Experimental Investigations and Modelling of the Reaction of Zirconium Alloys in Nitrogen/Oxygen or Nitrogen/Steam Atmospheres

KIT / Institute for Applied Materials / Program NUSAFE **M. Grosse, M. Steinbrueck, Y. Maeng, J. Sung**

Outline

- Introduction

- Experiments with contradictory results

- Atomistic description of the process

- Proposed model of the kinetics

- First experimental validations

- Hydrogen uptake during oxidation in steam/nitrogen mixture

- Conclusions and further plans

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).
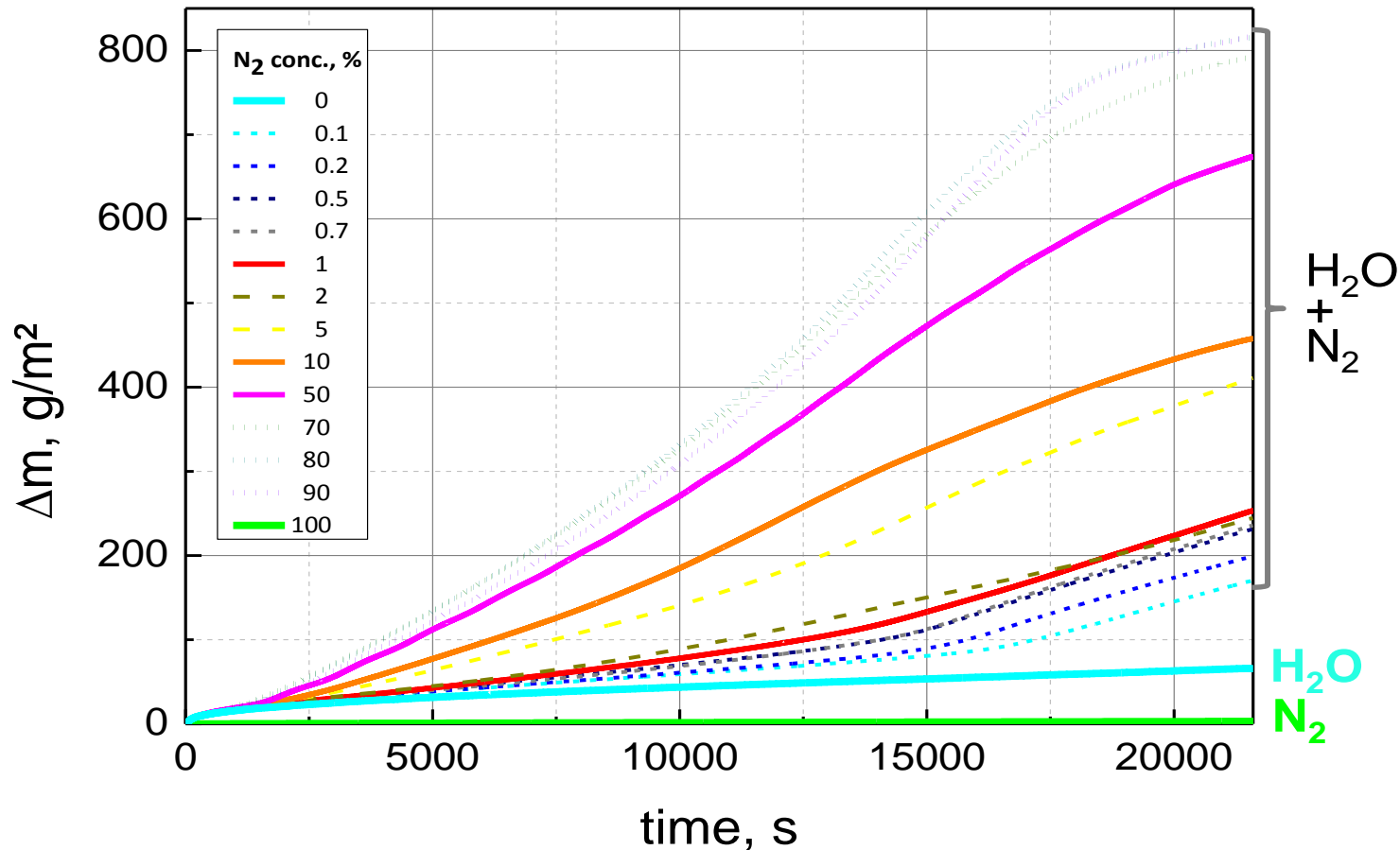
- The reaction

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

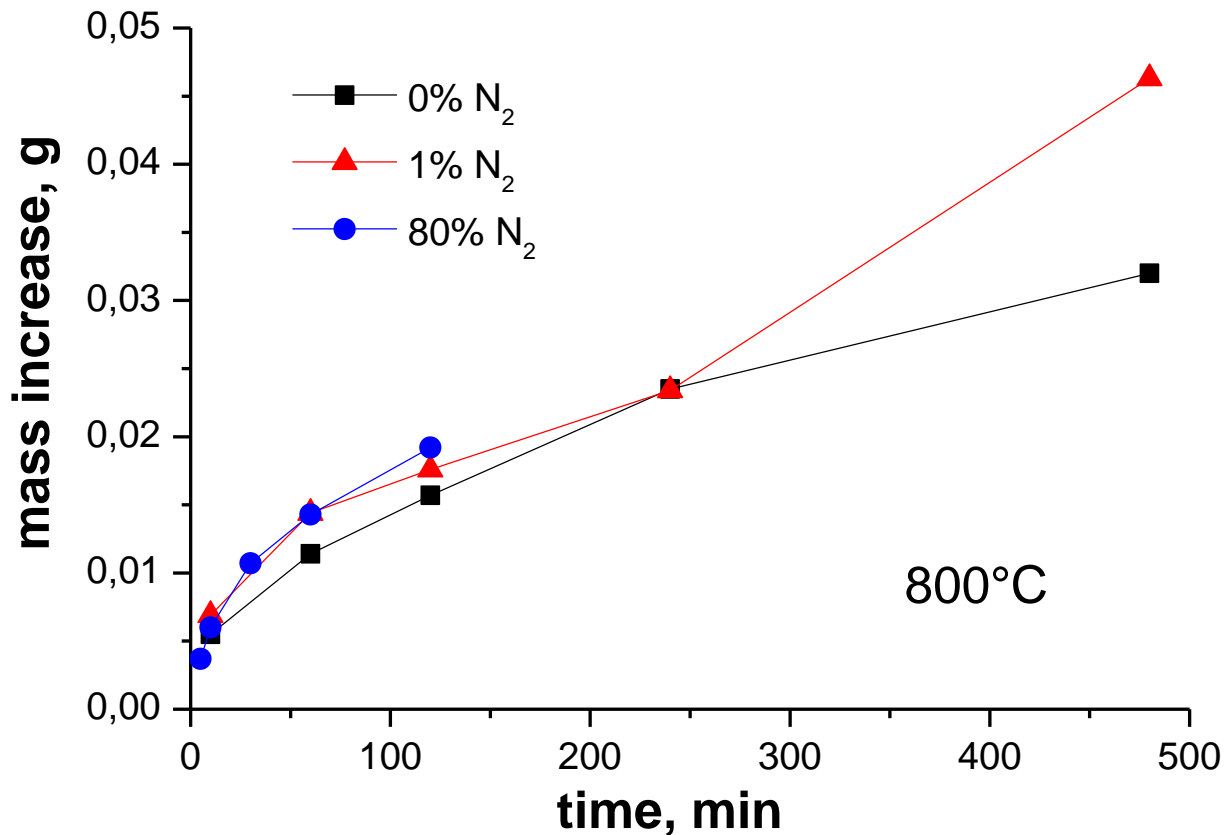 occurs only under oxygen and steam starvation conditions.

