# Kinetics of dissolution of oxide layer on cladding surface under oxygen starvation conditions at temperatures between 900°C and 1200°C

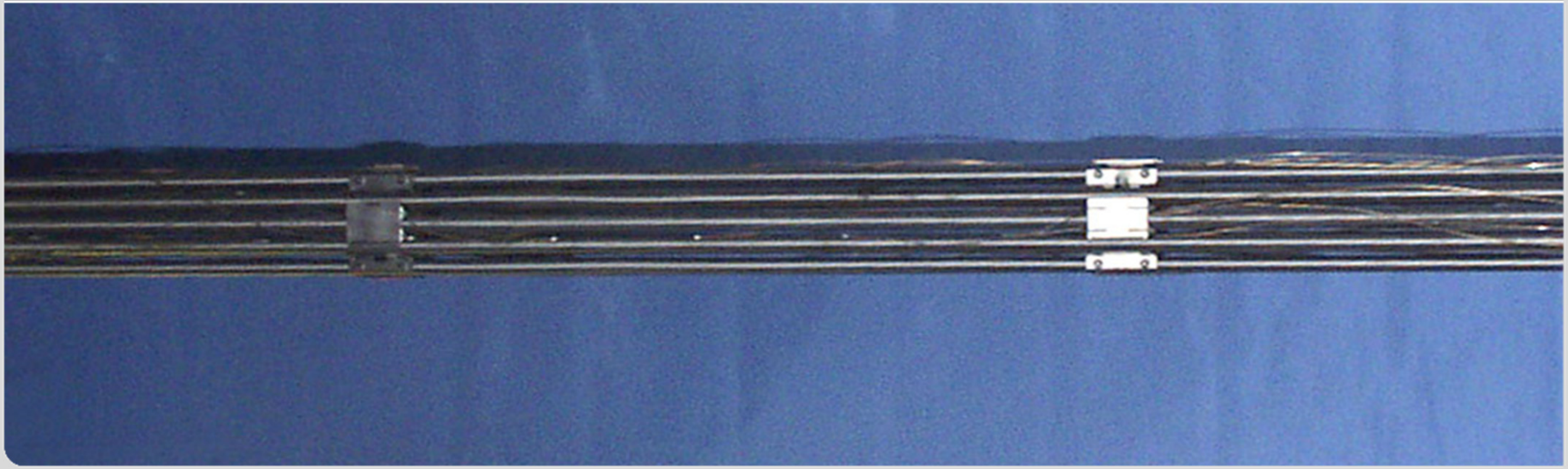
**J. Stuckert, A. Pshenichnikov, U. Peters**

*QWS20, Karlsruhe 2014*

Karlsruhe Institute of Technology

Institute for Applied Materials

Institute for Applied Materials, IAM-WPT, Program NUKLEAR



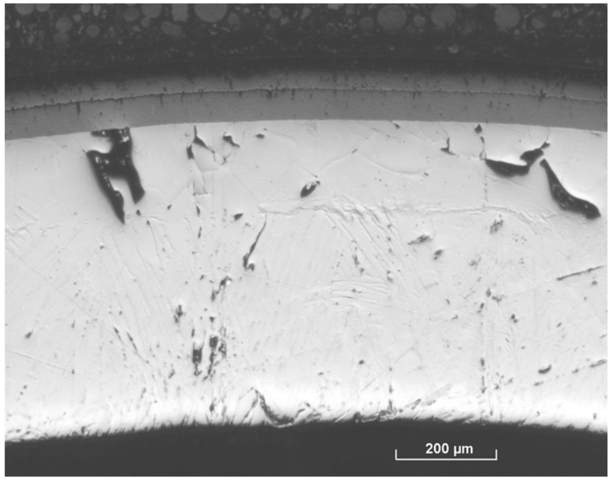
# History (QWS8, 2002): annealing of oxidised clads in Ar at 1700 K during 3 h

Karlsruhe Institute of Technology

**$ZrO_2$, 134 µm**

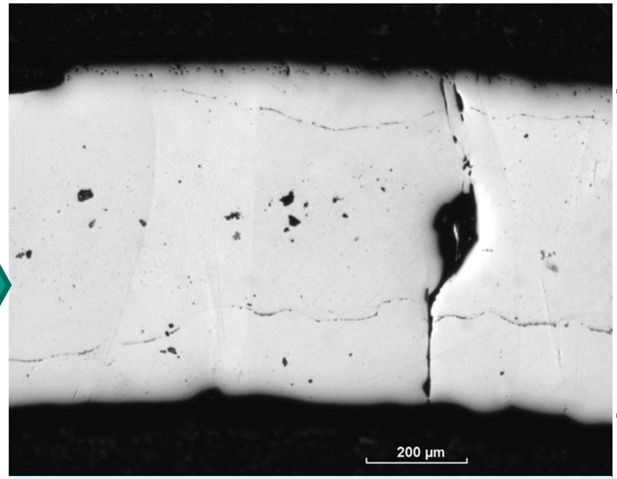
α-Zr(O), 182 µm

β-Zr, 431 µm




reference sample after pre-oxidation

complete dissolution of $ZrO_2$ for layer < 150 µm



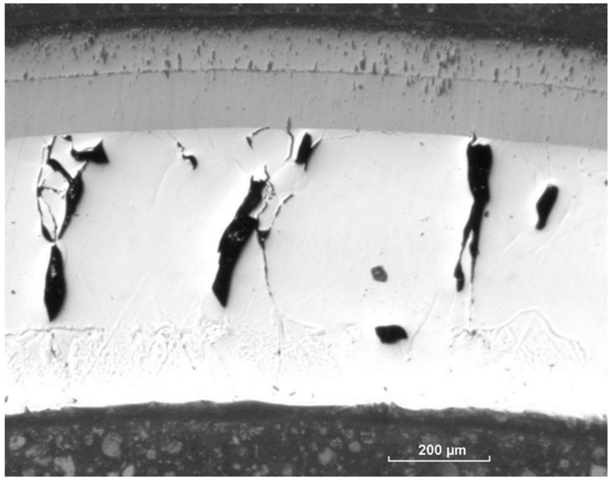

α-Zr(O), 733 µm

radial homogeneous redistribution of the oxygen across the tube wall

**$ZrO_2$, 228 µm**

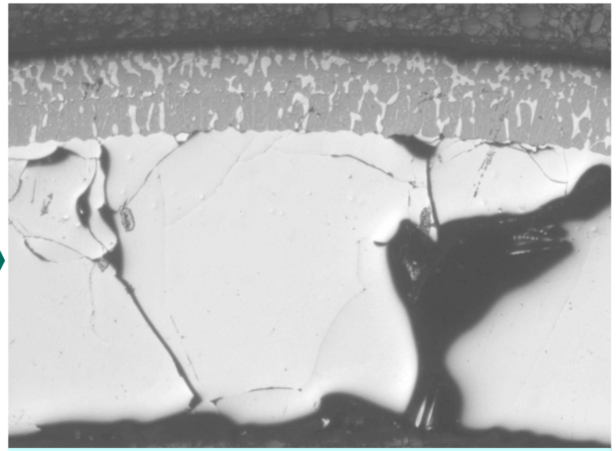
α-Zr(O), 397 µm

prior β-Zr, 177 µm




reference sample after pre-oxidation

partial dissolution of $ZrO_2$ and precipitates for layer > 150 µm



$ZrO_2$, 186 µm

α-Zr(O), 646 µm

redistribution of the oxygen between homogeneous inner α-Zr(O) layer and outer layer with α-Zr(O) precipitates

