# High-temperature single-rod tests on the oxidation of Cr coated cladding tubes, carried out at KIT within the IAEA project ATF-TS

*J. Stuckert, U. Peters, U. Stegmaier, K. Vizelkova, E. Vogel*

## Abstract

22 single rod oxidation tests with Cr coated zirconium alloy tubes were carried out within the framework of the IAEA project ATF-TS under DBA and BDBA transient conditions in an induction furnace. Eight M5® and four ZIRLO™ claddings PVD coated to 7 µm thick Cr layer, four E110 claddings with arc ion Cr plating to 8 µm thick Cr layer, six opt. ZIRLO™ claddings PVD coated to 5, 18 µm thick Cr layer and 18+8 µm thick Cr+CrN layer were tested.

The tests performed with ZIRLO claddings coated to 7 µm Cr layer showed that for Tmax<1300 °C, only small oxidation of Cr layer with low hydrogen release (factor 15 in comparison to not coated claddings) occurred. For higher temperatures, formation of numerous local swellings at the outer cladding surface due to Zr-Cr eutectic at 1350 °C occurred and significant hydrogen release due to oxidation of Zr substrate was measured.

The tests performed with E110 claddings coated to 8 µm Cr layer showed significant decrease of hydrogen release under extended LOCA conditions (max 1250 °C) in comparison to not coated samples (factor 15). For peak cladding temperature of 1350 °C, numerous local swellings at the outer cladding surface formed and intensive hydrogen release (factor 18 in comparison to 1250 °C) was measured.

The tests performed with opt. ZIRLO claddings coated to three different layer thicknesses showed that an increase in the thickness of the Cr layer by 3 times (from 6 to 18 µm) reduced the hydrogen release by 30% under DBA conditions (transient to 1200 °C), however, only by 3% under BDBA conditions (1400 °C). Barrier layer CrN has only moderate influence on hydrogen release under DBA, but strong reduced hydrogen release under BDBA (reduction factor 4). A local temperature escalation and formation and relocation of (Zr,Cr)+Zr melt for Cr/CrN coating occurred perhaps due to the lack of intermediate oxidation of part of the zirconium substrate, which could not react with steam due to the barrier effect of CrN layer.

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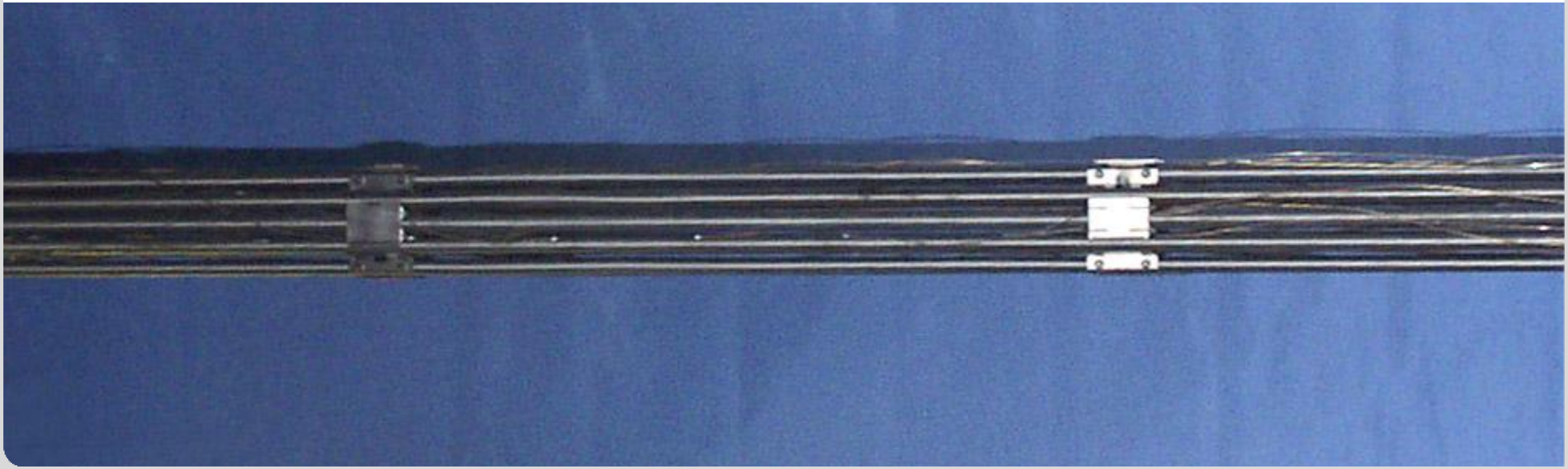
**29th QWS**

Institute for Applied Materials;  Program NUSAFE



# Three sets of HT oxidation tests

I. ZIRLO and M5® tubes, PVD coated by Oerlikon/Balzers GmbH with Cr to the layer thickness of 7 µm.

II. ZIRLO tubes, PVD coated by UPM/Prague with Cr to the layer thicknesses of 5 and 18 µm as well as with Cr/CrN to the layer thickness 18/8 µm (Cr/CrN.

III. E110 tubes, treated by AEOI with arc ion coated method to the Cr layer thickness of 8 µm.

# Transient tests in inductive furnace: cladding oxidation in steam

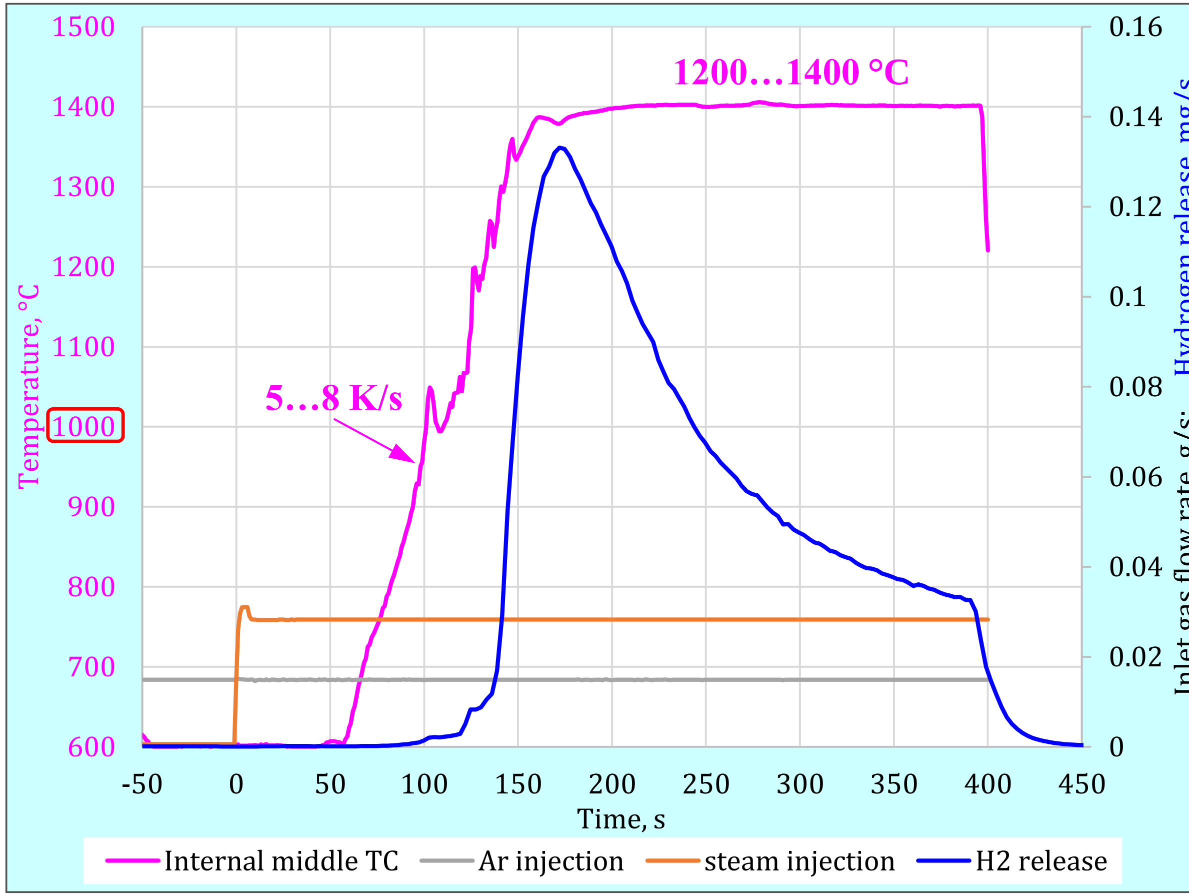
mass spectrometer

$H_2$+Ar + steam

$Zr + 2H_2O = ZrO_2 + 2H_2$

$2Cr + 3H_2O = Cr_2O_3 + 3H_2$

**Ar (30 l/h) + steam (100 g/h)**




Instrumentation: 1) TC inside the sample; 2) TC at the sample surface; 3) pyrometer; 4) mass spectrometer at furnace outlet

Control of generator according to internal TC or pyrometer; oscillations above 1000 °C

# Tests with 12 KIT samples coated by OERLIKON to 7 µm Cr

MC tubes: OD=10.75 mm, wall 725 µm;  MCs and ZOs tubes: OD=9.5 mm, wall 570 µm

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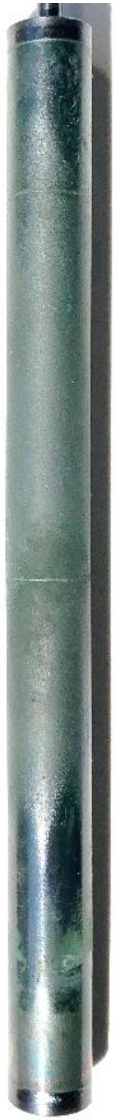
| Sample | Heating rate [K/s] | Maximal clad temperature $T_{max}$ [°C] | Duration of oxidation at $T_{max}$ [min] | Cooldown | Comment |
|---|---|---|---|---|---|
| MC-4 | 7 | 1200 | 10 | steam + Ar | performed |
| MC-5 | 7 | 1200 | 15 | steam + Ar | performed |
| MC-6 | 8 | 1300 | 5 | steam + Ar | performed |
| MC-7 | 6 | 1250 | 10 | steam + Ar | performed |
| MCs-2 | 8 | 1360 | 6 | steam + Ar | performed |
| MCs-3 | 8 | 1360 | 0 | steam + Ar | performed |
| MCs-4 | 5 | 1250 | 6 (1250°→900°) | **water** | performed |
| MCs-5 | 5 | 1250 | 0 | steam + Ar | performed |
| ZOs-2 | 5 | 1200 | 4 | steam + Ar | performed |
| ZOs-3 | 5 | 1380 | 0 | steam + Ar | performed |
| ZOs-4 | 5 | 1200 | 4 | steam + Ar | performed |
| ZOs-5 | 5 | 1400 | 4 | steam + Ar | performed |

**MC – for coated M5®**
**ZO – for coated ZIRLO™**

# Appearance of coated cladding samples oxidized in inductive furnace



MC-4: 1200 °C
during 10 min

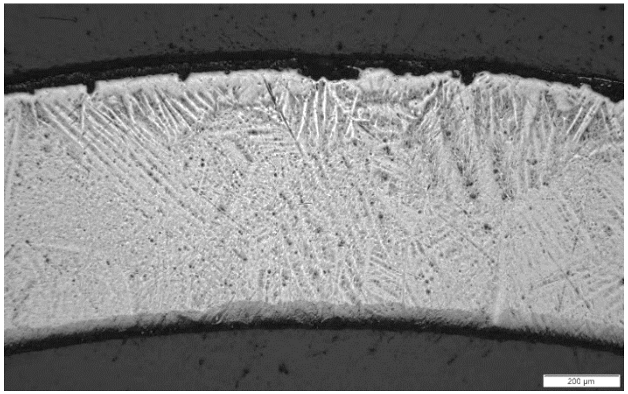
MC-5: 1200 °C
during 15 min

MC-7: 1250 °C
during 10 min

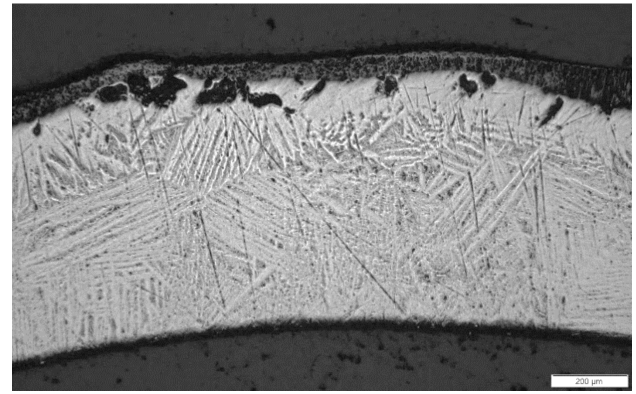
MC-6: 1350 °C
during 5 min

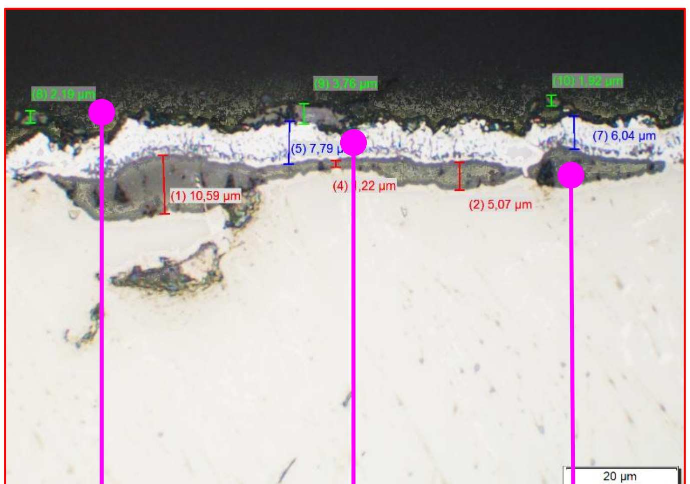
# Cladding microstructure after heating with 7 K/s and oxidation at 1200 °C

