Karlsruhe Institute of Technology

Hydrogen Uptake of Zry-4 during Reaction in N_2/H_2O Atmosphere in the Temperature Range of 600 - 1100°C

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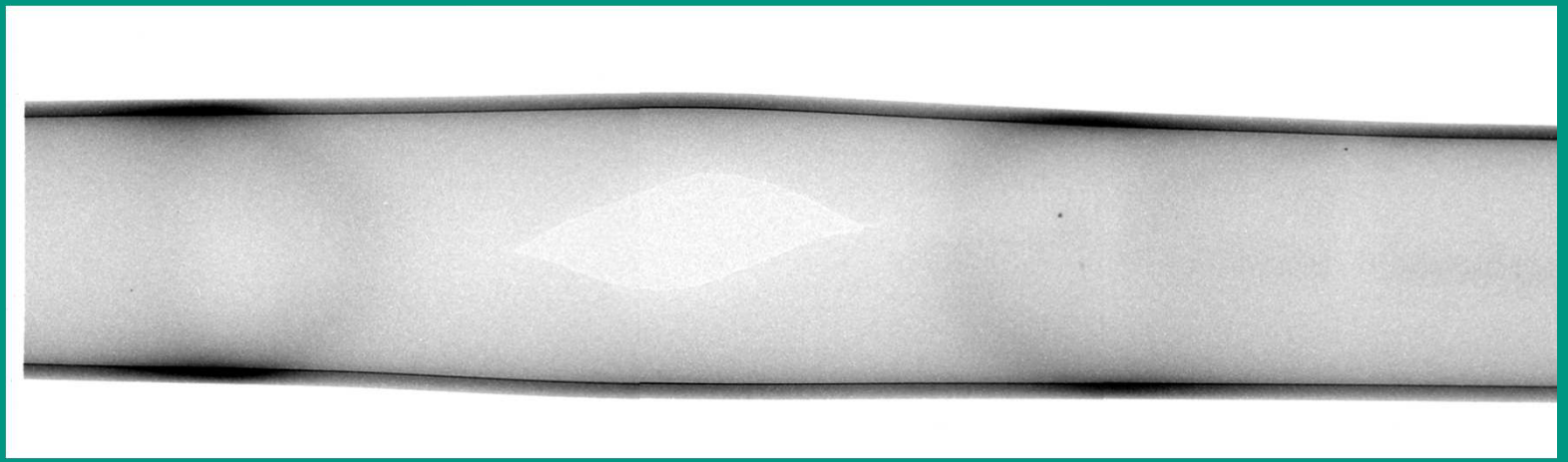


Outline

- Introduction
- Annealing of zirconium alloys in steam/nitrogen atmosphere
- Neutron radiography
  - Measurements
  - Calibration
  - Results
  - Discussion
- Conclusions

Introduction

- High temperature oxidation of the zircaloy claddings in nitrogen/steam atmosphere can occur for instance:
  - During severe accidents in BWR where the containment is inerted by nitrogen
  - Spent fuel pool (SFP) accidents (The hydrogen released consumes the oxygen from the air and steam/nitrogen atmosphere remains at the fuel rods).

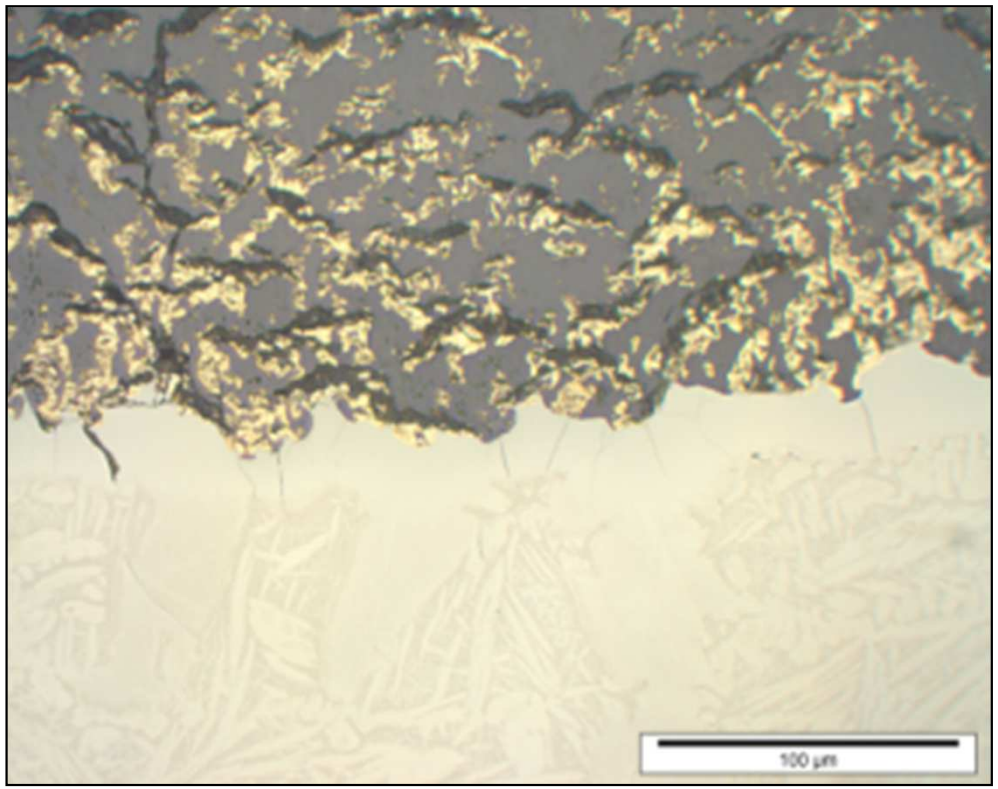
- The reaction

$$2\ Zr + N_2 = 2\ ZrN \qquad \text{(very simplified)}$$

occurs only under oxygen and steam starvation conditions.

