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# Progress Report on the Development of a nitriding model

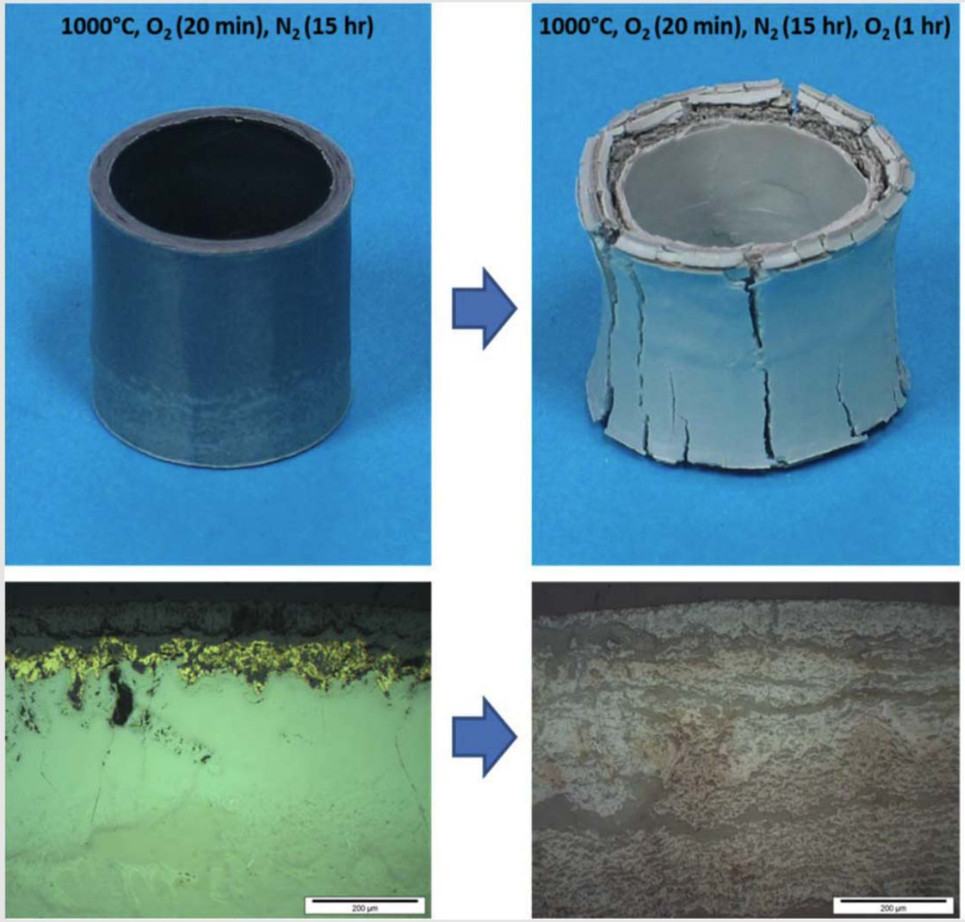
EMUG Meeting, April 6th+7th, 2017, Madrid, Spain

# Content

# Introduction

**The influence of Nitrogen in the air-oxidation of zircaloy based cladding materials has been known since a long time.**

**A period of nitriding leads to a macro cracked oxide scale after reoxidation.**



# Introduction

**First strong evidence, that Nitrogen is not only a catalyst for the cladding degradation by oxidation, but also an important reaction partner was found from the off gas analysis in the Sandia Fuel Project phase 2.**