# Experimental procedure

Karlsruhe Institute of Technology

**LORA furnace**

**Specimen before oxidation**

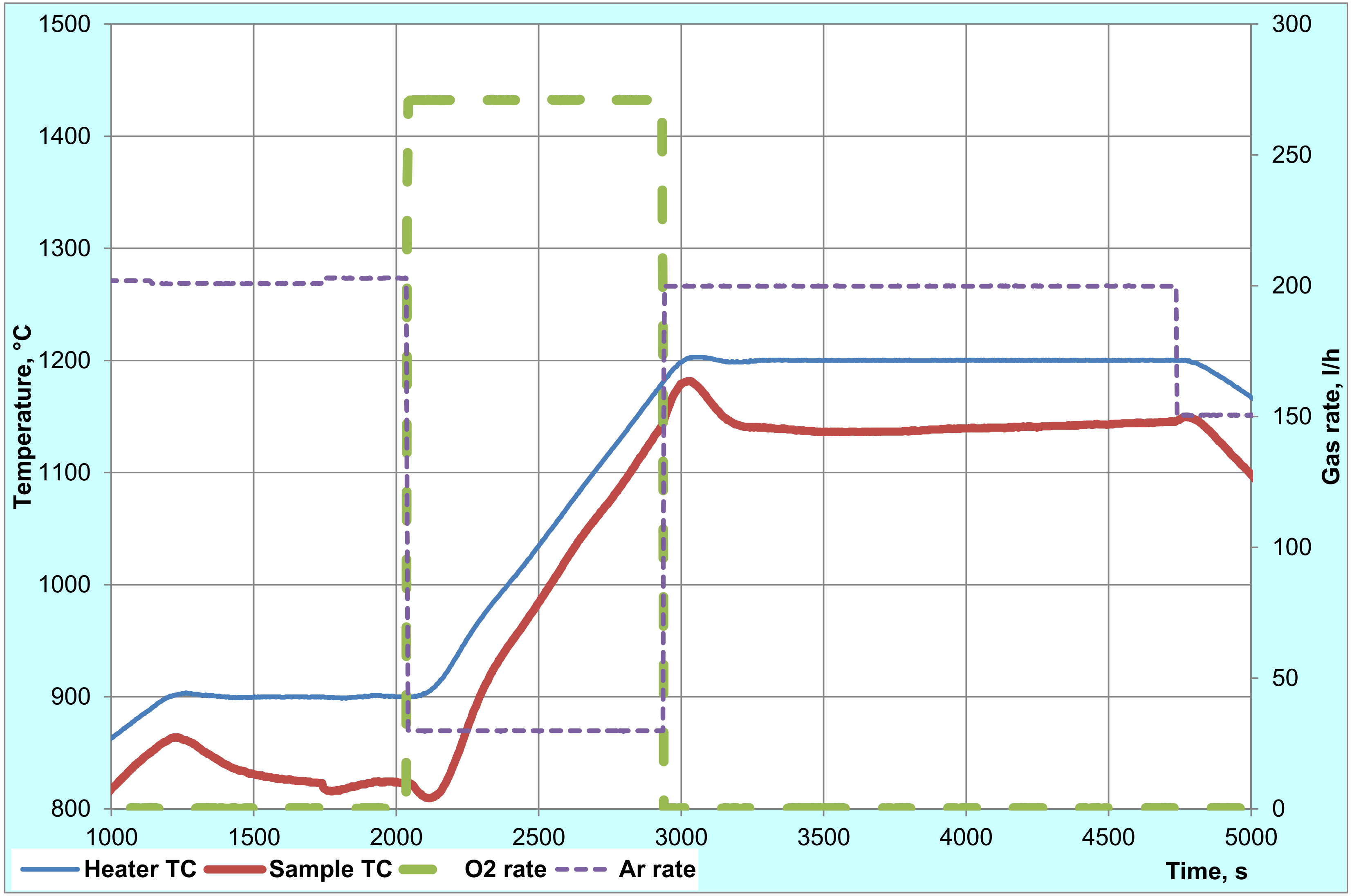
**Specimen withdrawal in air after test**

**Estimated cooling rate was 5 K/s**

**Cooled specimen after pre-oxidation and annealing**

# Example of test progress for annealing at 1150°C:

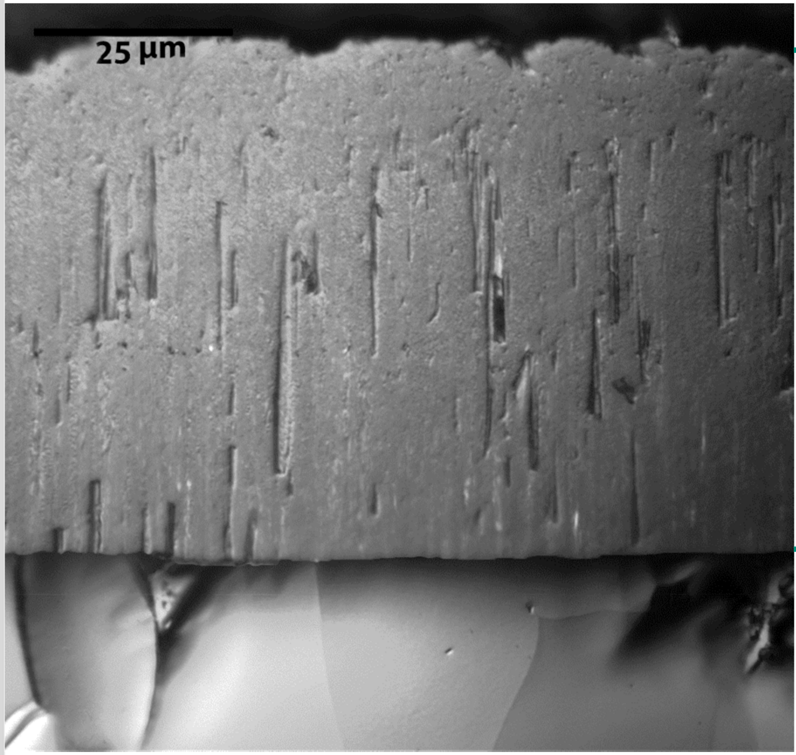
pre-oxidation to 66 µm in $O_2$+Ar during transient,
Annealing in Ar during 1800 s.



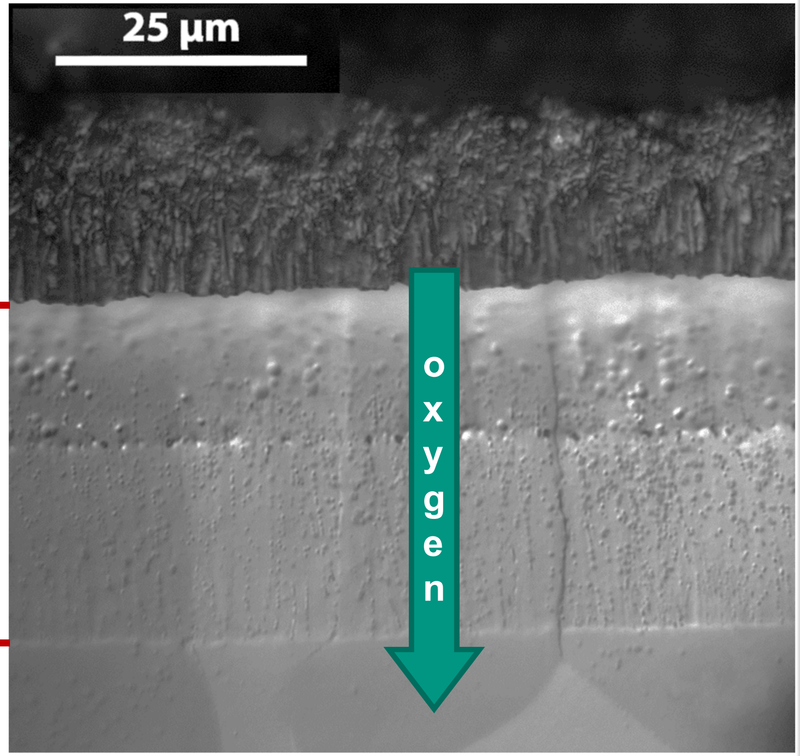
# Test matrix

| T, K | $ZrO_2$ $\delta_0$, µm | time, s → | 900 | 1800 | 3600 | 5400 | 7200 |
|---|---|---|---|---|---|---|---|
| 1170 | 20 | | X | X | X | X | X |
| 1280 | 63 | | | X | X | X | X |
| 1373 | 70 | | X | X | | | |
| 1373 | 85 | | | X | X | | |
| 1420 | 66 | | X | X | X | | X |