Introduction

- Porous oxide scale is formed:



- Do we get an enhanced hydrogen uptake like it happens during the so called breakaway oxidation at around 1000°C?

Annealing of zirconium alloys in steam/nitrogen atmosphere

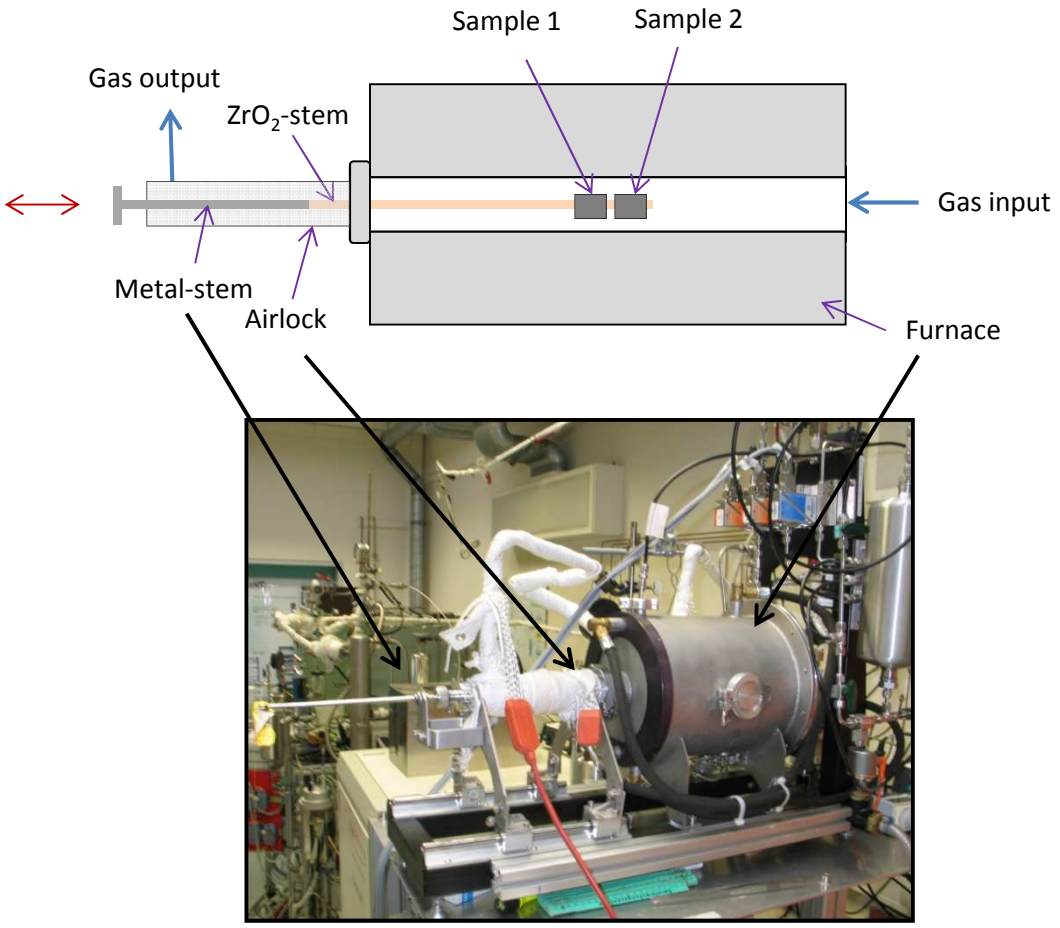
INRRO furnace

2 Zry-4 cladding tube segments (2 * 10 mm length) per annealing

Loading and withdrawal of the samples at test temperature

Cool down to nearly RT during about 5 min.

Atmospheres:
- pure steam
- 99 % steam + 1 % N_2
- 20 % steam + 80 % N_2.

