mm. Image analysis of the Zr-O melt, frozen in these pools and inside rods, allows estimating the hydrogen release due to melt oxidation to 25 g.
- 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.
- The total hydrogen production during QUENCH-16 was higher compared to QUENCH-10, i.e., 144 g (QUENCH-10: 53 g), 128 g of which were released during reflood (QUENCH-10: 5 g).

## Acknowledgement

The QUENCH-16 test was performed in framework of the LACOMEKO program at KIT with financial support from the HGF Program NUKLEAR and the European Commission.

The authors would like to thank Mr. Große, Mr. J. Moch, Mr. Rössger, Mrs. J. Laier, Mrs. Stegmaier and Mrs. U. Peters for intensive work during the test preparation and post-test investigations.

*Thank you for your attention*

<http://www.iam.kit.edu/wpt/english/471.php/>

<http://quench.forschung.kit.edu/>