MC-4: 1200 °C during 10 min after heating



MC-5: 1200 °C during 15 min after heating






$Cr_2O_3$: 5µm

Cr: 5…8 µm

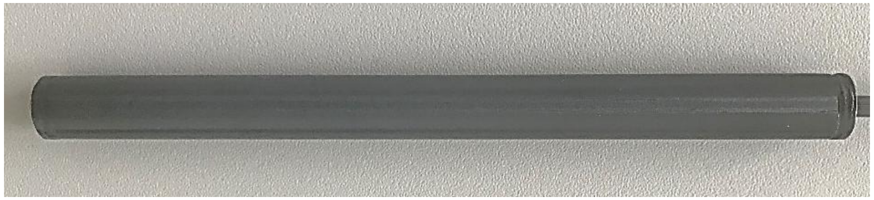
$ZrO_2$: 2…25 µm

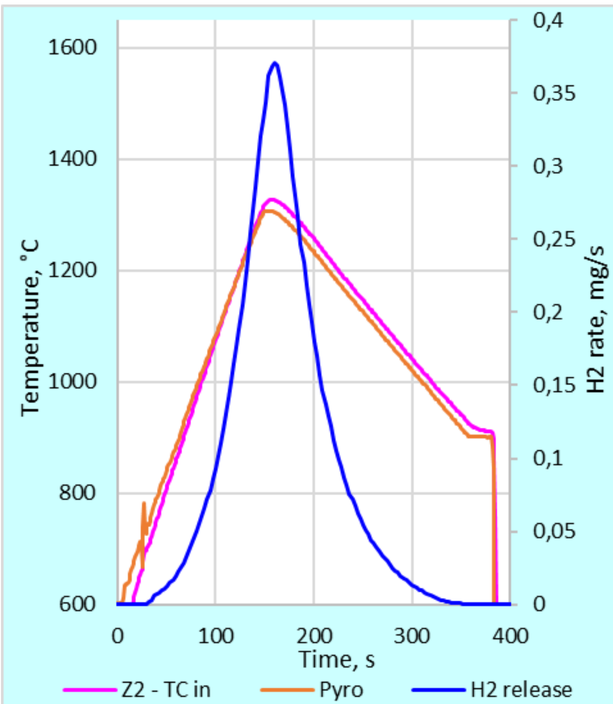

$Cr_2O_3$: 3…7 µm

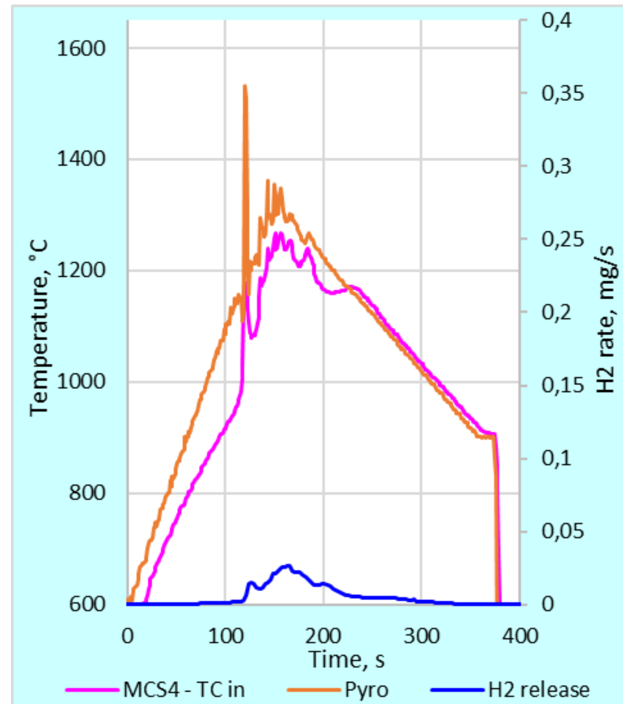
Cr: 0…7 µm

$ZrO_2$: 75 µm

# Influence of coating on hydrogen release
# (LOCA transient 5 K/s from 600 to1250 °C, then cooldown to 900 °C and quenching)




not coated sample Z2 (Zry-4): significant hydrogen release

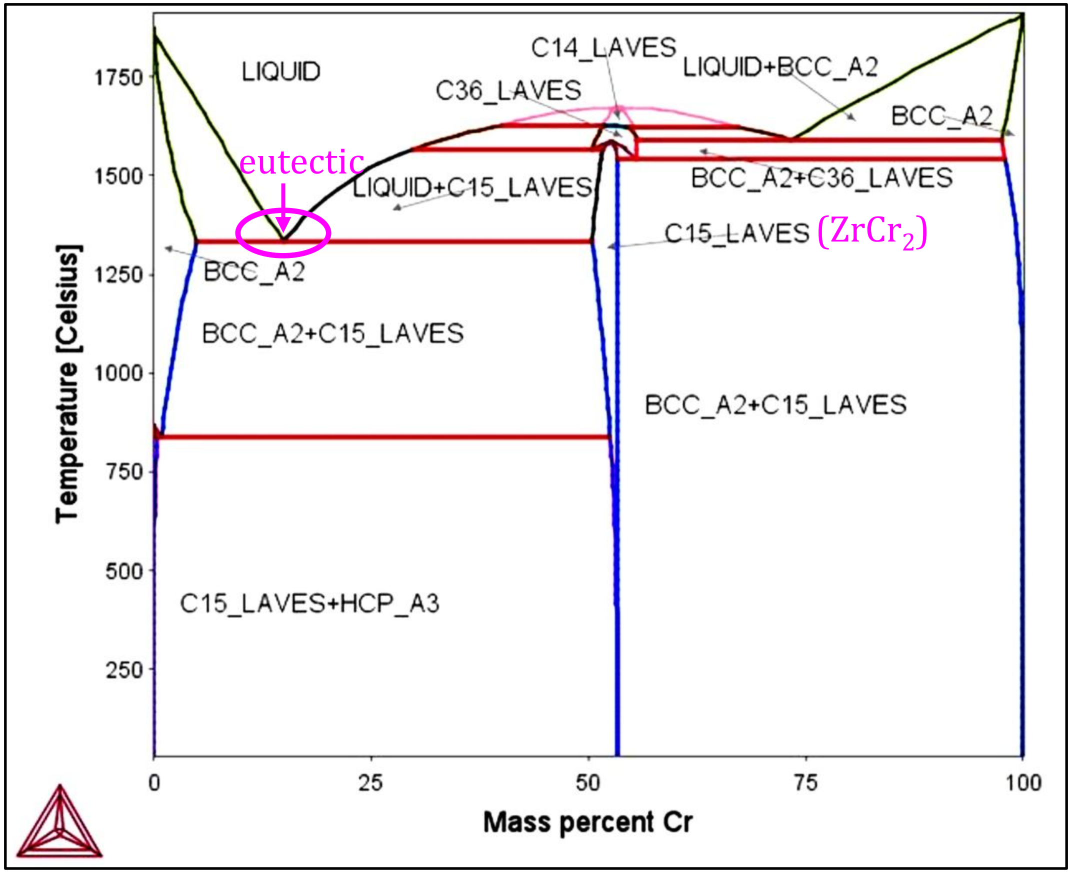
coated sample MCs-4 (M5®): strong reduced hydrogen release (factor 15)

# LOCA transient followed by a constant temperature of 1400 °C: influence of duration of oxidation in steam

sample MCs-3: transient with 8 K/s, then 1400 °C during 3 s

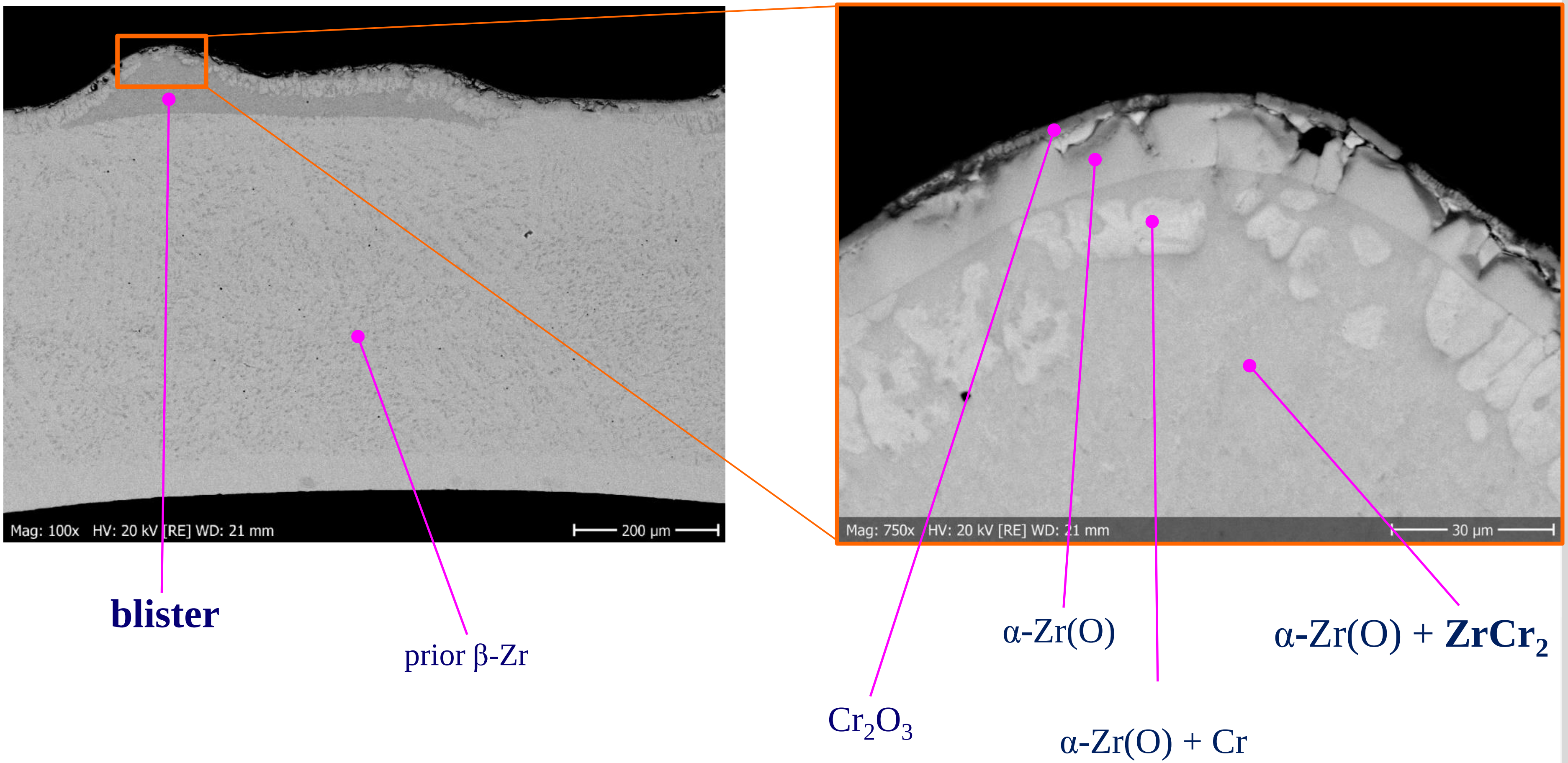
sample MCs-2: transient with 8 K/s, then 1400 °C during 240 s

# Binary Zr-Cr phase diagram




**The eutectic Zr/Cr forms at ≈1330 °C**

# Result of SEM/EDX analysis of MCs3 sample: cladding microstructure immediately after LOCA transient from 600 to 1400 °C: formation of surface swellings containing Laves phase $ZrCr_2$



# No influence of Zr alloy (as substrate) on hydrogen release for coated samples tested under similar high temperature conditions

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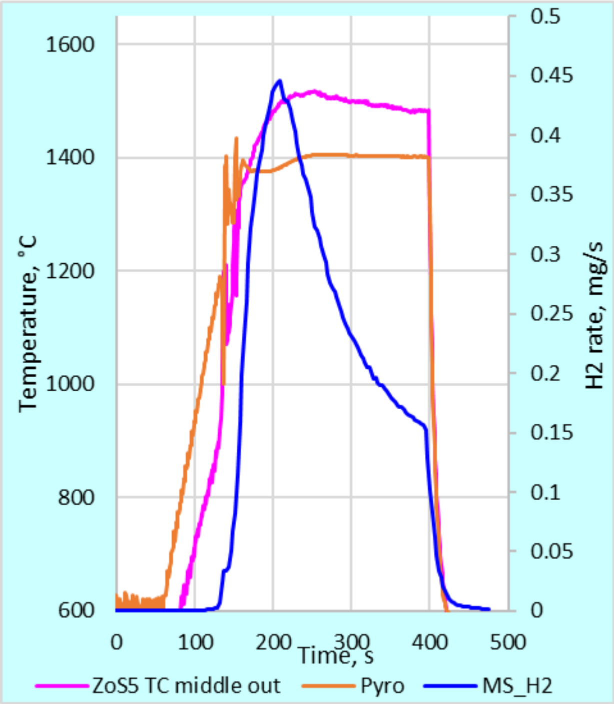
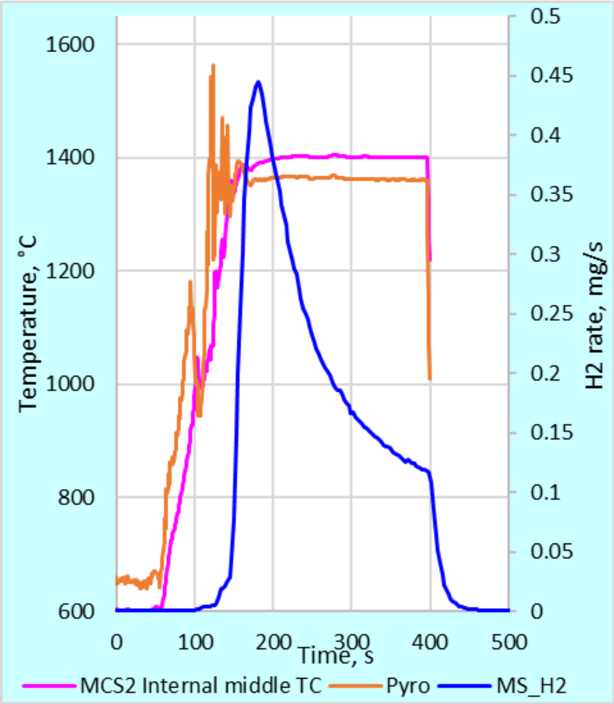
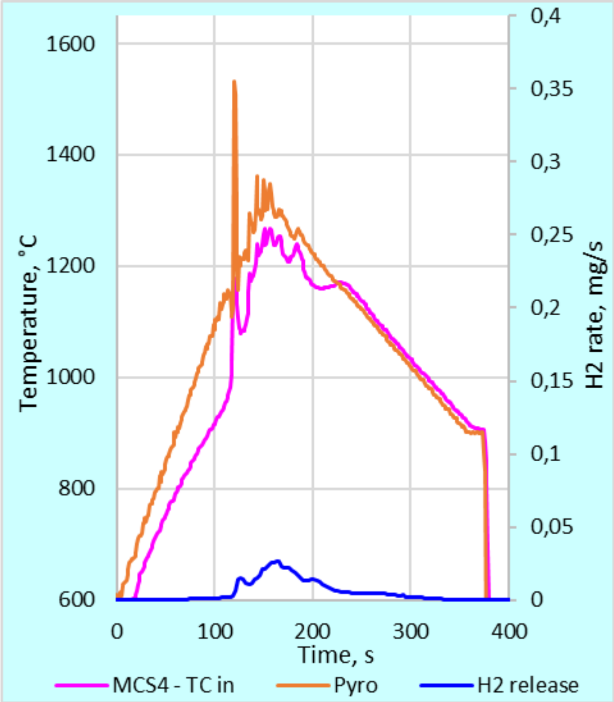
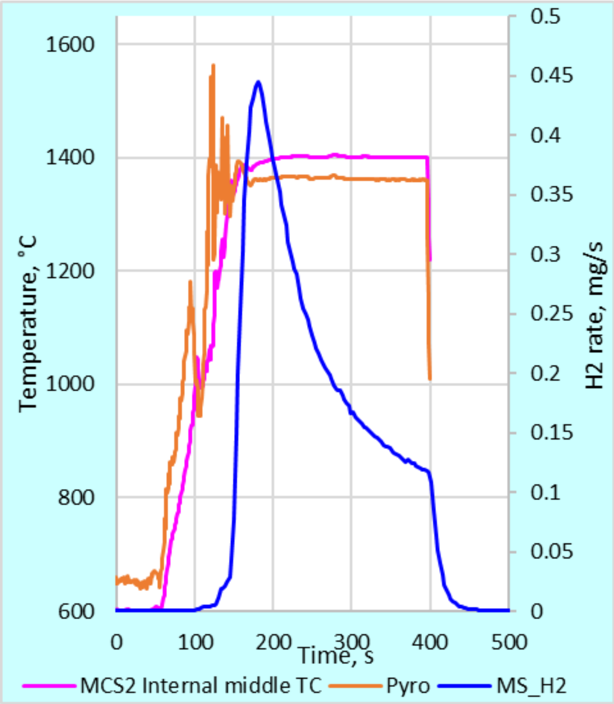
|---|---|
|  |  |
| sample ZOs5 (ZIRLO™) | sample MCs2 (M5®) |