- Modelling in severe accident simulation codes is unsatisfying

Experiments with contradictory results

Mass gain of Zircaloy-4 oxidized at 800°C in steam-nitrogen mixtures (annealing in TG)

Experiments with contradictory results

Mass gain of Zircaloy-4 oxidized at 800°C in steam-nitrogen mixtures (annealing in BOX furnace)
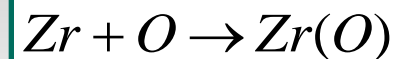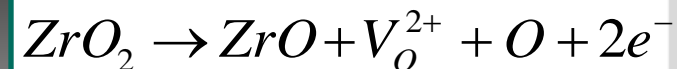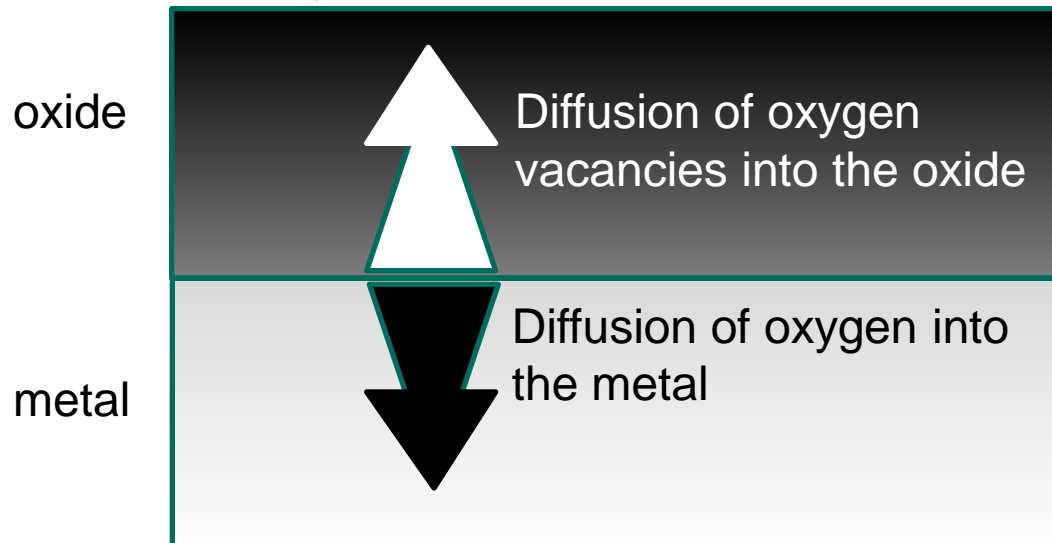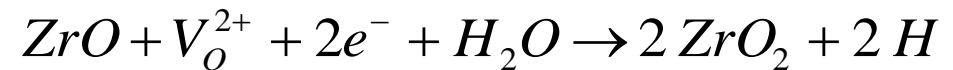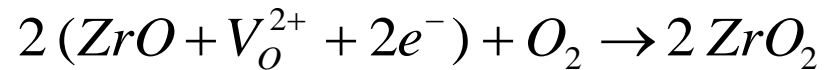
What make the difference?

Main difference between the two furnaces is the gas flow!

Atomistic description
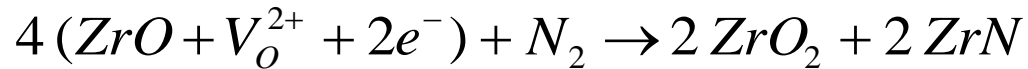
oxygen or steam saturation conditions:

Oxygen or steam transport to the surface

$$2\,(ZrO + V_O^{2+} + 2e^-) + O_2 \rightarrow 2\,ZrO_2$$

$$ZrO + V_O^{2+} + 2e^- + H_2O \rightarrow 2\,ZrO_2 + 2\,H$$

oxide

Diffusion of oxygen vacancies into the oxide

$$ZrO_2 \rightarrow ZrO + V_O^{2+} + O + 2e^-$$

metal

Diffusion of oxygen into the metal

$$Zr + O \rightarrow Zr(O)$$

Wagner (1968)

Atomistic description

Oxygen and steam starvation conditions:

$$4\,(ZrO + V_O^{2+} + 2e^-) + N_2 \rightarrow 2\,ZrO_2 + 2\,ZrN$$

How many oxygen vacancies are available at the surface reaction zone?

How many oxygen vacancies reach this zone per time unit? Do we know it?

YES, we know!

The molar amount of oxygen vacancies is equal the molar amount of oxygen reacted under oxygen saturation conditions.

$$\dot{n}_{V_O^{2+}} = \dot{n}_{ox} = \frac{K_{n_{ox}}}{2\sqrt{t^*}}$$

$$t^* = \left(\frac{K_{D_{oxide}}}{D_{oxide}}\right)^2$$

Oxygen and steam starvation conditions:

$$\dot{n}_{V_O^{2+}}^{remain} = \frac{K_{n_{ox}}}{2\sqrt{t*}} - \left(2\,\dot{n}_{O_2} + \dot{n}_{H_2O}\right) = \frac{\dot{n}_N}{2}\,(reacting)$$

The nitrogen concentration in the oxide is given by:

$$n_N = \int_t \left[1 - \frac{\left(2\,\dot{n}_{O_2} + \dot{n}_{H_2O}\right)}{\dfrac{K_{n_{ox}}}{2\sqrt{t}}}\right] dt + n_{N_0}$$

If a critical nitrogen concentration is reached then zirconium nitride precipitations are formed.
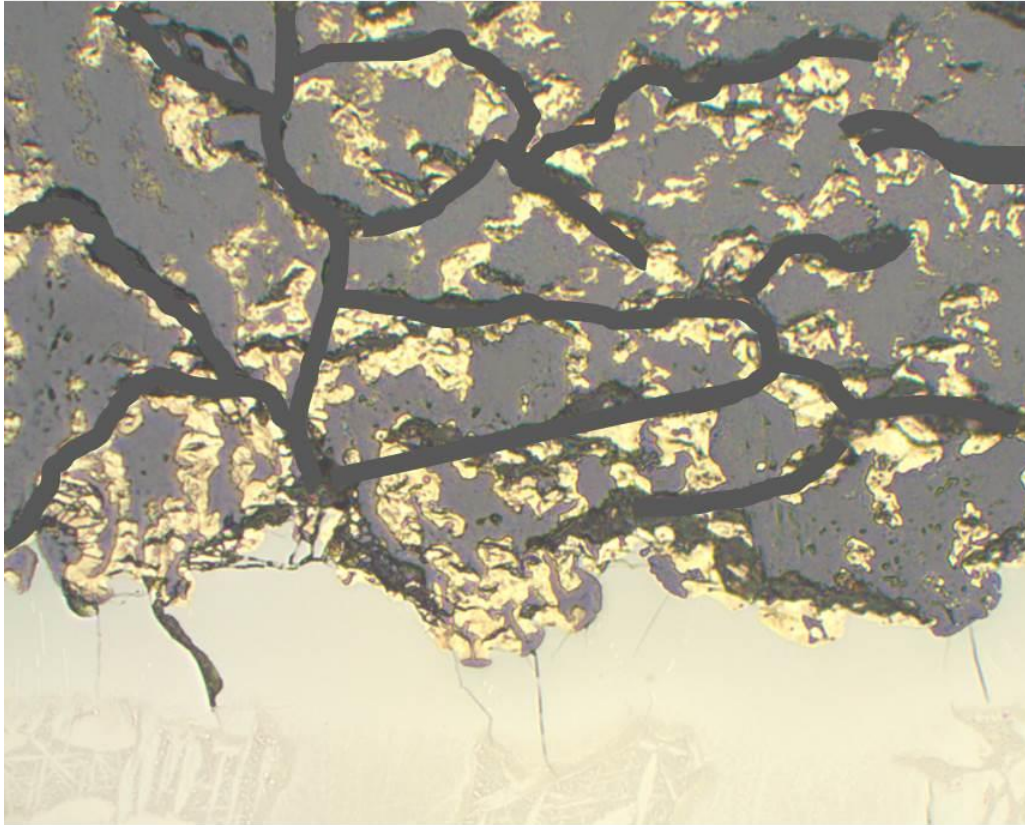
Atomistic description

Why exists a critical nitrogen concentration?

        - formation enthalpy has to be greater than the interface energy

          between nitride and oxide

        - solubility of nitrogen in the oxide (possibly)

If new oxygen becomes available then ZrN is re-oxidized. Zirconium nitride act as an "**oxygen vacancy storage**".

ZrN precipitation is connected with crack formation.

Atomistic description

Cracks are barriers for oxygen vacancy diffusion

Oxygen vacancies will be more or less completely consumed in the outer cells.

→ reoxidation of ZrN

High vacancy concentration in the cells between metal/oxide interface and first crack parallel (= reaction zone) to this interface.

