# Investigation of flow condition on the oxidation of Zircaloy-4 in air at 850°C and 1100°C

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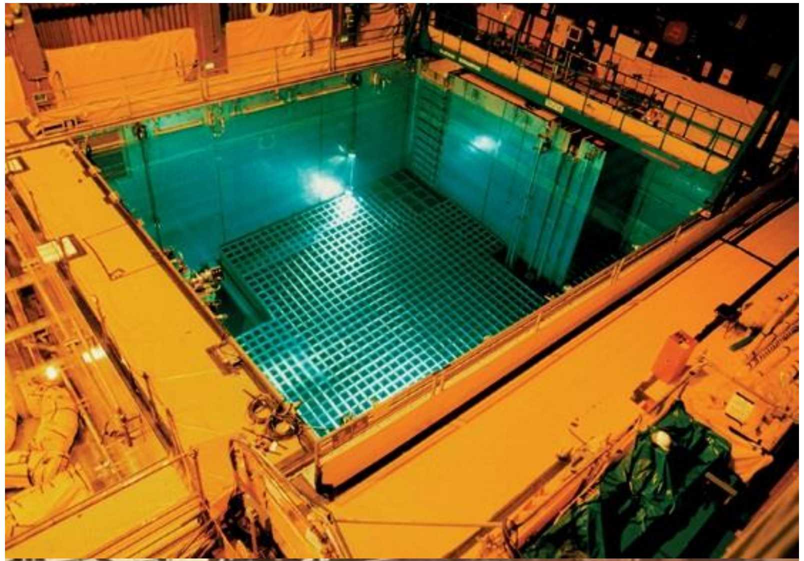
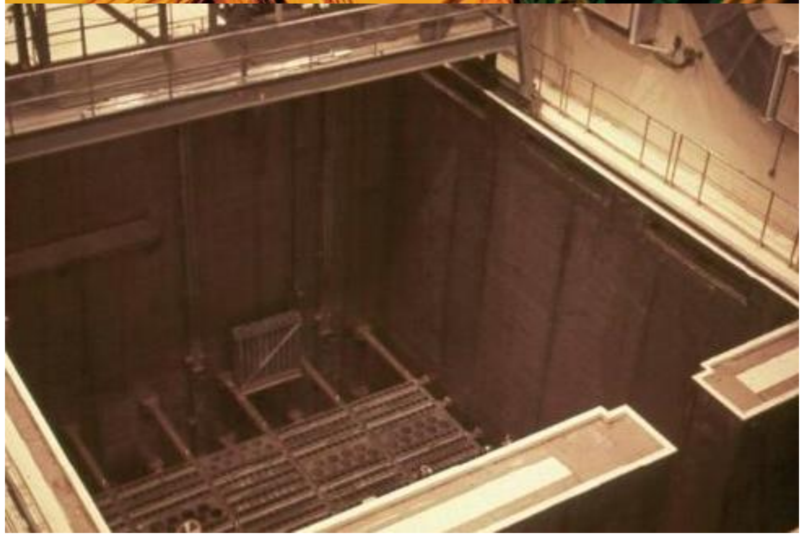
# Contents