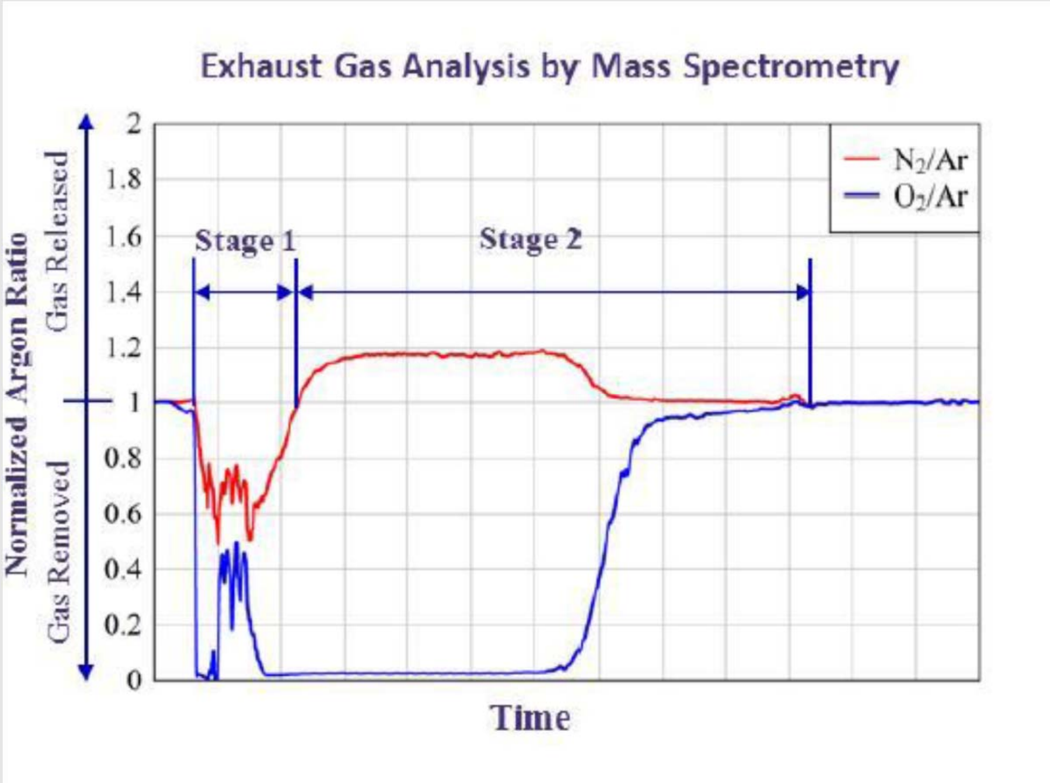



Figure from SFP final seminar 2013, Paris

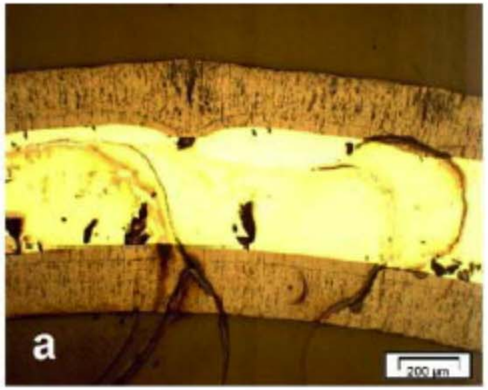
# Introduction

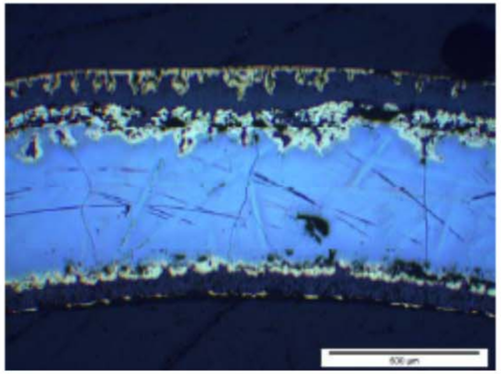
Three experimental phases were selected to investigate the dependency of the reaction parameters on different controled conditions for oxidation and nitriding.

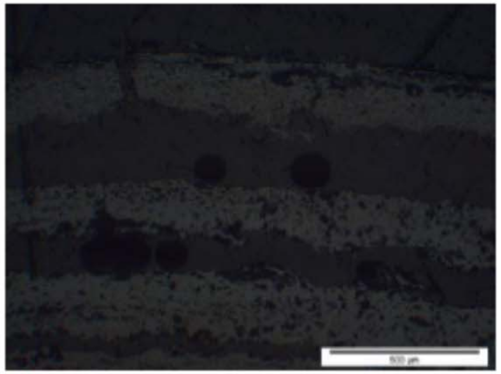
In the first phase a pre oxidation is selected to produce an oxide layer with different thickness (pre breakaway and post breakaway).

The second phase is the nitriding of the pre oxidized sample with different duration to check for the nitriding mechanism.

The final phase includes a reoxidation of the sample to investigate the reaction rates after nitriding.





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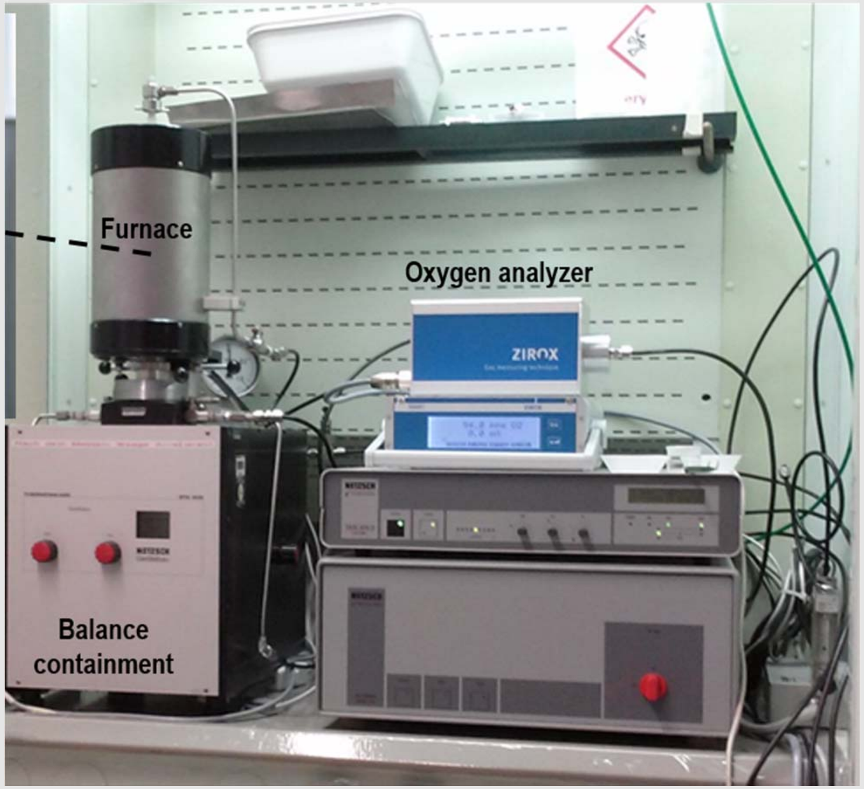
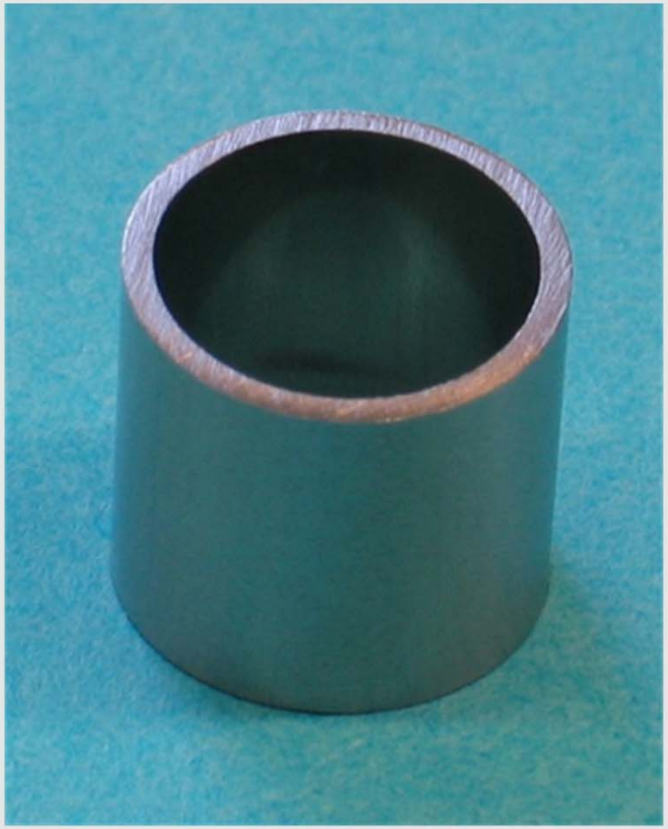
# Experimental Conditions

**Two different thermal balance systems were used to perform the experiments at KIT, Germany: Netzsch STA-409 and Setaram TAG.**