# Influence of peak cladding temperature on hydrogen release





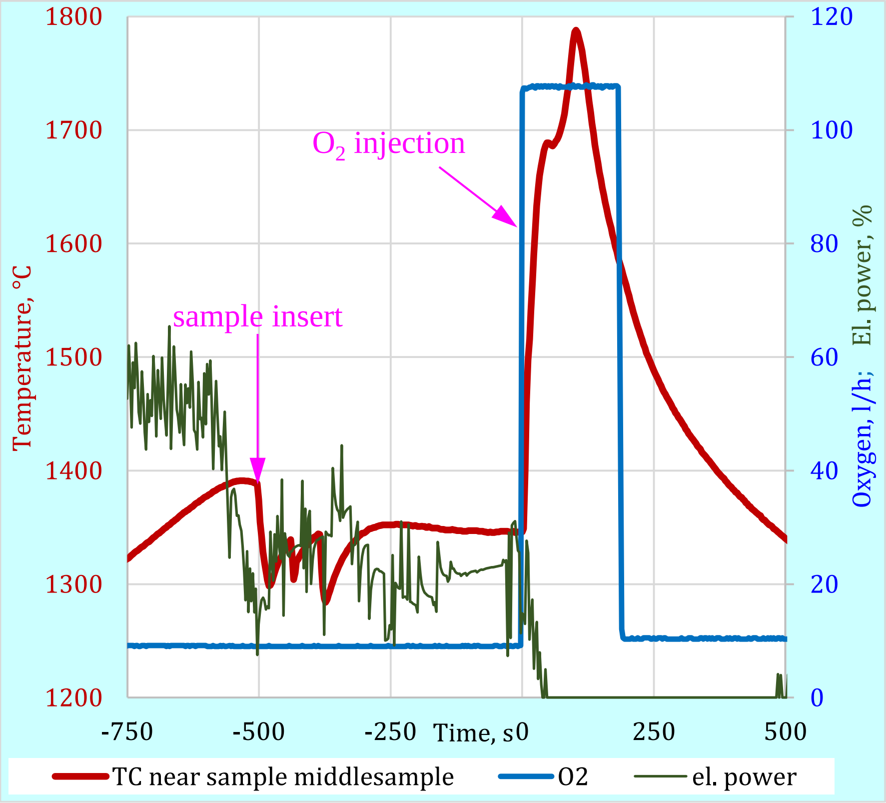




Cr coated sample MCs-4 oxidized with $T_{max}$=1250 °C
(***only oxidation of Cr layer***)

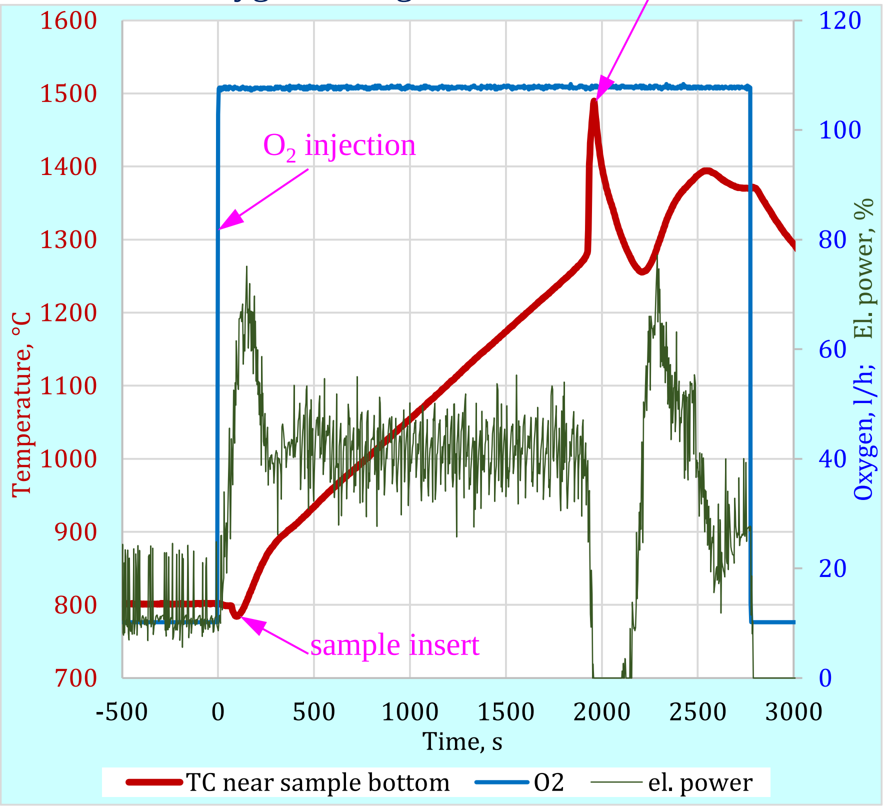
Cr coated sample MCs-2 oxidized with $T_{max}$=1400 °C: factor 20 for $H_2$
(***additional oxidation of Zr substrate***)

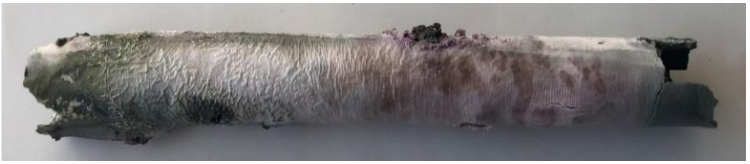
# Catastrophic oxidation and temperature escalation at T>1300 °C in tube furnace (without radiation heat loss)

sample MC-1: injection of oxygen at 1350°C




sample ZOs-1: temperature escalation in oxygen during slow transient



sample completely destroyed

# Summary on KIT samples

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➢ Inductive furnace:

1) for Tmax<1300 °C, only small oxidation of Cr layer with low hydrogen release (factor 15 in comparison to not coated claddings),

2) For higher temperatures, formation of numerous blisters (local swellings) at the outer cladding surface due to Zr-Cr eutectic at 1350 °C and significant hydrogen release due to oxidation of Zr substrate.

➢ Tube furnace: catastrophic oxidation at T>1300 °C due to the absence of radiation heat loss.

# E110 sample with arc ion Cr plating (AEOI) with a layer thickness of 7…8 µm

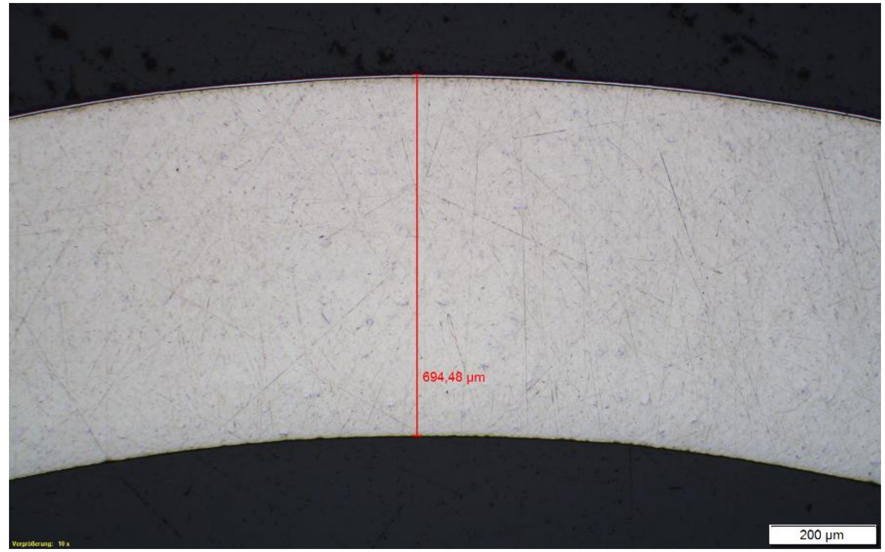
capillary Zr tube (sample holder and pressure normalizer)

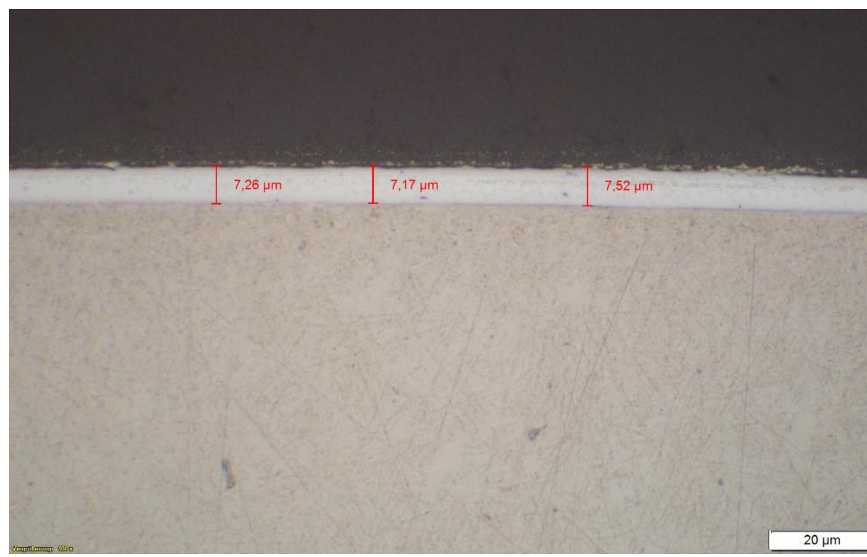
Zr plug

Zr alloy cladding coated by Cr; OD=9.14 mm ID=7.72 mm

Zr plug

coated empty sample welded at KIT and prepared for SETs




*Cr layer*

optical microscopy

# Appearance of coated cladding samples oxidized by steam in inductive furnace

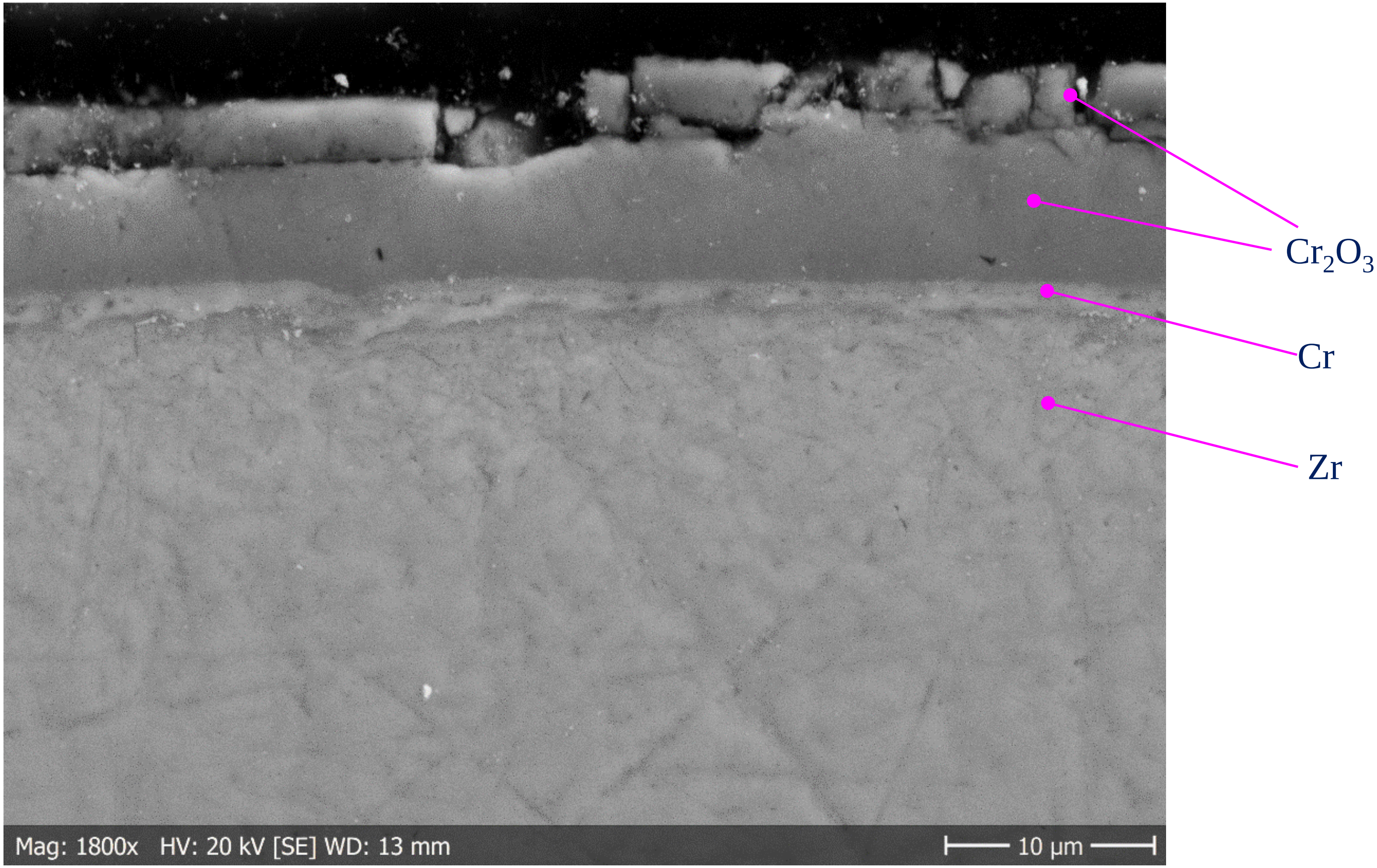
EC2: 5 K/s to $T_{max}$=**1250 °C**
cooldown 2 K/s, quench at 900 °C