# Background





■ An effect of air on oxidation of Zr alloy

Acceleration of oxidation kinetics of Zirconium alloy cladding

Degradation of cladding due to an effect of nitrogen

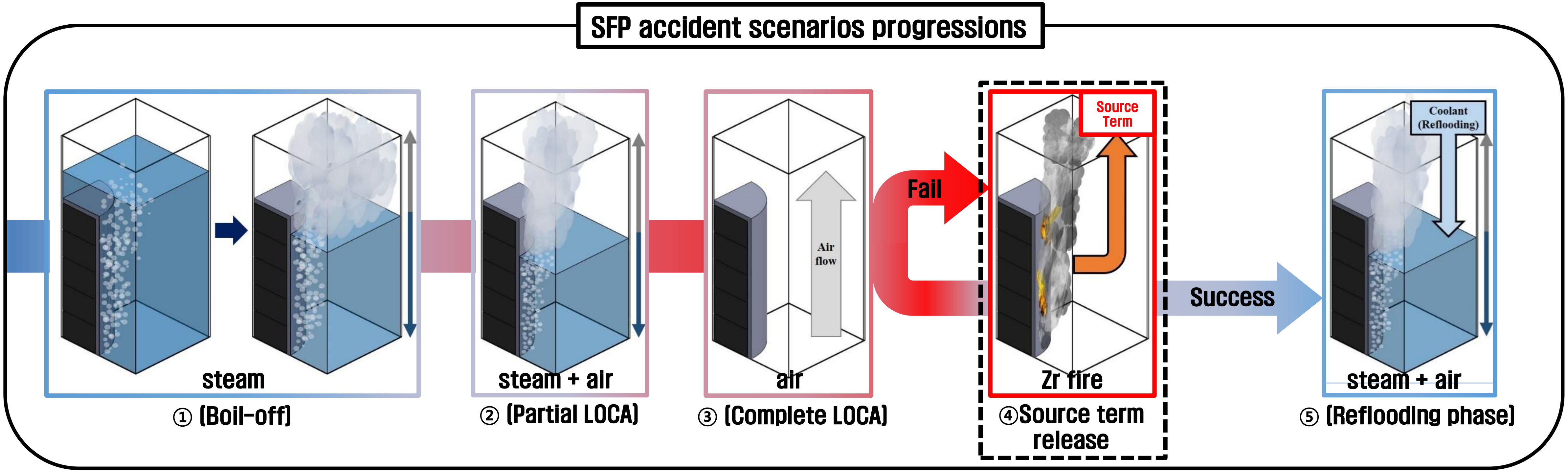
■ Air ingress scenario

For example, SFP LOCA scenario

■ Research/Experimental data on air oxidation

Various leading groups (KIT, EDF, IRSN… in Europe, ANL, SNL in United States) and international research project have been studying oxidation of cladding in air