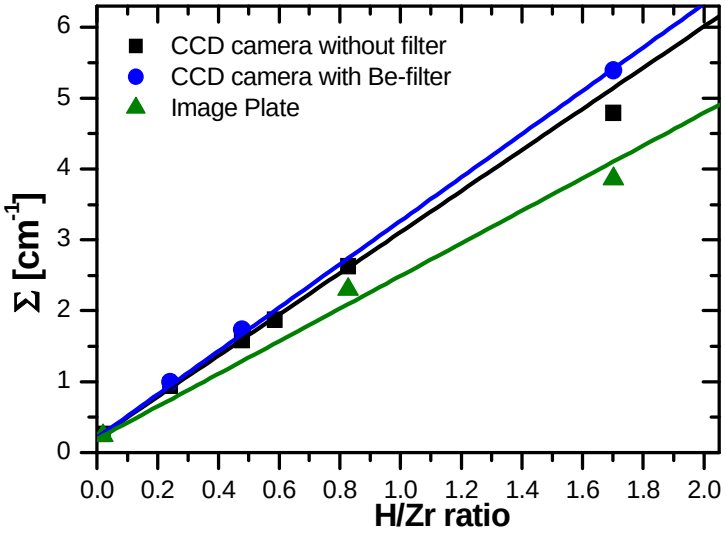


Neutron radiography investigations

X-ray radiography

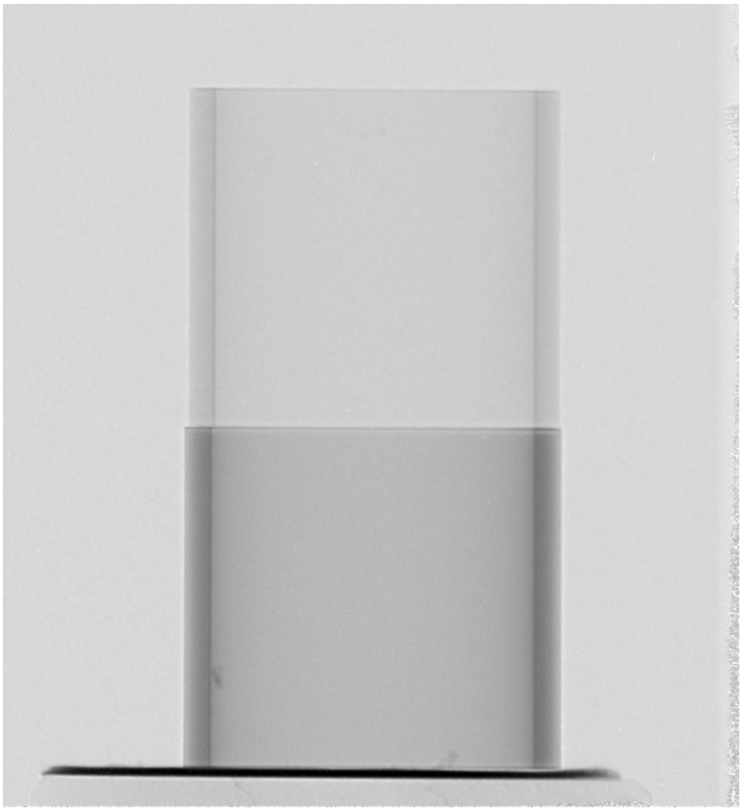
neutron radiography

GKSS Geesthacht 1991

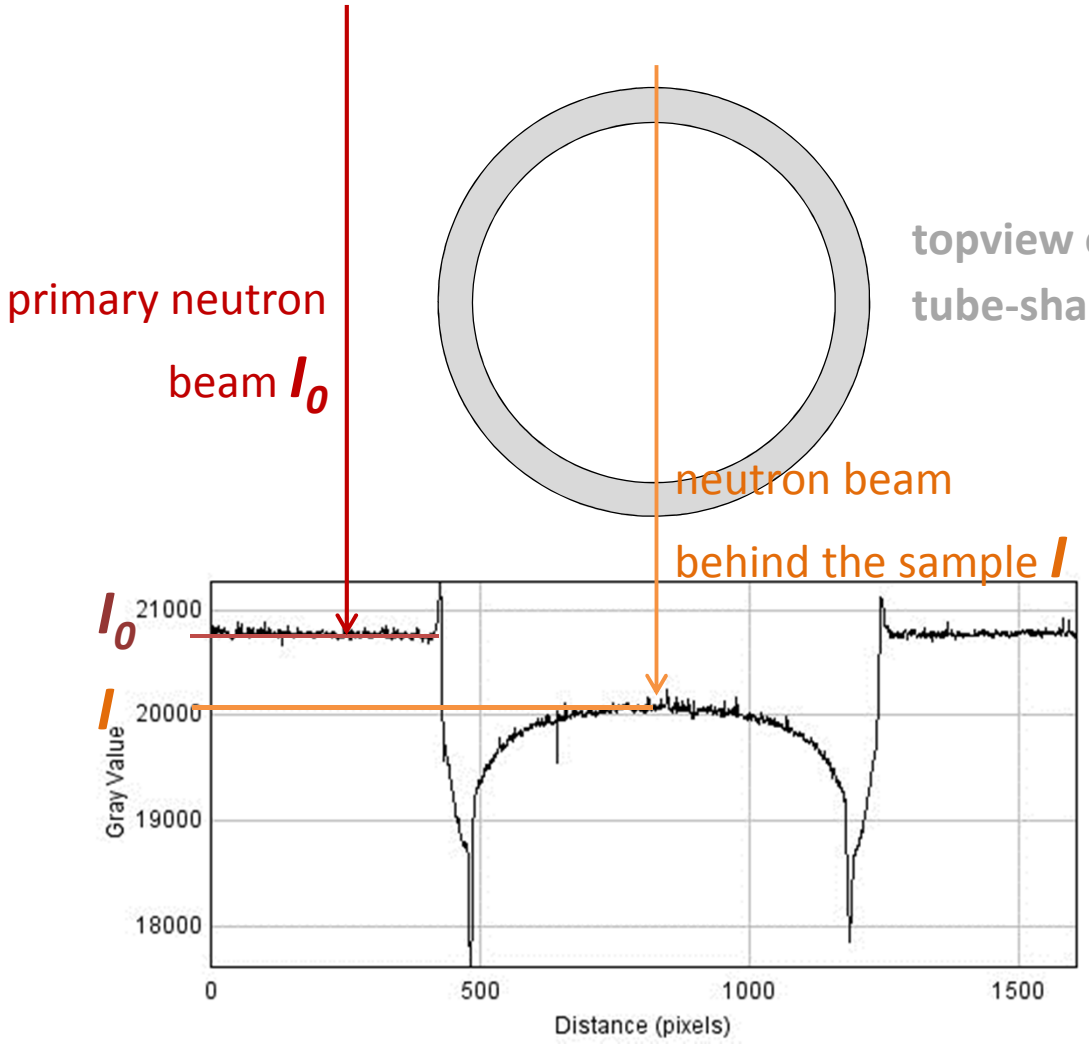


Neutron radiography investigations

facility	ICON
neutron source	SINQ
institution	PSI Villigen
resolution	~ 25 µm
time per image	300 s