# Experimental Conditions

**The specimen are slightly different for the two facilities.**



Specimen for Netzsch STA-409

Specimen for Setaram TAG

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# Experimental Conditions

## Experimental Test Matrix for Netzsch STA-409

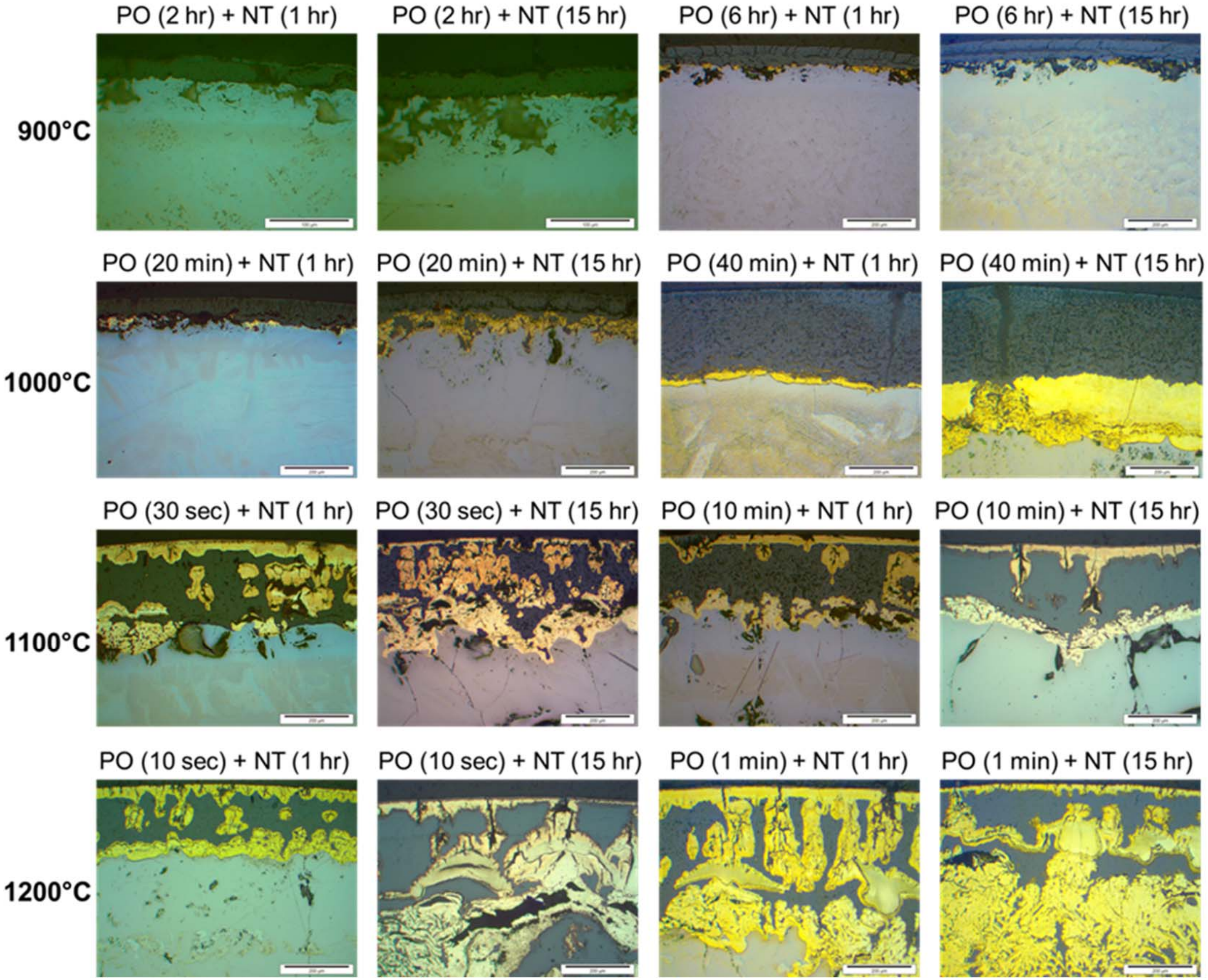
| Temperature | Pre-Oxidation | Nitriding | Re-Oxidation |
|---|---|---|---|
| 900°C | 2 h, 6 h | 1 h, 15 h | no, 2 h |
| 1000°C | 20 min, 40 min | 1 h, 15 h | no, 1 h |
| 1100°C | 30 s, 10 min | 1 h, 15 h | no, 20 min |
| 1200°C | 10 s, 1 min | 1 h, 15 h | no, 10 min |

**Setaram TAG: (1000°C and 1100°C) additional nitriding (0.5 h, 3 h, 6 h)**

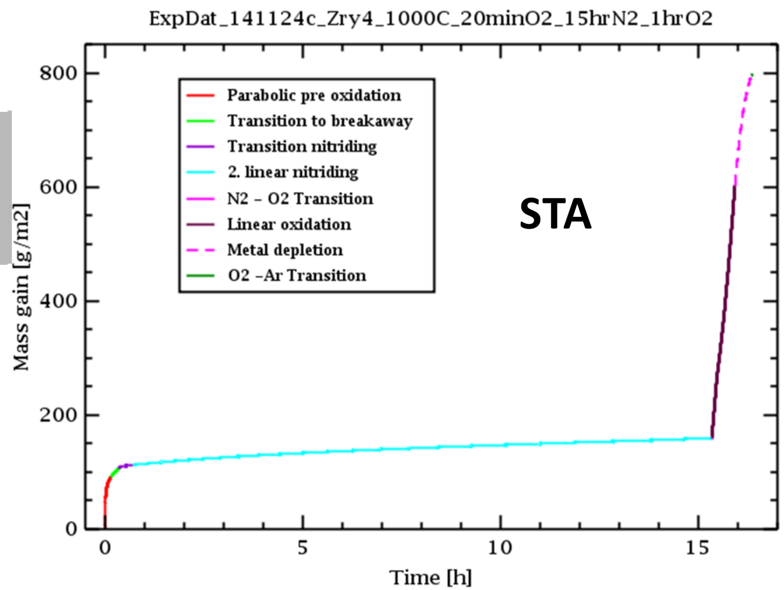
**Inclusive repetition experiments 75 tests were performed and analysed**