# Transformation of $ZrO_2$ into α-Zr(O) due to oxygen diffusion



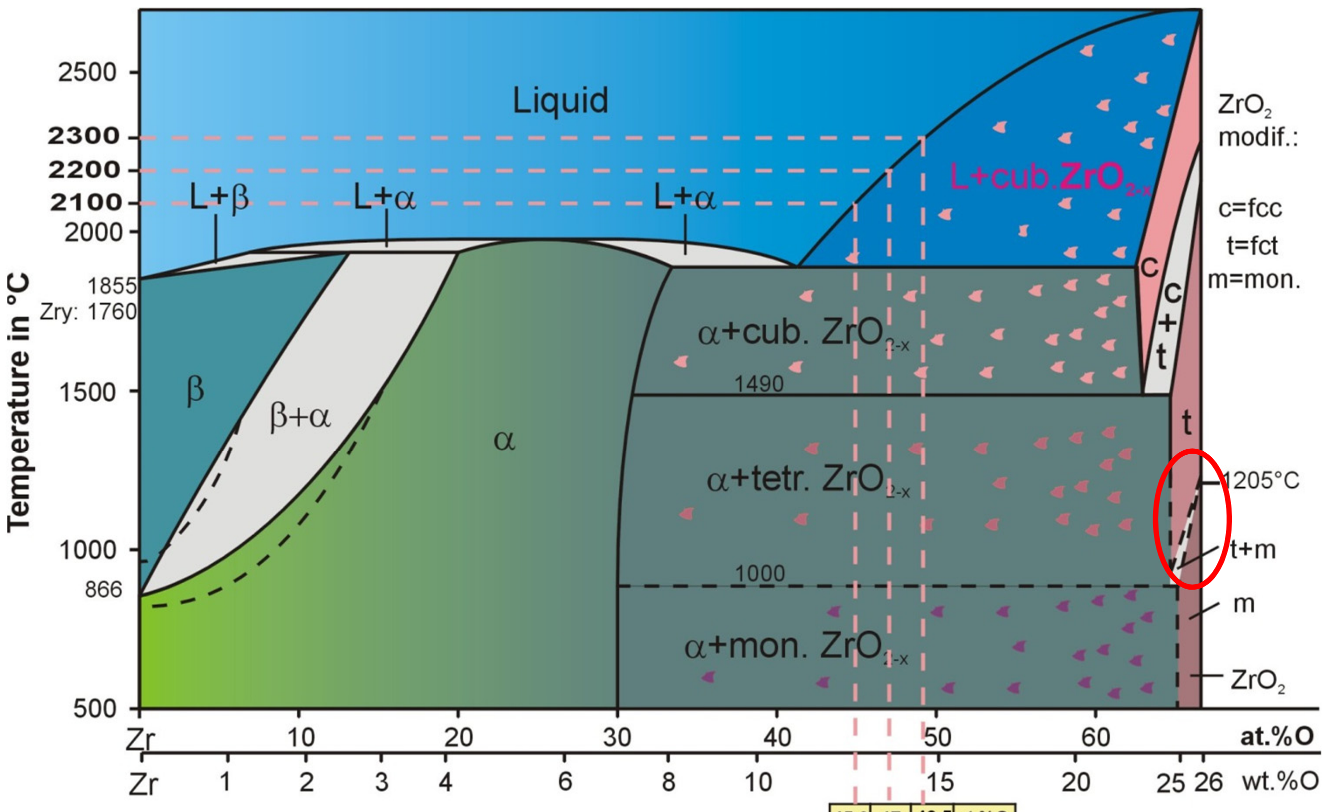

dissolved $ZrO_2$




**Annealing in Ar at 1420 K during 3600 s**

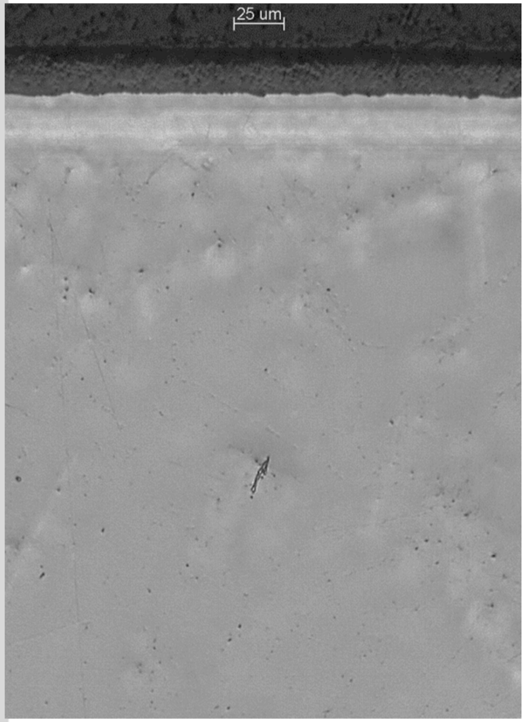
**Sample oxidised in $O_2$ to $ZrO_2$ = 73 µm**

