Karlsruhe Institute of Technology

In-situ Investigations of the Hydrogen Uptake of Zirconium Alloys during Steam Oxidation

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- Neutron Imaging
- Results
  - Examples
  - In-situ Calibration
  - Analyse of the data
- Discussion
- Conclusions

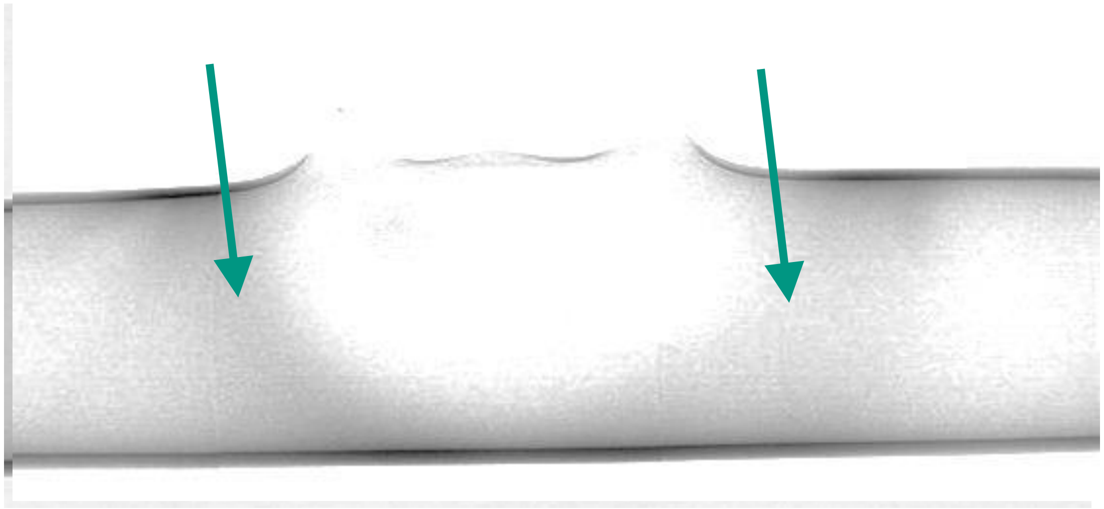
Introduction

- Zirconium alloys absorb hydrogen during corrosion in water or steam oxidation at higher temperatures

- Hydrogen uptake reduces the ductility of zirconium alloys

- Consequences for the thermo-shock stability during LOCA

- QUENCH-LOCA program was initiated at KIT to study the hydrogen uptake during LOCA and its consequences on the mechanical properties



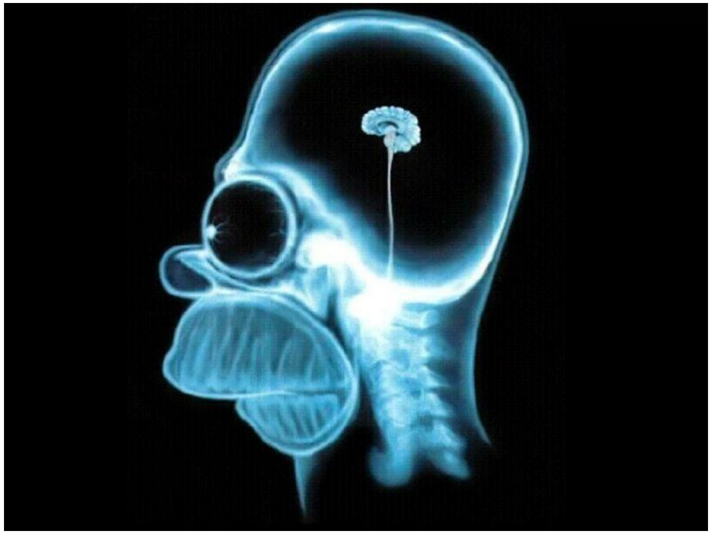
Neutron radiograph of the balloning zone of rod #08 of the QUENCH-L0-test