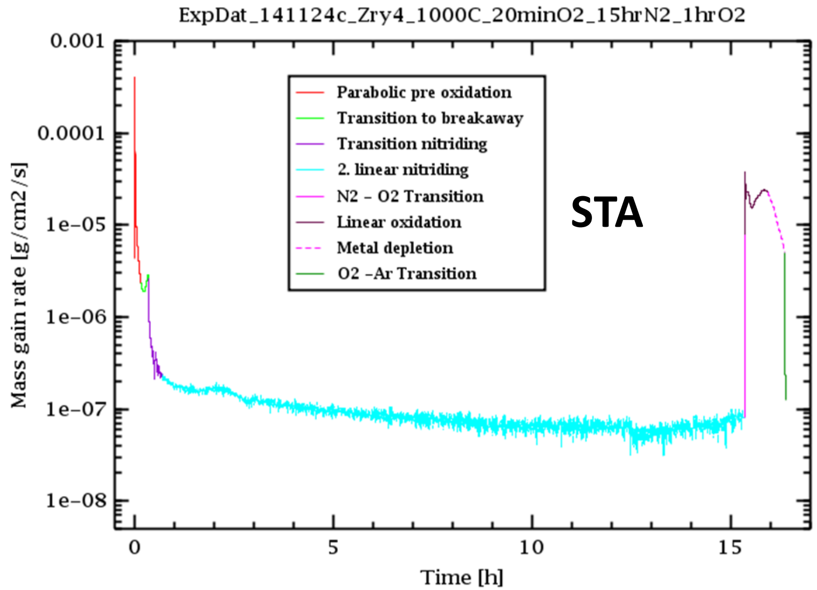
# Content

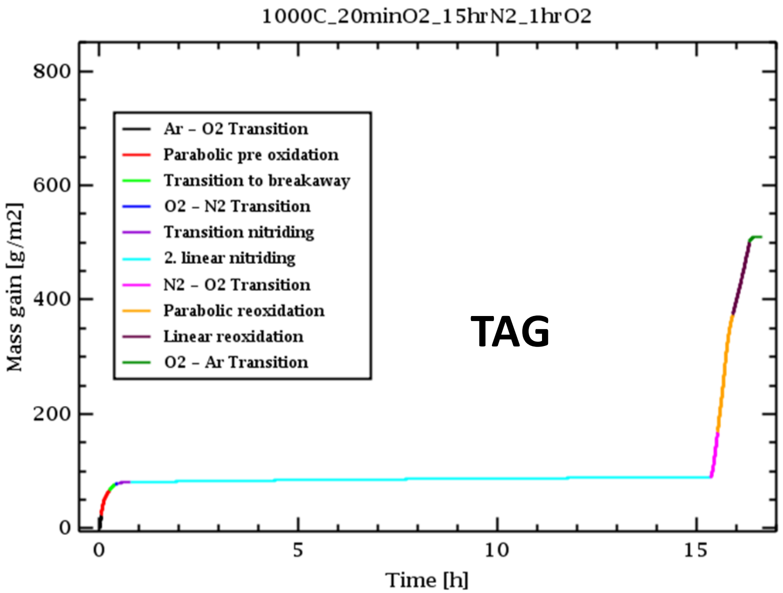
# Experimental data

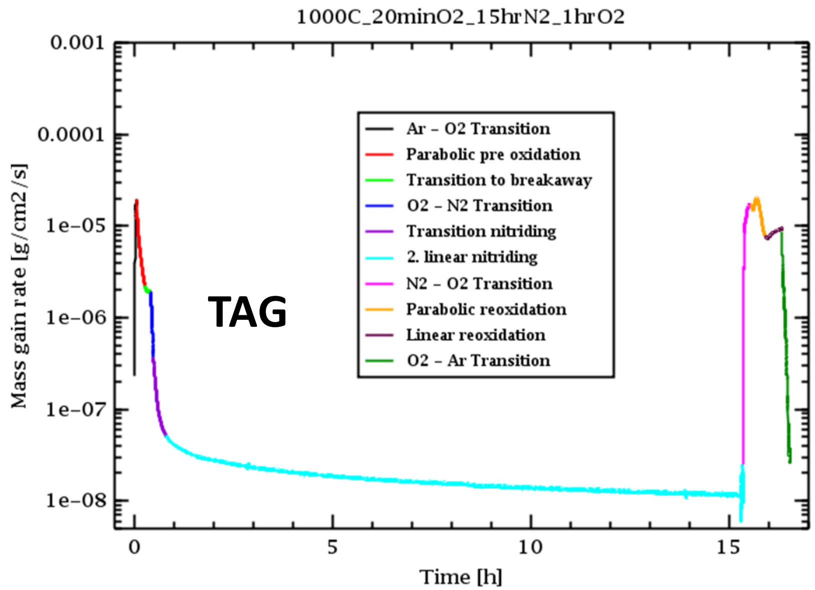


# Experimental data



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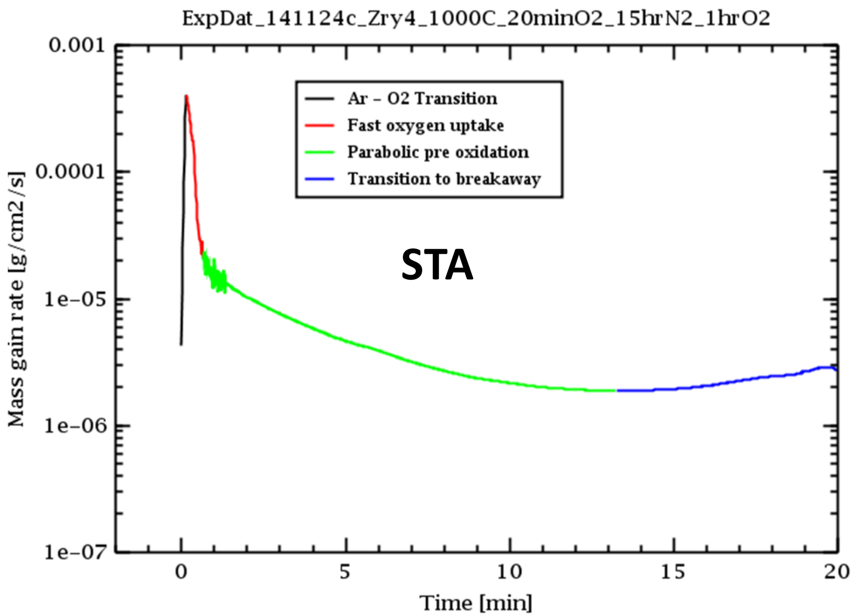
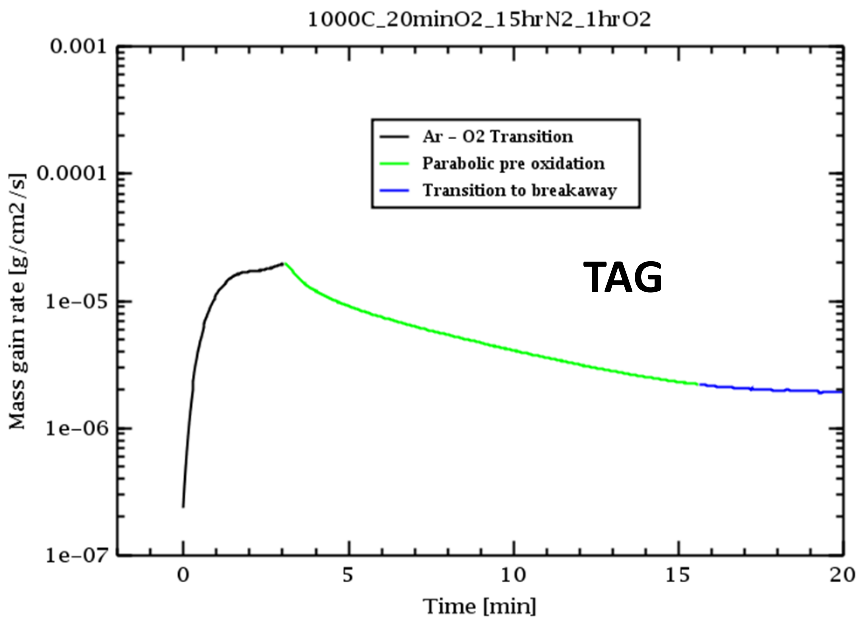
