Development of the Metallic Layer on the Surface of Oxidised Zry-Cladding under Steam Starvation Conditions

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OBJECTIVES

- Steam starvation conditions are typical for some scenarios of reflooding

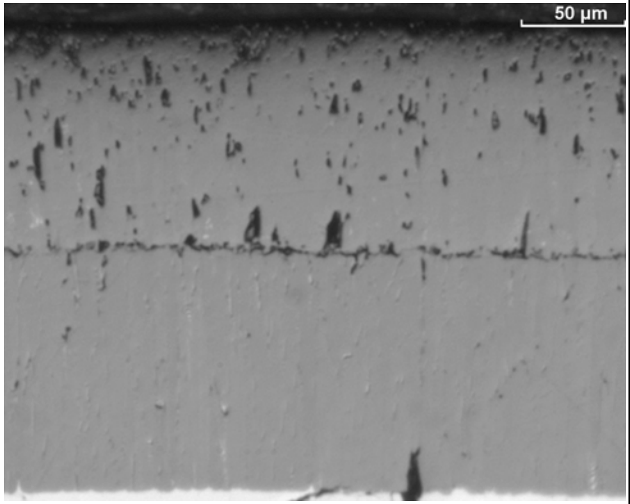
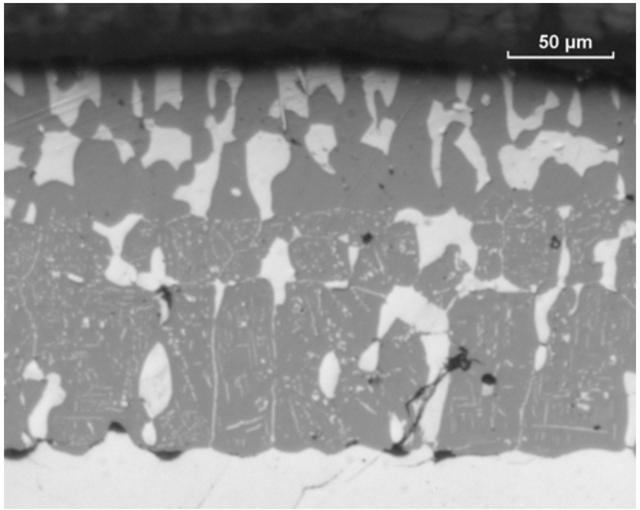
- Former FZK tests on oxide layer reduction performed under non-isothermal conditions in a temperature range between 1400 °C and 1480 °C showed formation of metallic α-Zr(O) large-scale precipitations inside of oxide layer.

- Former FZK isothermal BOX-tests at 1400 °C show the development of metallic small-scale precipitations inside of oxide layer and formation of α-Zr(O) layer on the outer surface of oxide layer. Uncertainty factor: slow transient heating.

- Former non-isothermal tests on oxide layer reduction at lower temperature (~1300 °C) showed formation of metallic small-scale precipitations inside of oxide layer and formation of α-Zr(O) layer on the outer surface of oxide layer.

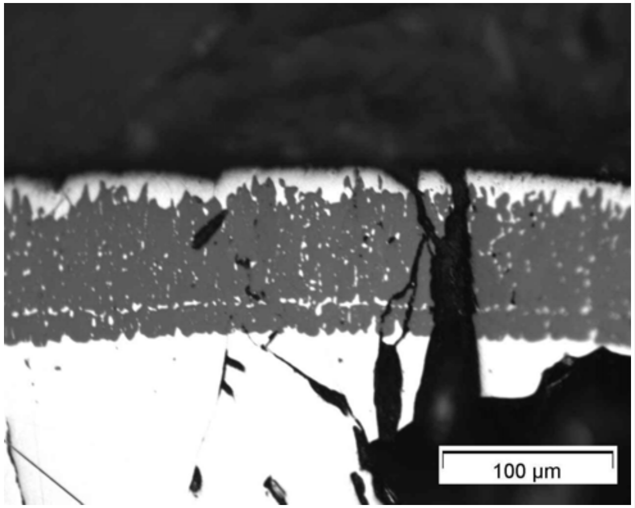
- New FZK tests were performed to analyze of outer metallic layer formation under isothermal conditions.