# Peculiarities of ZrO2 between 900 and 1200°C: mixture of sub-stoichiometric tetragonal and monoclinic phases

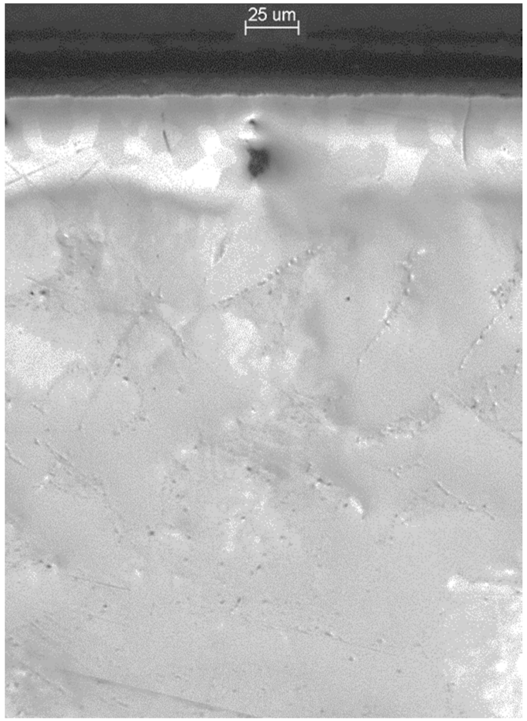



| 45.3 | 47 | 49.5 | at.%O |
|---|---|---|---|
| 12.7 | 13.5 | 14.7 | wt.%O |

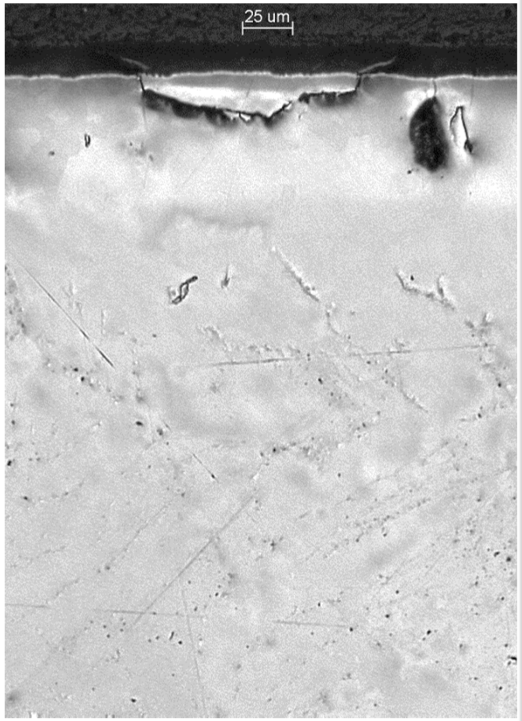
# Oxidation and annealing at 1170 K




**Sample oxidised to**
**$ZrO_2$ 20 µm, α-Zr(O) 28 µm**



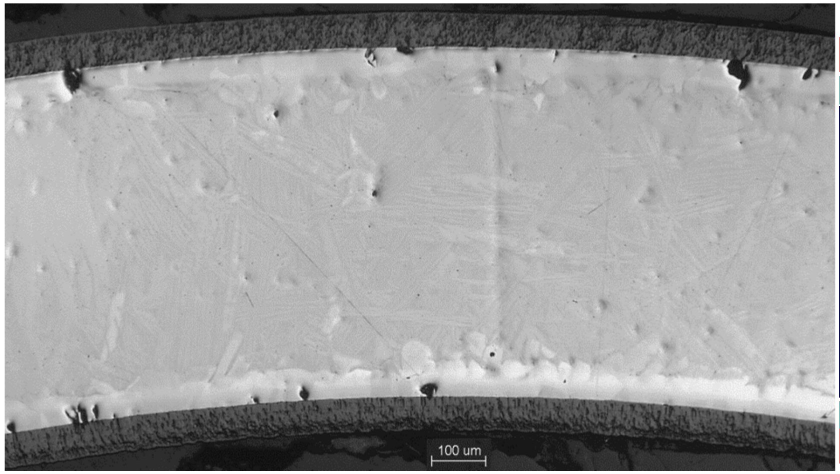

**Annealing in Ar during 3600 s:**
**$ZrO_2$ 8 µm, α-Zr(O) 47 µm**



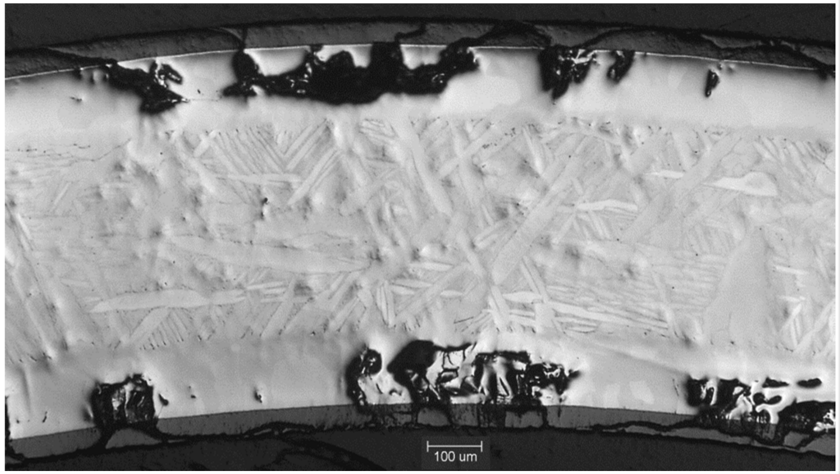

**Annealing in Ar during 7200 s:**
**$ZrO_2$ 5 µm, α-Zr(O) 60 µm**

# Oxidation and annealing at 1280 K

Karlsruhe Institute of Technology