# Experimental phases

16 phases could be identified in the experiments
(some may be covered in some experiments):

1: Gas phase transition from Ar to $O_2$
2: Fast oxygen uptake of zirconium
3: Parabolic pre oxidation

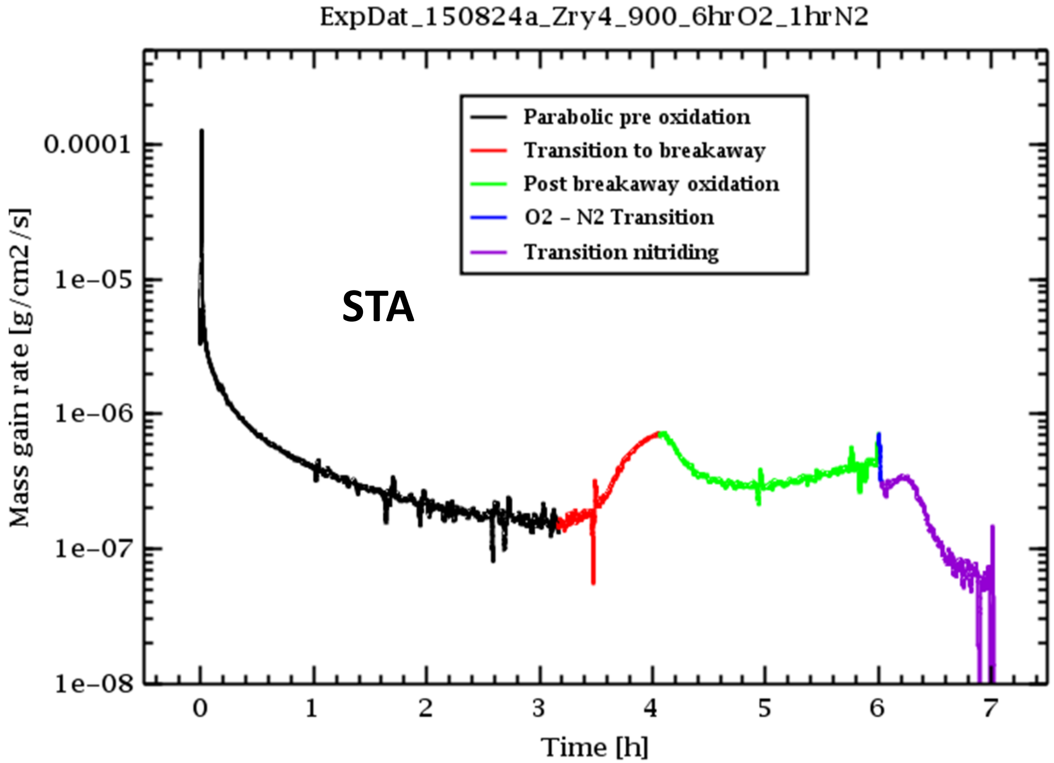


# Experimental phases

16 phases could be identified in the experiments
(some may be covered in some experiments):