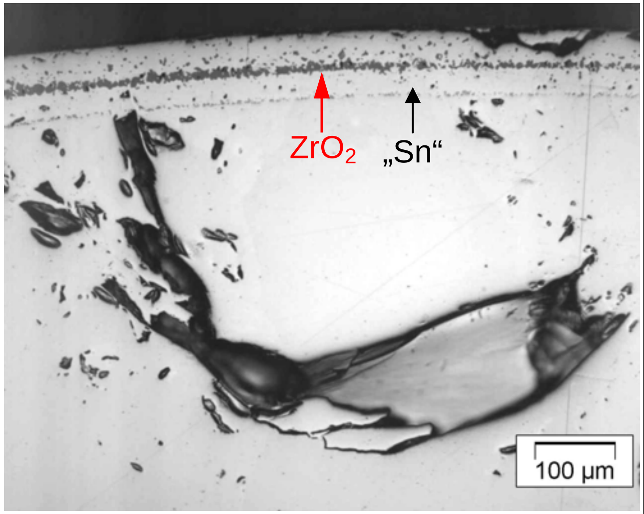
2002: First QUENCH-Rig tests (not isothermal) on annealing of Zry-4 oxidised claddings under Ar at ~1475 °C during 10800 s

			
initial oxide layer: ~230 µm (755 s); no annealing	bulk precipitates content: no surface metallic layer: no	bulk precipitates content: 24% surface metallic layer: no	pre-oxidation: 750 s; annealed oxide layer: ~190 µm

2003: BOX-Rig tests (isothermal, slow transient) on annealing of Zry-4 oxidised claddings under Ar during 5400 s

Annealing of tube at 1400°C





Annealing of rod at 1450°C

pre-oxidation: ~150µm (660 s);

annealed oxide layer: ~100 µm

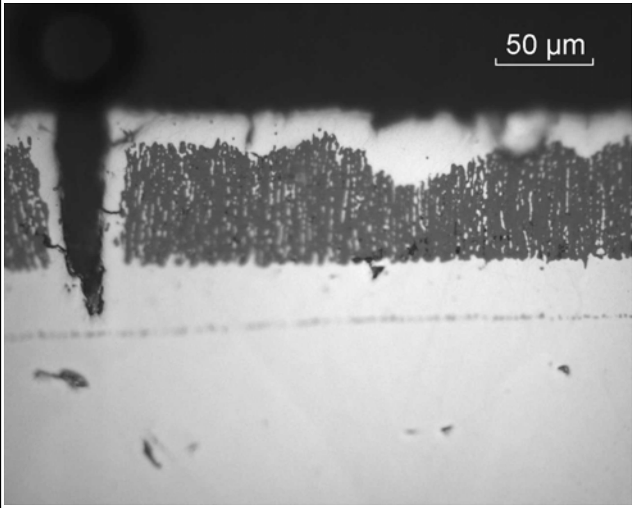
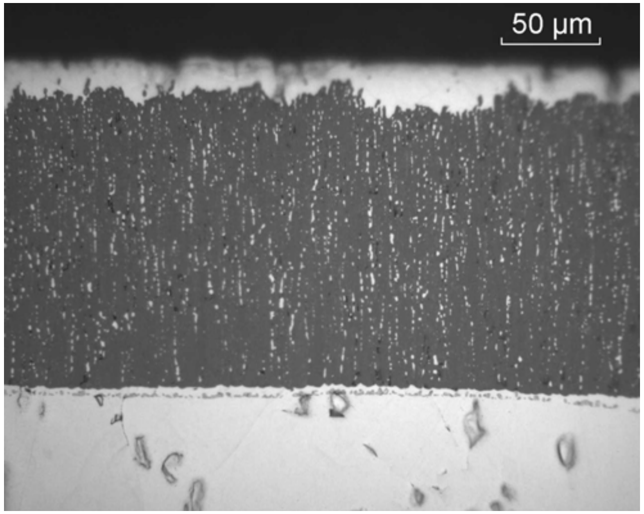
bulk precipitates content: 7 %

surface metallic layer: 15 µm

nearly complete dissolution of oxide layer

pre-oxidation: ~275µm (1080 s)

2004: QUENCH-Rig tests (not isothermal) on annealing of Zry-4 oxidised claddings under Ar at ~1350 °C during 9000 s

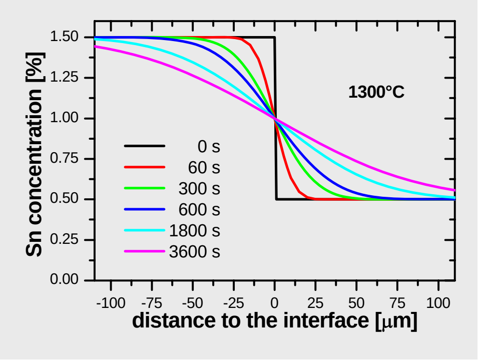
			
initial oxide layer: ~180 µm (720 s) annealed oxide layer: 75 µm	**bulk precipitates content: 10%** **surface metallic layer: ~35 µm**	**bulk precipitates content: 8%** **surface metallic layer: ~30 µm**	**initial oxide layer: ~240 µm (1190 s) annealed oxide layer: 155 µm**