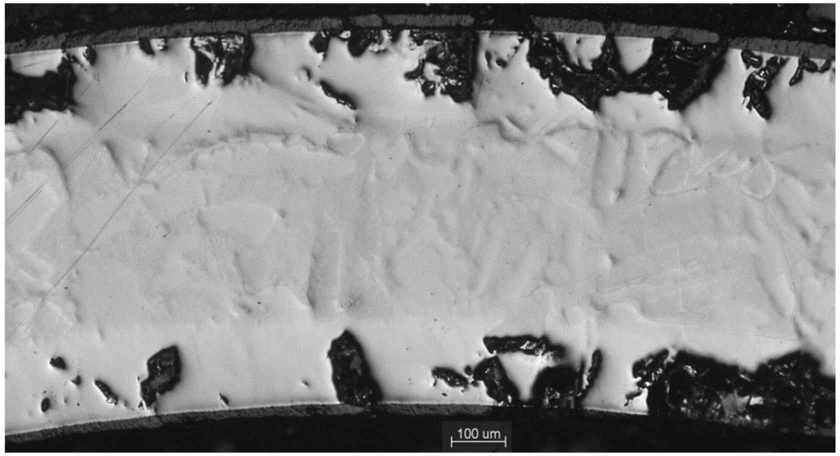



$ZrO_2$
α-Zr(O)
prior β-Zr
α-Zr(O)
$ZrO_2$



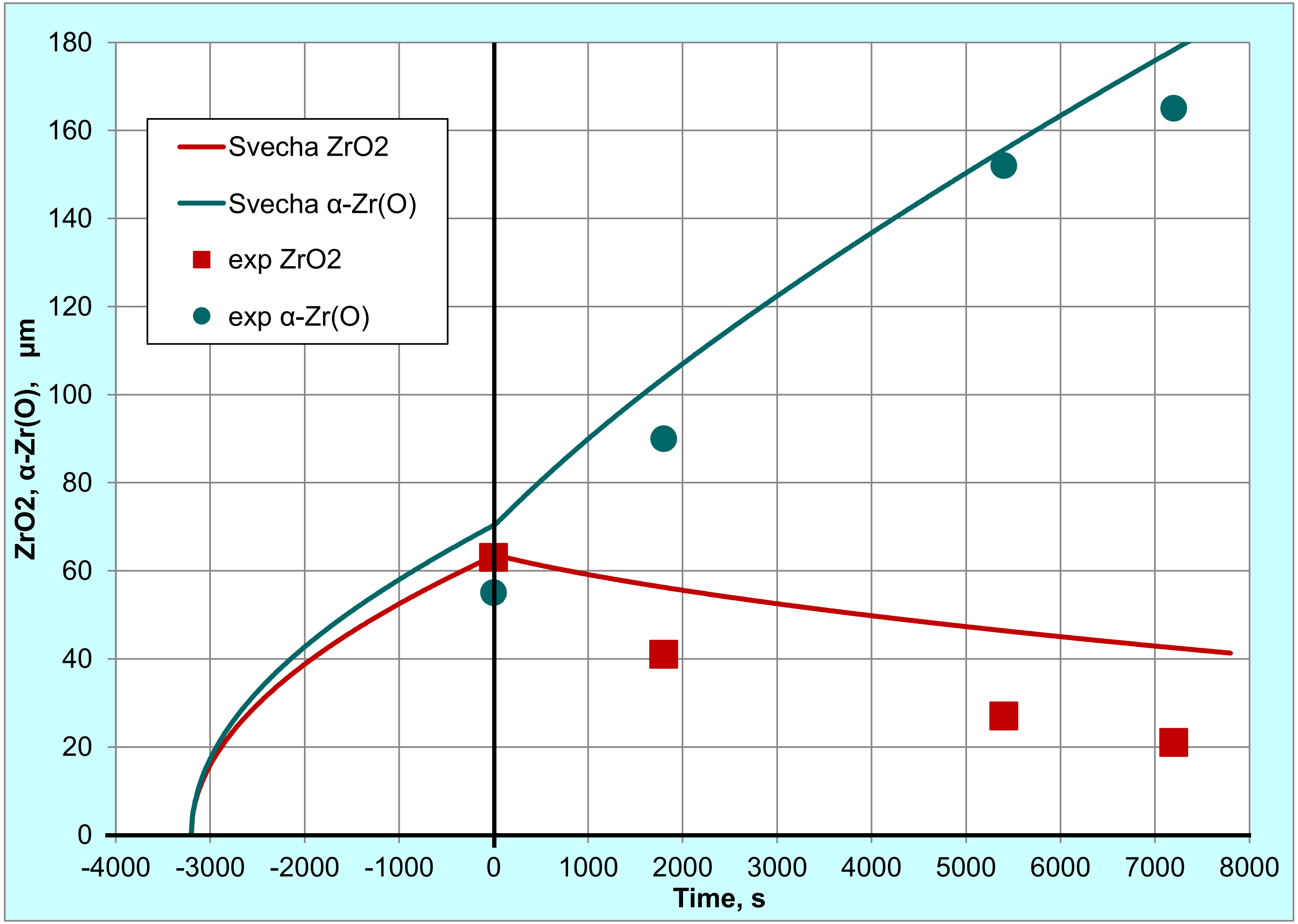

**Sample oxidised to**
**$ZrO_2$ 63 µm, α-Zr(O) 55 µm**

**Annealing in Ar during 3600 s:**
**$ZrO_2$ 42 µm, α-Zr(O) 130 µm**

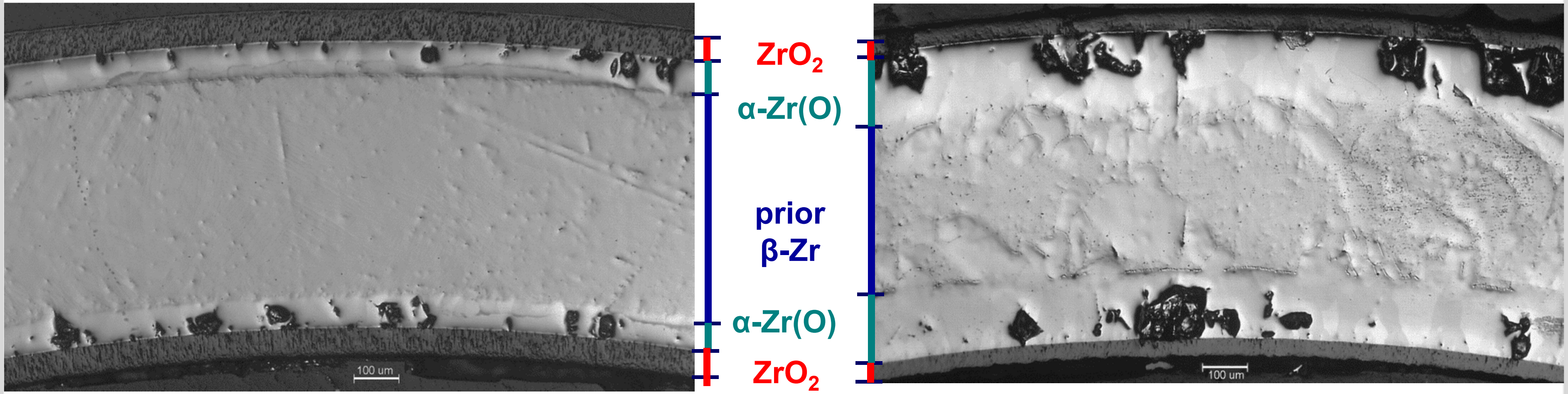



**Annealing in Ar during 7200 s:**
**$ZrO_2$ 21 µm, α-Zr(O) 165 µm**

# Comparison of experimental and calculation (SVECHA code) results for 1280 K

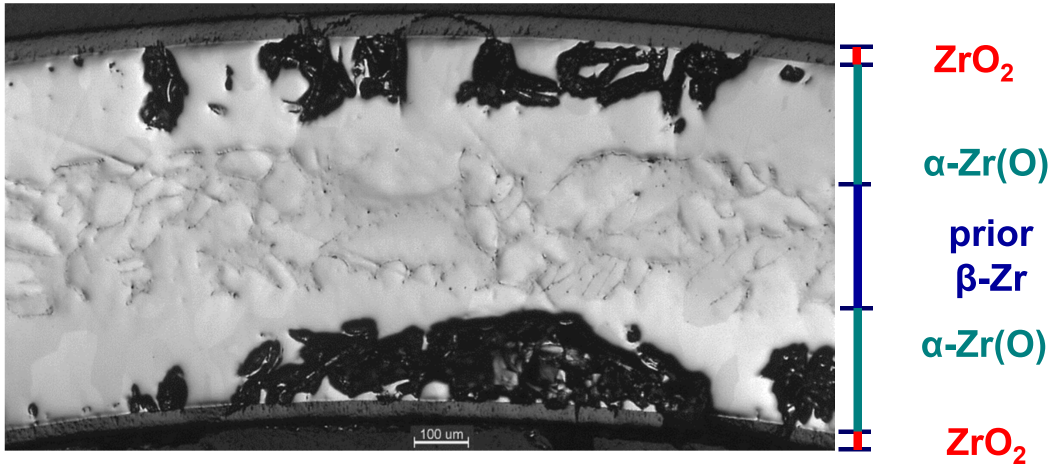


# Oxidation and annealing at 1373 K




**Sample oxidised to**
**$ZrO_2$ 70 µm, α-Zr(O) 79 µm**

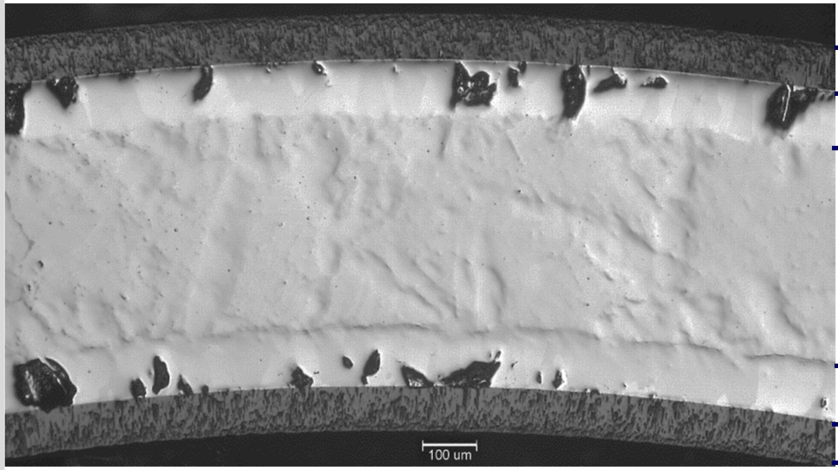
**Annealing in Ar during 900 s:**
**$ZrO_2$ 41 µm, α-Zr(O) 165 µm**