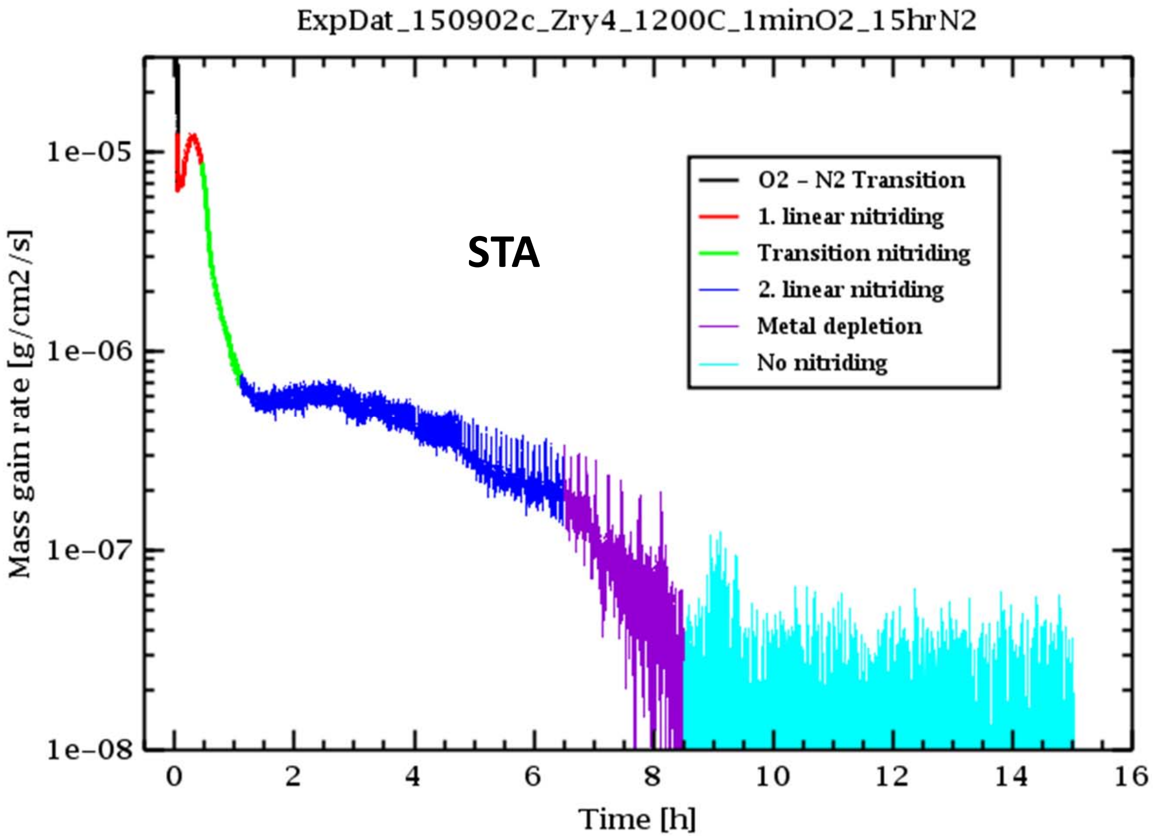
4: Transition to breakaway
5: Post breakaway oxidation
6: Gas phase transition from $O_2$ to $N_2$



# Experimental phases

16 phases could be identified in the experiments
(some may be covered in some experiments):

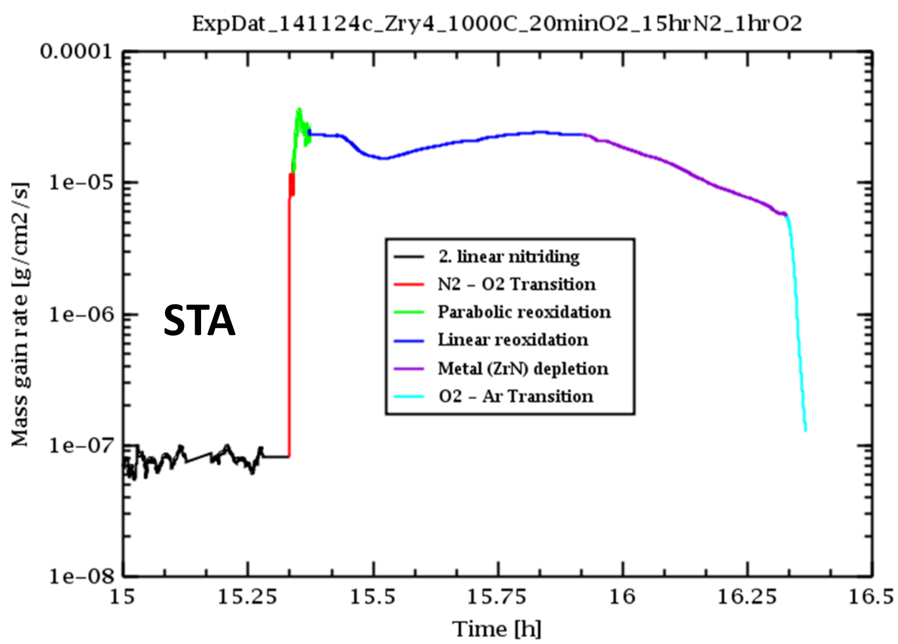
7: 1. linear nitriding
8: Transition nitriding
9: 2. linear nitriding
10: Metal depletion
11: No nitriding

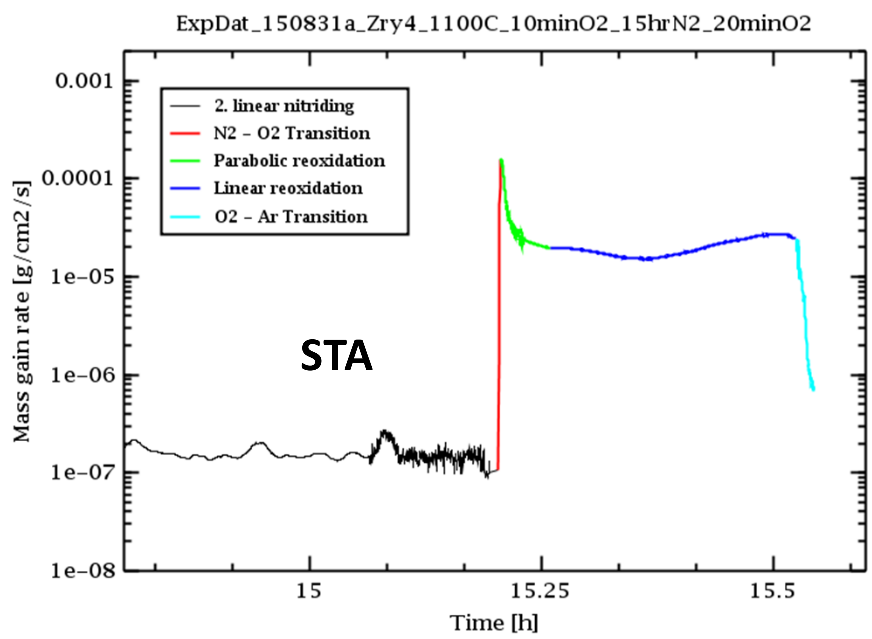


# Experimental phases

16 phases could be identified in the experiments
(some may be covered in some experiments):

12: N2 – O2 Transition
13: Parabolic reoxidation
14: Linear reoxidation
15: Metal (ZrN) depletion
16: O2 – Ar Transition