New tests (2006). Investigated materials:

- Zry-4
- E110 (WWER)
- Framatome Duplex:

D4-layer (150 µm) + Zry-4-layer (575 µm)

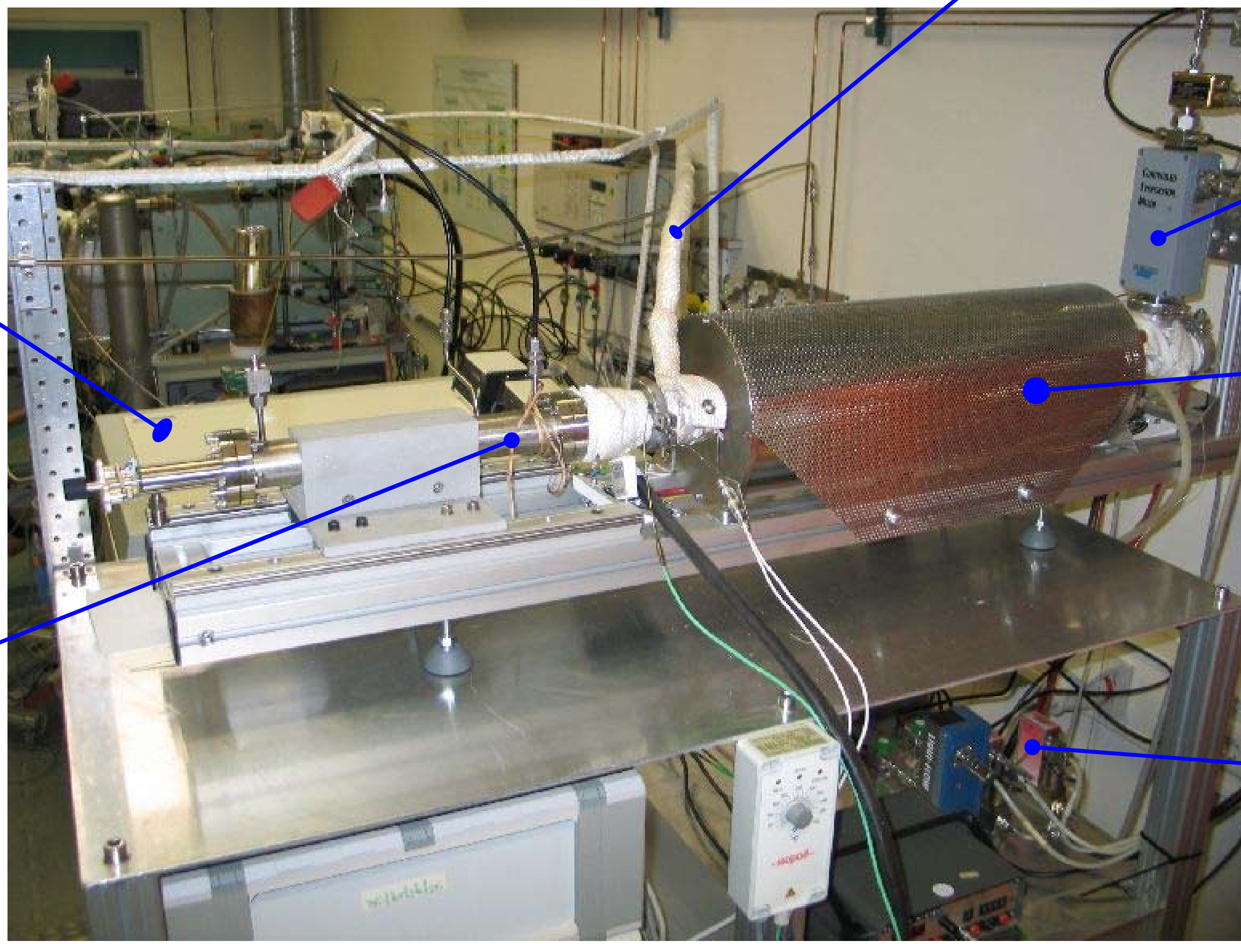
Diffusion of Sn in Zr



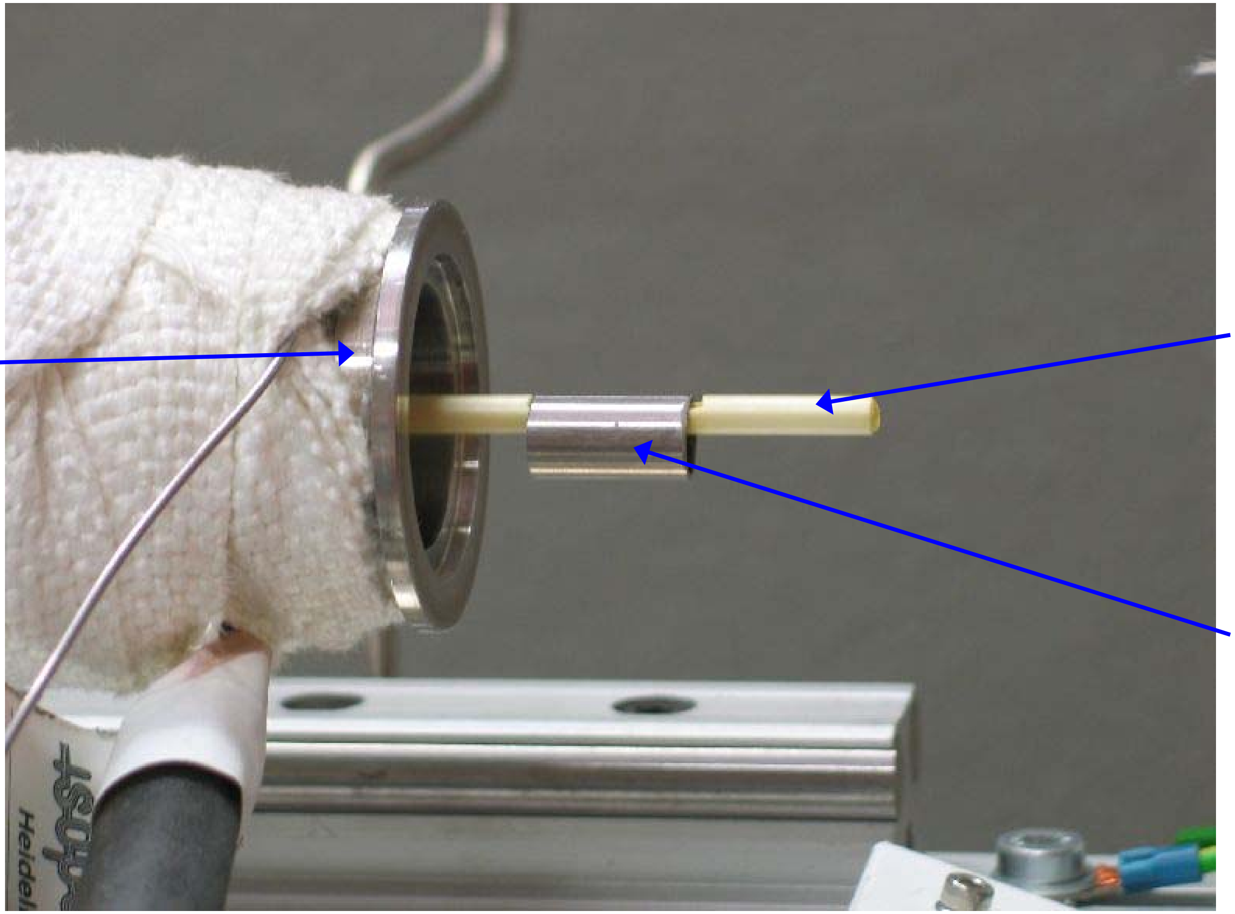
Chemical composition

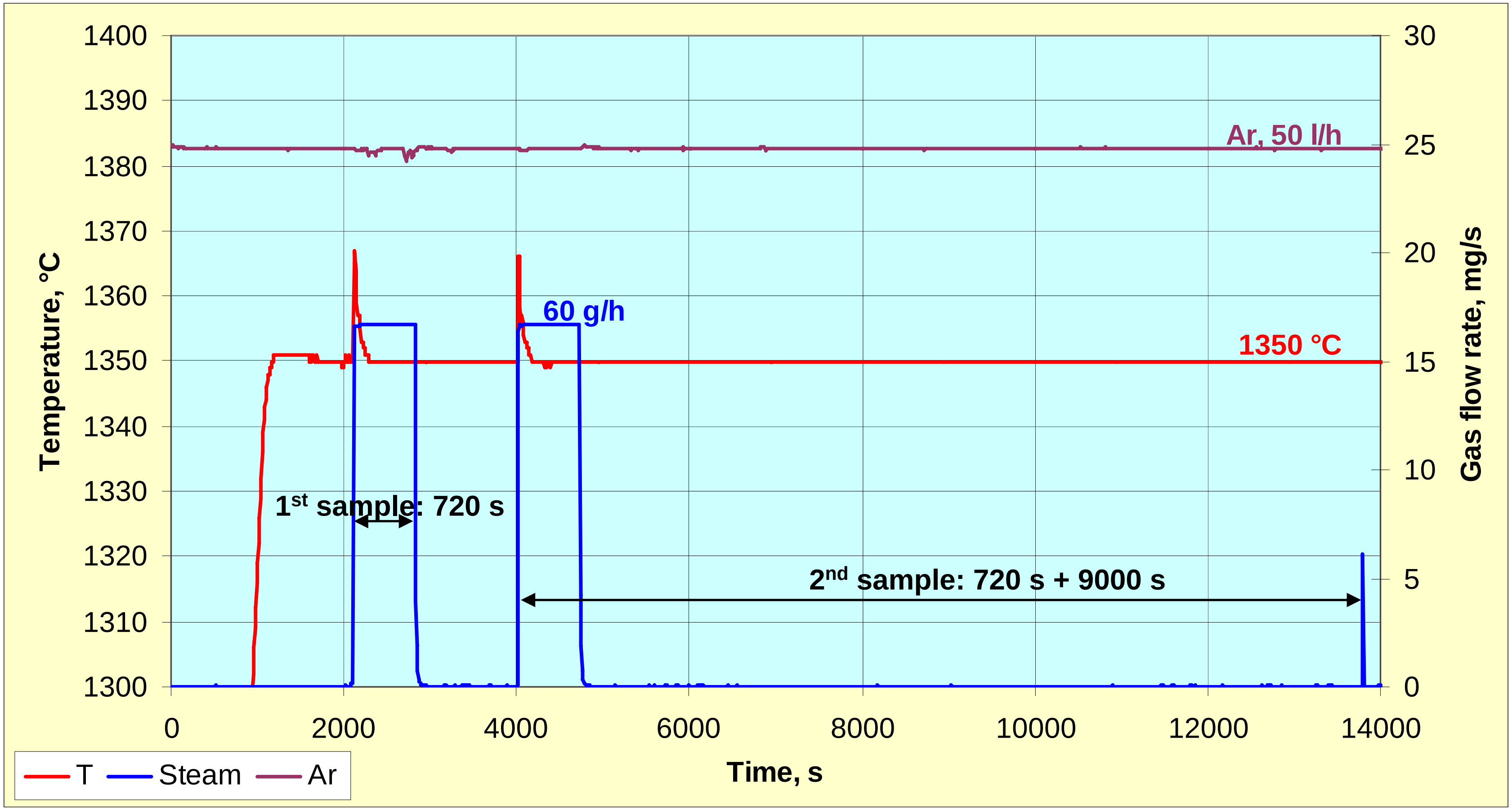
Material	Nb	Sn	Hf	Fe	Cr	Ni
E110	**0.97**	<0.04	0.025	0.008	0.002	0.002
Zry-4	0.0001	**1.5**	0.0001	0.21	0.10	0.00007
D4	0.0001	**0.5**	0.0001	**0.5**	**0.20**	**0.03**

BOX Rig for oxidation experiments under quasi isothermal conditions



BOX Rig: movable sample holder
allows the fast probe positioning in furnace and the fast probe removal from furnace





Test progression with two samples:
1st sample – oxidation in steam at 1350 °C
2nd sample – oxidation in steam and annealing in Ar at 1350 °C

Zircaloy-4: oxidation in BOX-rig at 1350 °C in steam flow of 60 g/h (with Ar 50 l/h)