Basis of neutron radiography



$$T = \frac{I}{I_0} = \exp\left(\Sigma_{total}\ s\right)$$

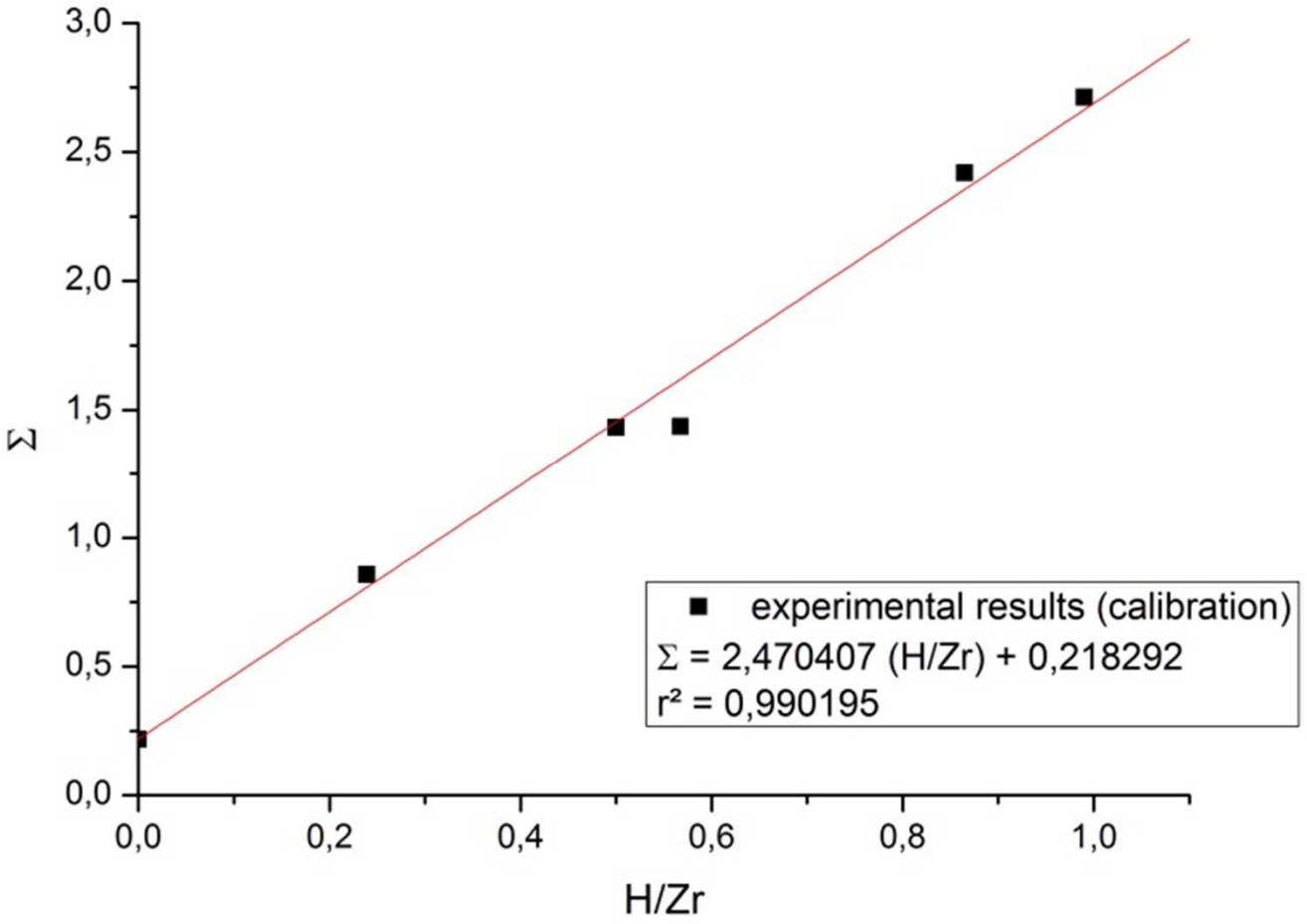
Basis of neutron radiography

$$\Sigma_{total} = \frac{-\ln\left(\frac{I - I_B}{I_0 - I_B}\right)}{s}$$

$$= \sum_i N_i \sigma_i$$

$$= \underbrace{N_{Zr}\sigma_{Zr} + \ldots}_{\Sigma_{Zry}} + N_H\sigma_H + N_O\sigma_O + N_N\sigma_N$$

Basis of neutron radiography



Calibration of the hydrogen contribution on the neutron attenuation

Basis of neutron radiography

Correction of the effect of oxygen:

$$\Sigma_O = \frac{a}{\delta_m \, S} \cdot \Delta m = 0.32 \; g^{-1} \cdot \Delta m$$

(former work:
M. Grosse et al.;
Nucl. Instr.& Meth. In Phys. Res.
A 651, (2011), 253)