EC4: 5 K/s to **1250 °C**,
5 s 1330 °C, imm. cooldown

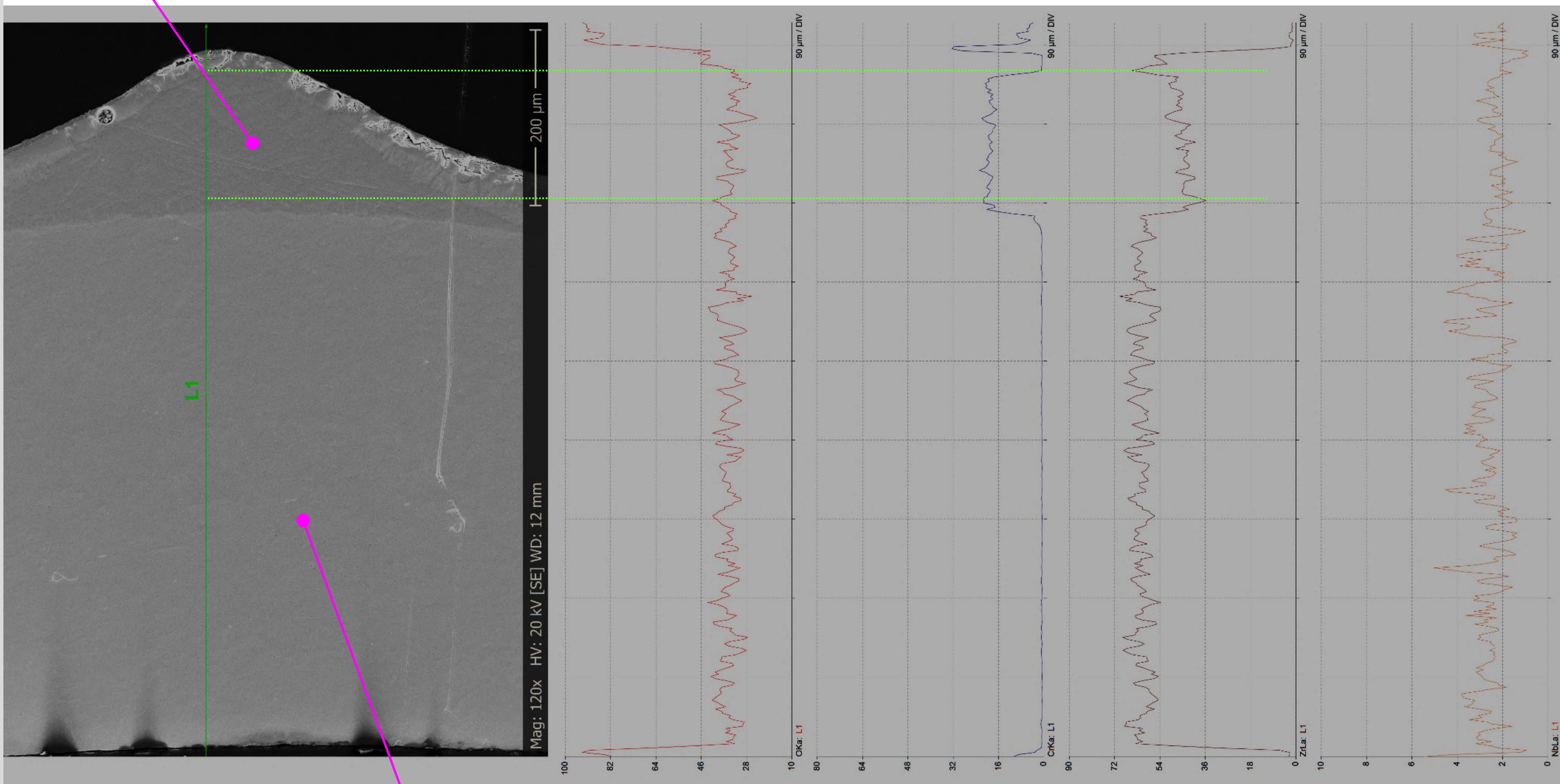
EC1: 8 K/s to $T_{max}$=**1390 °C**,
immediate cooldown

EC3: 8 K/s to **$T_{max}$=1400 °C**,
240 s 1400 °C, imm. cooldown

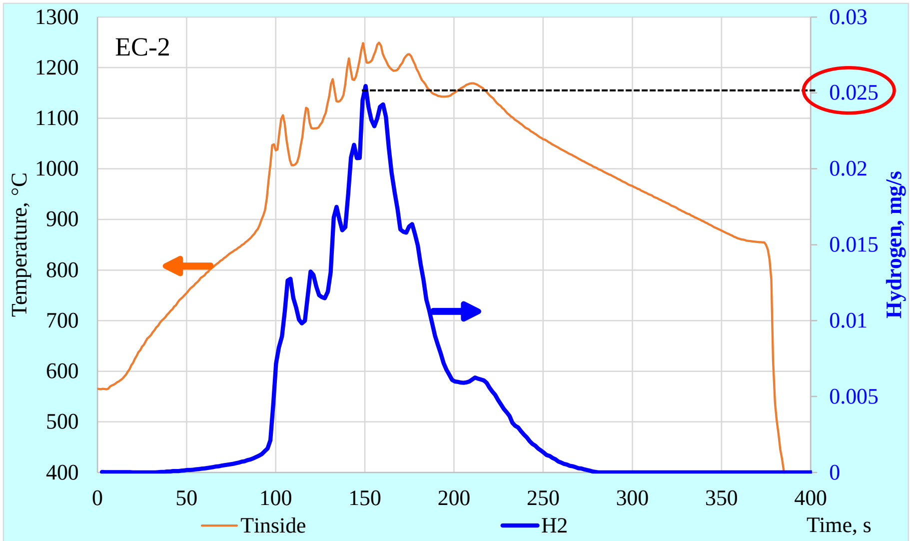
# EC4 (1250 °C, immediate cool-down), SEM/EDX



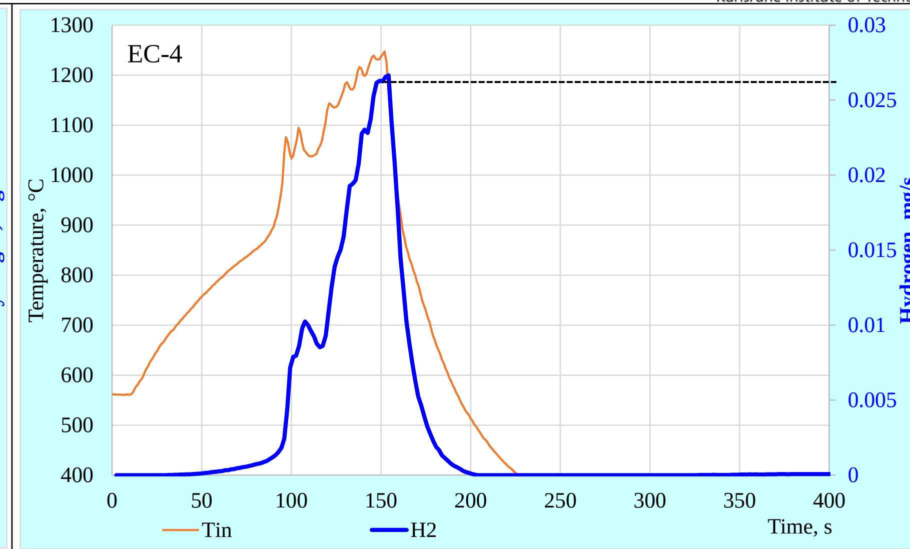
# EC1 (1400 °C, immediate cool-down), SEM line scan: formation of Laves phase inside the blister



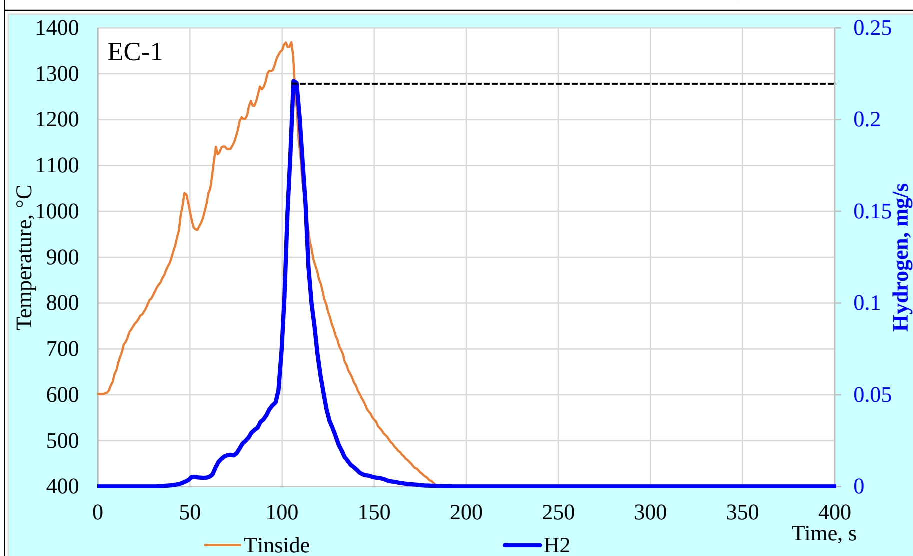
# Coated AEOI samples: hydrogen release



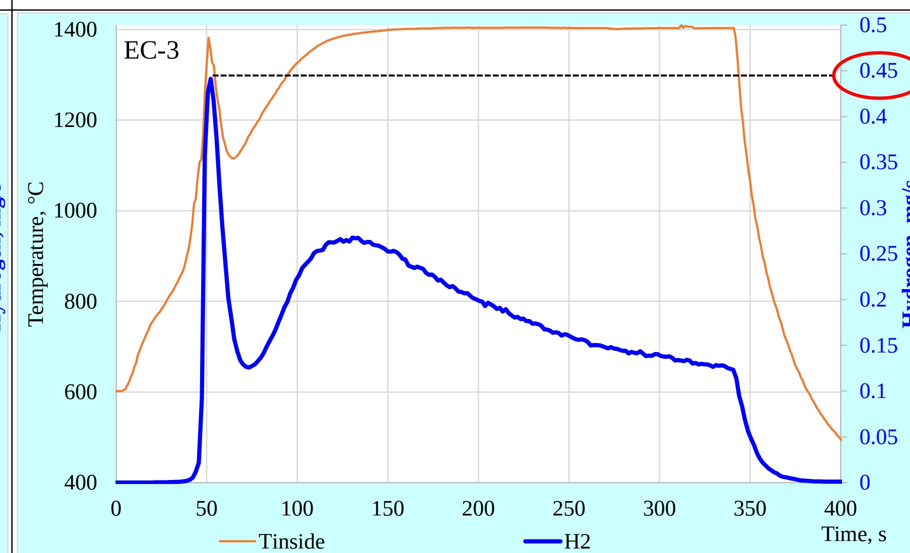

5 K/s, Tmax=**1250 °C**, cool-down 1.5 K/s to 900 °C, quench




5 K/s, Tmax=**1250 °C**, immediate cool-down



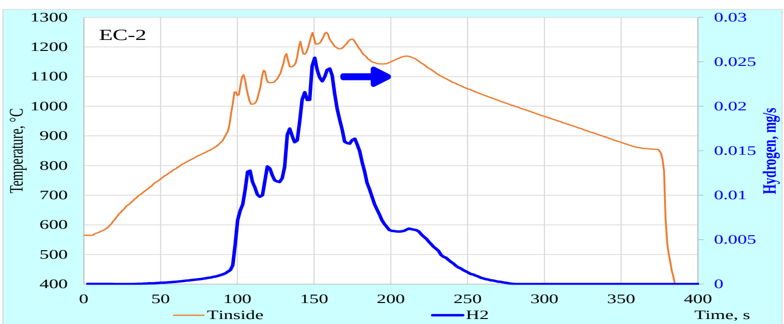

8 K/s, Tmax=**1390 °C**, immediate cool-down



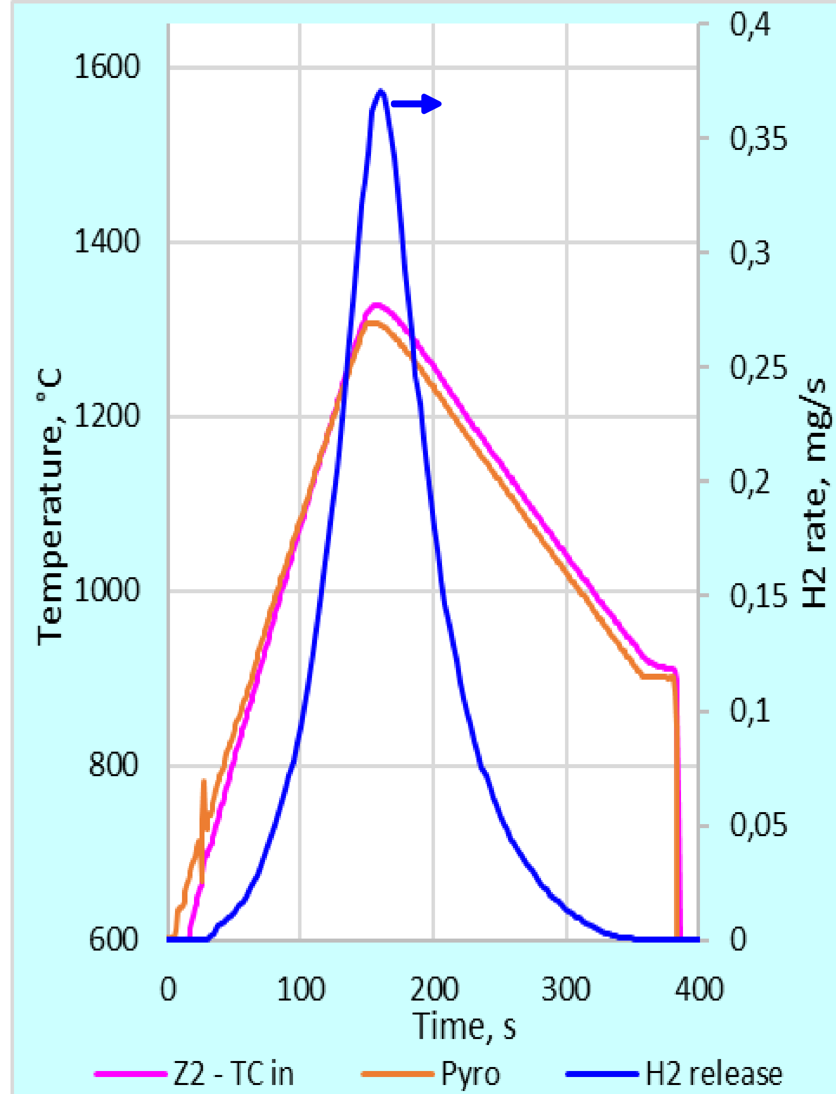

8 K/s, Tmax=**1400 °C** during 240 s, cool-down

# Comparison of coated E110 (2022) and not coated Zry-4: significant lower hydrogen release for coated cladding under extended LOCA (max 1250 °C, cool-down, quench)

E110




coated E110




not coated Zry-4

# Summary on AEOI samples

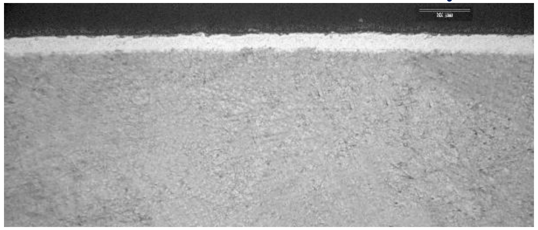
- significant decrease of hydrogen release under extended LOCA conditions (max 1250 °C) in comparison to not coated samples (factor 15).