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<tr>
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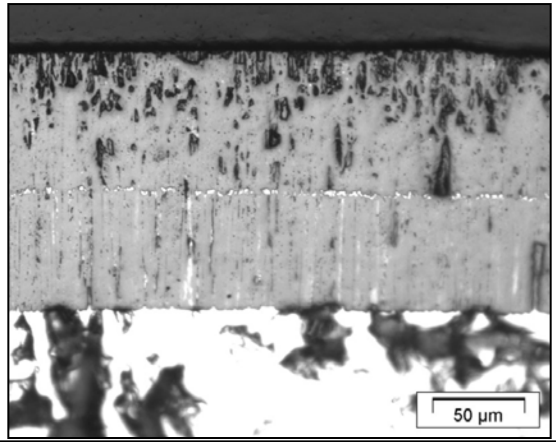
<td></td>
<td>↔ Similar structure of inner oxide layer</td>
</tr>
<tr>
<td>Oxidation: 720 s
El. resistance of outer surface : ∞</td>
<td>Outer oxide layer: 142 µm.
2 sub-layers divided with Sn interlayer</td>
<td>Inner oxide layer: 140 µm</td>
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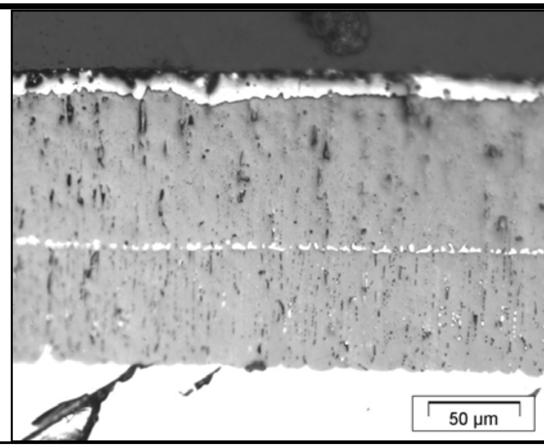
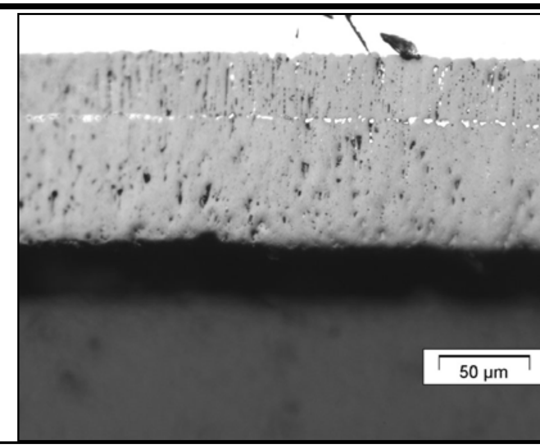
<td></td>
<td></td>
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<td>Pre-oxidation: 790 s; annealing: 9000 s
El. resistance of outer surface : 20 Ωm</td>
<td>Outer oxide layer: 150 µm
Outer α-Zr(O) layer: 11 µm</td>
<td>Inner oxide layer: 109 µm
Inner α-Zr(O) layer: 0 µm</td>
</tr>
</table>

<u>Duplex</u>: oxidation in BOX-rig at 1350 °C in steam flow of 60 g/h (with Ar 50 l/h)