Neutron Imaging

Beer-Lamberts law: $I = I_0 \exp(-\Sigma s)$

with $\Sigma = \sum_i (N_i \sigma_i)$

X-ray



$\sigma = f(Z)$

Neutrons

$\sigma \neq f(Z)$

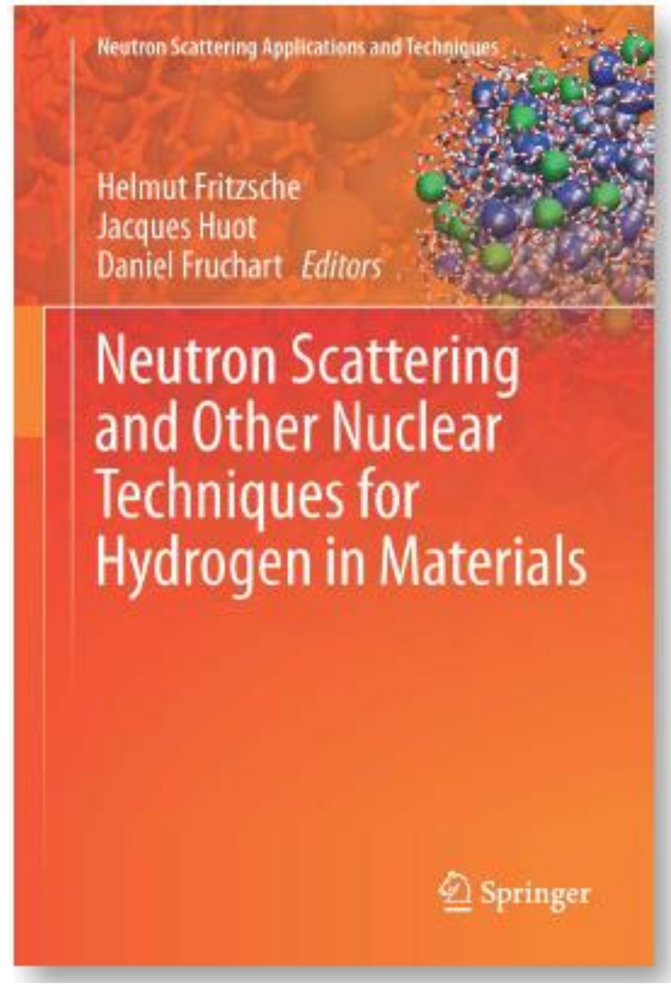
$\sigma_H >> \sigma_{Zr}$

Neutron Imaging

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

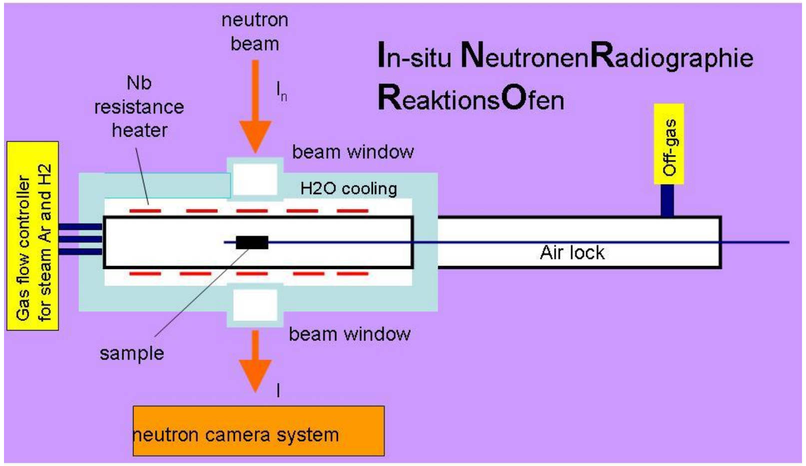
$$= \sum_i N_i \sigma_i$$

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

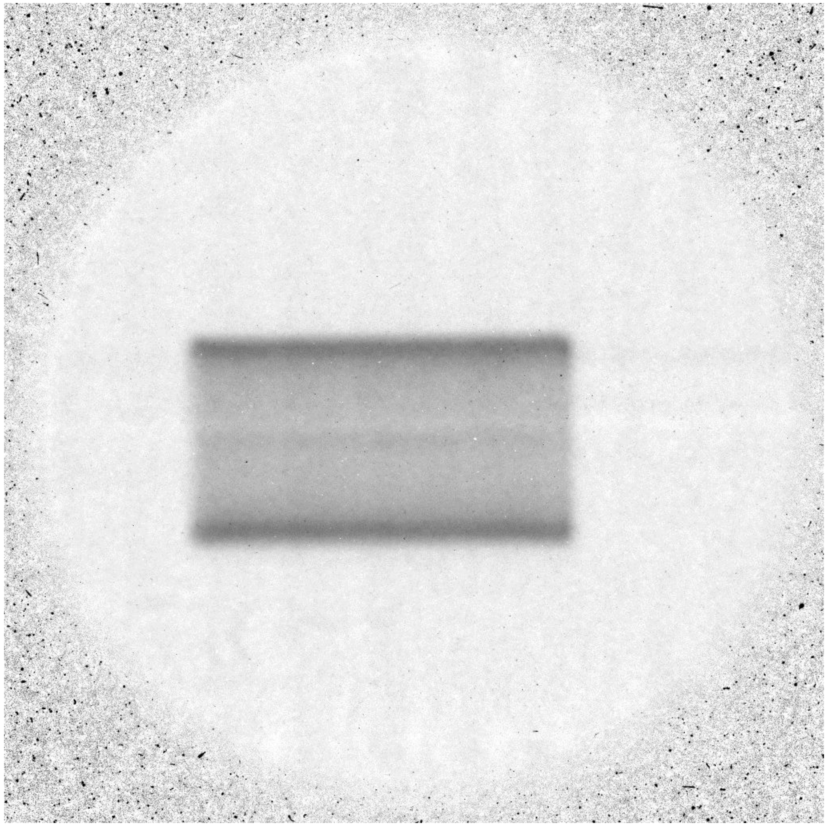


Materials and Experiments

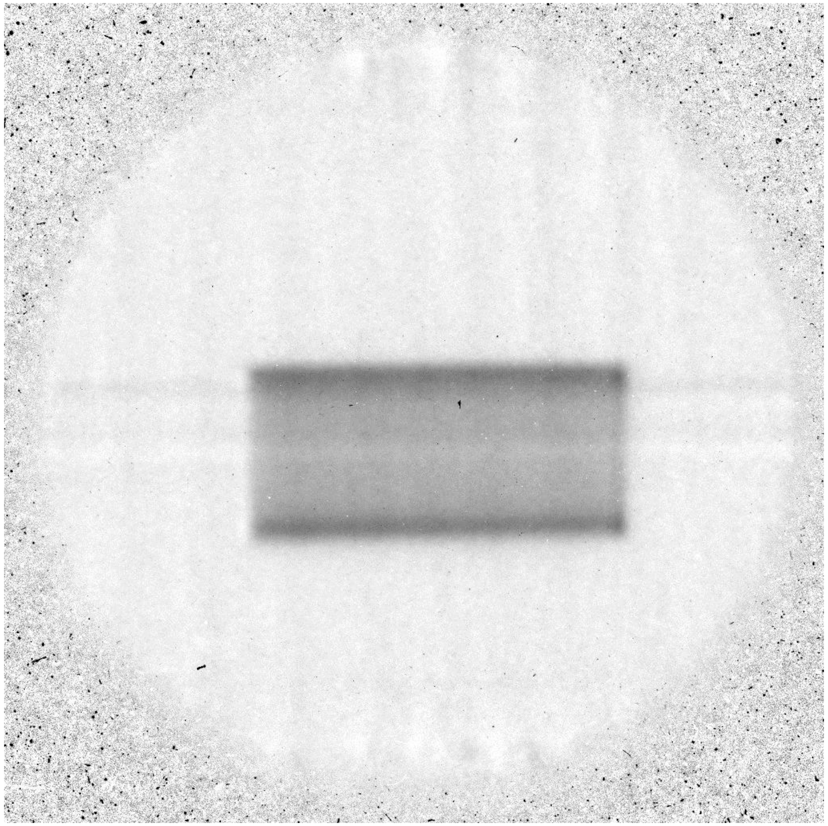
- Materials: Zry-4 and traditional E110
- Temperatures: Zry-4: 1273, 1373, 1473 and 1573 K
  E110: (1123, 1173,) 1273,1373, 121473 and 1573 K
- Neutron radiography measurements:
  - ICON at SINQ, 120 and 20 s illumination per image
  - ANTARES at FRM-2, 10 s illumination per image
- INRRO furnace:



Results Examples



Zry-4, 1373 K



E110, 1473 K

Mirco Grosse et al. / 18th Inten. Symposium on Zirconium in Nuclear Industries /
Hilton Head Island / May 15 – 18 2016