→ enhanced ZrN formation

Nitrides in the oxide layer at Zry-4 (1100°C, 40min, 20% steam + 80% nitrogen
Placement work of Laetitia Ott

Experiments with contradictory results
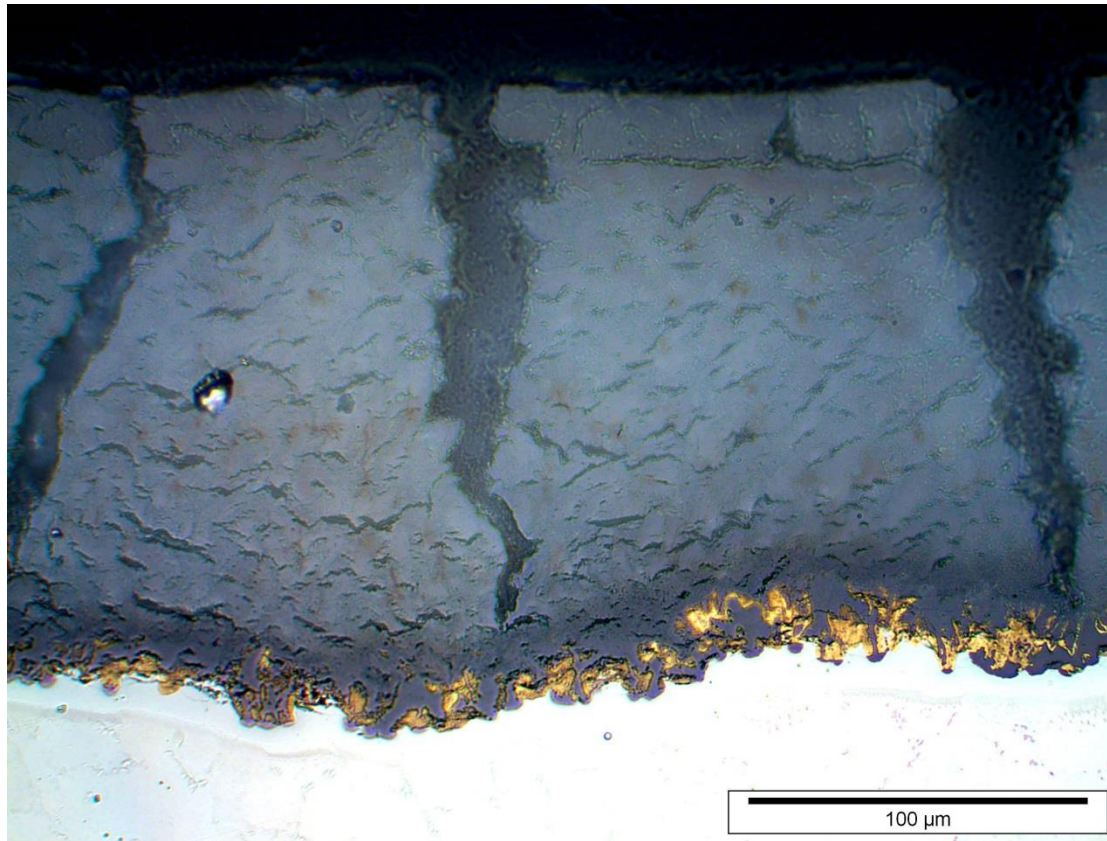
Metallographic image of the nitride containing layer at the metal/oxide interface (oxidation in air at 850°C, air and argon flow rates are 12 l/h and 4 l/h, respectively). Placement work of Yunhwan Maeng

Atomistic description

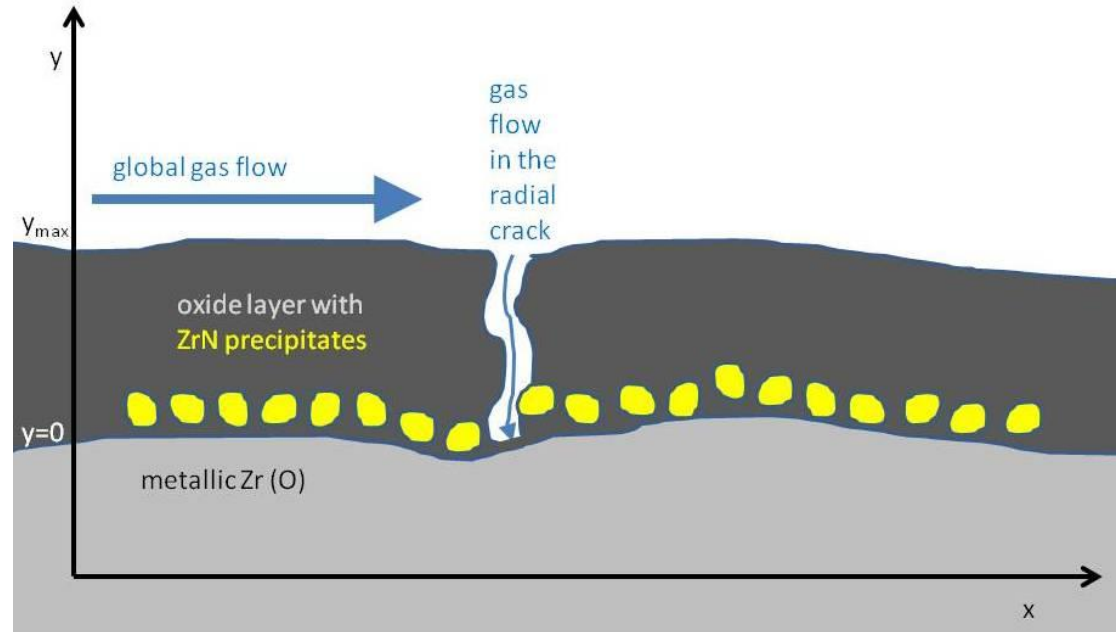**2 cases for the spatial extension of the starvation:**

global (the whole sample surface) or
local (e.g. in cracks)

2 cases for the general degree of the starvation:

partial (only oxygen and steam starvation + nitrogen saturation) or
total (oxygen and steam starvation + nitrogen starvation)

Atomistic description

Air oxidation: 2 cases of starvation conditions in cracks:

Case I: Complete starvation (both, O_2 and N_2 are consumed completely)
- Consumption of O_2 and N_2 in the reaction zone results in a total pressure drop in the crack. To compensate it, the same amount of air as it was consumed has to be sucked into the crack.

→ **The reaction rate is completely independent of the oxide layer thickness as well as of shape, length and cross section of the crack.**

→ **It depends on the oxygen + nitrogen flux**

Atomistic description

Air oxidation: 2 cases of starvation conditions in cracks:
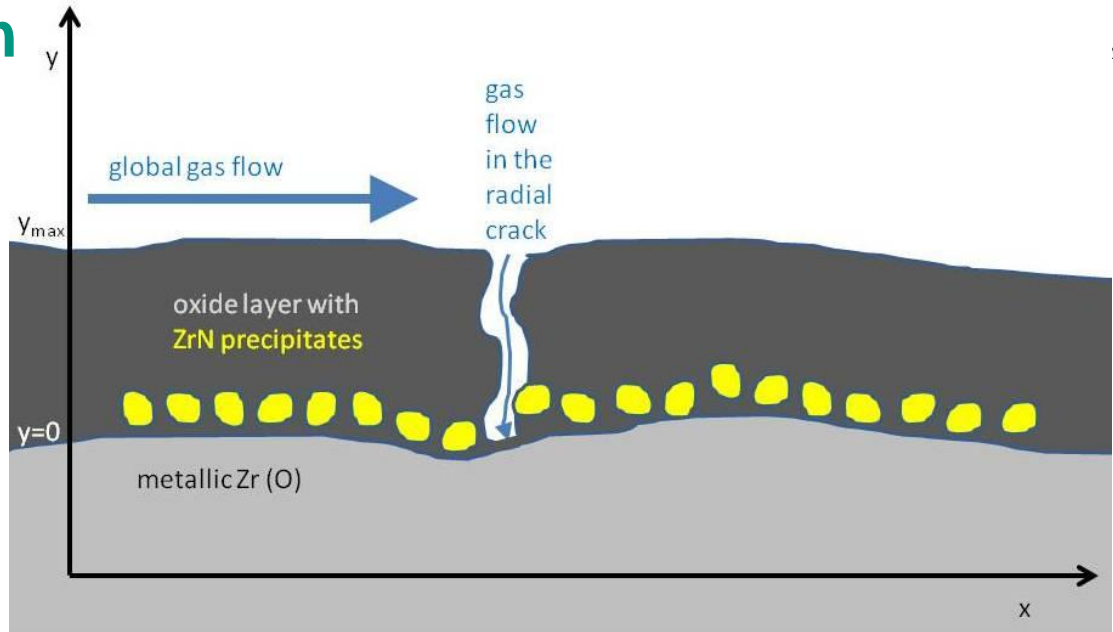
Case II: O_2 starvation but N_2 saturation (similar valid for steam/nitrogen oxidation)
- Enrichment of N_2 in the crack, Oxygen has to diffuse through the nitrogen to the reaction zone. The same happens if other gases are in the mixture (H_2, Ar). However, the gas diffusion rate is high and the deceleration of the process weak.