- Numerous blisters (local swellings) at the outer cladding surface. Zr-Cr eutectic at 1350 °C and formation of Laves phase $ZrCr_2$.

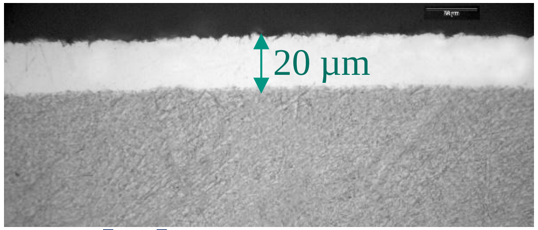
# Six coated (UPM/Prague) opt. ZIRLO™ samples with length 130 mm

## *Opt. ZIRLO claddings with OD=9.15 mm; wall thickness 650 µm:*

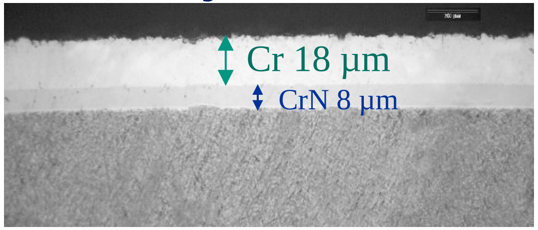
- 2 PVD coated samples with Cr layer thickness of ≈5 µm



- 2 PVD coated samples with Cr layer thickness of >17 µm




- 2 PVD coated samples with CrN/Cr multilayer




- *Samples are welded with Zr bottom and top plugs*
- *Top plug connected with Zr capillary tube*

# Test matrix
## and mass gains

| Sample | 1.1 (230418a) | 1.2 (230419a) | 2.1 (230419c) | 2.2 (230420a) | 3.1 (230421a) | 3.2 (230420b) |
|---|---|---|---|---|---|---|
| coating | Cr 5 µm | | CrN/Cr | | Cr 17 µm | |
| heat-up, K/s | 5 | 8 | 5 | 8 | 5 | 8 |
| $T_{max}$, °C | 1250 | 1400 | 1250 | 1400 | 1250 | 1400 |
| oxidation duration at $T_{max}$, s | 0 | 240 | 0 | 240 | 0 | 240 |
| cool-down, K/s | 1.5 to 900 °C | immediately | 1.5 to 900 °C | immediately | 1.5 to 900 °C | immediately |
| quench | water | in Ar+steam | water | in Ar+steam | water | in Ar+steam |
| $m_0$, g | 26.0662 | 25.5293 | 26.2996 | 26.1545 | 26.1584 | 26.1517 |
| $m_{pt}$, g | 26.1036 | 26.1948 | 26.3287 | 26.3265 | 26.1865 | 26.7329 |
| **Δm, mg** | **37.4** | ***665.5*** - *(TC wires)* | **29.1** | ***172 + (spalled scales)*** - *(TC wires)* | **28.1** | ***581*** - *(TC wires)* |

# Outer views of samples oxidized during DBA transients ($T_{max}^{surf}$=1200 °C)

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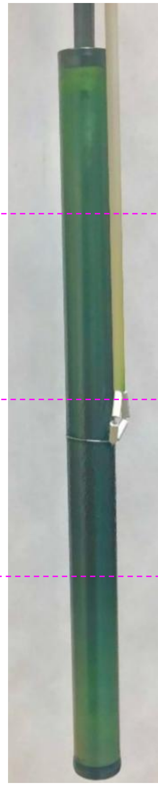
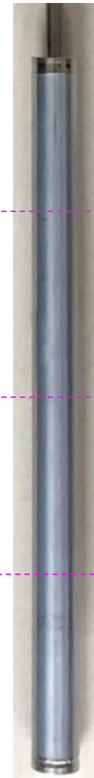
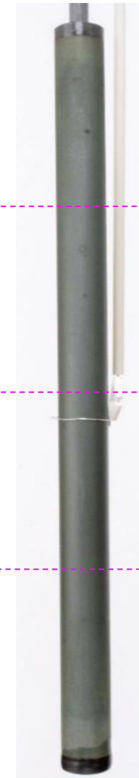
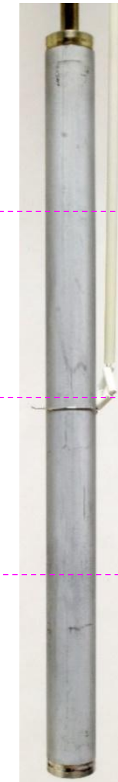
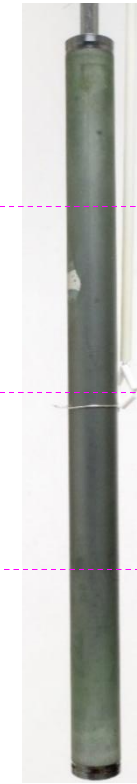
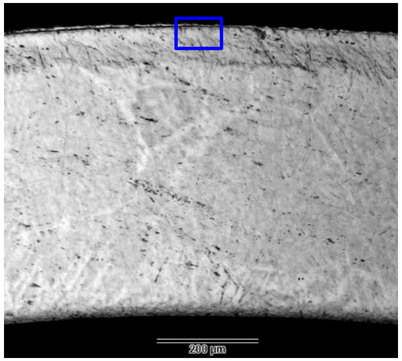
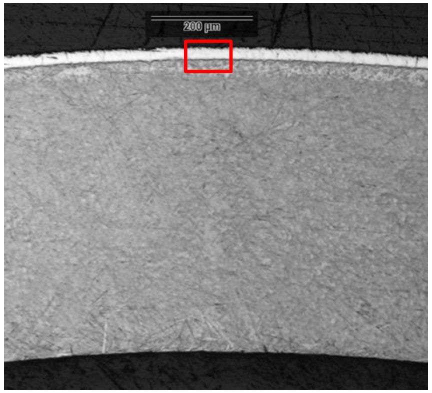
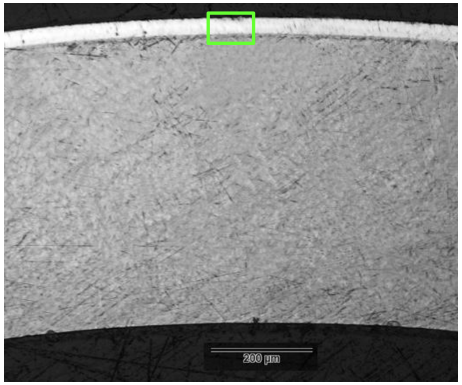
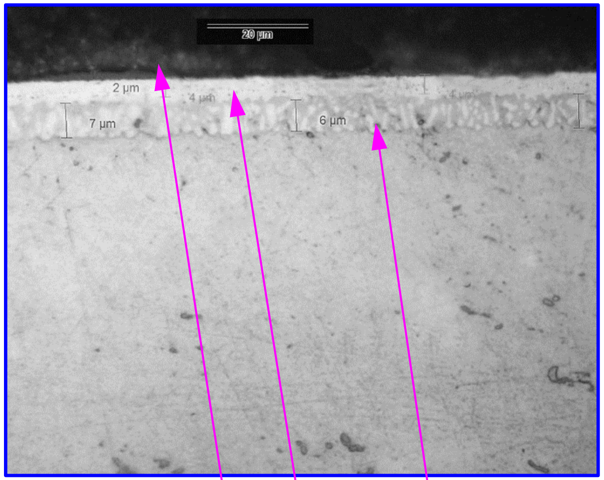
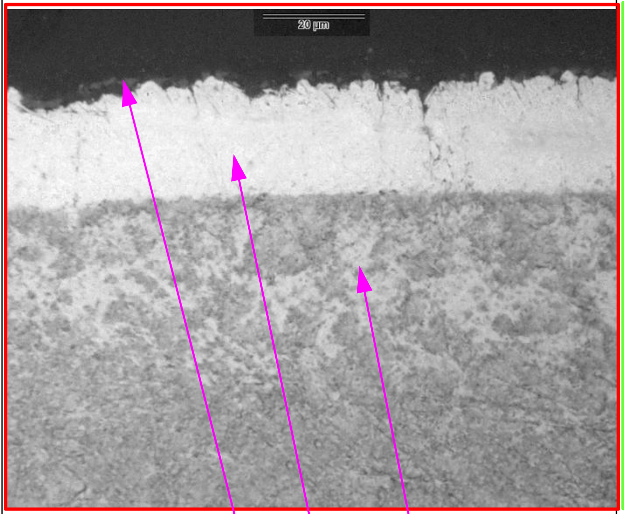
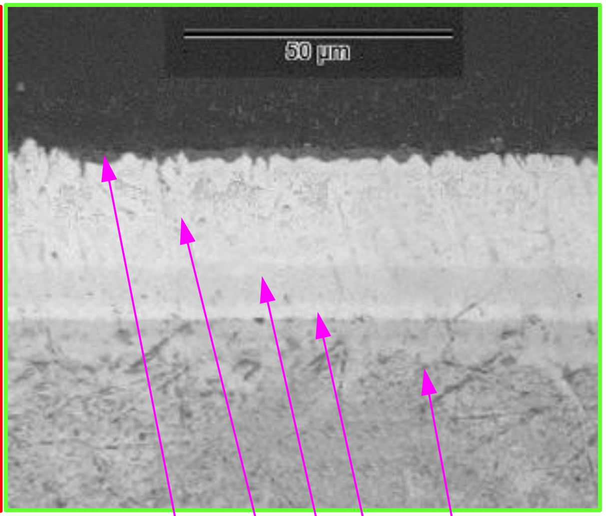
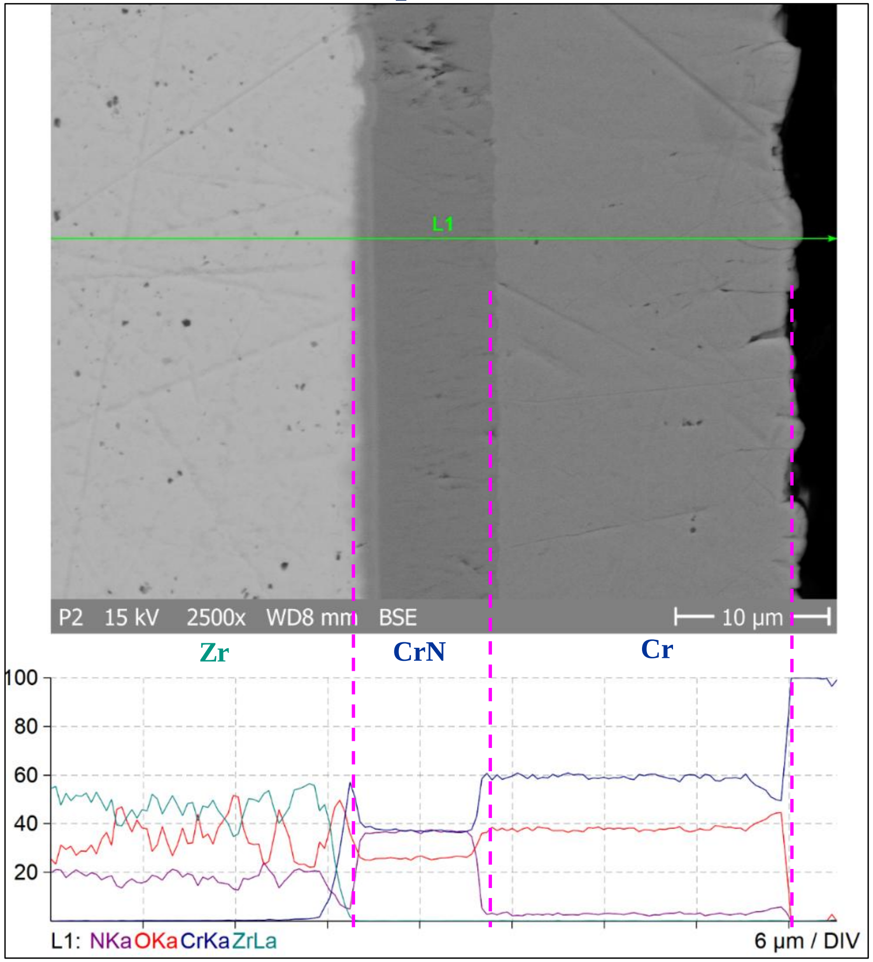
| *1.1*<br>*pre-test* | **1.1 (Cr≈5 µm)**<br>(sample 230418a) | *3.1*<br>*pre-test* | **3.1 (Cr>17 µm)**<br>(sample 230421a) | *2.1*<br>*pre-test* | **2.1 (CrN/Cr; 18/8 µm)**<br>(sample 230419c) |
|---|---|---|---|---|---|
| 100 mm<br>65 mm<br>hottest<br>elevation<br>35 mm<br> |  |  |  |  |  |
| |  | |  | |  |
| | **wrinkled surface** | | **glossy surface** | | **partial oxide spalling** |