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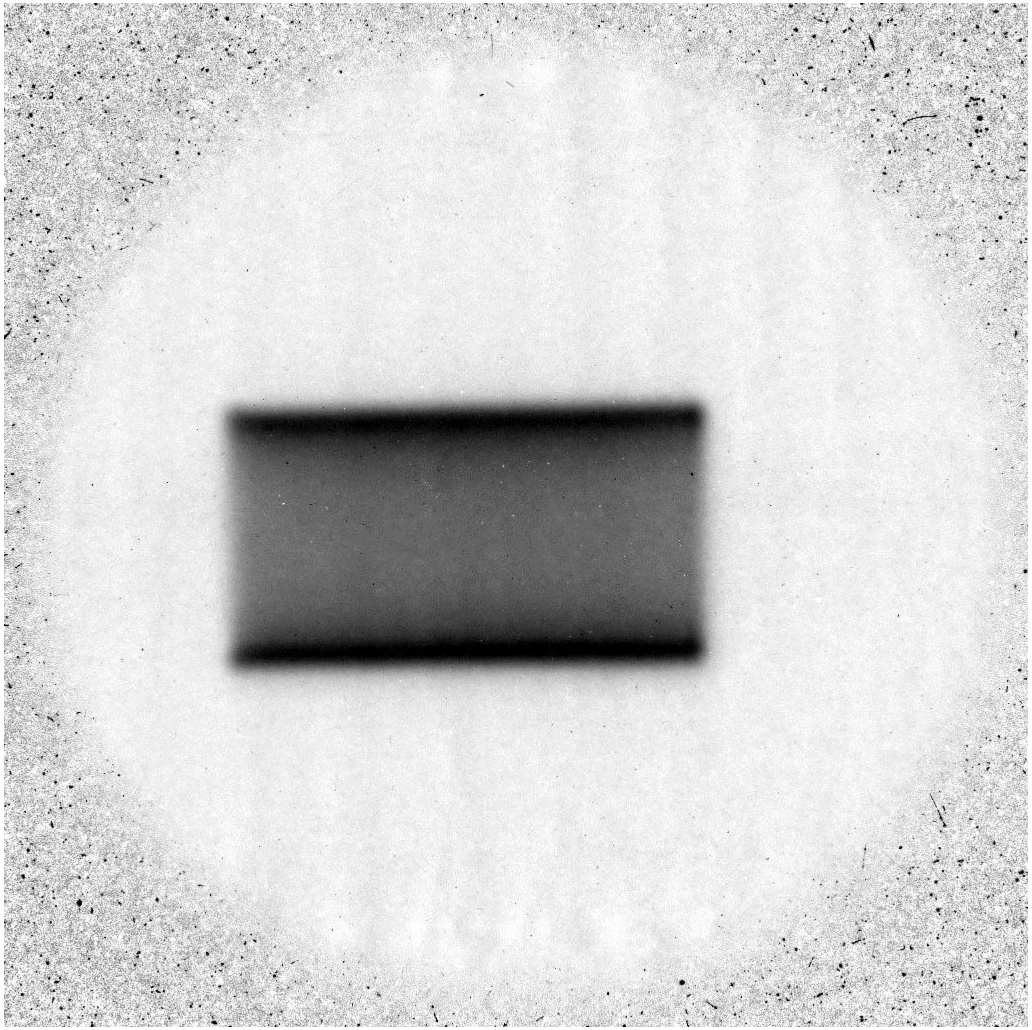
Results Examples



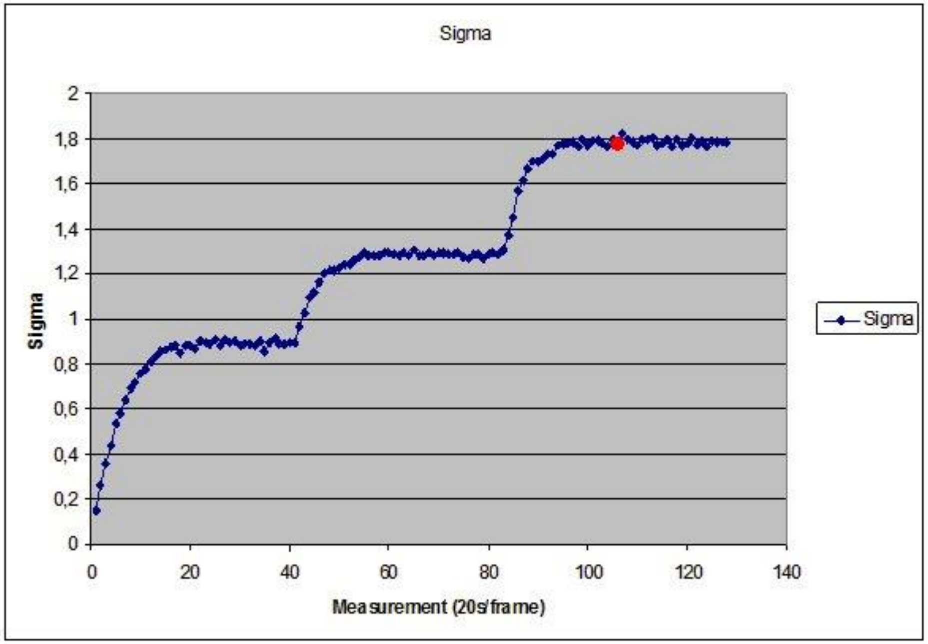
Zry-4, 1273 K

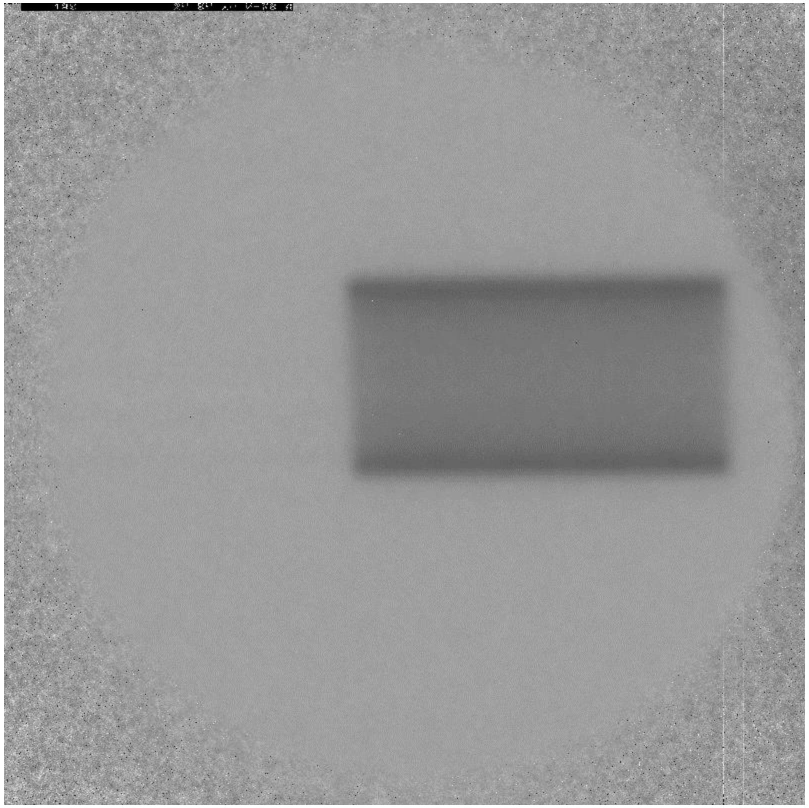
Calibration – Effect of Hydrogen

Sieverts´ law:

$$C_H^{(m)} = K_S \cdot \sqrt{p_{H_2}}$$

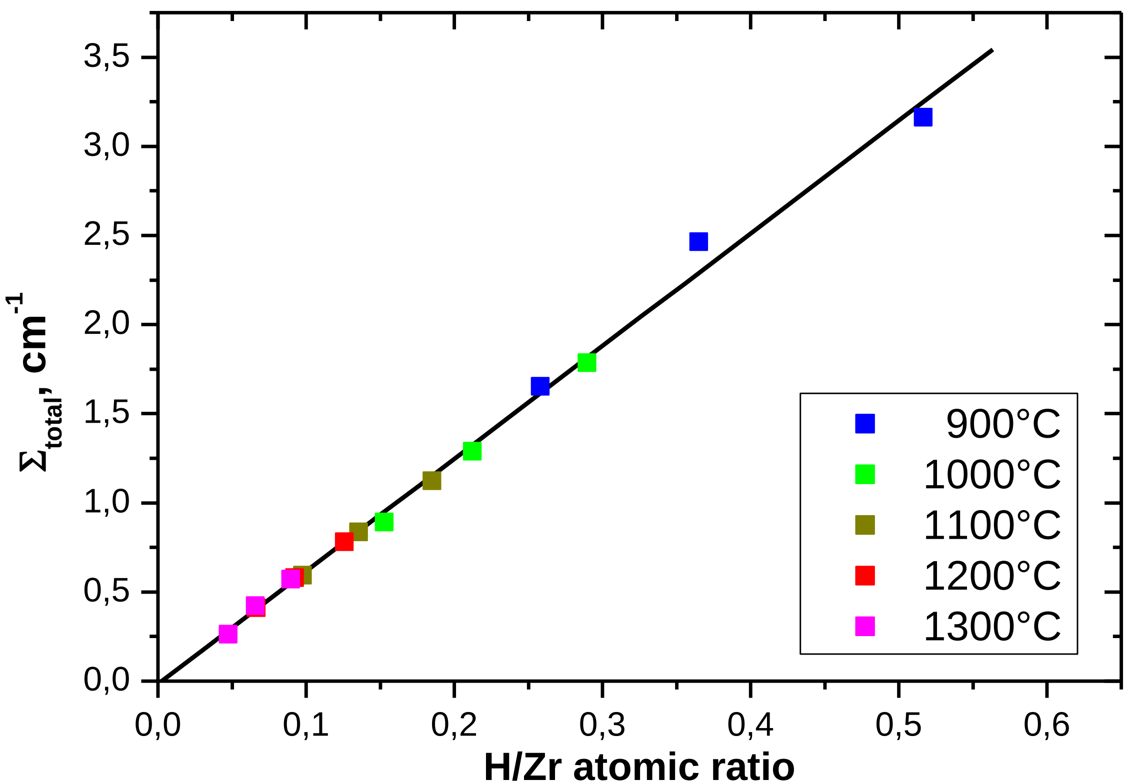
$$K_S = \exp\left(\frac{\Delta_S S}{R} - \frac{\Delta_S H}{R \cdot T}\right)$$





2 l/h 4 l/h 8 l/h H_2, 50 l/h Ar 1273 K

Calibration – Effect of Hydrogen



For in-situ NR experiments at SINQ:

Σ_{total} = 6.32 ± 0.12 H/Zr

For in-situ NR experiments at FRM2:

Σ_{total} = 5.61 ± 0.28 H/Zr

Calibration - Effect of Oxygen

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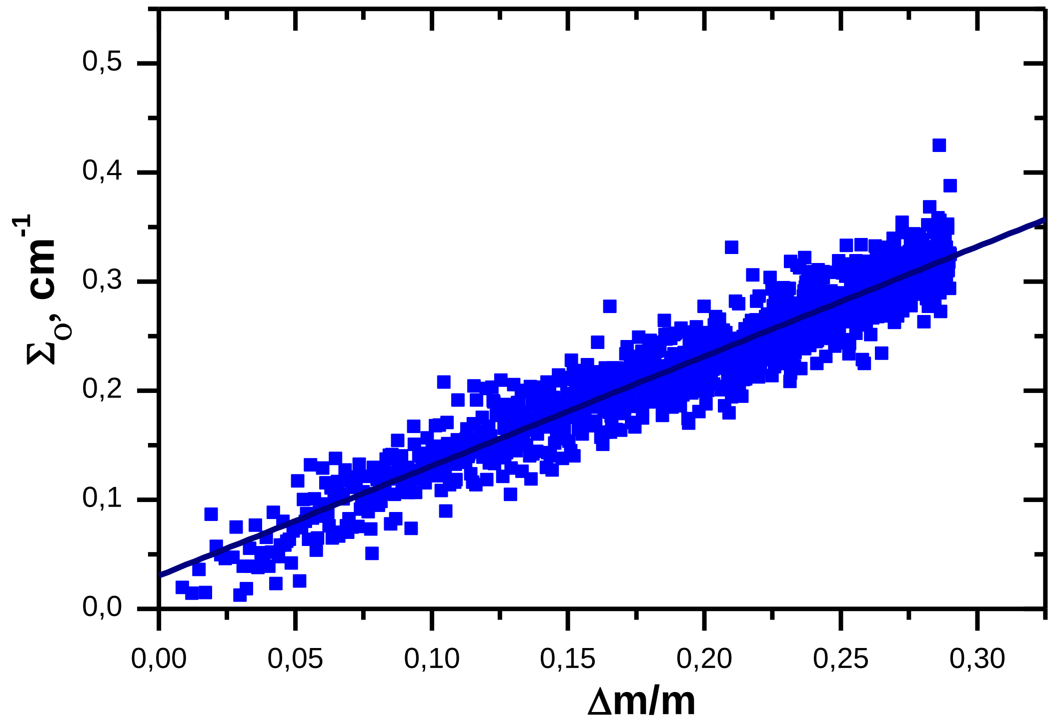
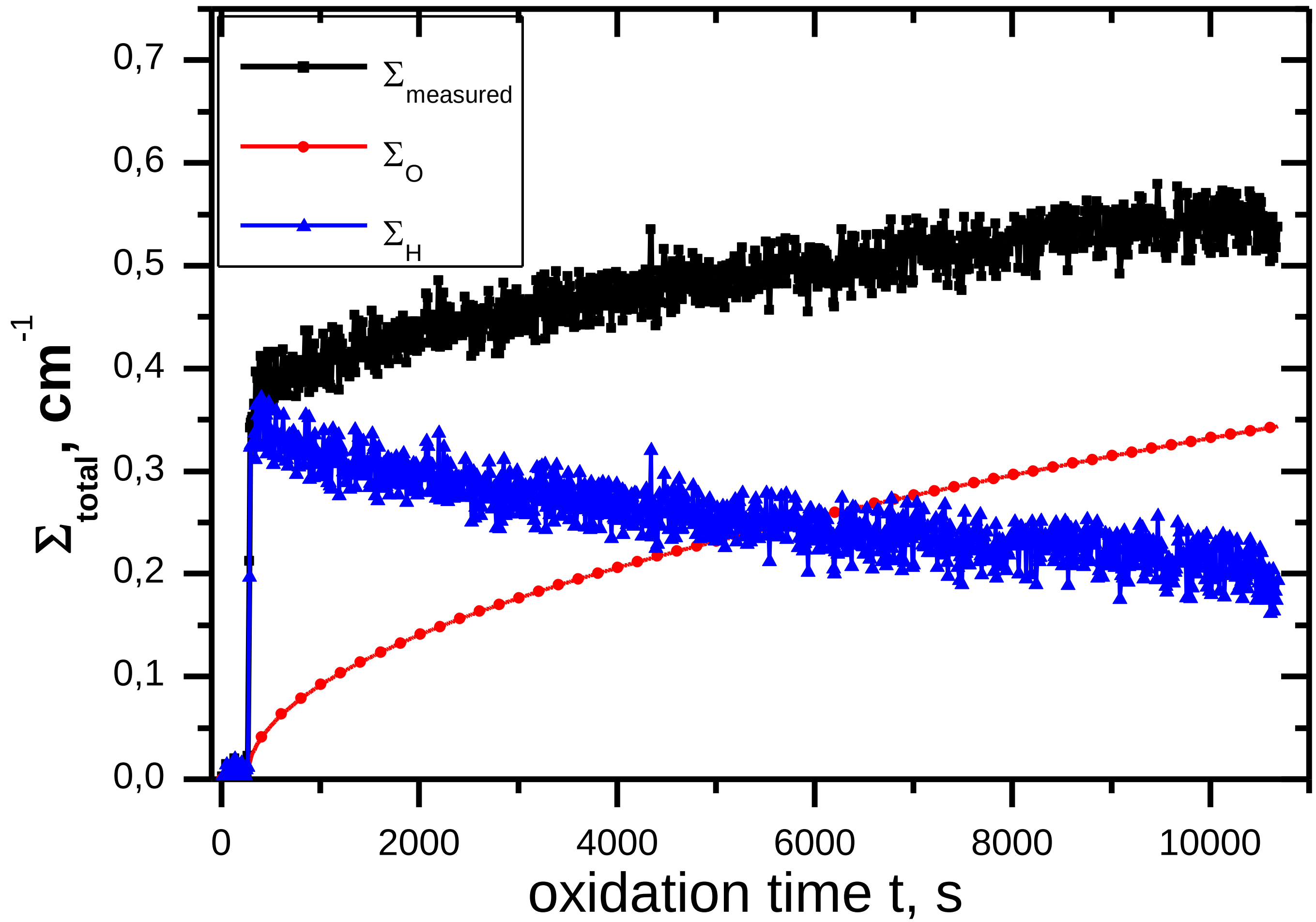