→ **The reaction rate slightly depends on the oxide layer thickness, shape, length and cross section of the crack.**
→ **It depend s on the oxygen flux but not on the nitrogen flux**

Proposed simplified model of the kinetics

From the atomistic description of the process the following can be concluded: The deviation from the parabolic reaction kinetics occurs if a critical nitrogen concentration in the oxide is reached.

$$n_{N=} \begin{cases} \displaystyle\int_{t=0}^{t_1} \frac{\dfrac{K_{n_{ox}}}{2\sqrt{t*}} - \left(2\,\dot{n}_{O_2} + \dot{n}_{H_2O}\right)}{2}\, dt & (for\ N_2\ saturation) \\[4ex] \displaystyle\int_{t=0}^{t_1} \frac{\dot{n}_{N_2}}{2}\, dt & (for\ N_2\ starvation) \end{cases} > n_N^{critical}$$

Consequences: In the case of N saturation, the smaller the O_2 flow rate, the earlier is the nitride formation and with it the transition of the kinetics. Otherwise it increases with the N_2 flow rate.

On the basis that the size of the nitrides does not depend on the nitrogen concentration, their number N_{ZrN} is linearly proportional to the amount of absorbed nitrogen.

Proposed simplified model of the kinetics

- The number of cracks N_{cracks} in the oxide formed due to the ZrN precipitation is linear proportional to the number of nitrides and with it its interface fraction.

$$IF_{cracks} = A \cdot n_N$$

- The reaction rate in the cracks is exactly or nearly constant depending on the starvation conditions.

$$\dot{n}_{crack} = const.$$

Proposed simplified model of the kinetics

- The effective reaction rate is the sum of the reactions via the cracks and via a more or less undamaged oxide layer weighted by their interface fractions IF_{cracks} and $(1 - IF_{cracks})$, respectively:

$$\dot{n}_{effective} = \dot{n}_{cracks} \cdot IF_{cracks} + \dot{n}_{parabolic} \cdot \left(1 - IF_{cracks}\right)$$

with

$$IF_{cracks} = \begin{cases} A\left(\int_t \frac{\dot{n}_{N_2}}{2} \, dt\right) - n_N^{critical} & (for\ N_2\ starvation) \\ A\left(\int_t \dot{n}_{effective} - 2\,\dot{n}_{O_2} - \dot{n}_{H_2O} \, dt\right) - n_N^{critical} & (for\ N_2\ saturation) \end{cases}$$

Consequences: in the case of only partial starvation, the smaller the oxygen flux, the higher the reaction rate because $\dot{n}_{cracks} > \dot{n}_{parabolic}$.

In the case of total starvation only the O_2 + N_2 gas flows determine the reaction rate. Therefore, the reaction rate is proportional to the O_2 + N_2 gas flow.

First experimental validations

$$\dot{n}_{H_2O} : \dot{n}_{N_2} : \dot{n}_{Ar} = const.$$
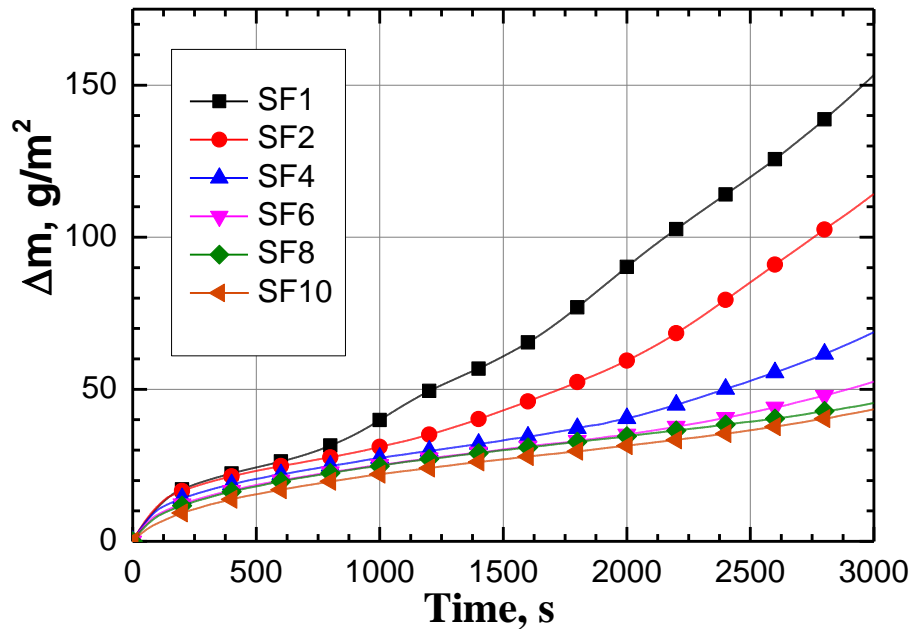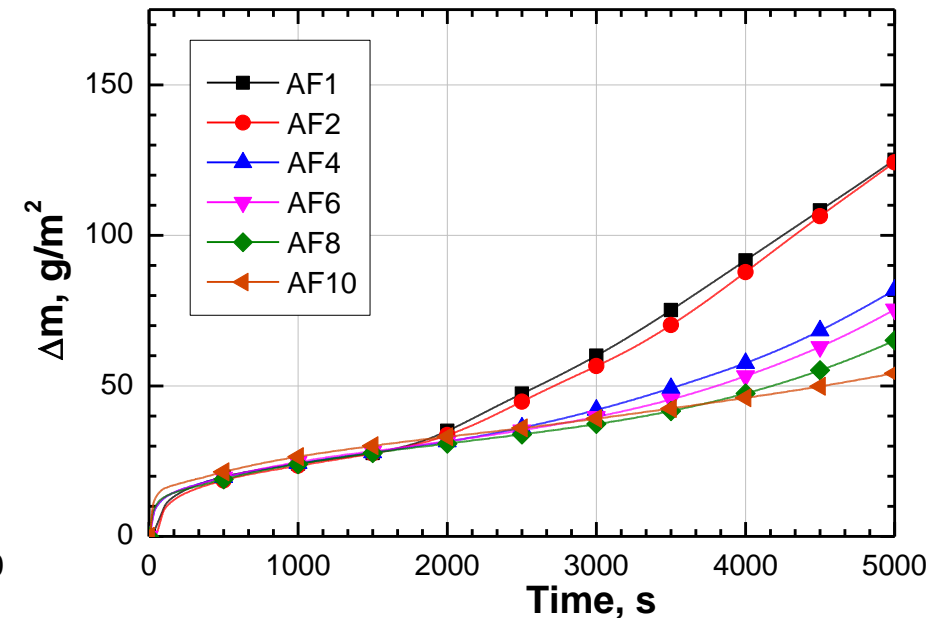
850°C