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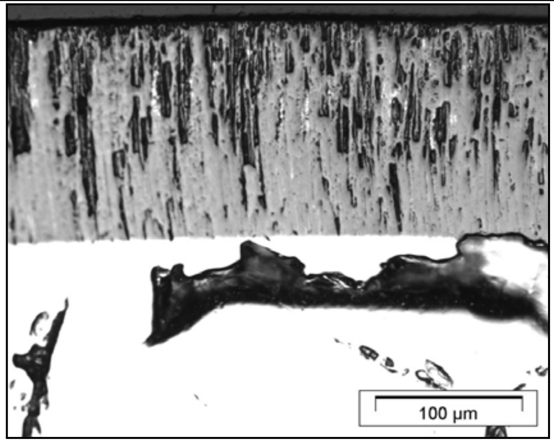
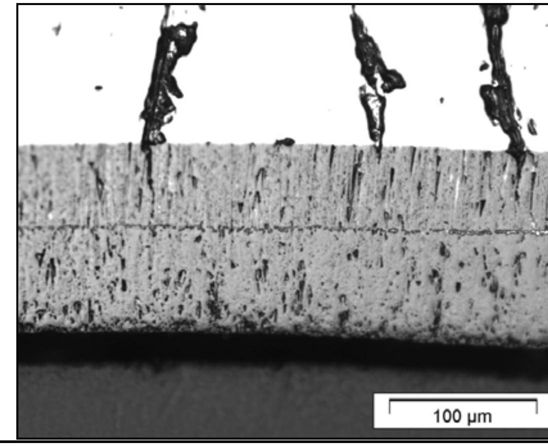
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation: 720 s
El. resistance of outer surface : ∞</td>
<td>Outer oxide layer: 148 µm
/Oxidised only outer D4-layer/</td>
<td>Inner oxide layer: 133 µm</td>
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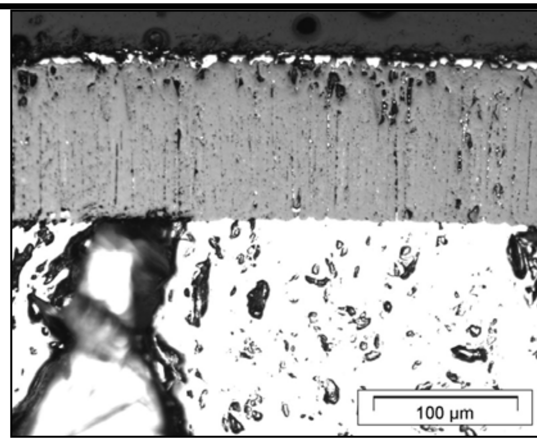
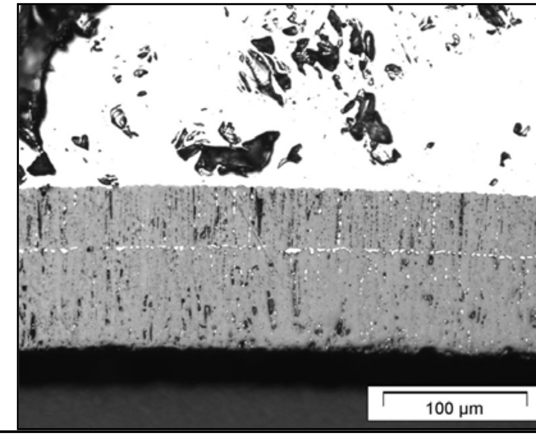
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-oxidation: 720 s; annealing: 9000 s
El. resistance of outer surface : 4 Ωm</td>
<td>Outer oxide layer: 110 µm
Outer α-Zr(O) layer: 5 µm</td>
<td>Inner oxide layer: 114 µm
Inner α-Zr(O) layer: 0 µm</td>
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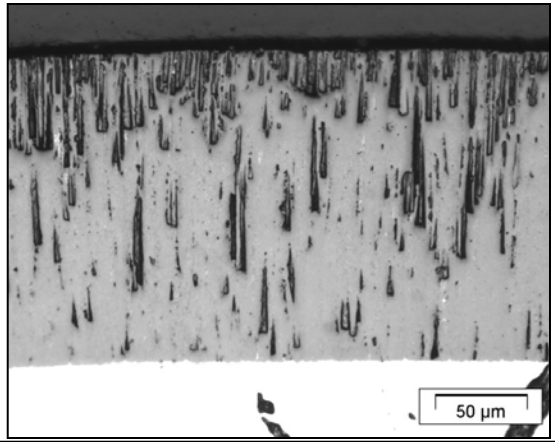
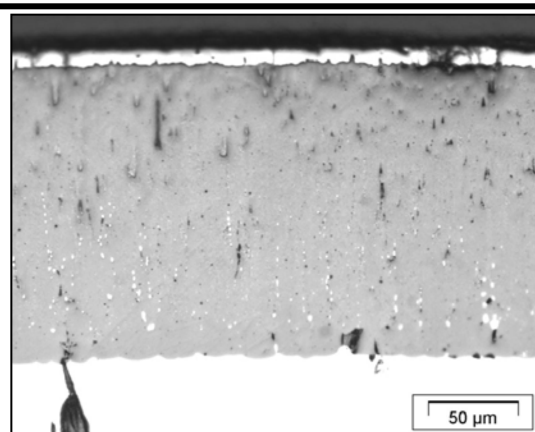
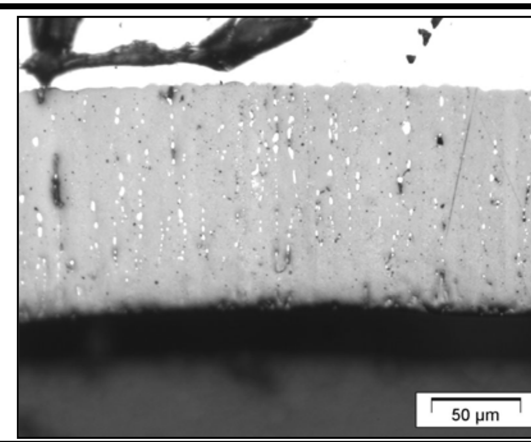
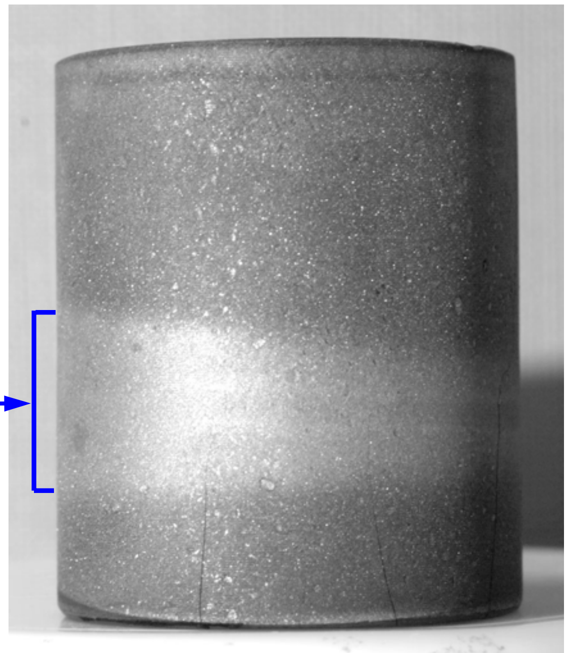
</table>