Annealing in Ar/O_2 at1200°C

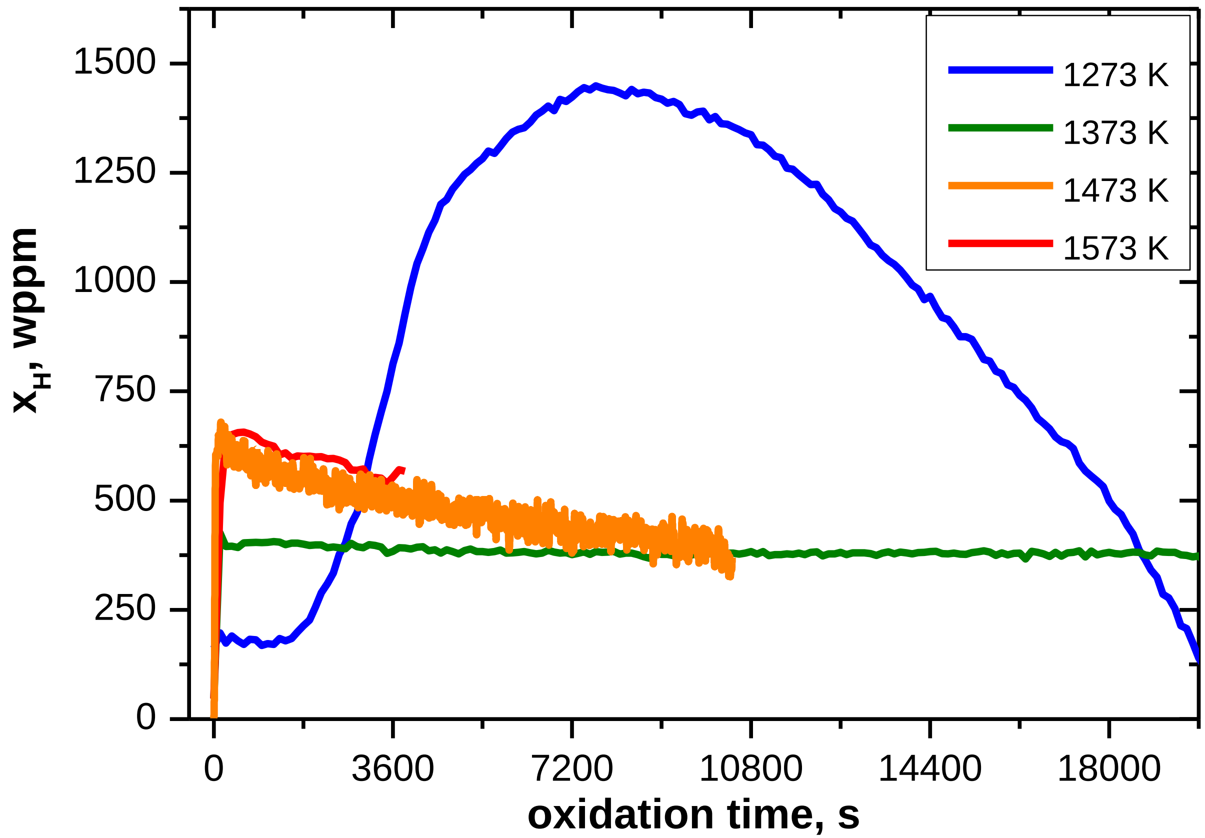
$$\Sigma_O = N_O \sigma_O = (0.98 \pm 0.04)\ cm^{-1} \frac{\Delta m}{m}$$