in steam /nitrogen

in air

Experimental validation

$$\dot{n}_{O_2} : \dot{n}_{N_2} : \dot{n}_{Ar} = const.$$
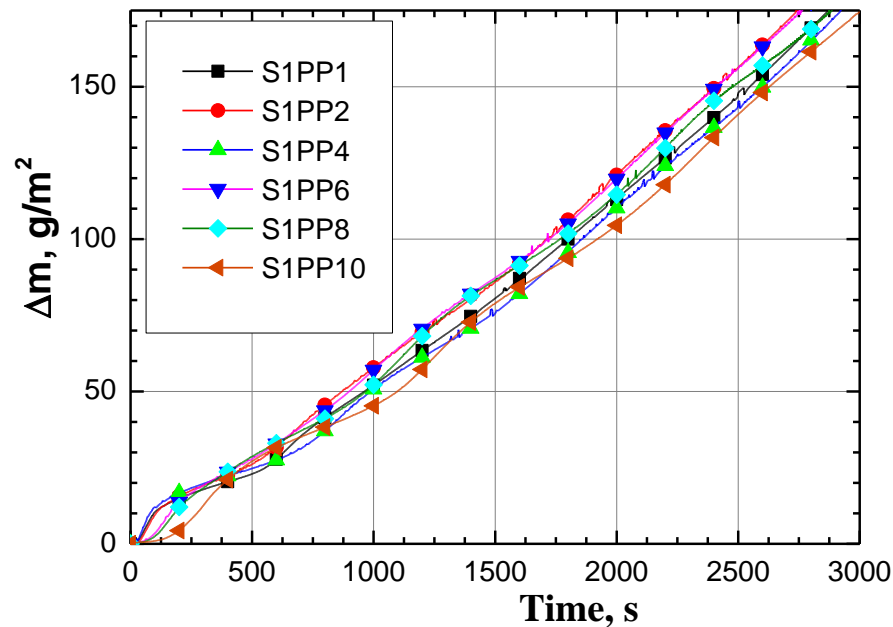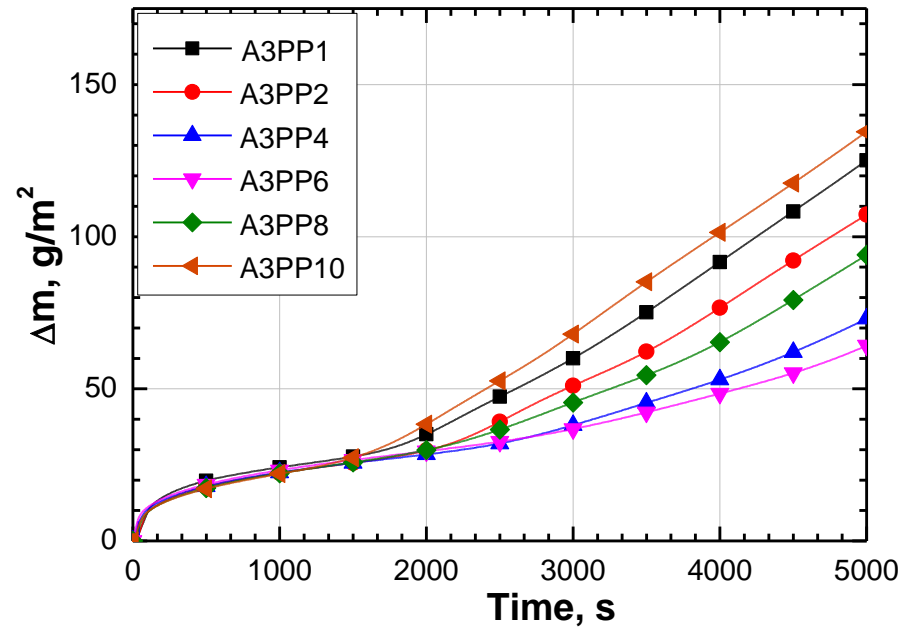

1100°C

in steam /nitrogen

in air

Experimental validation

$$\dot{n}_{O_2}, \dot{n}_{N_2} = const., \dot{n}_{Ar} \; changed$$

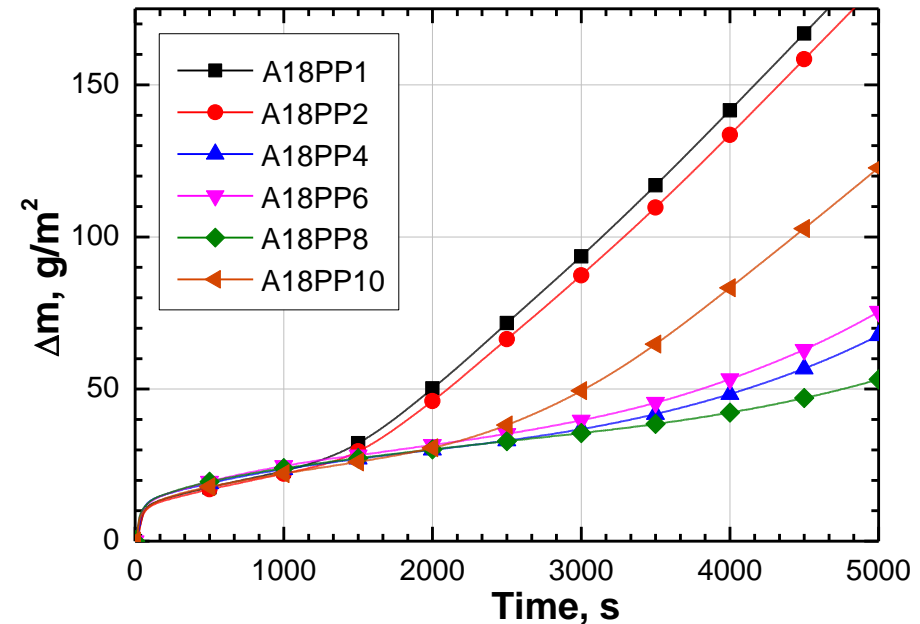850°C, low gas flux

in steam /nitrogen   in air
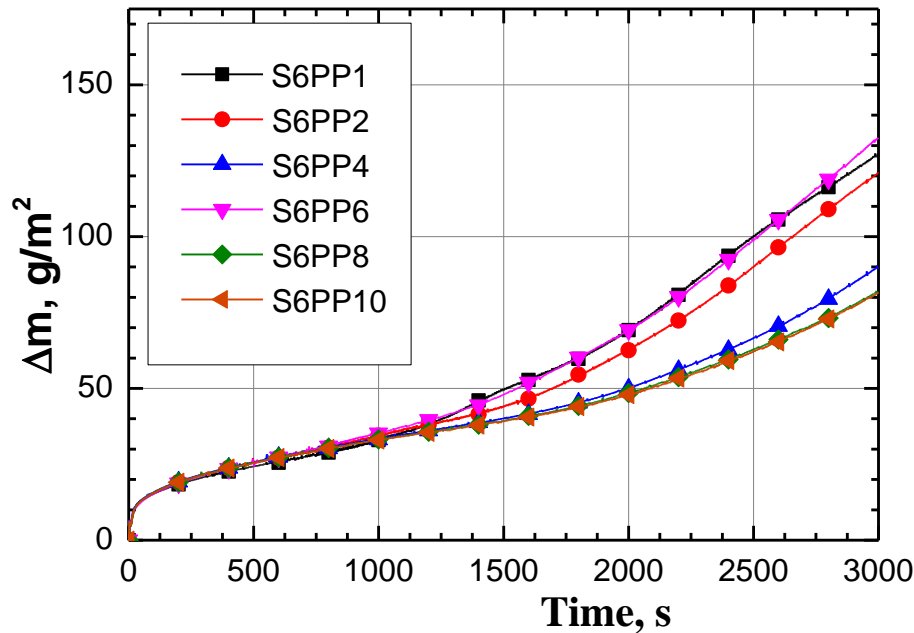
Experimental validation