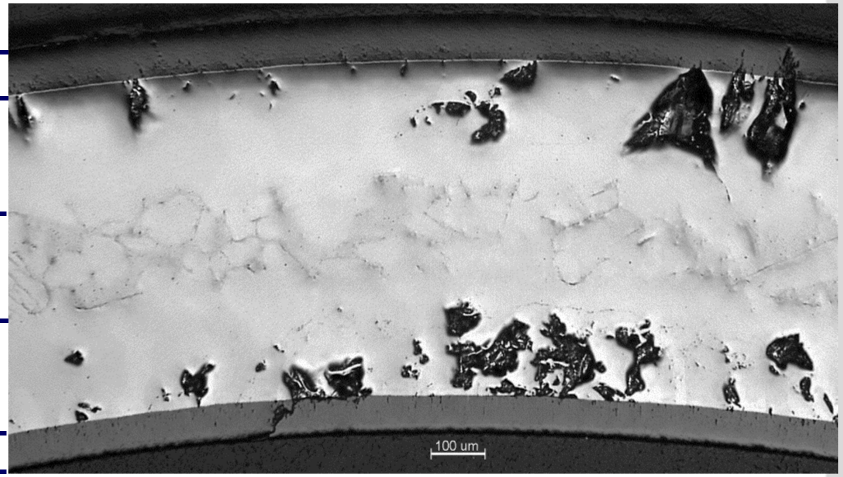

**Annealing in Ar during 1800 s:**
**$ZrO_2$ 34 µm, α-Zr(O) 240 µm**

# Oxidation and annealing at 1373 K

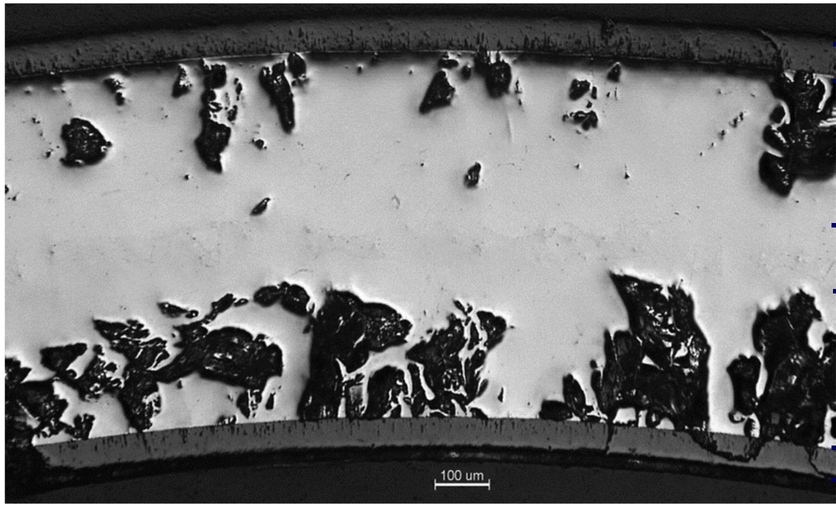
Karlsruhe Institute of Technology




**Sample oxidised to**
**$ZrO_2$ 85 µm, α-Zr(O) 107 µm**

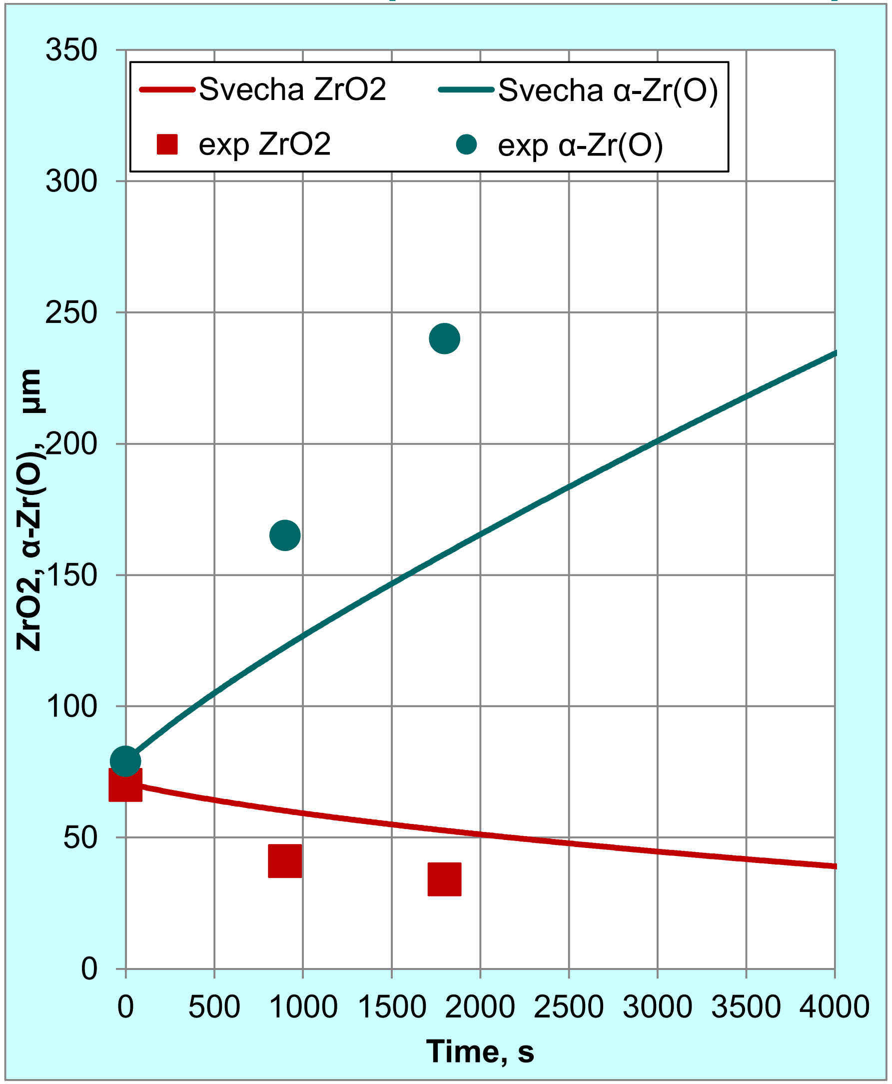



**Annealing in Ar during 1800 s:**
**$ZrO_2$ 75 µm, α-Zr(O) 220 µm**

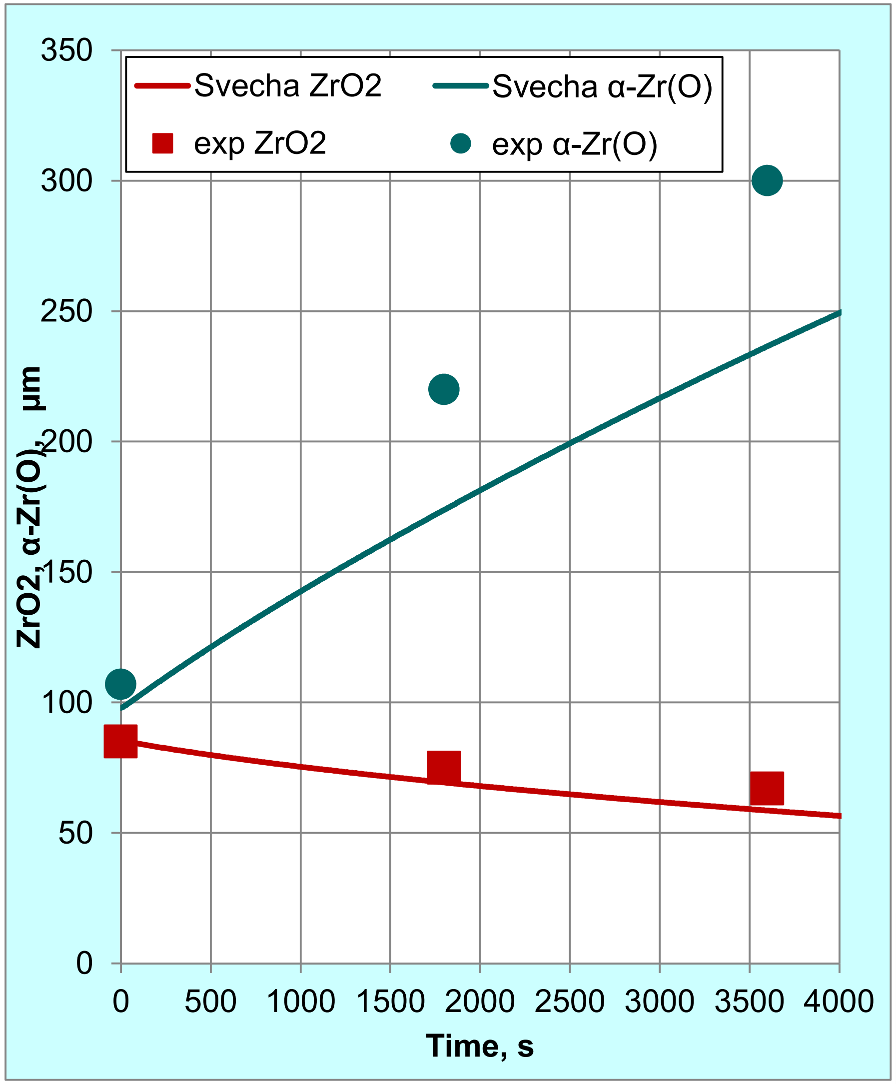



**Annealing in Ar during 3600 s:**
**$ZrO_2$ 67 µm, α-Zr(O) 300 µm**

# Comparison of experimental and calculation (SVECHA code) results for 1373 K

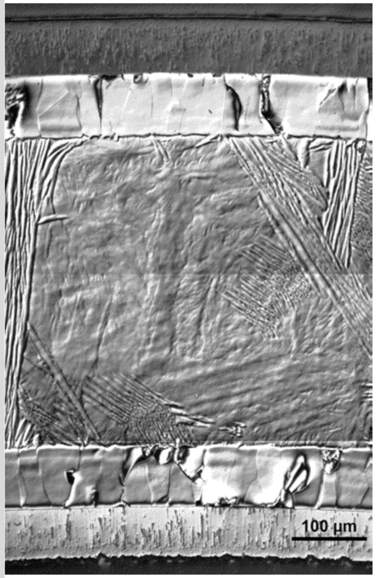



**After pre-oxidation to $ZrO_2$ = 70 µm: underestimation of dissolution**



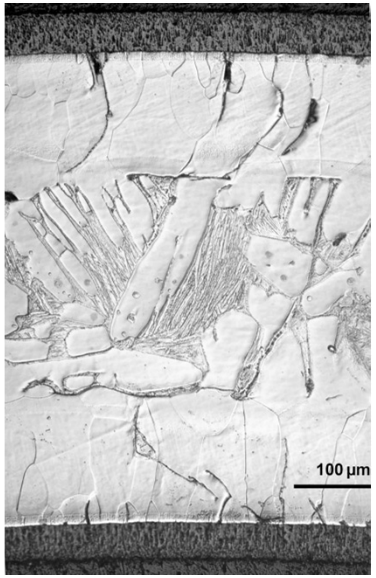

**After pre-oxidation to $ZrO_2$ = 85 µm: well prediction $ZrO_2$ decrease, underestimation α-Zr(O)**

# Oxidation and annealing at 1420 K



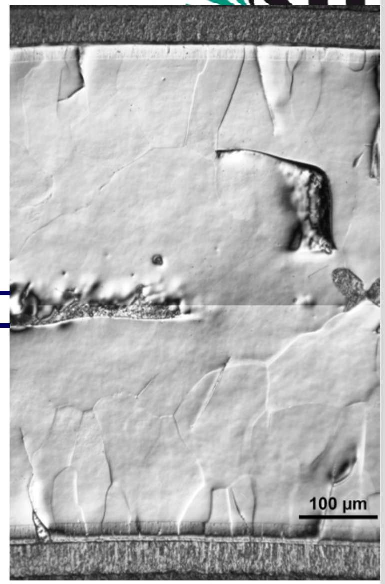

$ZrO_2$
α-Zr(O)
prior β-Zr
α-Zr(O)
$ZrO_2$

Sample oxidised to $ZrO_2$ 73 µm, α-Zr(O) 83 µm

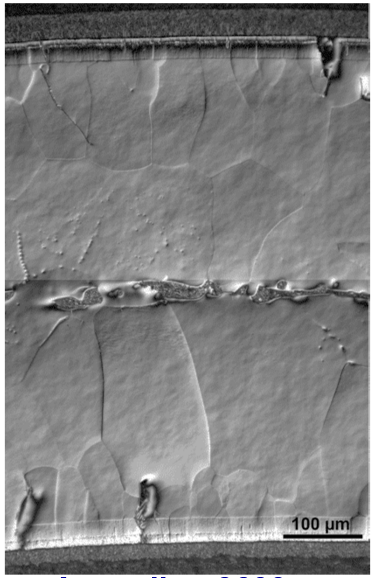



Annealing 900 s: $ZrO_2$ 52 µm, **dissolved 12 µm**, α-Zr(O) 165 µm

prior β-Zr 25 µm