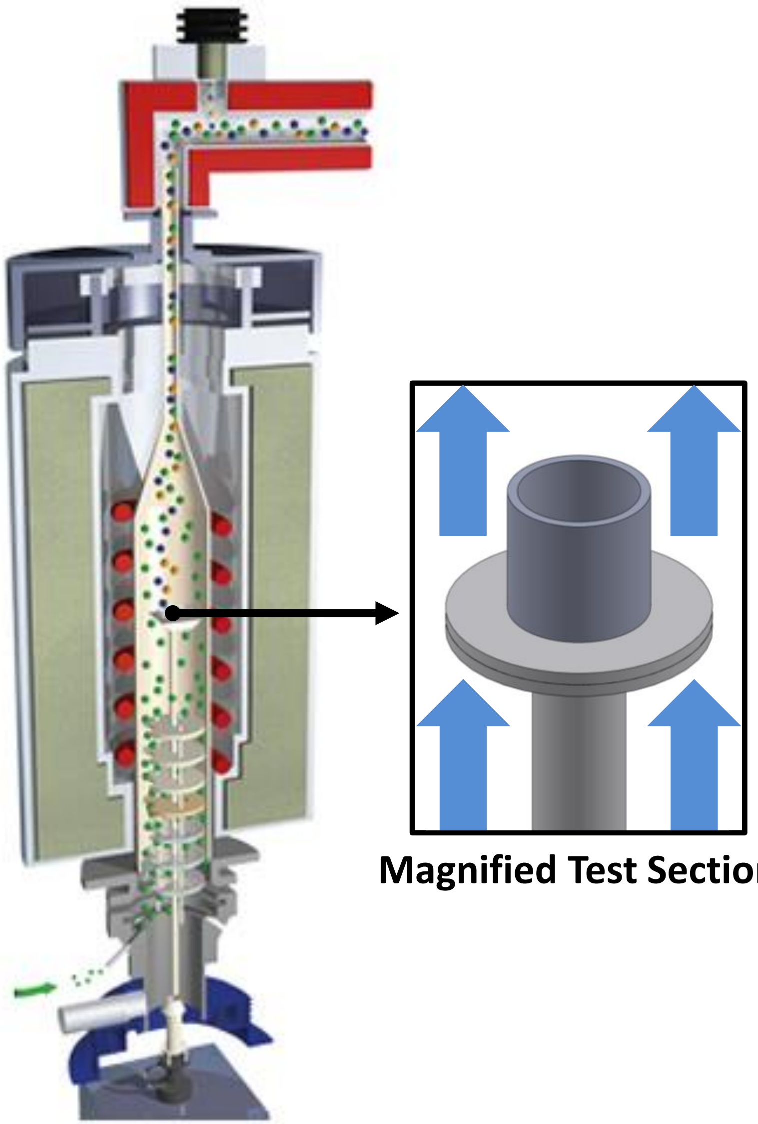
# Motivation – SFP Accident Scenario




By accident sequence, following conditions would be varied:

- Temperature
- Cladding oxidation atmosphere
- Flow condition (flow rate, partial pressure)