Results data correction



Zry-4, 1473 K

Results

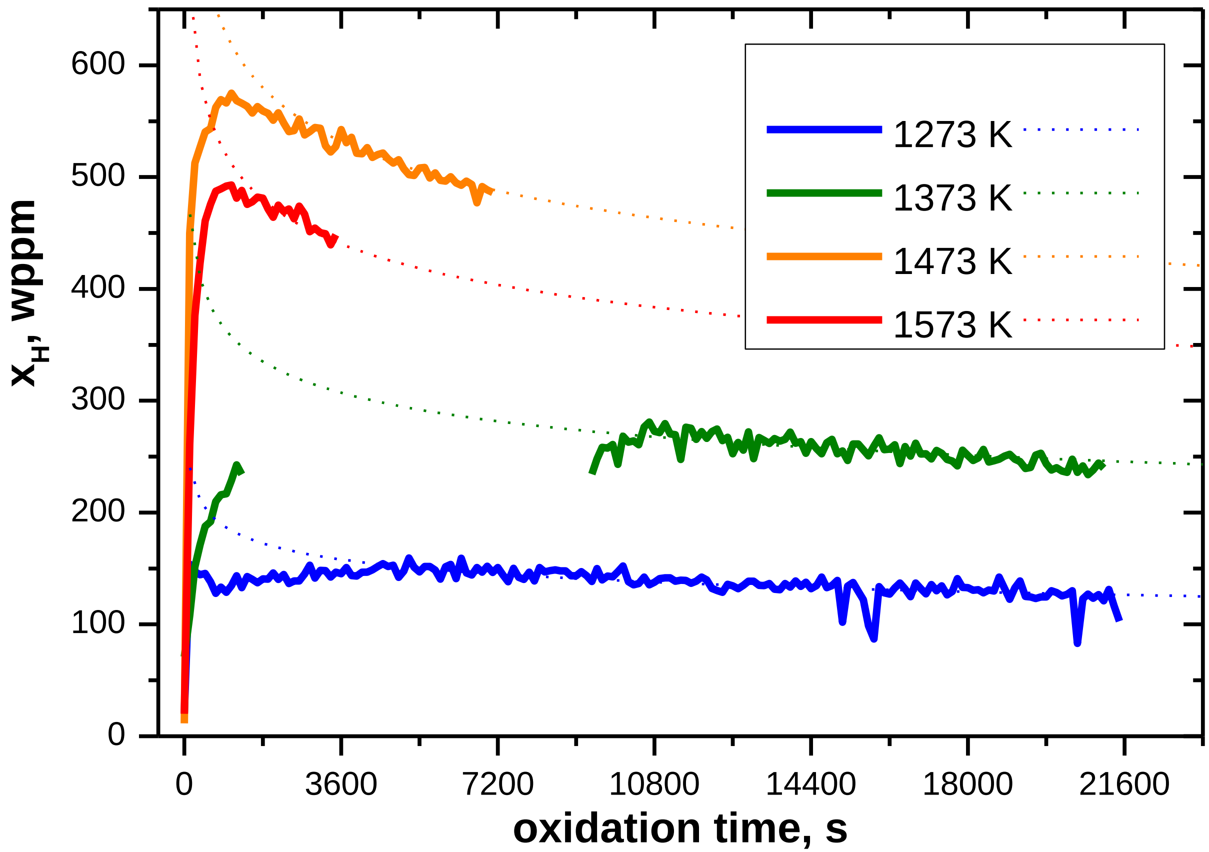


Very fast hydrogen uptake at the beginning

Later the hydrogen concentration decreases with time

Enhanced hydrogen uptake due to breakaway

Results



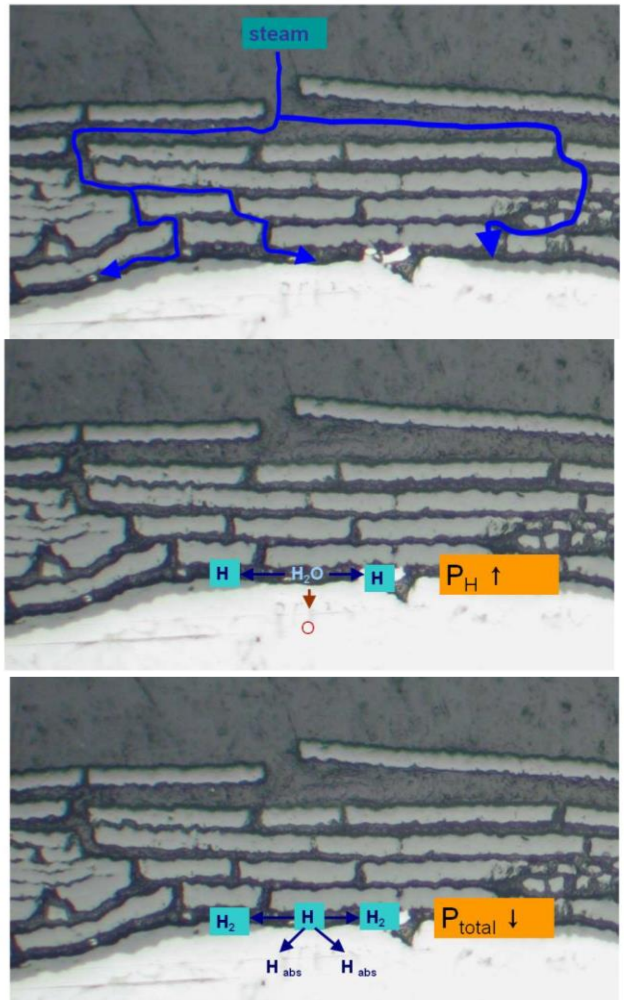
Very fast hydrogen uptake at the beginning

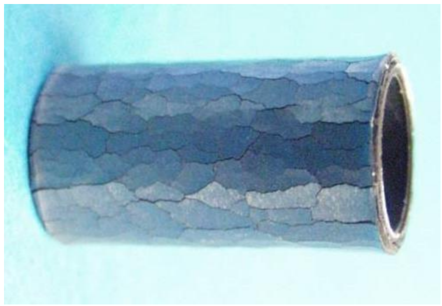
Later the hydrogen concentration decreases with time

Less influence of breakaway on the hydrogen concentration

Discussion

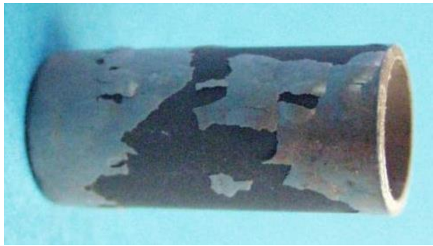
Hydrogen pump effect during breakaway oxidation