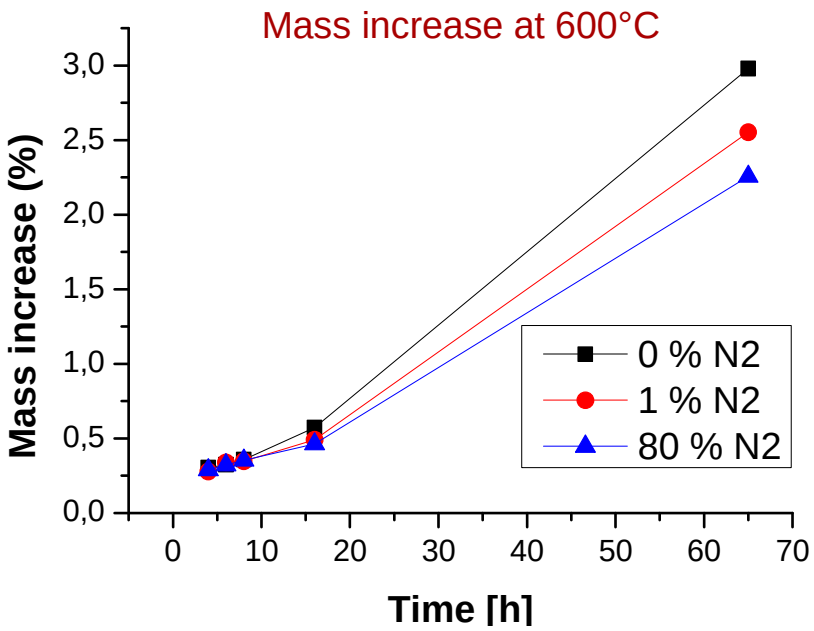
Correction of the effect of nitrogen:

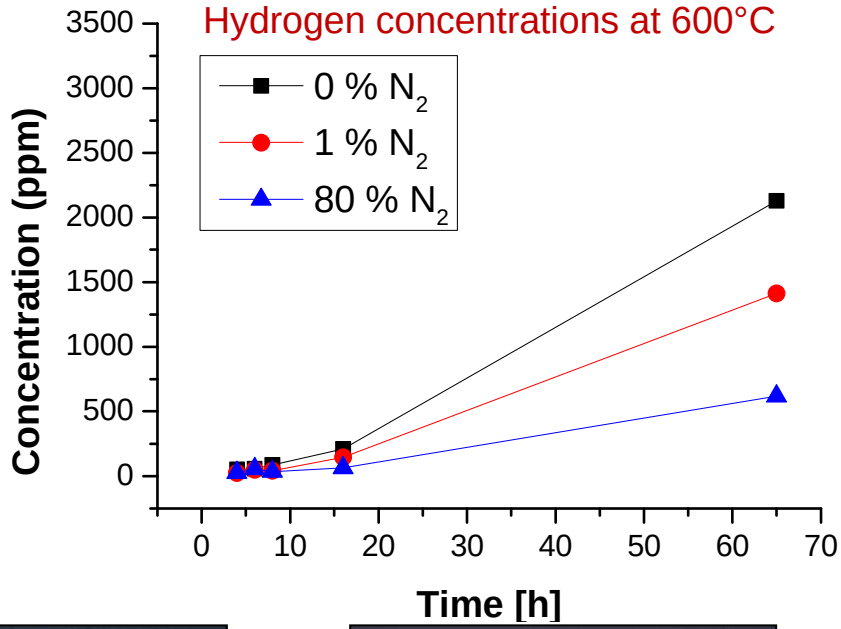
Using the samples annealed in synthetic air:

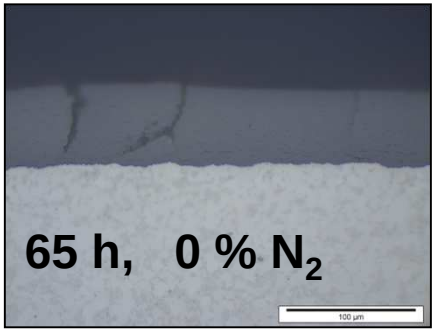
$$\Sigma_N = \; 0.60 \; mm^{-1} \cdot \overline{\delta_{ZrN}}$$

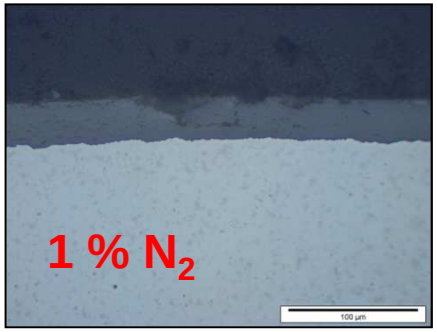
$\overline{\delta_{ZrN}}$ mean thickness of the nitride containing layer

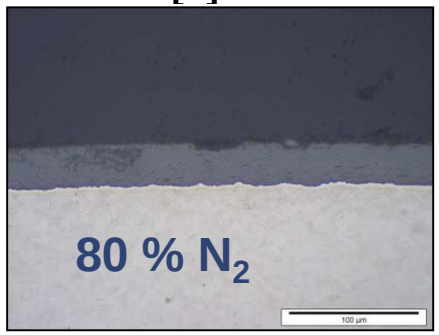
Results (600°C)