# Cross-sections (at hottest elevation of 65 mm) of samples oxidized during DBA transients ($T_{max}^{surf}$=1200 °C)

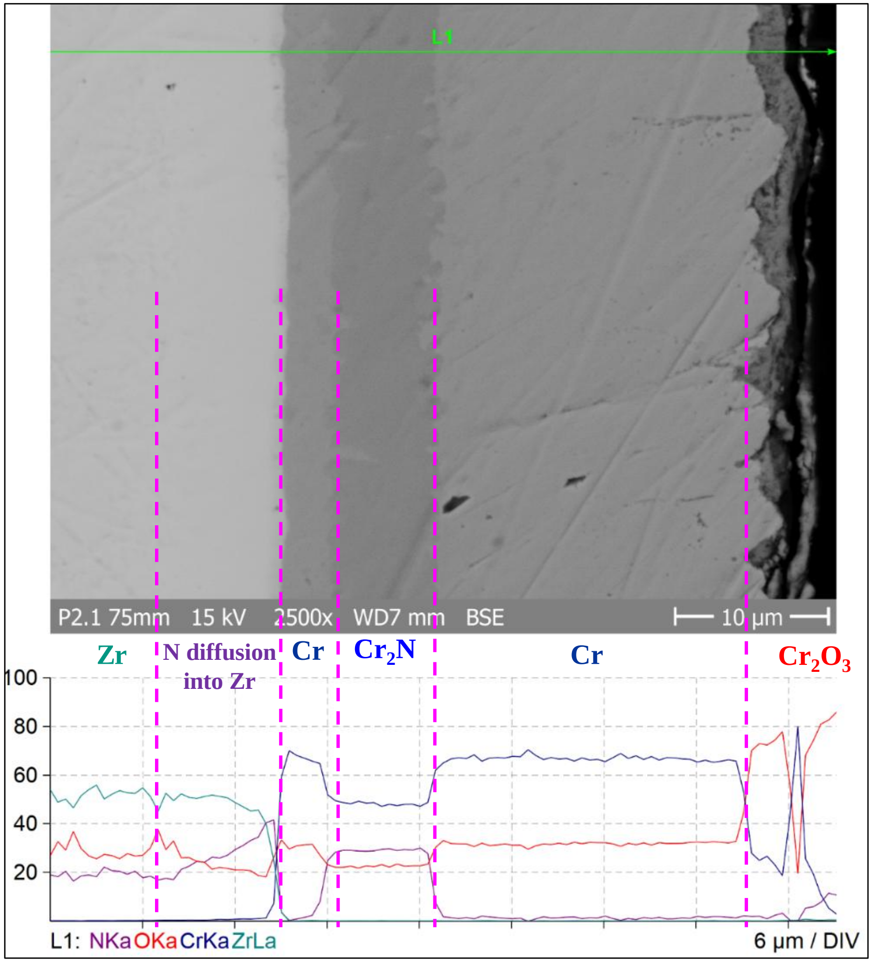
| sample 1.1, Cr 5 µm | sample 3.1, Cr 20 µm | sample 2.1, CrN/Cr multilayer 18/8 µm |
|---|---|---|
|  |  |  |
|  |  |  |
| 3 layers: $Cr_2O_3$, Cr, diffusion zone | 3 layers: $Cr_2O_3$, Cr, diffusion zone | 5 layers: $Cr_2O_3$, Cr, CrN, Cr, diffusion zone |

# Features of the behavior of the CrN/Cr sample under transient to $T_{max}^{surf}$=1200 °C

pre-test




post-test

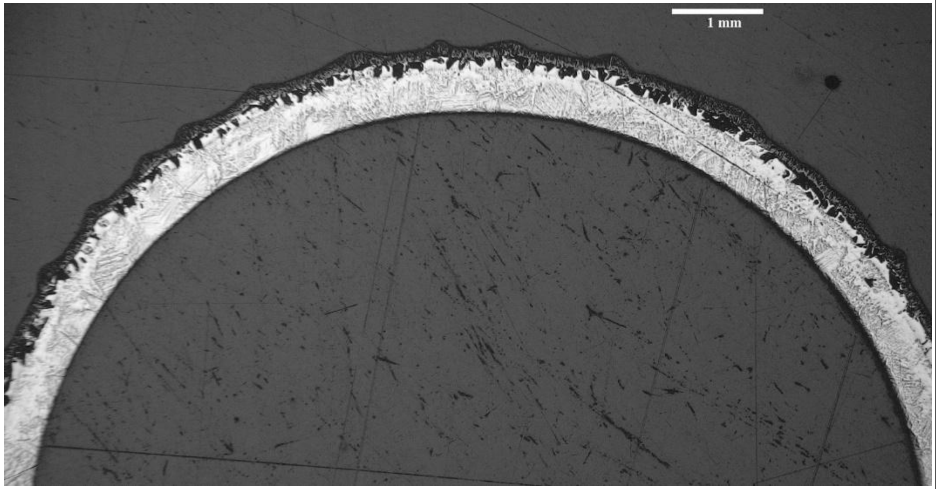


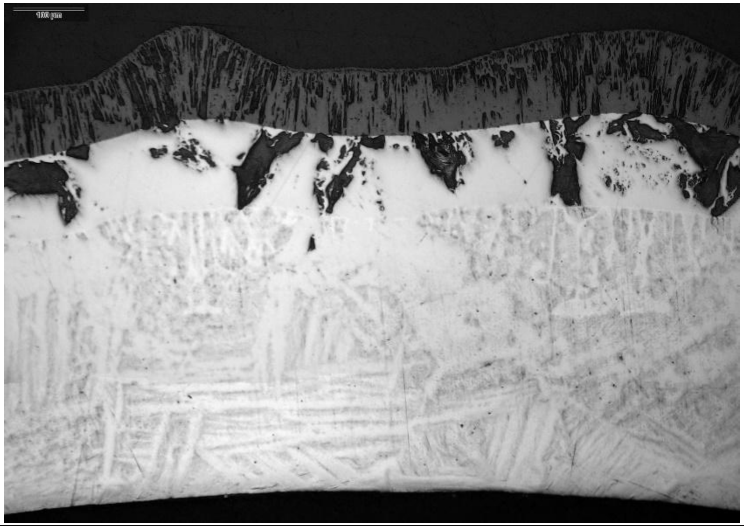
# Outer views of samples oxidized at $T_{max}^{surf}$=1400 °C

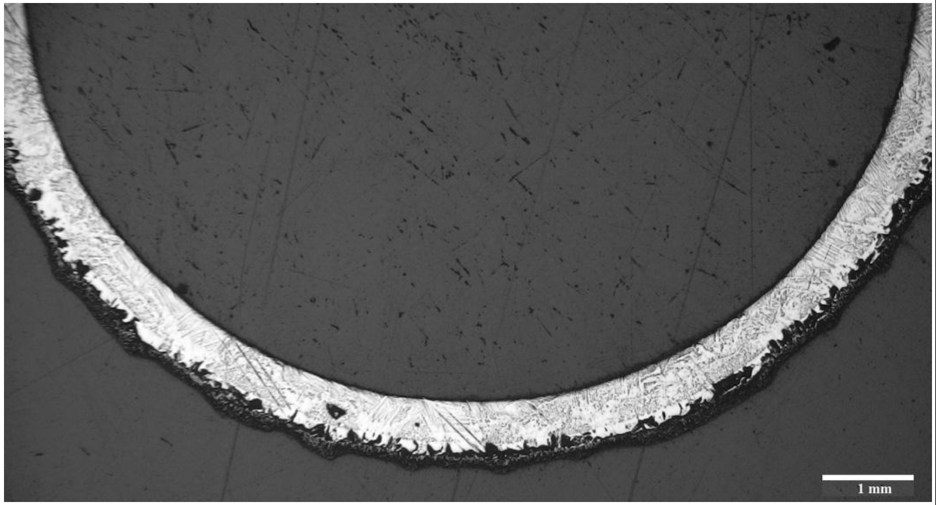
| ***1.1***<br>***pre-test*** | **1.2 (Cr≈5 µm)**<br>**(230419a)** | ***3.1***<br>***pre-test*** | **3.2 (Cr>17 µm)**<br>**(230420b)** | ***2.1***<br>***pre-test*** | **2.2 (CrN/Cr)**<br>**(230420a)** |
|---|---|---|---|---|---|
|  |  |  |  |  |  |
| |  | |  | |  |
| | fine surface blisters | | coarse surface blisters | | leaked (Zr, Cr) eutectic melt |

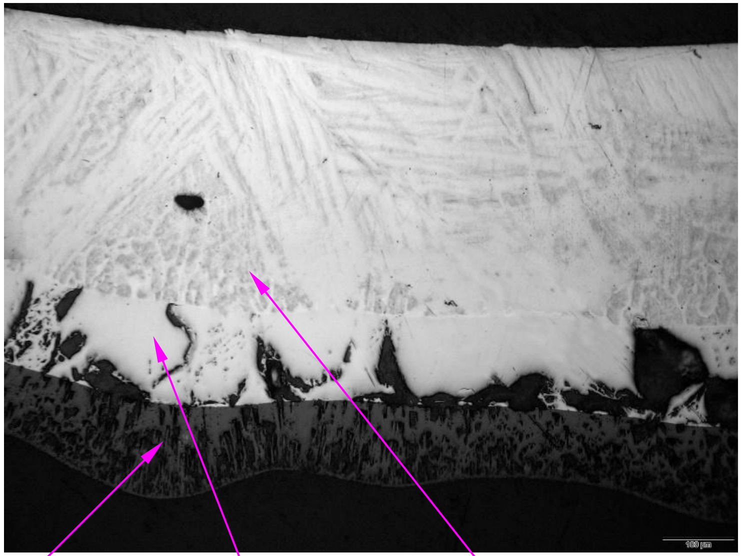
# Cross-sections of sample 1.2 (5 µm Cr) at 65 mm oxidized under BDBA conditions ($T_{max}^{surf}$=1400 °C)

Karlsruhe Institute of Technology



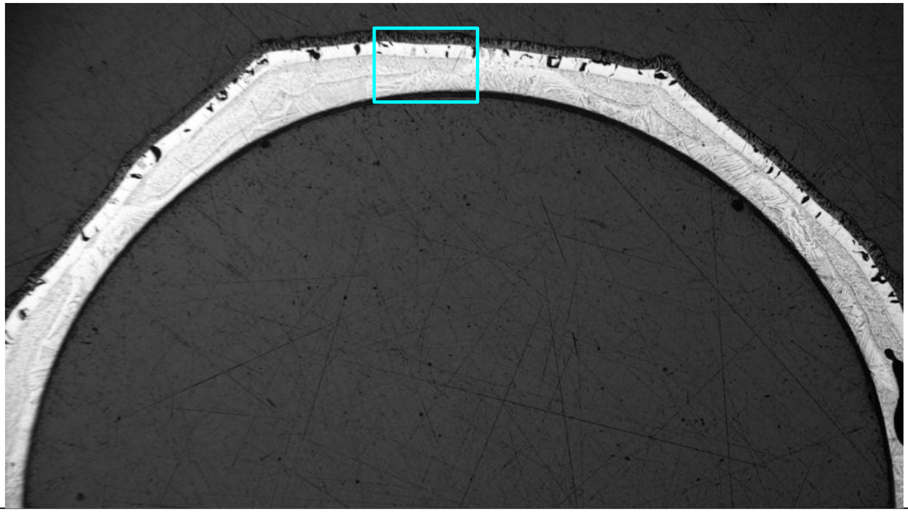



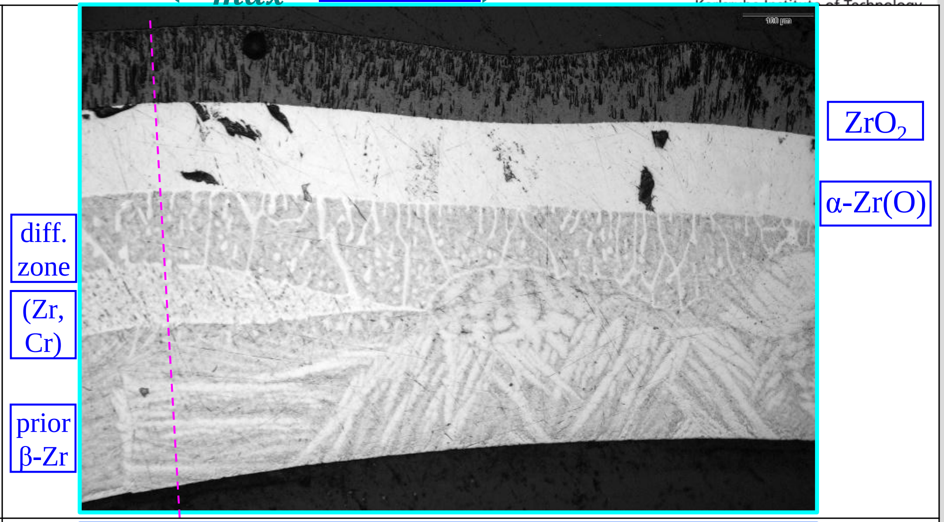


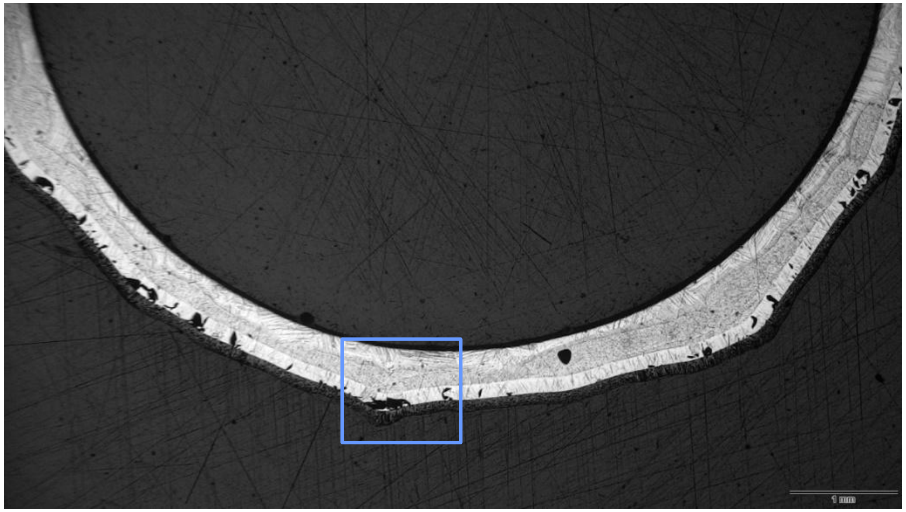



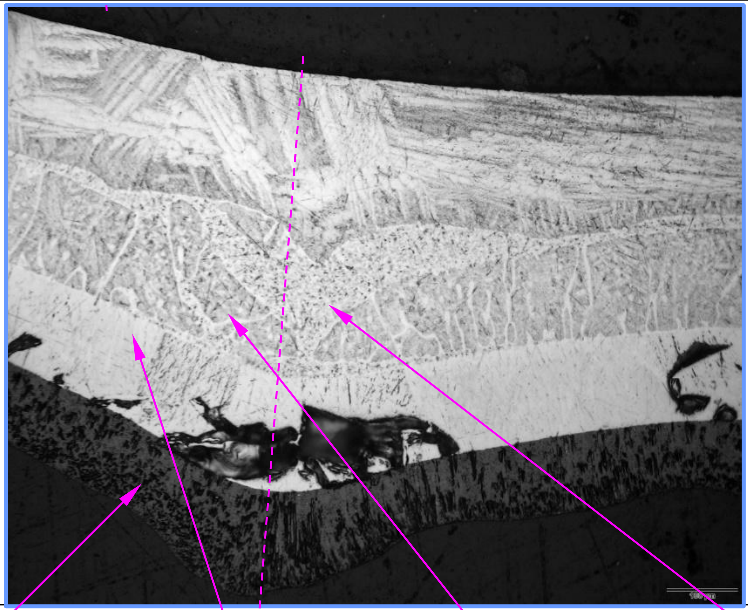
| | |
|---|---|
| **overview: ≈1.2 blisters per mm of circumference** | **$ZrO_2$ 95-130 µm; α-Zr(O) 125-140 µm; $Cr_{diffusion\ in\ Zr}$** |