$$\dot{n}_{O_2}, \dot{n}_{N_2} = const., \dot{n}_{Ar} \; changed$$
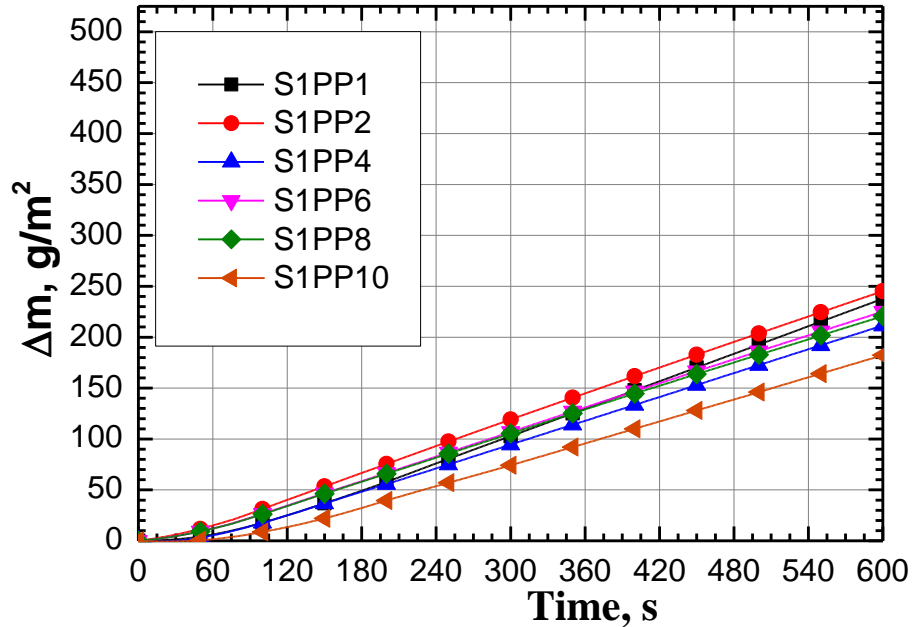
850°C, high gas flux
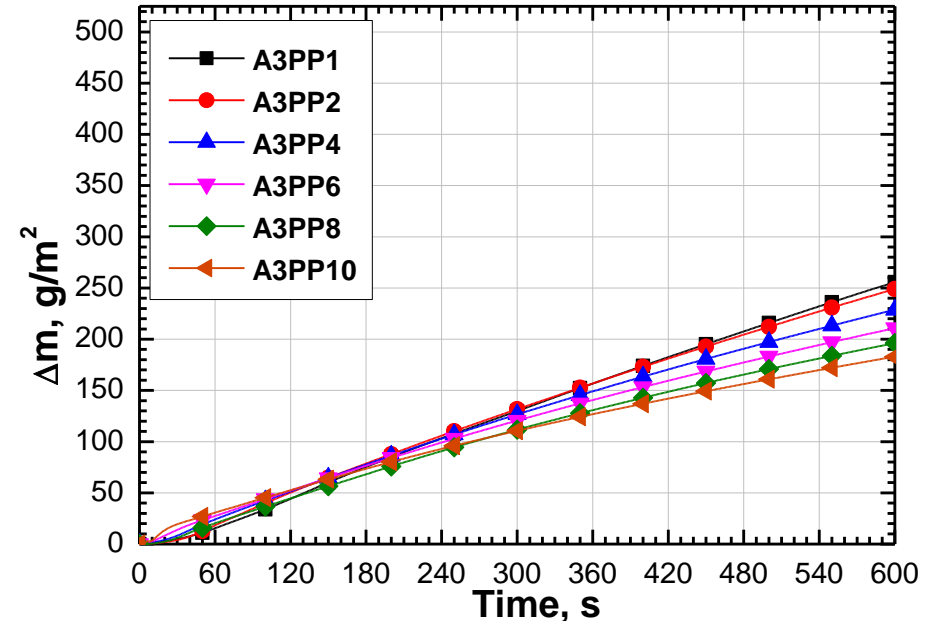
in steam /nitrogen   in air

$$\dot{n}_{O_2}, \dot{n}_{N_2} = const., \dot{n}_{Ar} \ changed$$

1100°C, low gas flux

in steam /nitrogen

in air

$$\dot{n}_{O_2}, \dot{n}_{N_2} = const., \dot{n}_{Ar} \ changed$$

1100°C, high gas flux

in steam /nitrogen

in air

Hydrogen uptake during oxidation in steam/nitrogen mixture

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

Mirco Grosse et al   Pohang (Rep. Korea), July 22, 2016 Mirco Grosse et al.   Institute for Applied Materials

Program NUSAFE
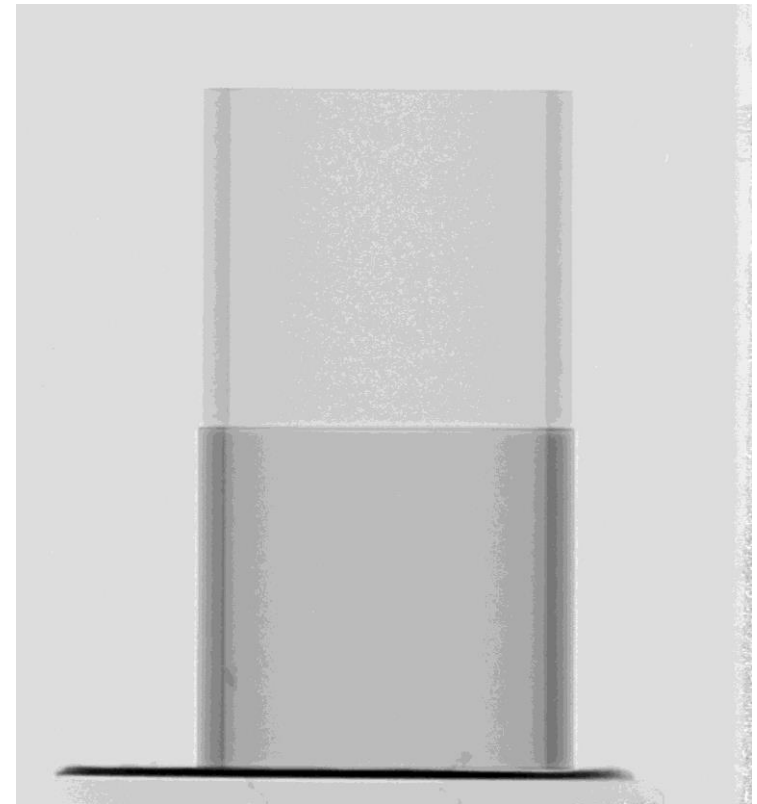
Hydrogen uptake during oxidation in steam/nitrogen mixture

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)

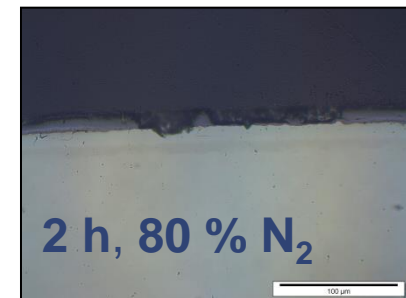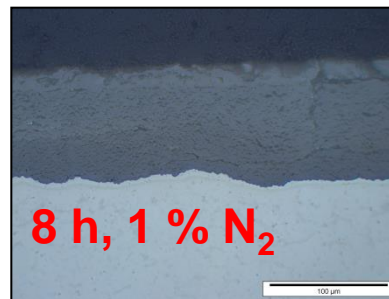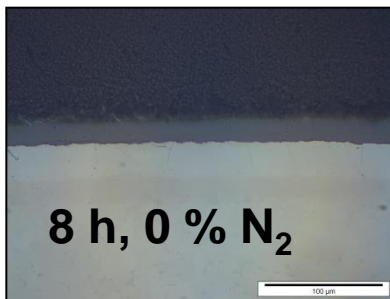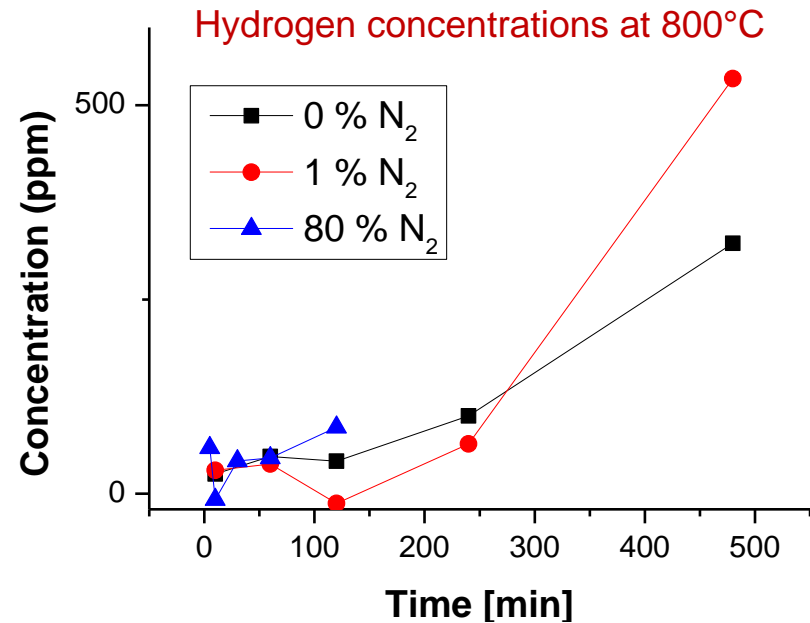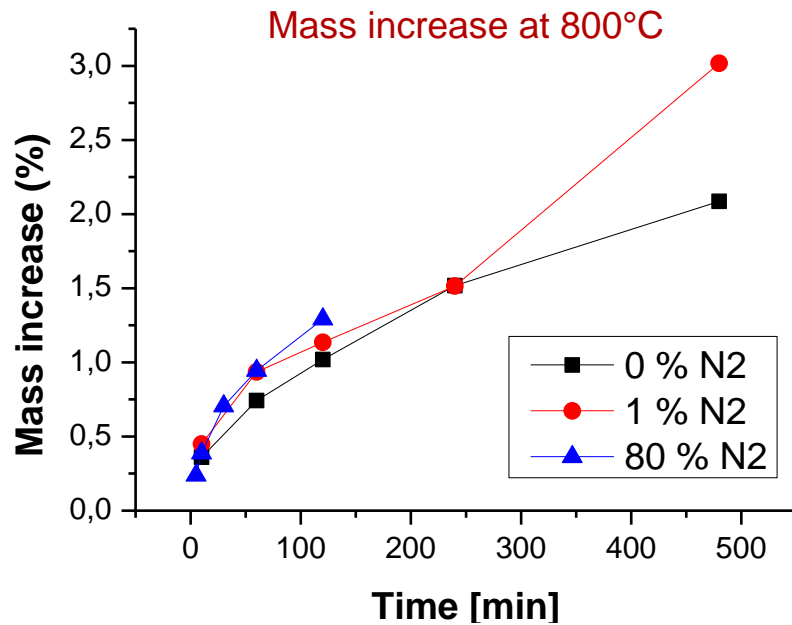**Correction of the effect of nitrogen:**