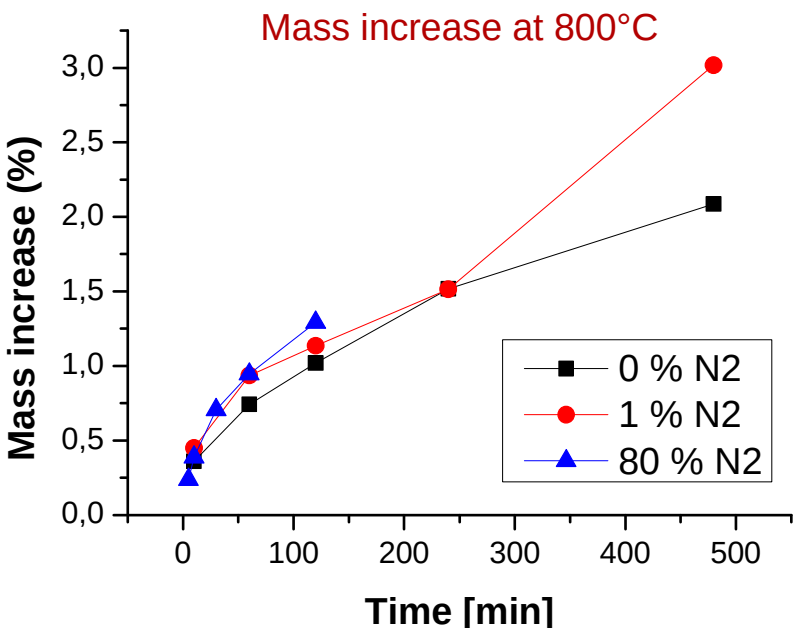


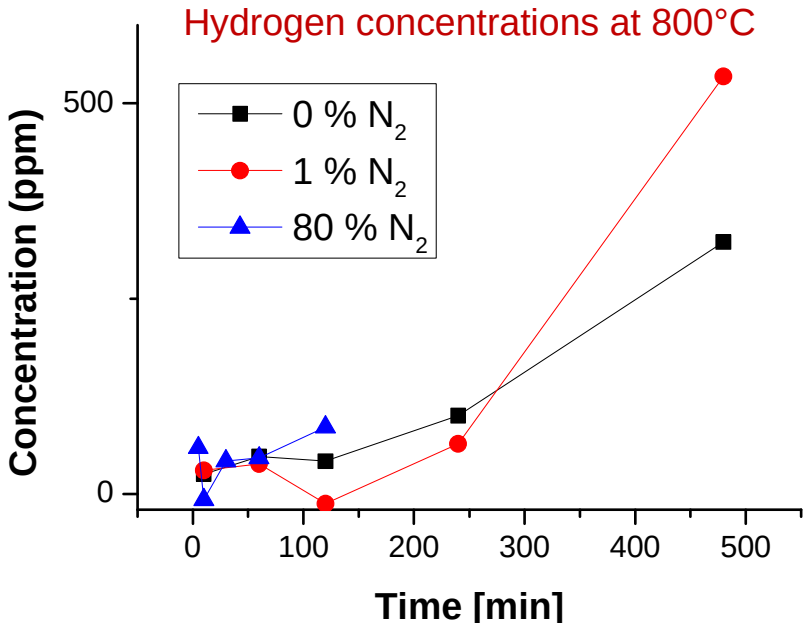


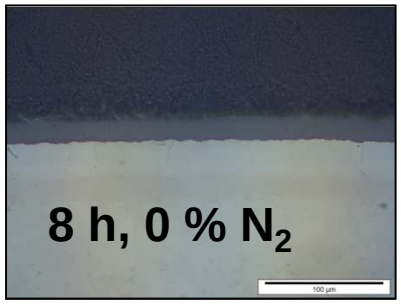


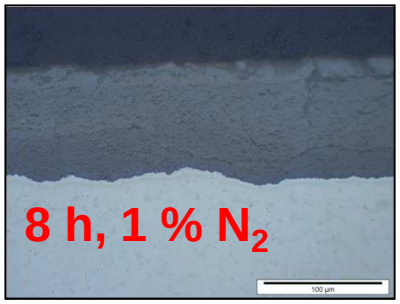


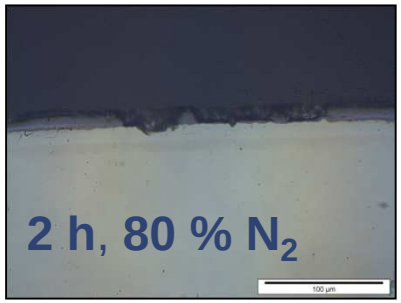
Results (800°C)