# Cross-sections of sample 3.2 (>17 µm Cr) at 65 mm oxidized under BDBA conditions ($T_{max}^{surf}$=1400 °C)





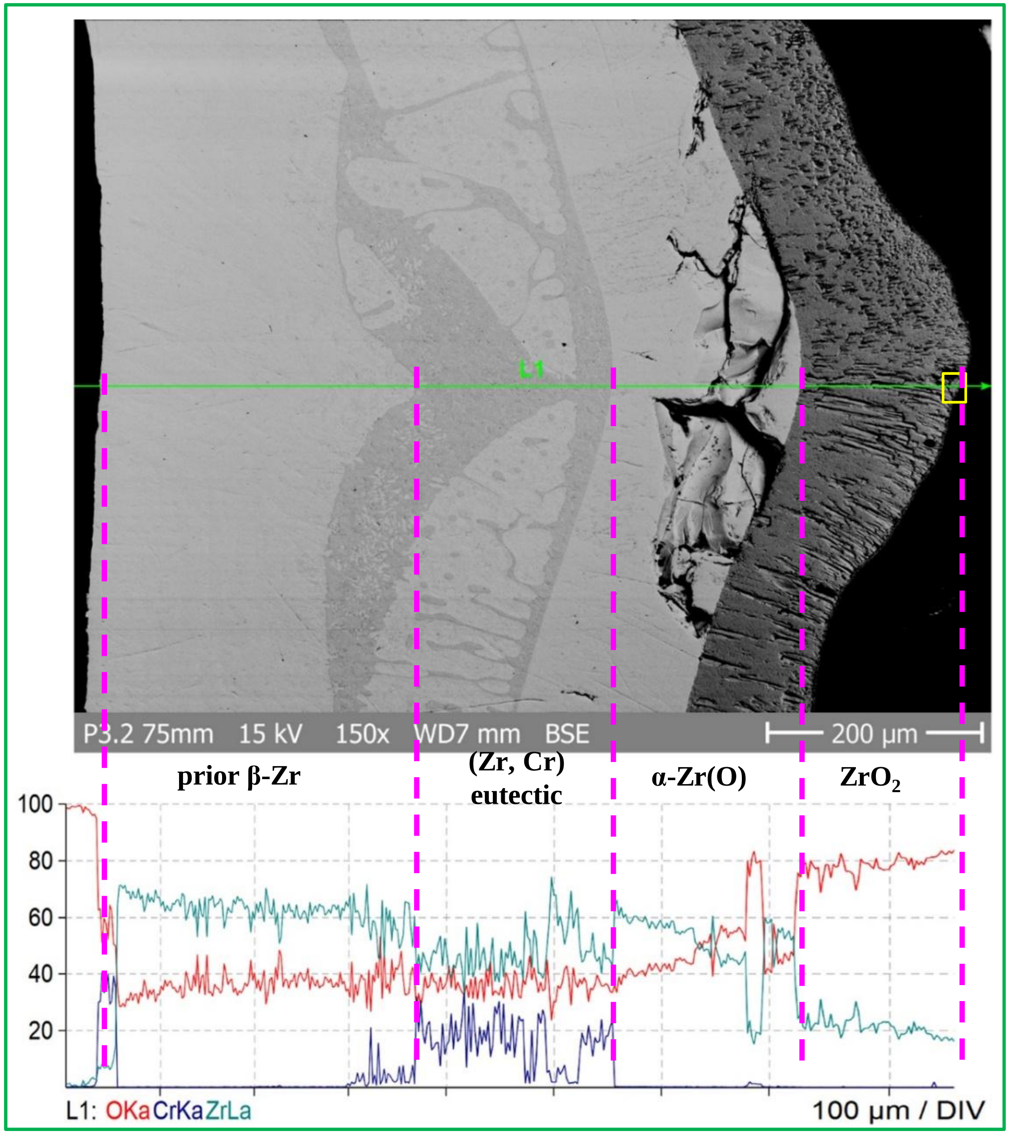


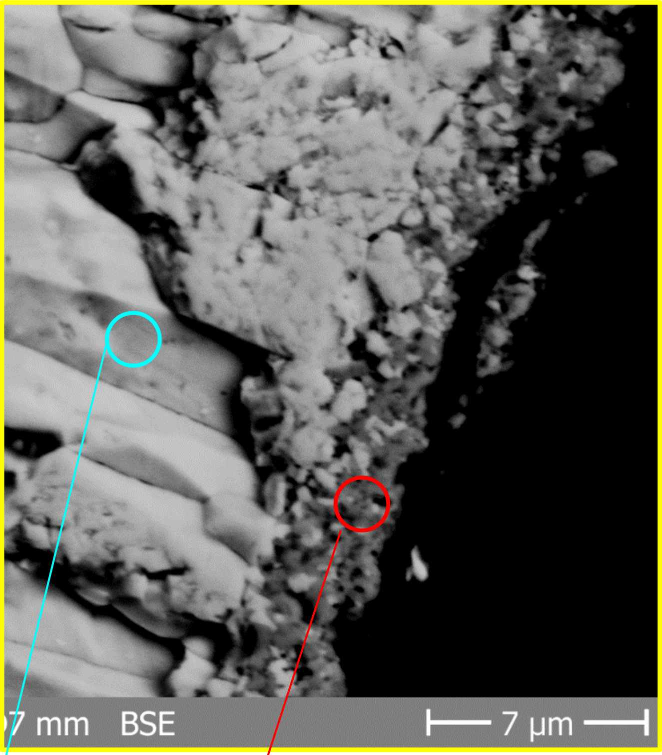
overview: ≈0.5 blisters per mm of circumference

$ZrO_2$ 95-155 µm; α-Zr(O) 130-160 µm; $Cr_{diffusion\ in\ Zr}$ 120 µm; $(Zr, Cr)_{max}$ 120 µm

# Cross-sections of sample 3.2 (>17 µm Cr) at 65 mm oxidized under BDBA conditions ($T_{max}^{surf}$=1400 °C)

Karlsruhe Institute of Technology



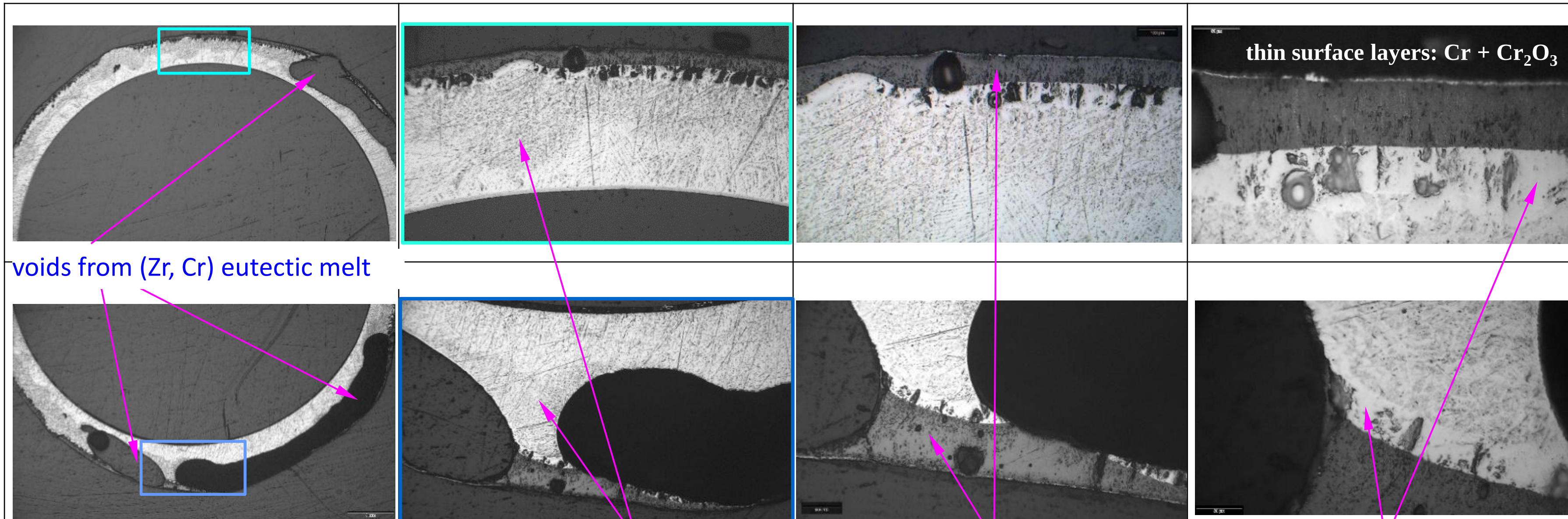

$Cr_2O_3$

| Elt | XRay | Int | Error | K | Kratio | W% | A% |
|---|---|---|---|---|---|---|---|
| O | Ka | 2563.5 | 64.5061 | 0.5452 | 0.4266 | 58.06 | 82.78 |
| Cr | Ka | 1630.6 | 1.9068 | 0.3948 | 0.3089 | 35.70 | 15.66 |
| Zr | La | 400.8 | 1.8673 | 0.0600 | 0.0469 | 6.24 | 1.56 |
| | | | | 1.0000 | 0.7825 | 100.00 | 100.00 |

$ZrO_2$

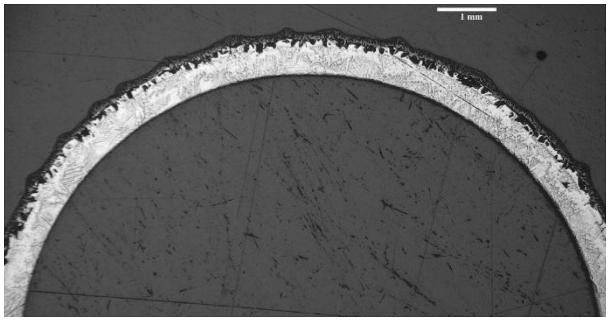
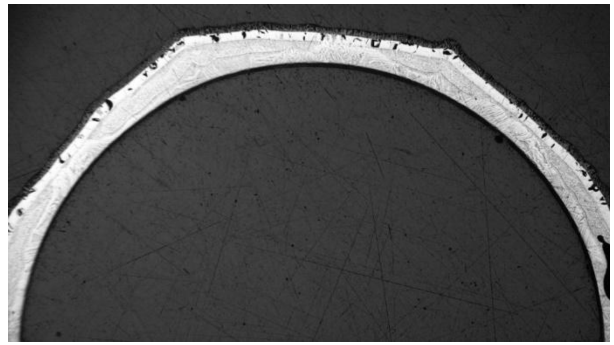
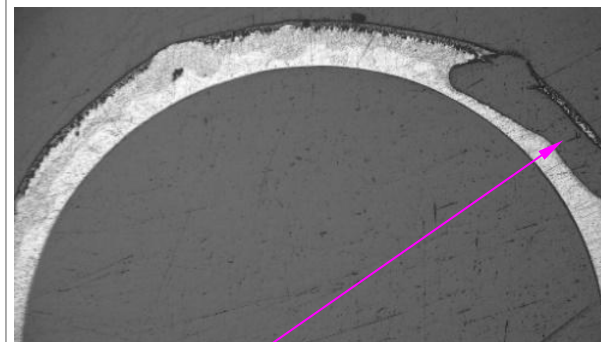
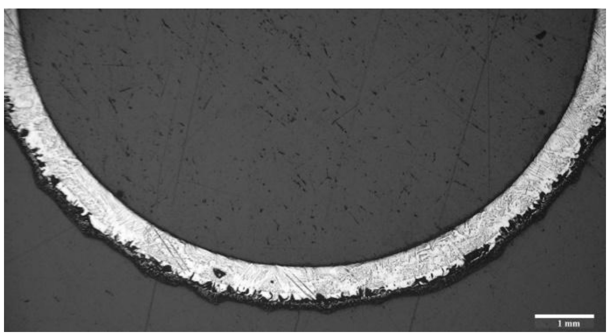
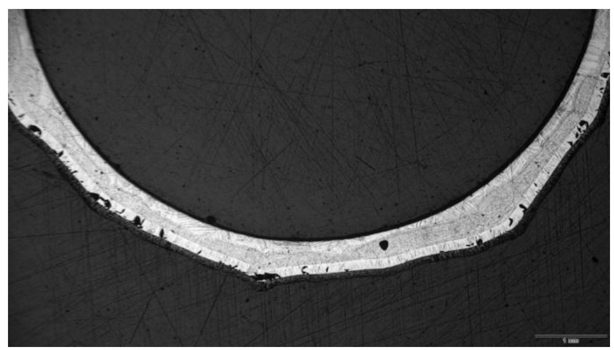
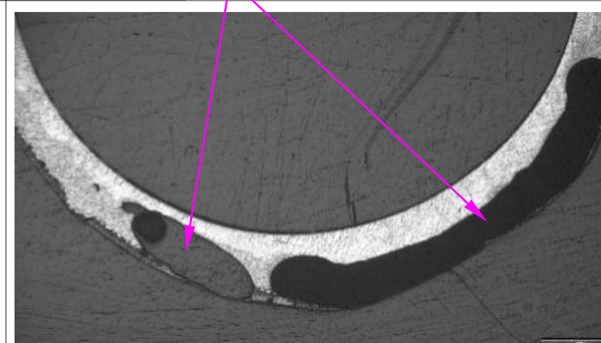
| Elt | XRay | Int | Error | K | Kratio | W% | A% |
|---|---|---|---|---|---|---|---|
| O | Ka | 673.1 | 1.3042 | 0.2139 | 0.1256 | 46.00 | 82.91 |
| Cr | Ka | 3.0 | 0.1818 | 0.0011 | 0.0006 | 0.07 | 0.04 |
| Zr | La | 3508.4 | 6.5569 | 0.7850 | 0.4609 | 53.93 | 17.05 |
| | | | | 1.0000 | 0.5872 | 100.00 | 100.00 |