Using the samples annealed in synthetic air:

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

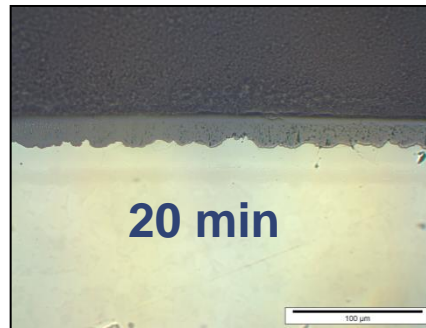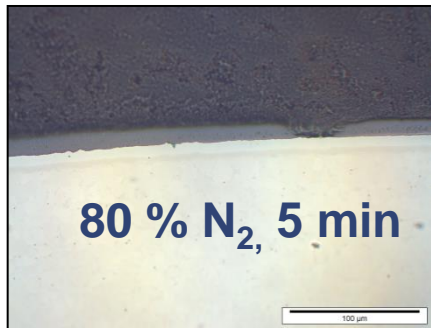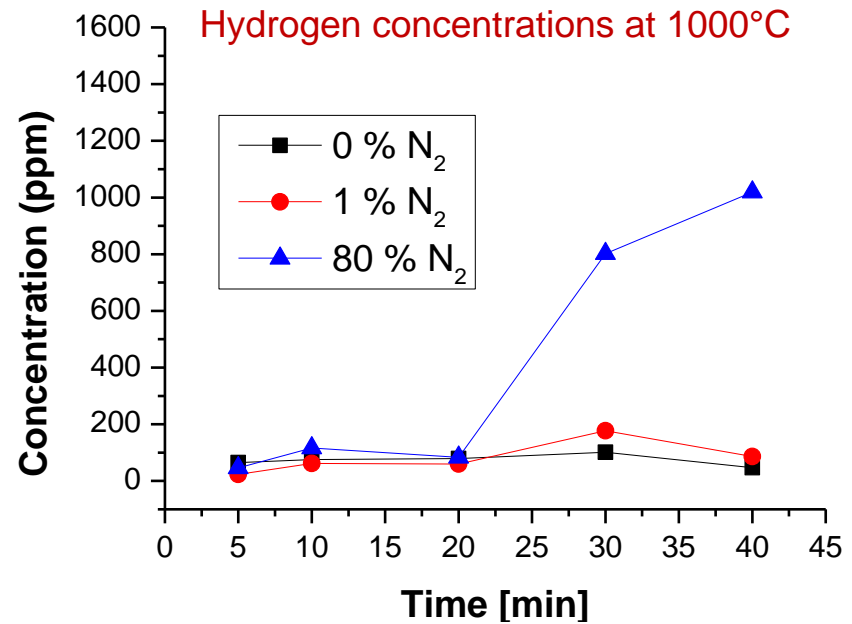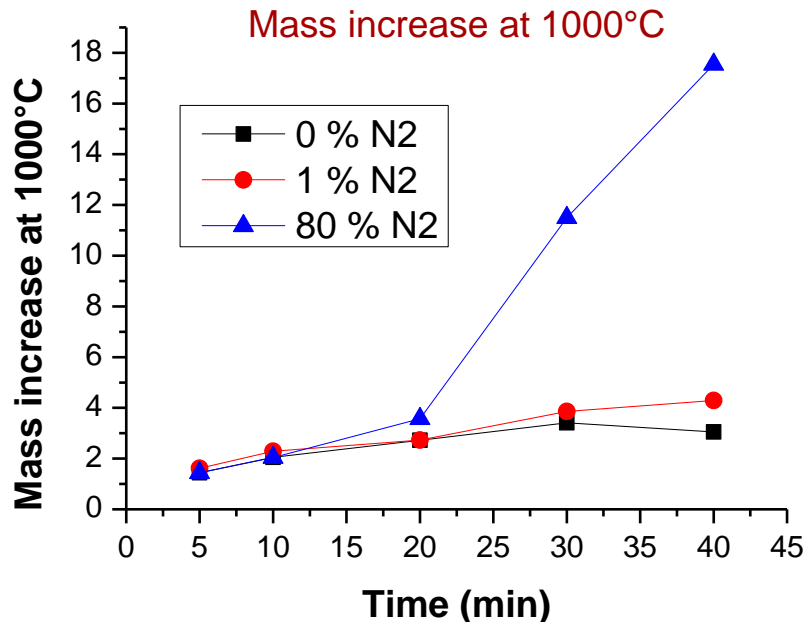$\overline{\delta_{ZrN}}$ mean thickness of the nitride containing layer

Hydrogen uptake during oxidation in steam/nitrogen mixture

Mass increase at 800°C

Hydrogen concentrations at 800°C

8 h, 0 % N$_2$

8 h, 1 % N$_2$

2 h, 80 % N$_2$

Hydrogen uptake during oxidation in steam/nitrogen mixture

Mass increase at 1000°C

Hydrogen concentrations at 1000°C

80 % N₂, 5 min

20 min

40 min

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Pohang (Rep. Korea), July 22, 2016

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Hydrogen uptake during oxidation in steam/nitrogen mixture