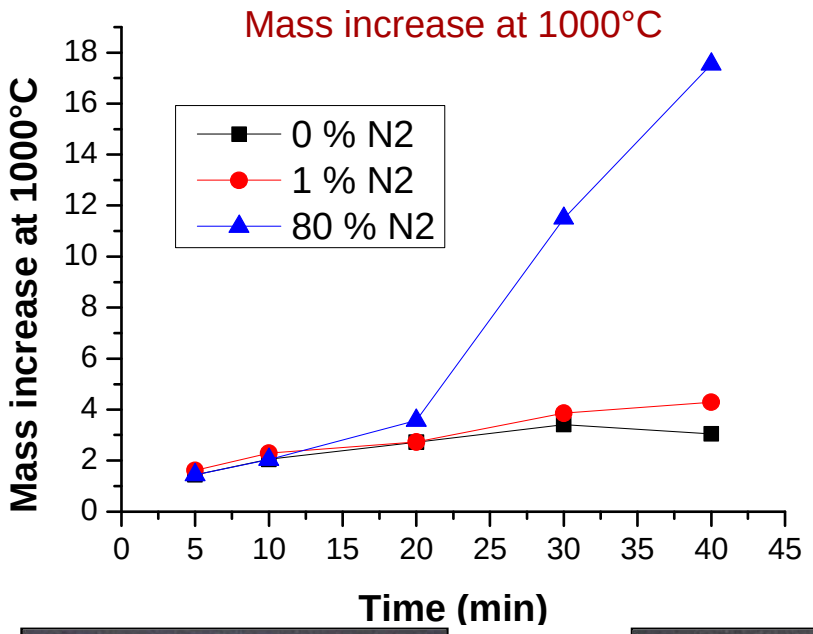


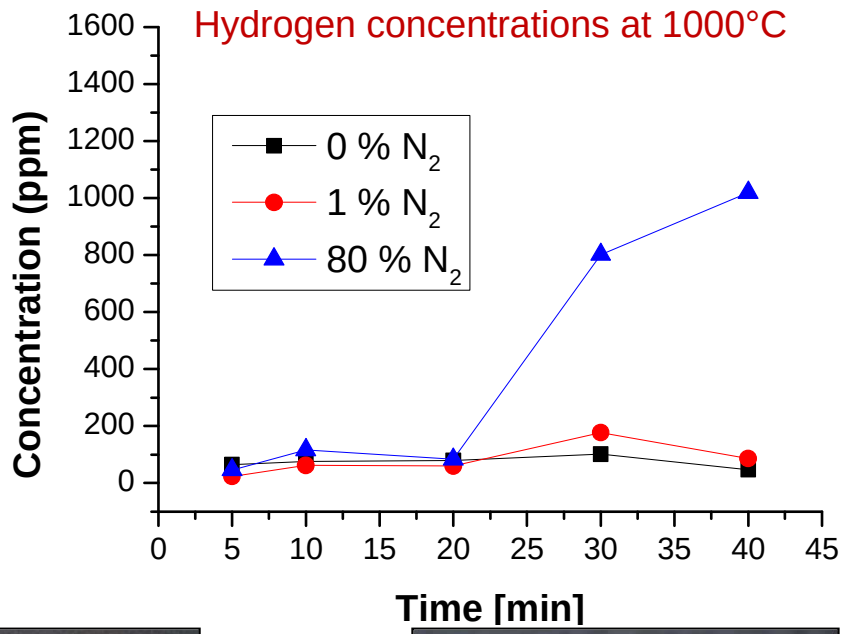


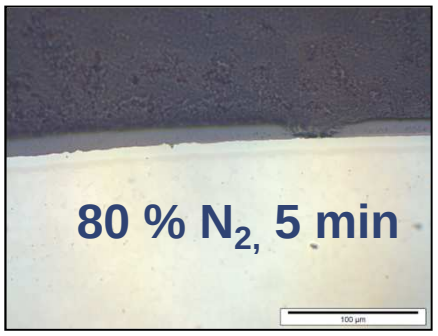


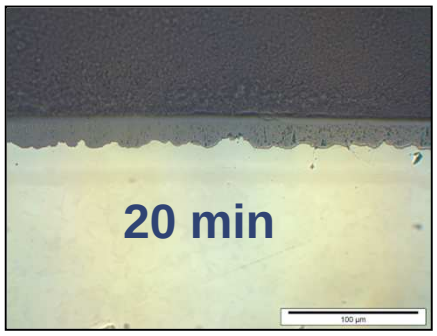


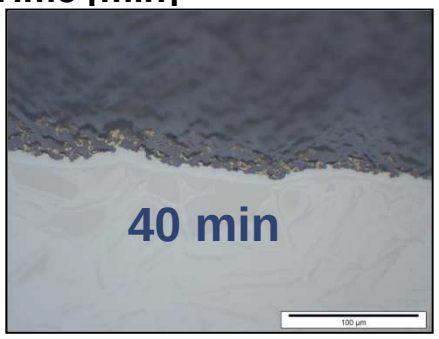
Results (1000°C)