# Test Parameter: Flow Condition

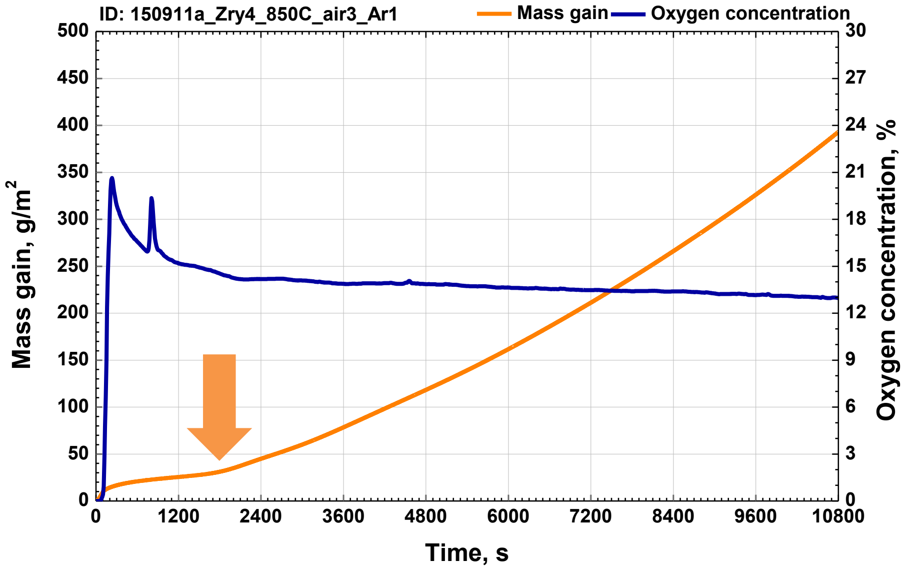


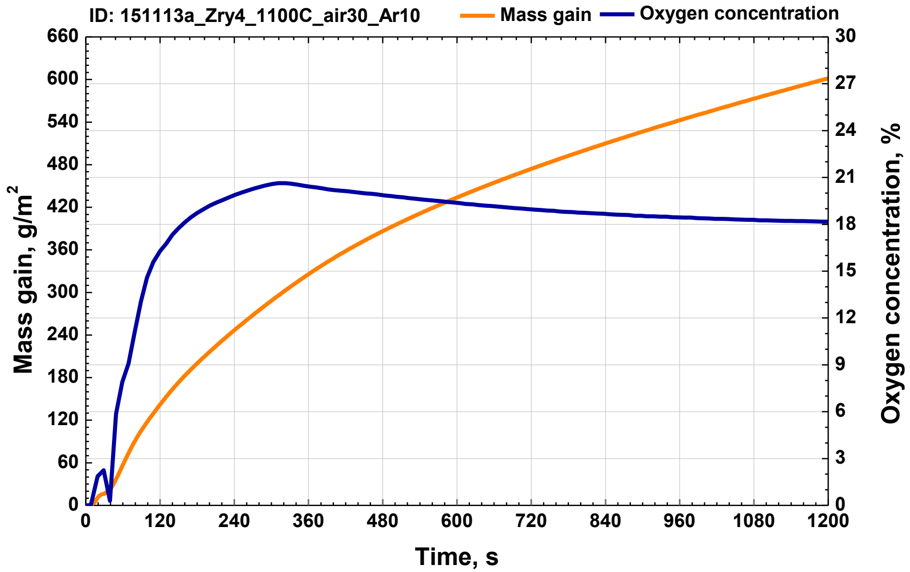
Magnified Test Section

- Flow condition inside the furnace could affect an oxidation kinetics of zirconium alloy cladding
- For this reason, an effect of flow condition (flow rate and partial pressure of oxygen) on oxidation kinetics was studied

Reference of image: https://www.netzsch-thermal-analysis.com/en/products-solutions/evolved-gas-analysis/tgasta-qms-403-d-aeolos/

# Test Parameter: Temperature



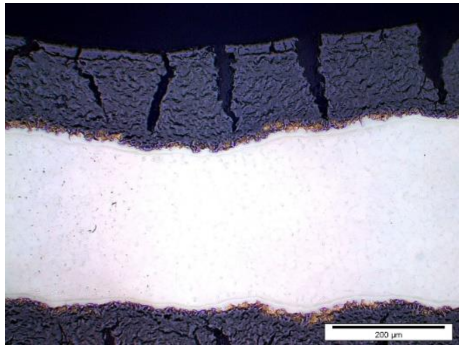

## ■ Oxidation kinetics at 850°C

**In the beginning, cubic or parabolic kinetics is observed**

**Acceleration of oxidation kinetics is observed (breakaway)**

**Pre-breakaway regime:** $\frac{dX}{dt} = \frac{k_p}{X}$

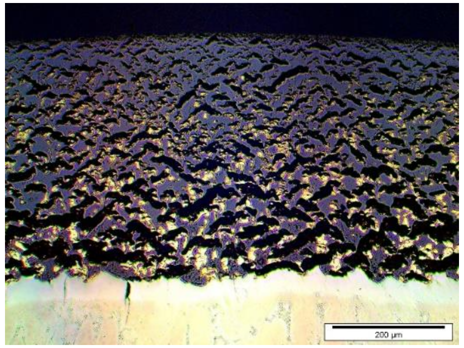
**Post-breakaway regime:** $\frac{dX}{dt} = k_l$



## ■ Oxidation kinetics at 1100°C

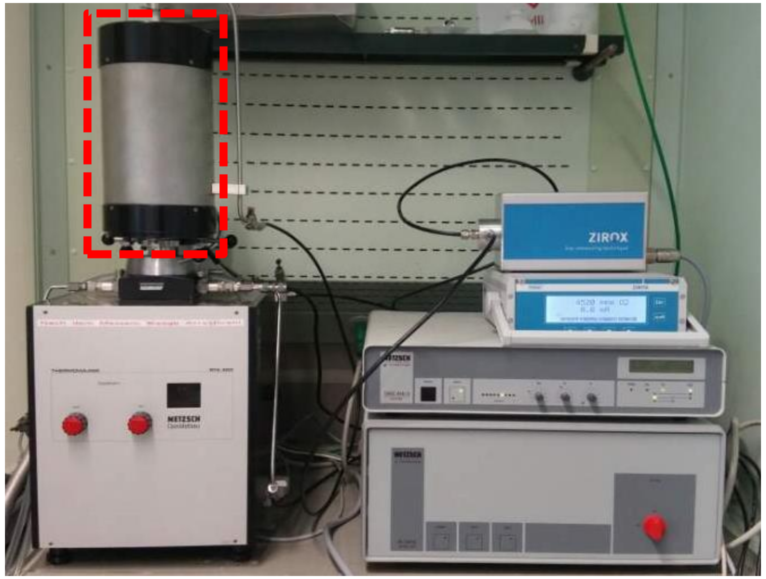
**Parabolic oxidation kinetics is observed**