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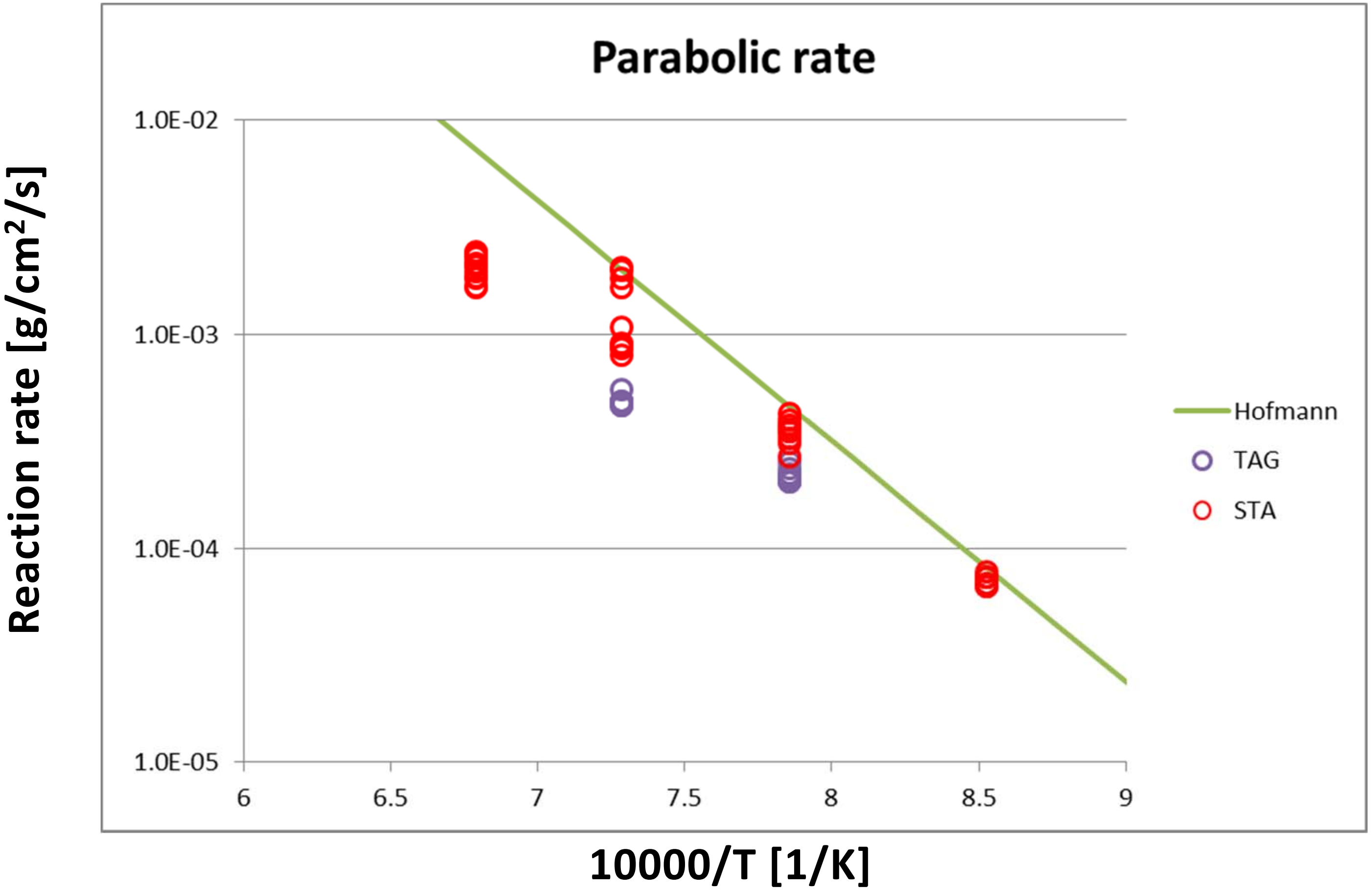
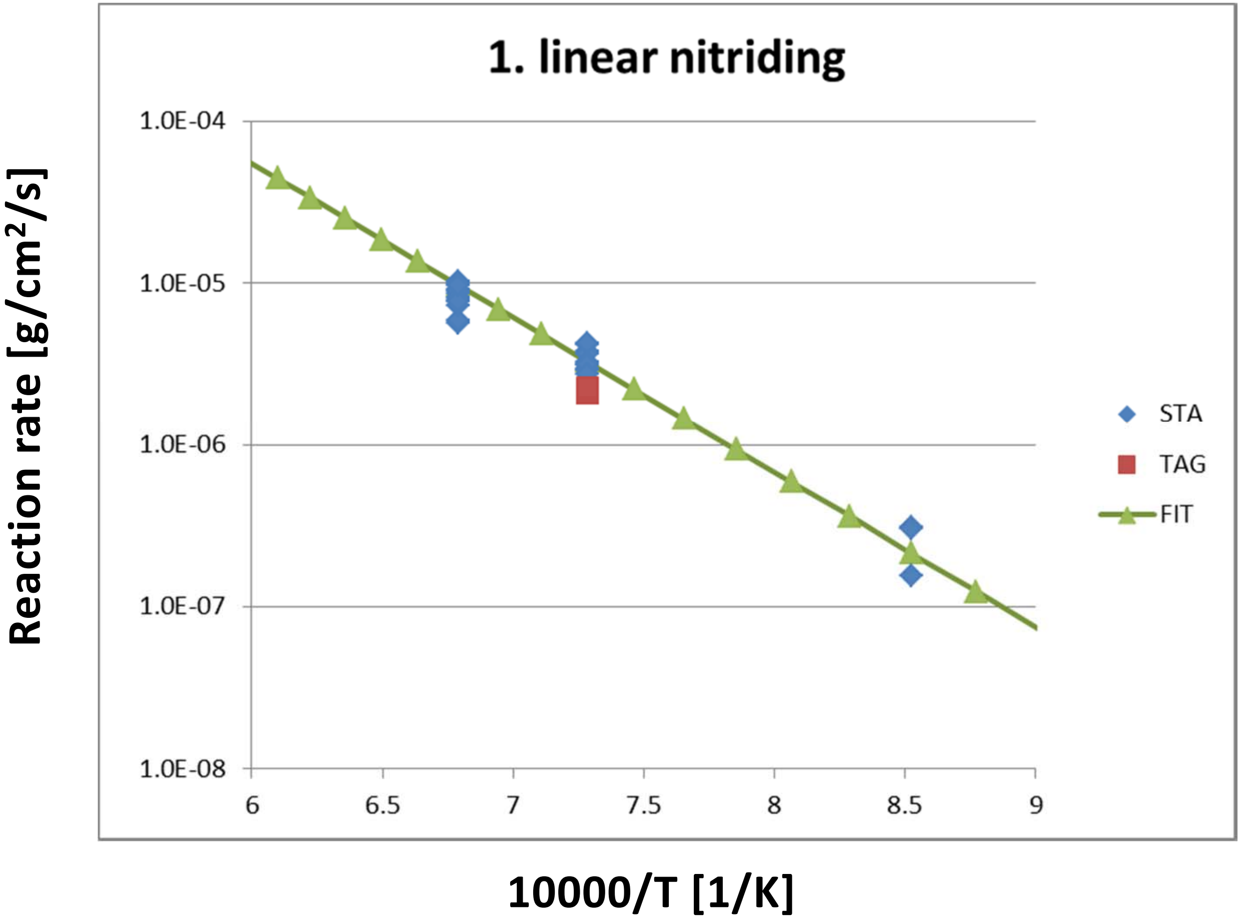
# Analysis and preliminary Results