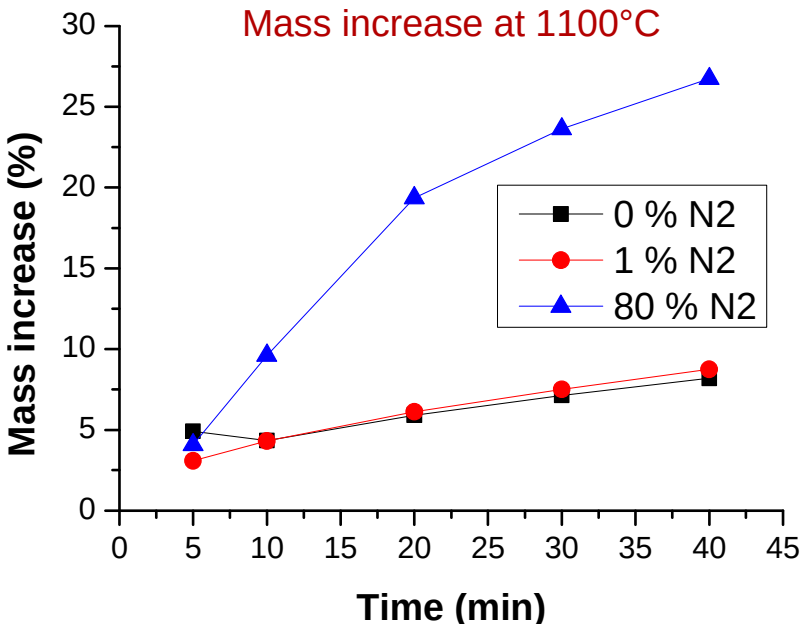


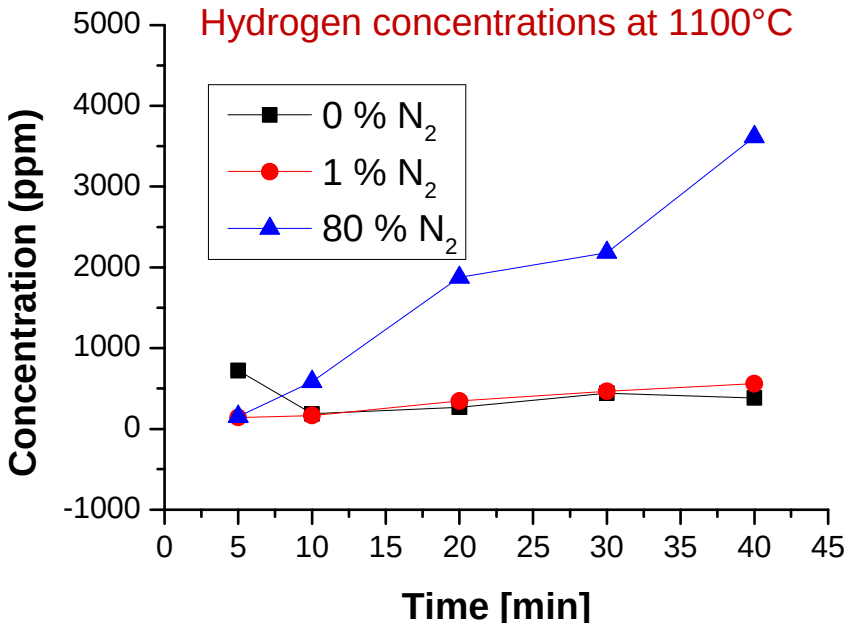


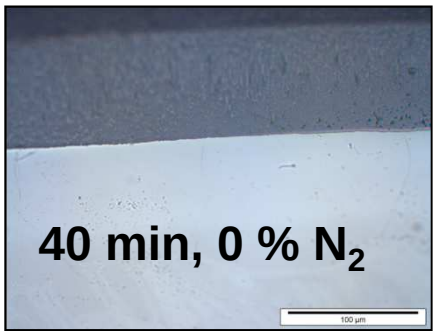


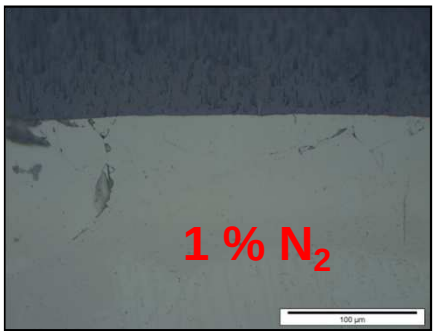


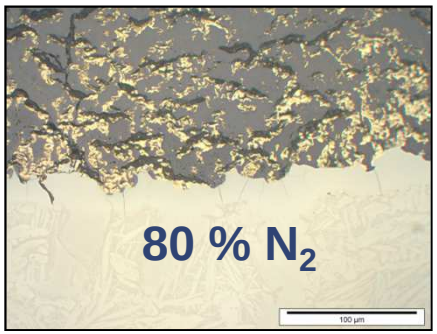
Results (1100°C)



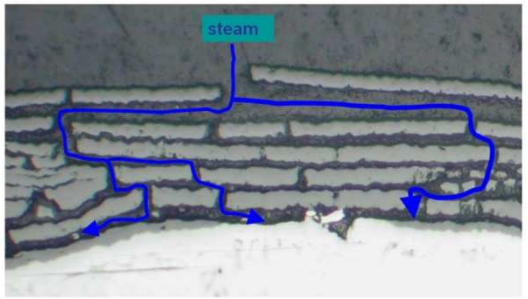




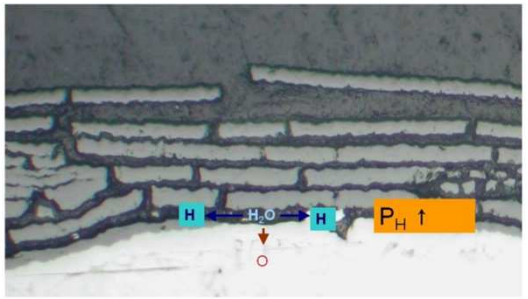




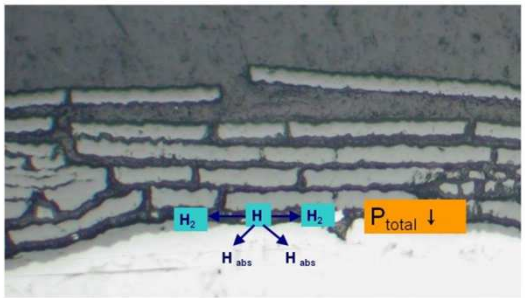
Discussion



a)



b)



c)

“Hydrogen pump” effect known for breakaway oxides:

- Steam penetrates into the cracks and reaches the oxide/metal interface

- Steam reacts at the interface, hydrogen remains in the cracks resulting in a high hydrogen partial pressure

- Higher hydrogen partial pressure results in a stronger hydrogen uptake by the metallic Zry (Sieverts law). The total pressure in the cracks decreases. New steam is sucked into the cracks and the process continues at the beginning.

Summary and Conclusion

- Nitrogen in steam strongly enhances oxidation and hydrogen uptake of Zircaloy-4.
- The effect is very strong at 1000 and 1100°C. Only some minutes annealing is needed to start the enhanced reaction.
- The formation of nitrides is accompanied by an strong increase in the hydrogen concentration. The effect is comparable with the effect occurring during breakaway oxidation
- Additionally to the faster degradation by the enhanced reaction, strong hydrogen embrittlement occurs.
- More details and discussions (e.g. hydrogen uptake fractions, influence of the total gas flow) are given in the proceedings.

Thanks

U. Stegmaier for the support in the annealings and P. Severloh for her help in the metallographic investigations.

The ICON facility at SINQ (PSI Villigen, Switzerland) was used for the neutron radiography investigations. Thanks for providing beam time and support.

Thanks for your attention, questions?

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