# Cross-sections of sample 2.2 (CrN/Cr) at the hottest elevation 65 mm oxidized under BDBA conditions ($T_{max}^{surf}$=1400 °C)



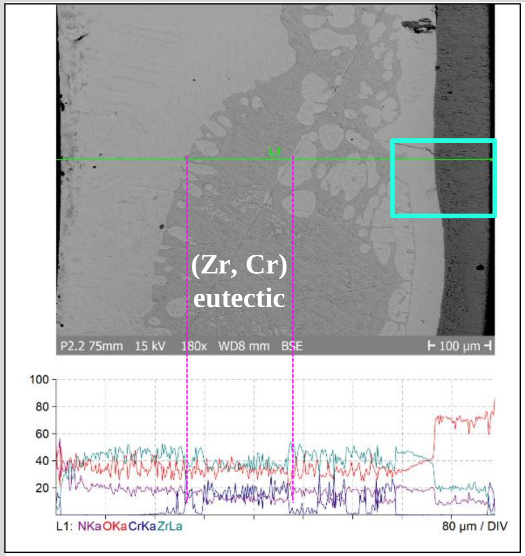

| | | | |
|---|---|---|---|
| overview: voids due to eutectic melt formation and relocation | thick diffusion layers | outer $ZrO_2$ layer | intermediate α-Zr(O) layer |

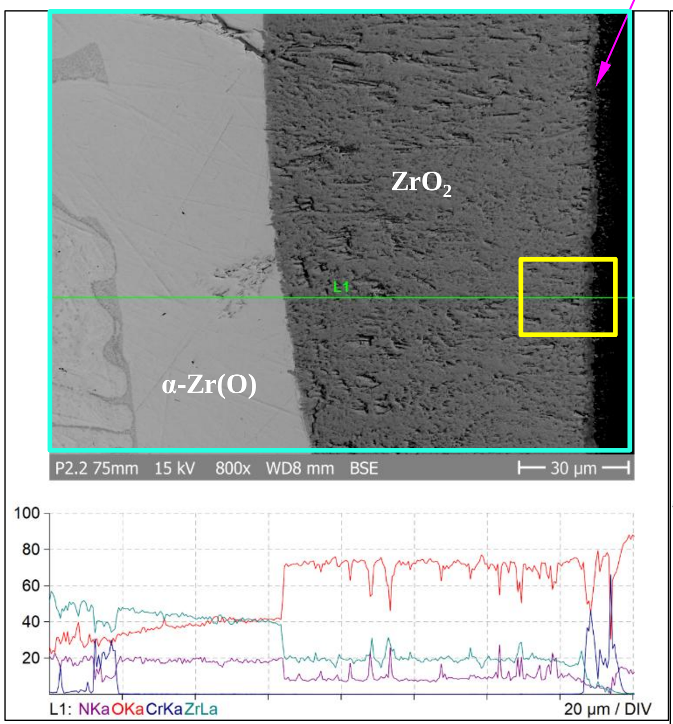
# Cross-sections of the UPM/Prague samples at the hottest elevation 65 mm oxidized under BDBA conditions ($T_{max}^{surf}$=1400 °C)

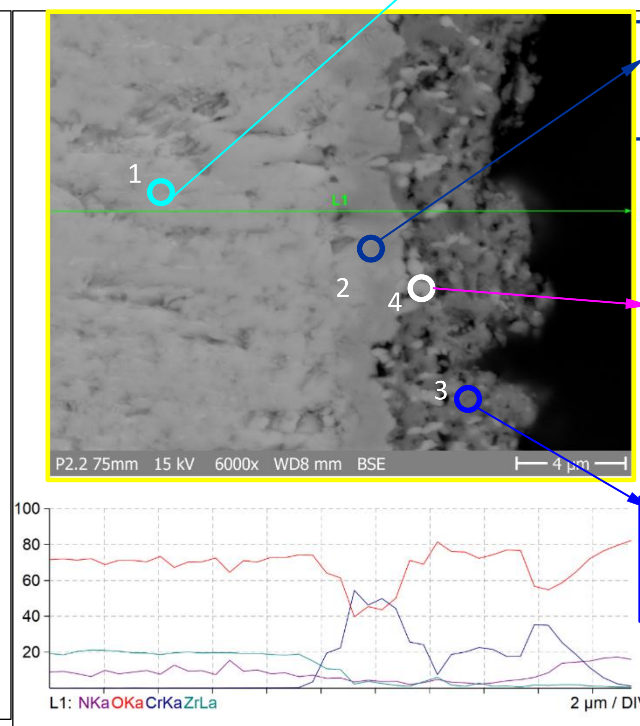
| | | |
|---|---|---|
|  |  |  |
| **≈1.2 blisters per mm of circumference** | **≈0.5 blisters per mm of circumference** | voids from (Zr, Cr) eutectic melt |
|  |  |  |
| **sample 1.2: 5 µm Cr** | **sample 3.2: >17 µm Cr** | **sample 2.2: Cr (18 µm)/CrN (8 µm)** |

- Formation and relocation of (Zr,Cr) eutectic **melt** for Cr/CrN coating perhaps due to the lack of intermediate oxidation of part of the zirconium, which could not react with steam due to the barrier effect of CrN layer.

# Cross-sections of BDBA sample 2.2 (Cr/CrN) at hottest elevation of 65 mm ($T_{max}^{surf}$=1400 °C), circumferential position outside voids




**$ZrO_2$ with ZrN inclusions**

| Elt | XRay | Int | Error | K | Kratio | W% | A% |
|---|---|---|---|---|---|---|---|
| N | Ka | 69.1 | 158.8994 | 0.0174 | 0.0103 | 5.37 | 11.41 |
| O | Ka | 866.9 | 158.8994 | 0.1519 | 0.0901 | 37.63 | 69.96 |
| Cr | Ka | 14.1 | 0.3705 | 0.0028 | 0.0017 | 0.18 | 0.11 |
| Zr | La | 6711.8 | 115.6367 | 0.8279 | 0.4910 | 56.81 | 18.52 |

**Cr**

| Elt | XRay | Int | Error | K | Kratio | W% | A% |
|---|---|---|---|---|---|---|---|
| N | Ka | 39.5 | 235.8792 | 0.0075 | 0.0065 | 1.35 | 3.46 |
| O | Ka | 1126.7 | 235.8792 | 0.1482 | 0.1299 | 19.46 | 43.74 |
| Cr | Ka | 5248.9 | 7.2788 | 0.7861 | 0.6889 | 72.62 | 50.21 |
| Zr | La | 629.0 | 11.3931 | 0.0582 | 0.0510 | 6.57 | 2.59 |

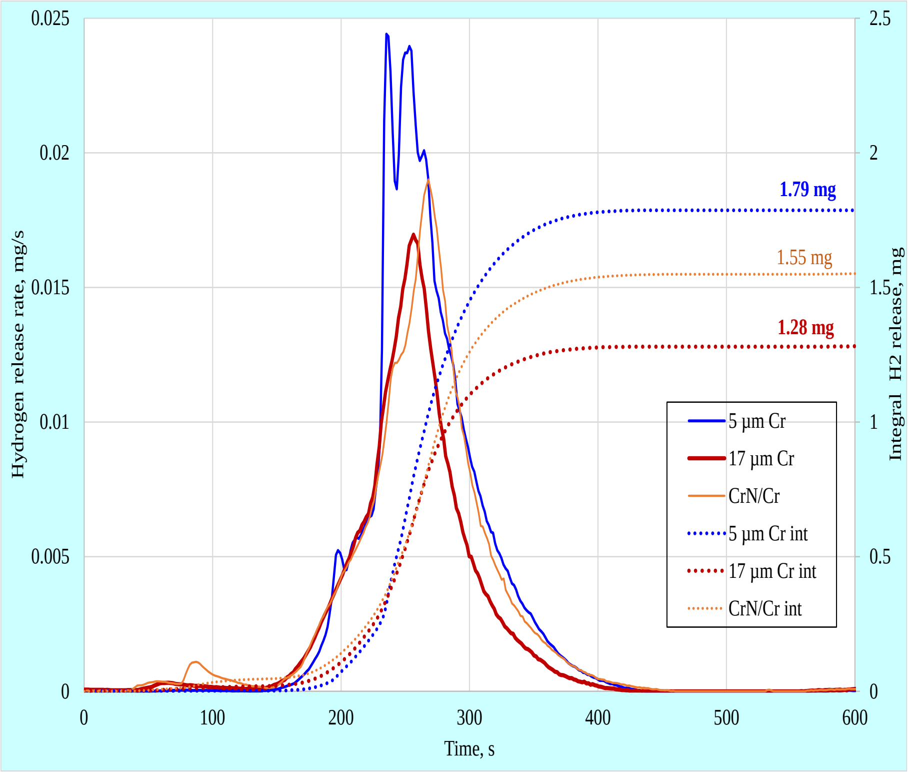
**$Cr_2O_3$ with Zr inclusions**

| Elt | XRay | Int | Error | K | Kratio | W% | A% |
|---|---|---|---|---|---|---|---|
| N | Ka | 50.5 | 205.6407 | 0.0111 | 0.0074 | 1.94 | 3.43 |
| O | Ka | 2452.0 | 205.6407 | 0.3755 | 0.2497 | 49.74 | 77.09 |
| Cr | Ka | 2351.1 | 1.9388 | 0.4099 | 0.2726 | 30.95 | 14.76 |
| Zr | La | 1886.9 | 37.5481 | 0.2034 | 0.1353 | 17.38 | 4.72 |

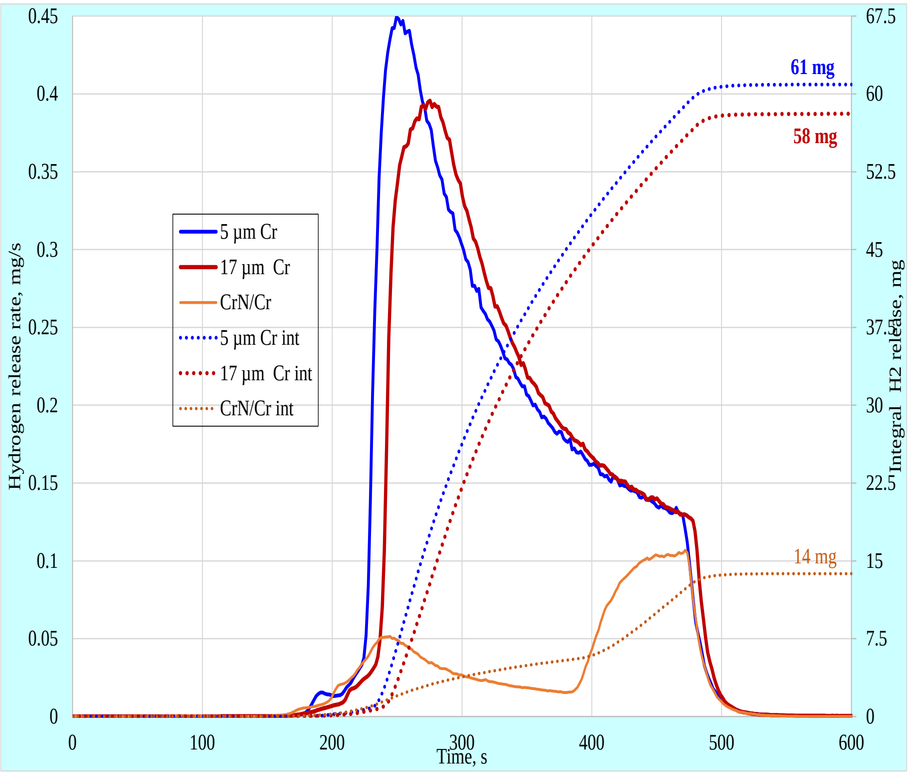
**$Cr_2O_3$**

| Elt | XRay | Int | Error | K | Kratio | W% | A% |
|---|---|---|---|---|---|---|---|
| N | Ka | 73.4 | 390.9179 | 0.0122 | 0.0098 | 1.69 | 2.88 |
| O | Ka | 4089.2 | 390.9179 | 0.4723 | 0.3791 | 50.62 | 75.79 |
| Cr | Ka | 3692.4 | 9.0070 | 0.4855 | 0.3897 | 44.47 | 20.49 |
| Zr | La | 370.5 | 12.8343 | 0.0301 | 0.0242 | 3.22 | 0.85 |

# Hydrogen release during the tests with the UPM/Prague samples




hydrogen release under DBA conditions ($T_{max}^{surf}$=1200 °C)




hydrogen release under BDBA conditions ($T_{max}^{surf}$=1400 °C)

- Increasing the thickness of the chromium layer by 3 times (from 5 to ≈17 µm) reduced the hydrogen release by 30% under DBA conditions (transient to 1200 °C), however, only by 3% under BDBA conditions (1400 °C). *The barrier CrN layer has only a moderate influence on hydrogen release under DBA, but strong reduced hydrogen release under BDBA (reduction factor 4).*

# Summary on Prague samples

- An increase in the thickness of the chromium layer by 3 times (from 6 to 18 µm) reduced the hydrogen release by 30% under DBA conditions (transient to 1200 °C), however, only by 3% under BDBA conditions (1400 °C). Barrier layer CrN has only moderate influence on hydrogen release under DBA, but strong reduced hydrogen release under BDBA (reduction factor 4).
- Formation of blisters (local swellings) at the outer cladding surface under BDBA conditions ($T_{max}$=1400 °C): fine blisters (1.2/mm) for thin Cr layer (6 µm) and coarse blisters (0.5/mm) for thick Cr layer (18 µm).
- Cr transport from the cladding surface to the boundary of α/β-Zr phases.
- Formation and relocation of (Zr,Cr) eutectic **melt** for CrN/Cr coating perhaps due to the lack of intermediate oxidation of part of the zirconium, which could not react with steam due to the barrier effect of CrN layer.

# Thank you for your attention

http://www.iam.kit.edu/awp/163.php
http://quench.forschung.kit.edu/