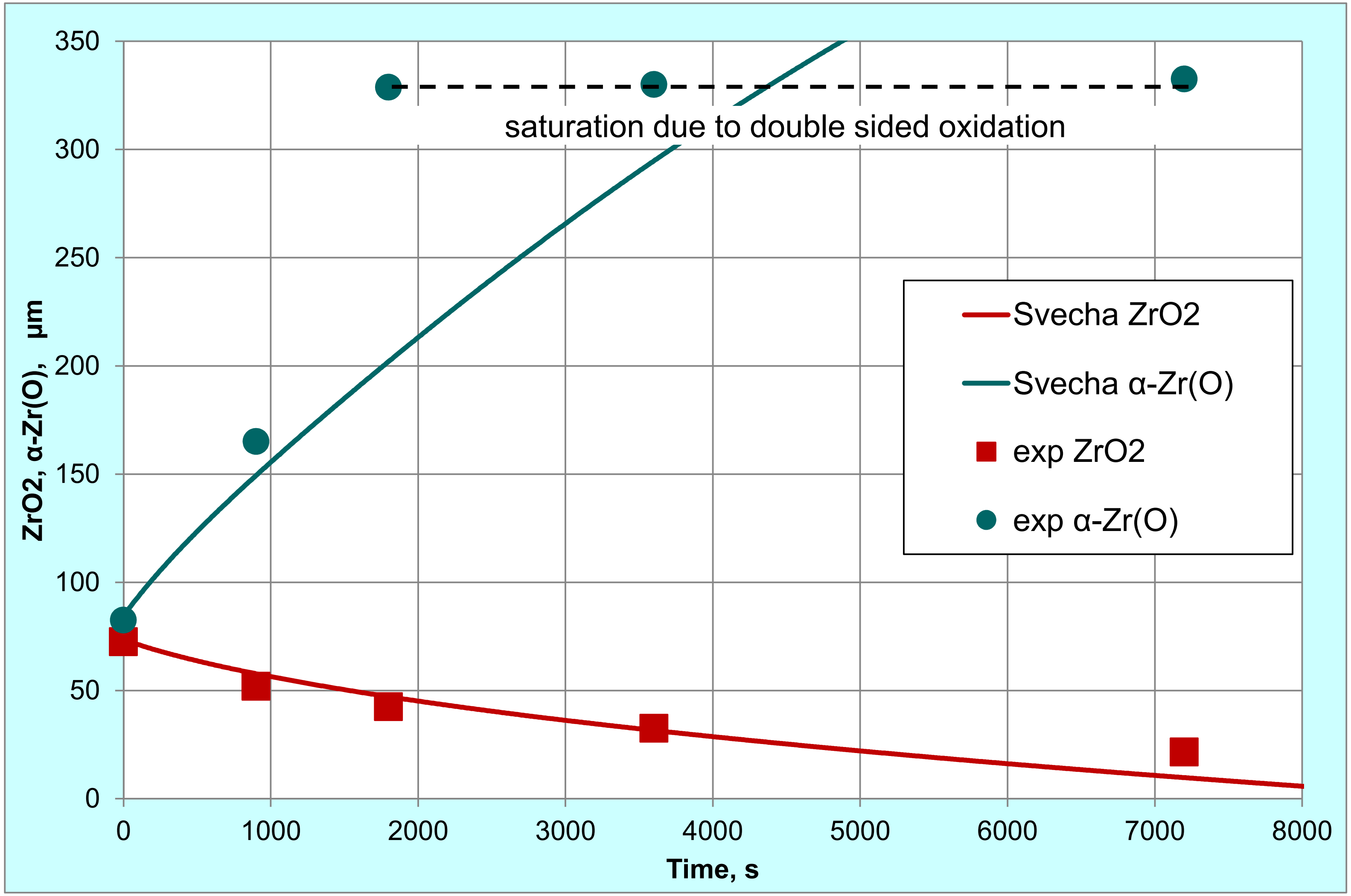

Annealing 1800 s: $ZrO_2$ 43 µm, **dissolved 22 µm**, α-Zr(O) 329 µm




Annealing 3600 s: $ZrO_2$ 33 µm, **dissolved 29 µm**, α-Zr(O) 330 µm

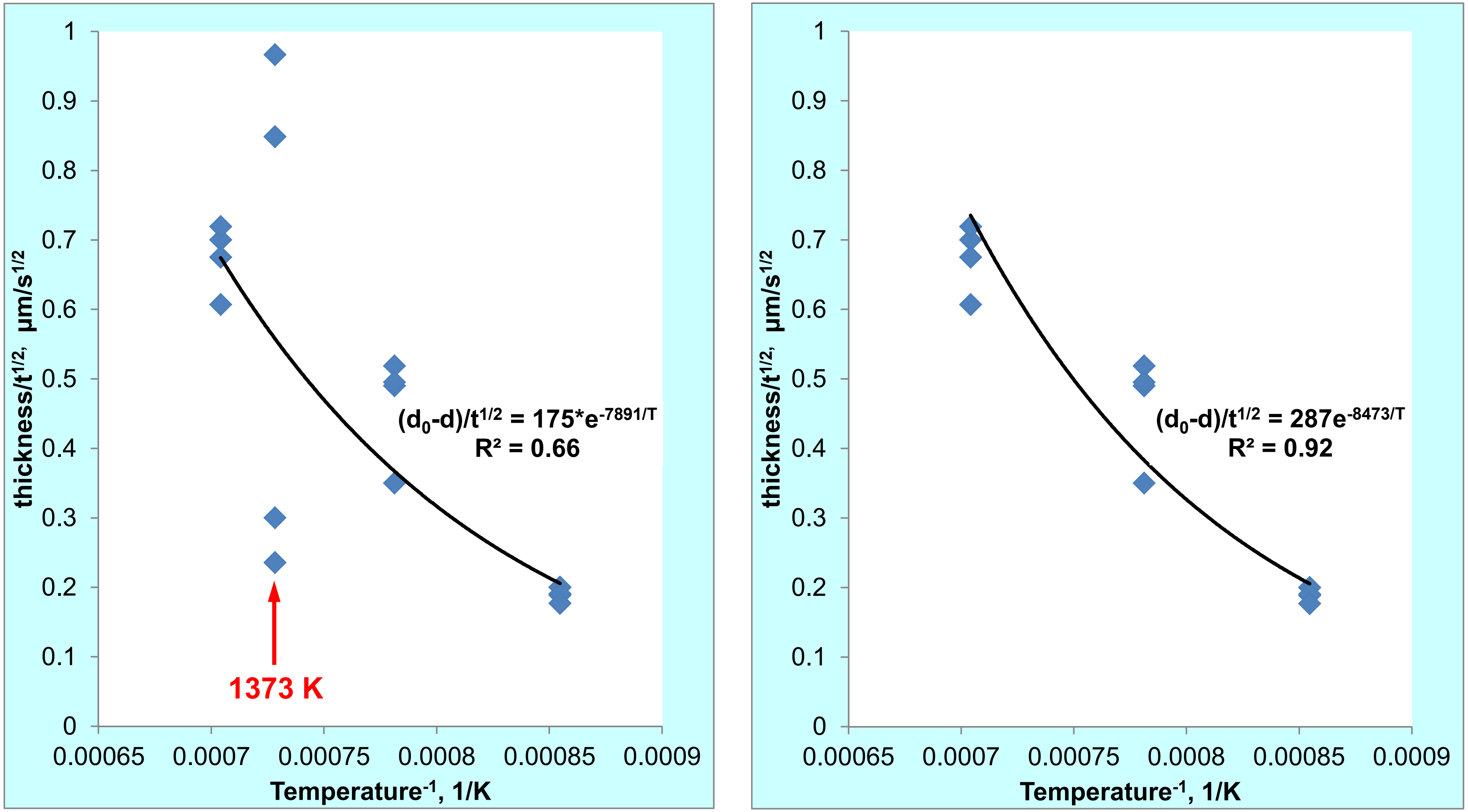

Annealing 7200 s: $ZrO_2$ 22 µm, **dissolved 39 µm**, α-Zr(O) 333 µm

# Comparison of experimental and calculation (SVECHA code) results for 1420 K




**After pre-oxidation to $ZrO_2$ = 73 µm: well prediction of $ZrO_2$ decrease, underestimation of α-Zr(O) increase**

# Arrhenius approximation of $ZrO_2$ dissolution



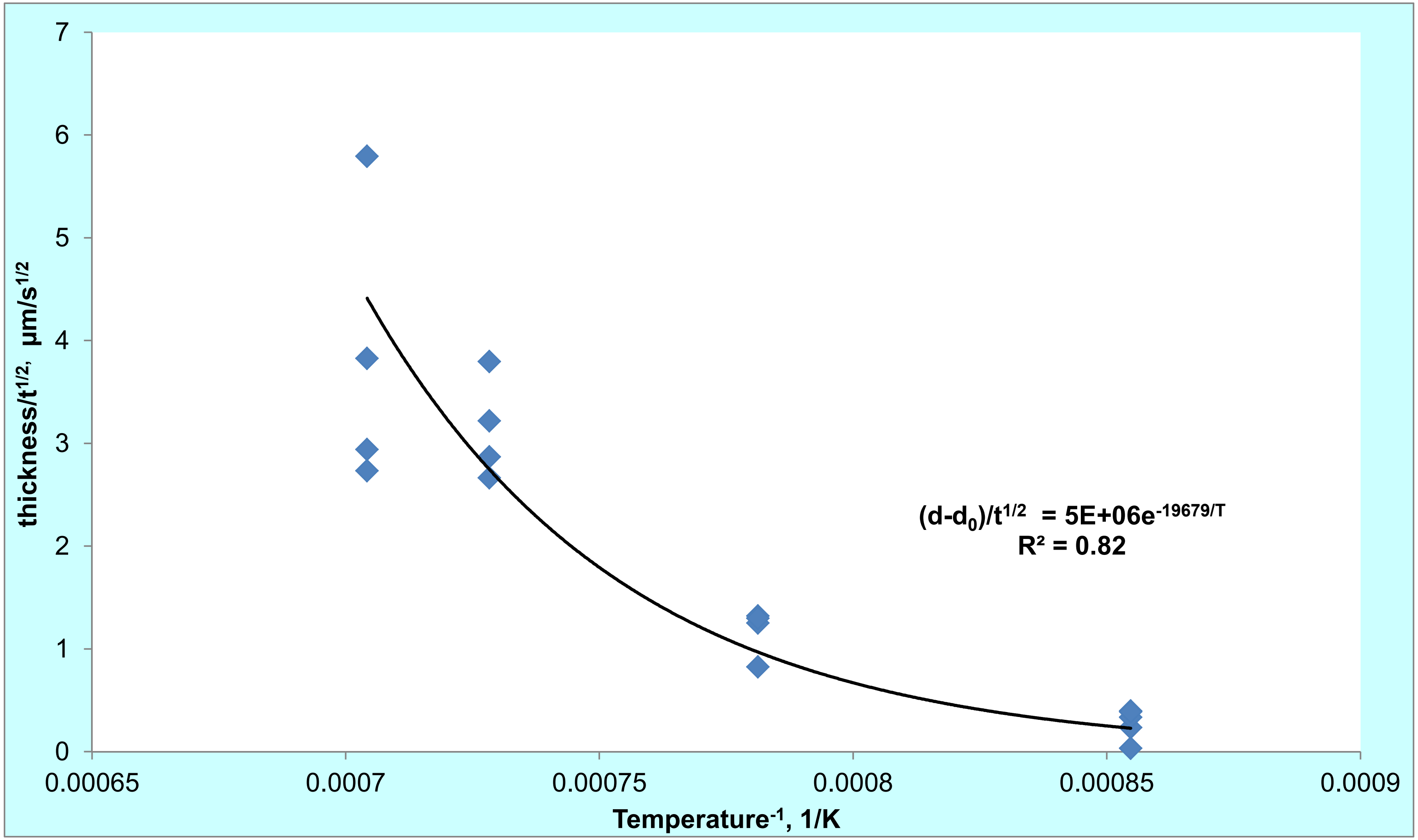

**Low value for coefficient of determination: $R^2 = 0.66$**

**Points for 1373 K excluded**

**Activation energy $E_{ZrO2} = R_g{*}8473 = 70326$ J/mol**

/Oxidation Cathcart-Pawel: 75008 J/mol/

# Arrhenius approximation for α-Zr(O) increase during $ZrO_2$ dissolution




**Moderate value for coefficient of determination: $R^2 = 0.82$**

**Activation energy $E_{zr(O)} = R_g*19679 = 163611$ J/mol**

/Oxidation Cathcart-Pawel: 101220 J/mol/