E110 Zry-4

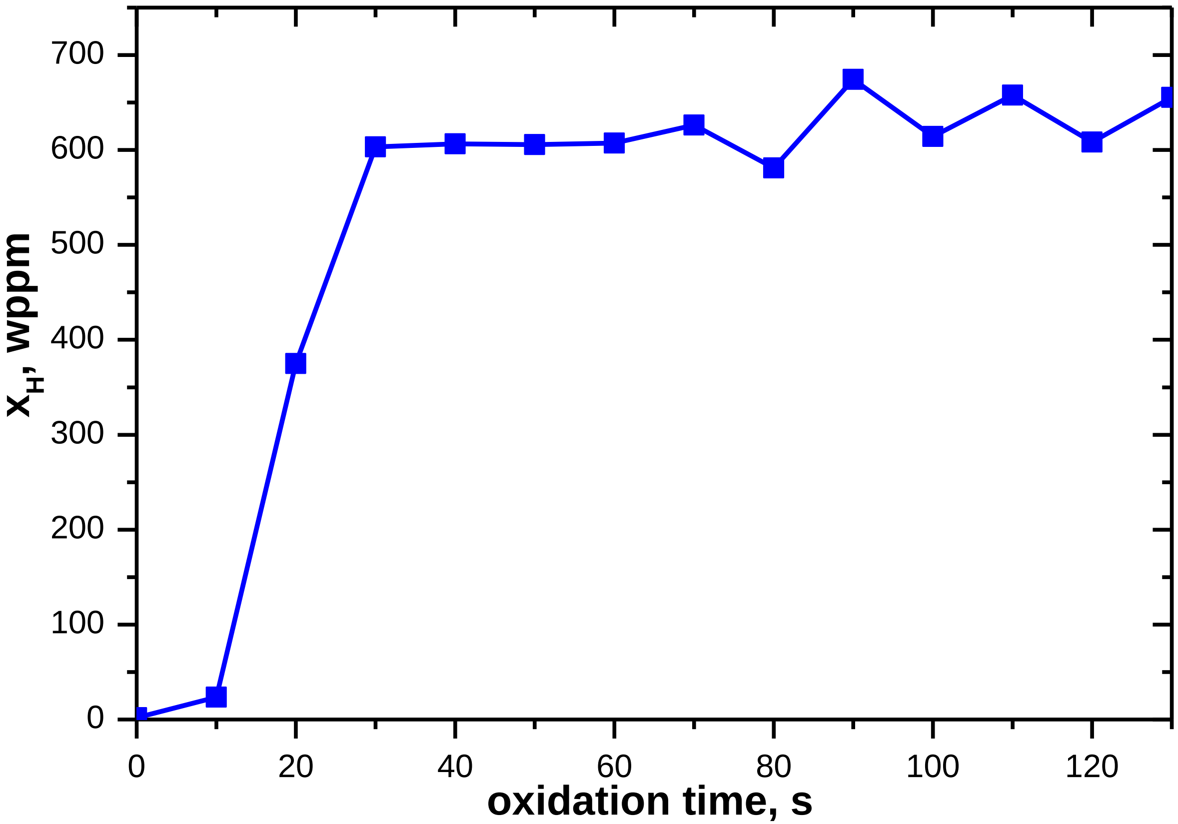
1273 K, 4 h in steam



E110, 1273 K, 6 h in steam

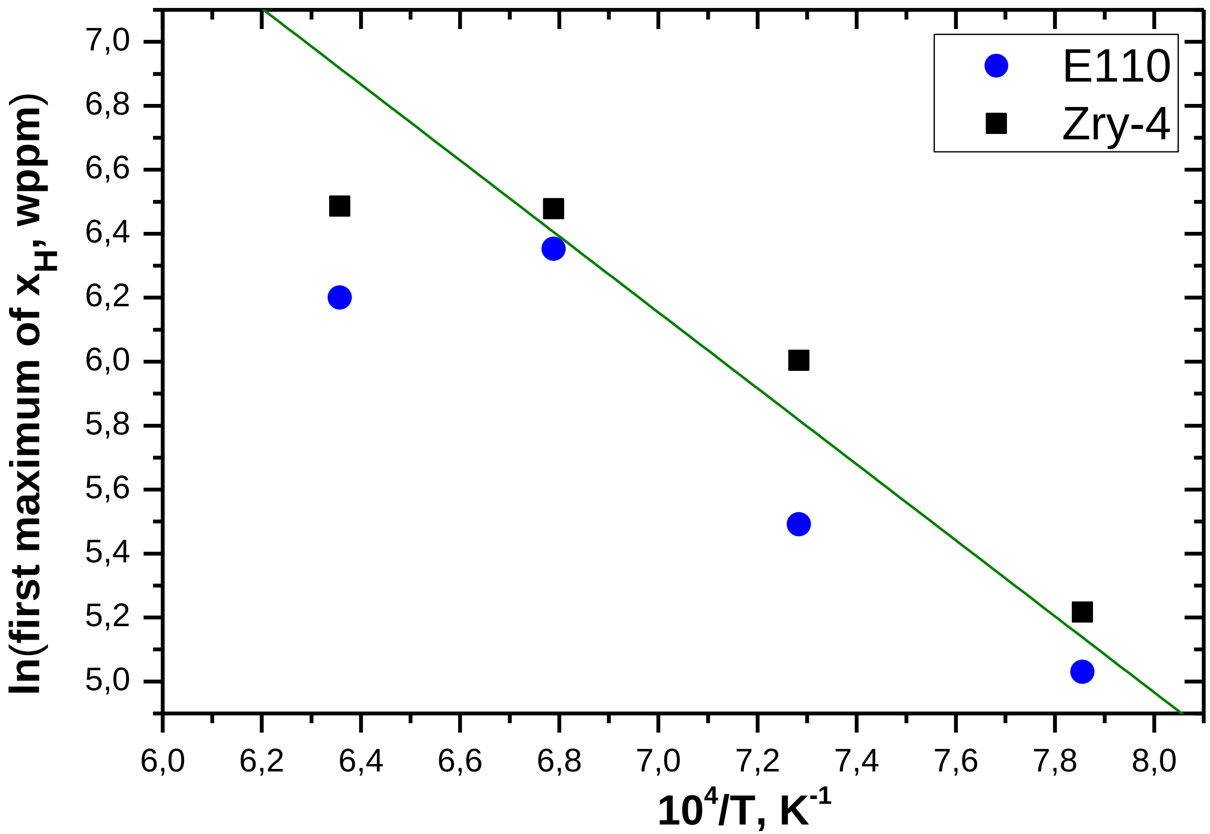
relative mass gain after 6 h at 1273 K during the in-situ experiments: Zry-4: 27.8 %, E110: -0.22%

Discussion



- very fast hydrogen uptake at the beginning
- during the first 20 s the whole hydrogen uptake occurs
- explains the results obtained from the QUENCH-LOCA tests