**The parabolic oxidation follows the oxidation rate function from Hofmann used for the zircaloy cladding oxidation in Oxygen. The data points below the curve reflect the time of dynamic concentration change of the oxidizing gas (Ar – $O_2$ Transition) which is reducing the reaction rate.**



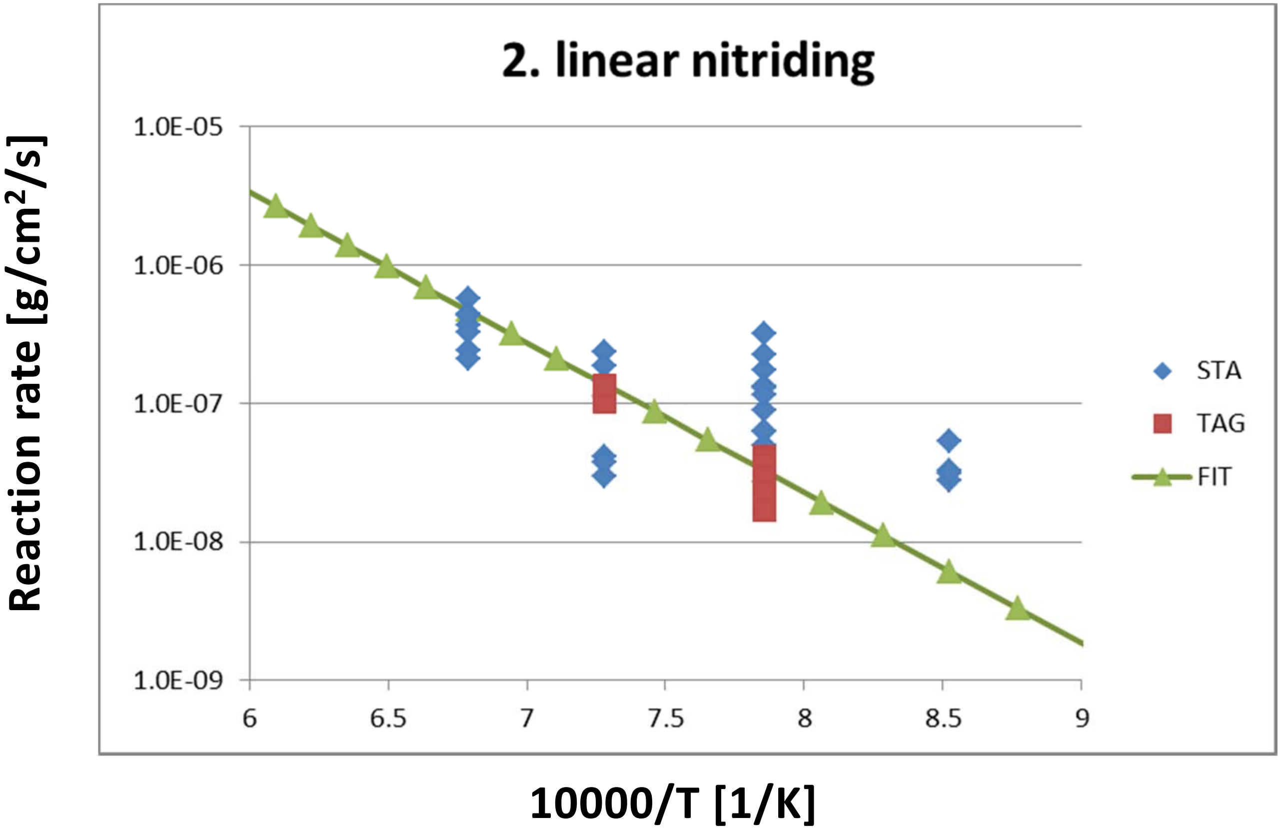
# Analysis and preliminary Results

**The first linear nitriding process is assumed to reflect the nitriding of the oxygen stabilized α-zirconium. This layer growths has to be modeled depending on the sample temperature to receive the right amount of available α-zirconium for nitriding.**



# Analysis and preliminary Results

**After oxidation of the α-zirconium the reaction rate dropped drastically. The further nitriding can be interpreted as reaction of nitrogen with the sub stoichiometric zirconium oxide (Breakaway effects can be observed at temperatures below 1100°C). Possible leakage of the facility may influence the measurement of very low reaction rates.**



# Analysis and preliminary Results

**For the development of the model it has to be assumed, that all processes are running in parallel (as far as the reacting gases are available). The reactions are:**

- **oxidation in steam or oxygen**
- **production of α-Zr(O) layer by oxygen diffusion**
- **production of sub stoichiometric zirconia by oxygen diffusion**
- **nitriding of α-Zr(O)**
- **nitriding of sub stoichiometric zirconia**
- **reoxidation of ZrN**

**The breakaway effect has also to be considered due to the reduction of the protective layer thickness to deliver higher reaction rates as observed in the tests below 1100°C.**

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# Outlook

**A model will be developed as stand alone programme to recalculate the oxidation and nitriding behavior of the different experiments.**

**The next phase is the testing of the model against independent experiments like QUENCH-10 and SFP Phase II or others.**

**Preparation of the model for implementation in severe accident codes.**

**Needs:**

- ❑ **Nitrogen as reacting and consumable gas**
- ❑ **ZrN as new material**
- ❑ **α-Zr(O) as new material**
- ❑ **sub stoichiometric zirconium oxide as new material (as in ASTEC)**


Questions?