# Summary

- Reduction of the oxide layer under steam starvation conditions was experimentally investigated with the Zircaloy-4 claddings oxidized double sided at temperatures between 900 and 1200°C. The oxygen from $ZrO_2$ layer redistributed during annealing during growing α-Zr(O) layer and decreasing β-Zr layer.
- During dissolution of oxide layer between 900 and 1200°C the $ZrO_2$ transformed from stoichiometric monoclinic phase to sub-stoichiometric tetragonal phase.
- The mechanistical SVECHA code underestimates the $ZrO_2$ dissolution at T<1150°C (mixture of sub-stoichiometric monoclinic and tetragonal $ZrO_2$).
- Due to continuous conversion of oxide phases during dissolution of oxide at 1100°C would be not correct approximate the $ZrO_2$ dissolution by Arrhenius approach.
- The SVECHA code can well predict the decrease of $ZrO_2$ layer at T>1150°C (only sub-stoichiometric tetragonal $ZrO_2$). However, the increase of α-Zr(O) layer is under-predicted.
- Correlations for change of layer thicknesses were established:
  - decrease of $ZrO_2$ (rough) $(d_0-d)/t^{1/2} = 287*\exp(-8473/T) = 287*\exp(-70326/RT)$
  - increase of α-Zr(O) $(d-d_0)/t^{1/2} = 5*10^6*\exp(-19679/T) = 5*10^6*\exp(-163611/RT)$

# Thank you for your attention!

http://www.iam.kit.edu/wpt/471.php

http://www.iam.kit.edu/wbm/552.php