Discussion



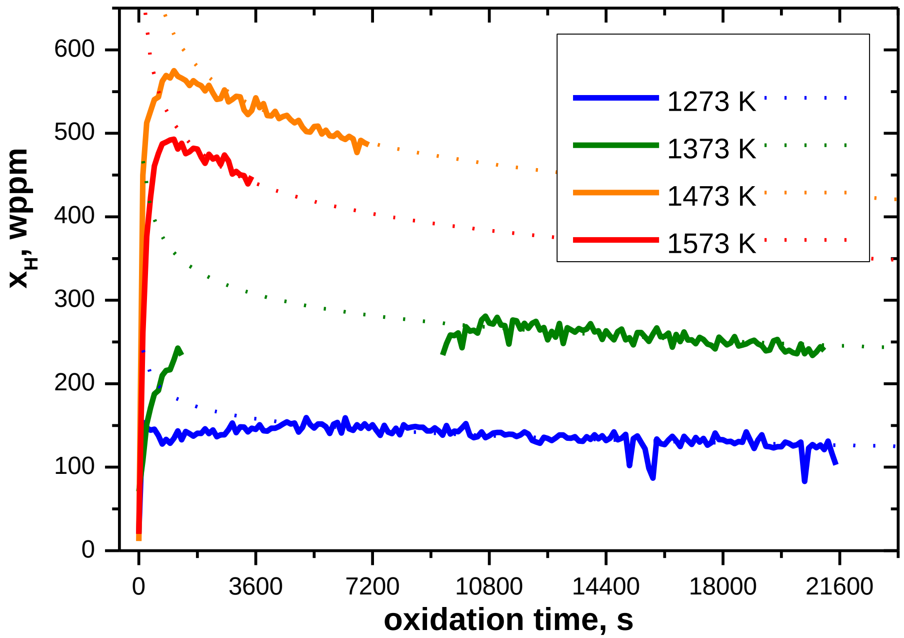
Arrhenius type dependence

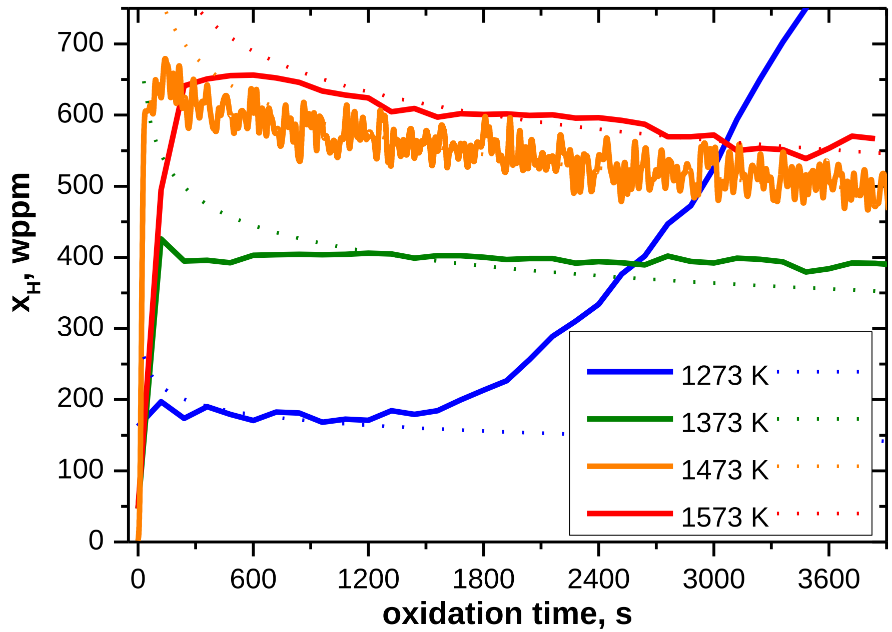
except values for 1573K because of temporary steam starvation

Hydrogen concentration increases with temperature

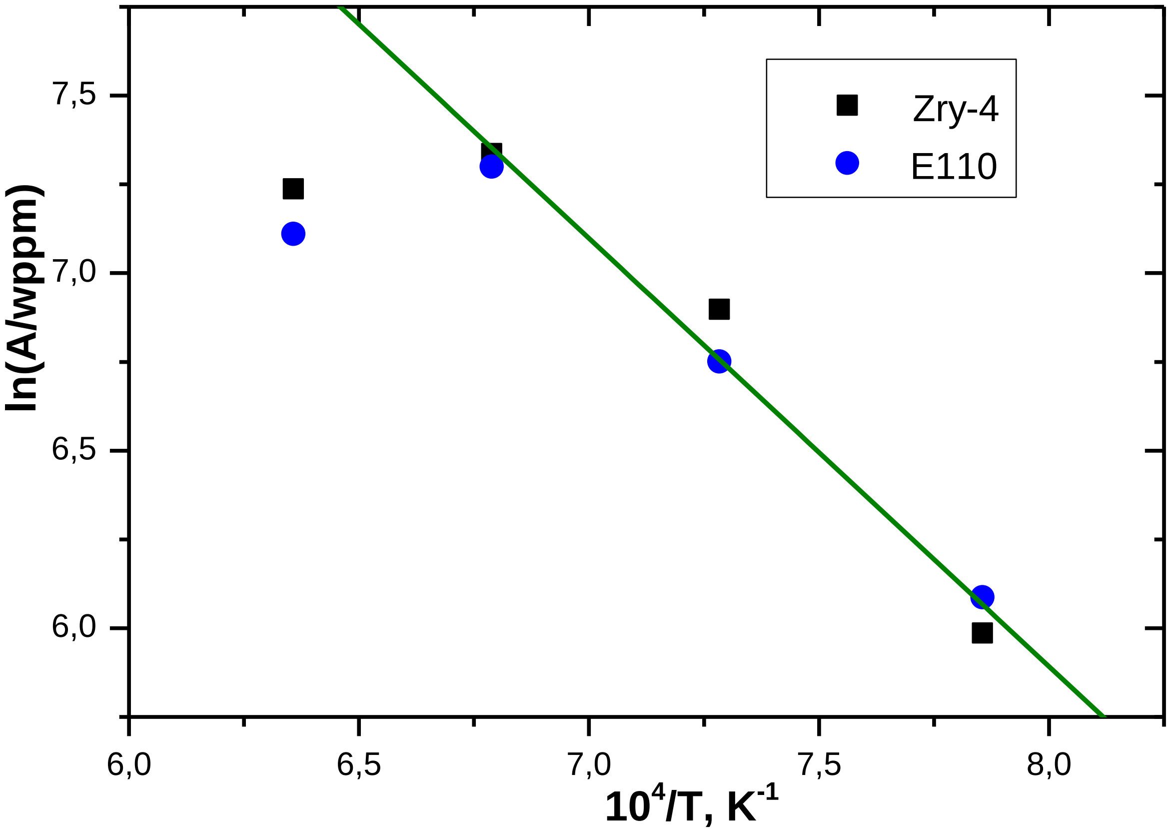
Discussion

Hydrogen release according the model of Veshchunov and Berdyshev with $t^{-1/8}$





Discussion



Arrhenius type dependence

except values for 1573K because of temporary steam starvation

Discussion

Sieverts´ law:

$$x_H^{metal} = K_S \sqrt{p_{H_2}}$$

$$K_S \sim \exp\left(\frac{-H_s}{RT}\right)$$

$$p_{H_2} = \frac{\dot{n}_H}{2\left(\frac{\dot{n}_H}{2} + \dot{n}_{H_2O} + \dot{n}_{Ar}\right)}$$

$$\dot{n}_H = 2\frac{d\left(K_O^m \sqrt{t}\right)}{dt} = -\frac{K_O^m}{\sqrt{t}}$$

$$K_O^m \sim \exp\left(\frac{-H_o}{RT}\right)$$

$$x_H^{metal} \sim \exp\left(\frac{-(H_s - H_O/2)}{RT}\right)$$

→ $H_O > H_S$

→ The hydrogen source term dominates the process not the Sieverts dependence

Conclusions

- Very fast hydrogen uptake as long as metallic surface exists or the oxide layer thickness is low enough. It explains the findings in the QUENCH-LOCA tests.

- The oxidation rate determines the amount of hydrogen absorbed, not the Sieverts´ law.

- After reaching maximal hydrogen concentrations, hydrogen will be released. The hydrogen concentration decreases according to the model of Veshchunov and Berdyshev with $t^{-1/8}$.

- Breakaway can enhance the hydrogen uptake significantly but only if the oxide is not spalled.

Thanks

We thank all involved in this investigations in particular our students Marius van den Berg and Camille Goulet.

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Thank you for your attention

Do you have questions?

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