Mass increase at 1100°C

Hydrogen concentrations at 1100°C

40 min, 0 % N_2

1 % N_2
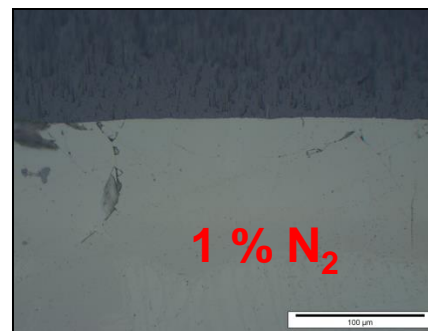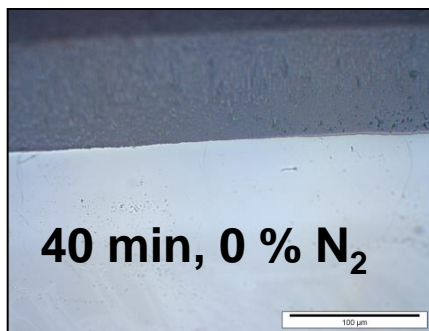
80 % N_2
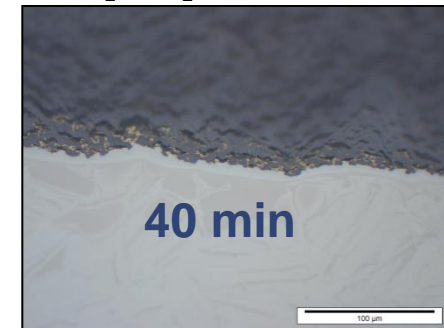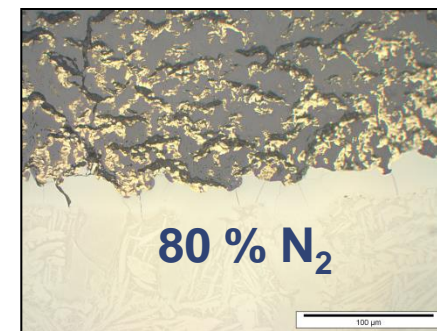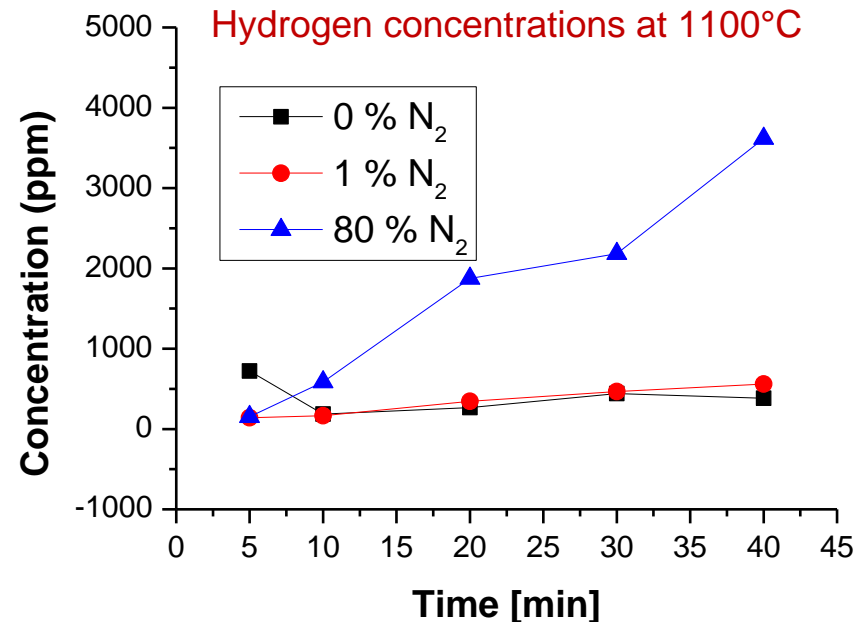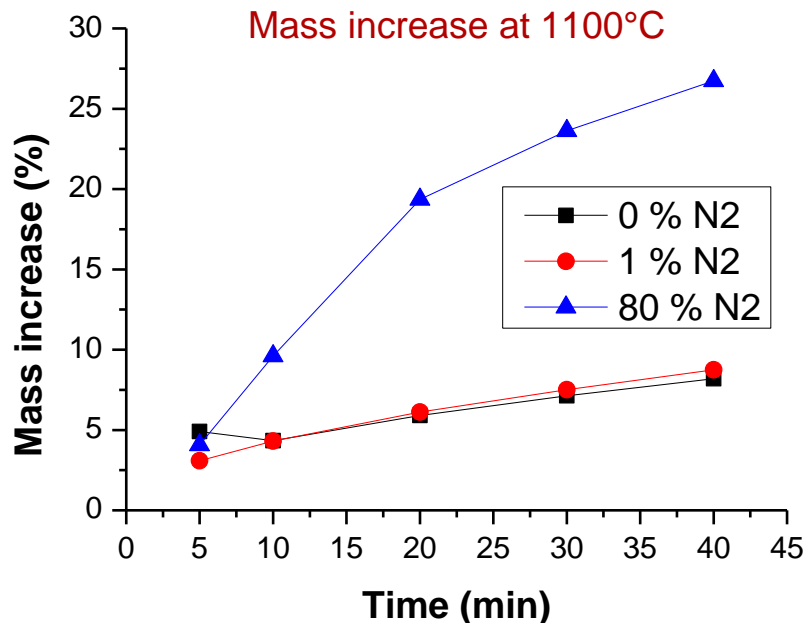
Hydrogen uptake during oxidation in steam/nitrogen mixture
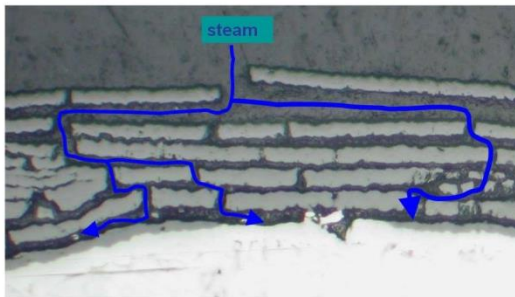
a)
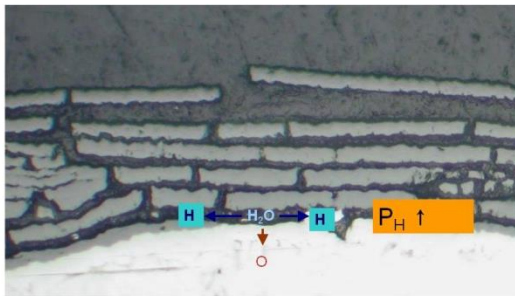
b)
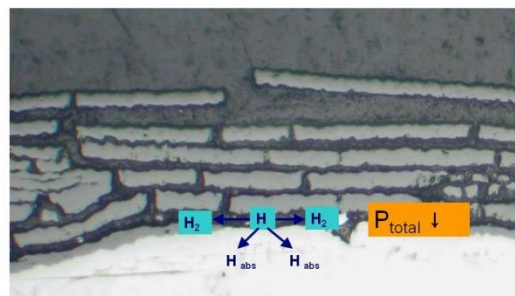
c)

"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 Conclusions

- The reaction of zirconium in air and/or steam/nitrogen mixtures depends strongly on the quantitative amount of oxygen and steam starvation.

- 2 times 2 cases can be divided:
  - by spatial extension: **global** or **local** starvation
  - by general degree of starvation: **partial** or **total**

- Partial starvation: The lower the oxygen flow rate, the earlier is the parabolic to linear kinetics transition and the higher is the reaction rate.

- Total starvation: The higher the oxygen + nitrogen flow rates, the higher is the reaction rate.

Summary and Conclusions

- In the model proposed three fitting parameters have to be determined:
  - The critical nitrogen concentration $n_N^{critical}$ at which ZrN precipitation starts
  - The constant reaction rate in the reaction zone at the crack tip $\dot{n}_{cracks}$
  - The coefficient A connecting nitrogen concentration and interface fraction of the cracks

- Influence of oxygen partial pressure:

  Investigation by varying of the argon flow while the oxygen or steam flow was kept constant.

  Result: No clear influence of the reaction kinetics on the oxygen partial pressure.

- The hydrogen uptake is enhanced by the crack formation. It shows a similar behaviour like the mass gain.

Thanks

I thank all involved in this investigations in particular our students Fabio da Silva and Laetitia Ott. The results of their placement works improve our understanding of the parameters influencing the reaction kinetics.

Thanks to all colleagues in particular Sanggil Park for the fruitful discussions of the mechanisms of the reactions of zirconium with air and steam/nitrogen mixture.

Thank you for your attention

Do you have questions?

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www.kit.edu

Proposed simplified model of the kinetics

$$IF_{cracks} = A \int_t \dot{n}_{effective} - \frac{\dot{n}_{O_2}}{2} - \dot{n}_{H_2O} \, dt - n_N^{critical} \quad \text{is recursive because}$$

$\dot{n}_{effective}$ depends on IF_{racks}. It can be calculated numerically *by:*

$$IF_{cracks}(i) = A \left[\sum_i \left(1 - \frac{\dfrac{\dot{n}_{O_2}(i)}{2} + \dot{n}_{H_2O}(i)}{IF_{cracks}(i-1)\,\dot{n}_{crack} + (1 - IF_{cracks}(i-1)) \dfrac{K_{n_{ox}}}{2\sqrt{t*(i)}}} \Delta t \right) - n_N^{critical} \right]$$