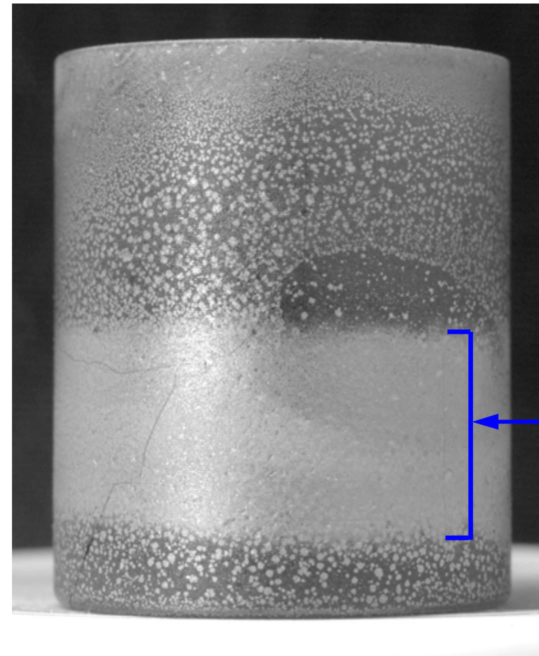
E-110 (Zr1%Nb): oxidation in BOX-rig at 1350 °C in steam flow of 60 g/h (with Ar 50 l/h)

		←→ Similar structure of inner oxide layer
Oxidation: 720 s El. resistance of outer surface : ∞	Outer oxide layer: 172 µm Homogeneous structure	Inner oxide layer: 136 µm
		
Pre-oxidation: 720 s; annealing: 9000 s El. resistance of outer surface : 1000 Ωm	Outer oxide layer: 164 µm **Outer α-Zr(O) layer: 9 µm**	Inner oxide layer: 128 µm Inner α-Zr(O) layer: 0 µm

Outer view of ZrO_2 crucibles used for the tests on dissolution of ZrO_2 with molten Zircaloy under Ar: formation of α-Zr(O) metallic strip with the height, corresponding to the melt height inside of crucible

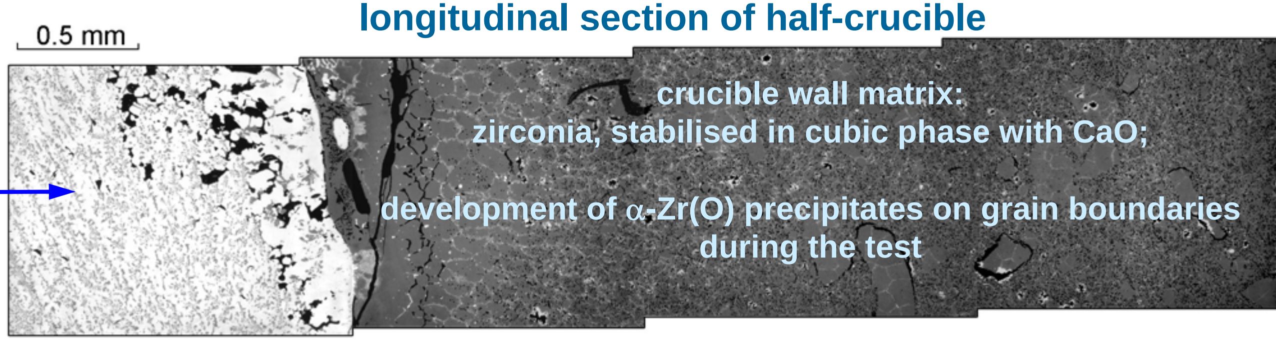


Test temperature 2100 °C, duration 750 s



Test temperature 2200 °C, duration 590 s

longitudinal section of half-crucible



SUMMARY

- New tests on annealing of pre-oxidised claddings in inert atmosphere under quasi isothermal conditions at 1350 °C during 9000 s were performed. The oxide layer thickness after pre-oxidation was about 140-170 µm on both sides of cladding tubes.

- Three different cladding materials were tested: Zircaloy-4, Duplex, Zr1%Nb.

- All probes showed a moderate decrease of oxide layers after annealing : about 5% for Zr1%Nb and up to 25 % for Zircaloy-4. This thickness decrease is significantly low in comparison with oxide layer decrease under not isothermal conditions (up to 60 % for Zircaloy-4).

- The development of α-Zr(O) precipitations in the bulk of the oxide layer under isothermal conditions is negligible in comparison with the bulk metallic precipitation development in the similar tests under not isothermal conditions.

- The α-Zr(O) layer developed during annealing only on the surface of outer oxide layer. No traces of metal there are on the oxidised inner surface of annealed tube probes.

- The thickness of developed α-Zr(O) layer for the isothermal annealed probes is much fewer in comparison with not isothermal cases (~10 µm instead of ~35 µm).