$$\frac{dX}{dt} = \frac{k_p}{X}$$



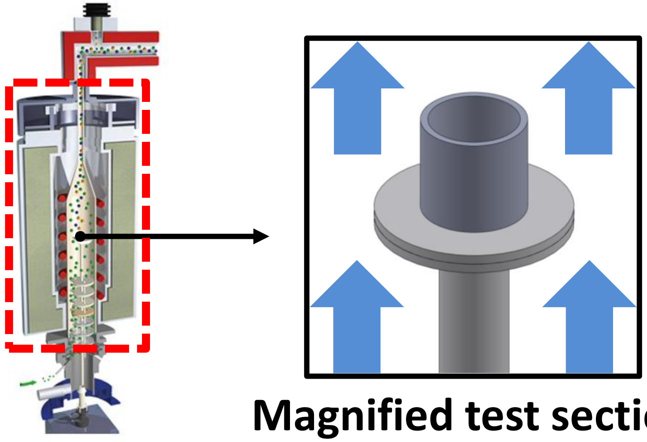
# Experimental Setup & Sample Preparation

## □ Experimental Devices



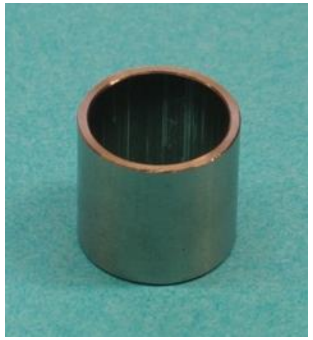

■ Thermogravimetric Analyzer (TGA, left)

■ $O_2$ concentration measuring device (ZIROX, right)



Magnified test section

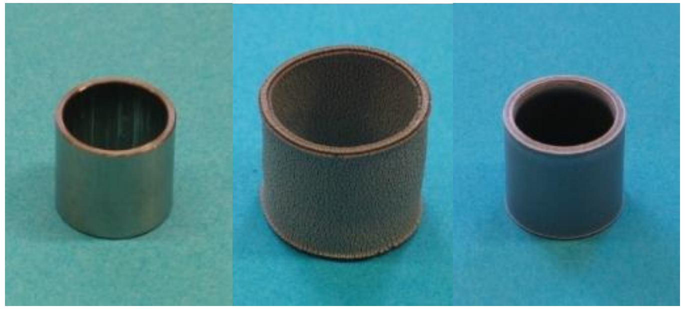
## □ Sample Preparation



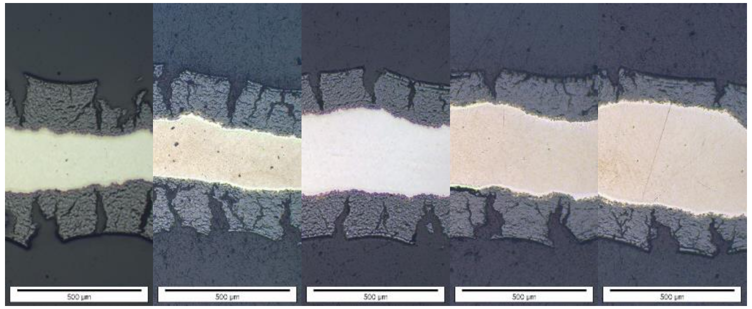
■ Zry-4 cladding sample

Zry-4 cladding tube was cut into 10 mm segments. After cutting and grinding process, samples were cleaned in acetone with ultrasonication.

## □ Post test analysis

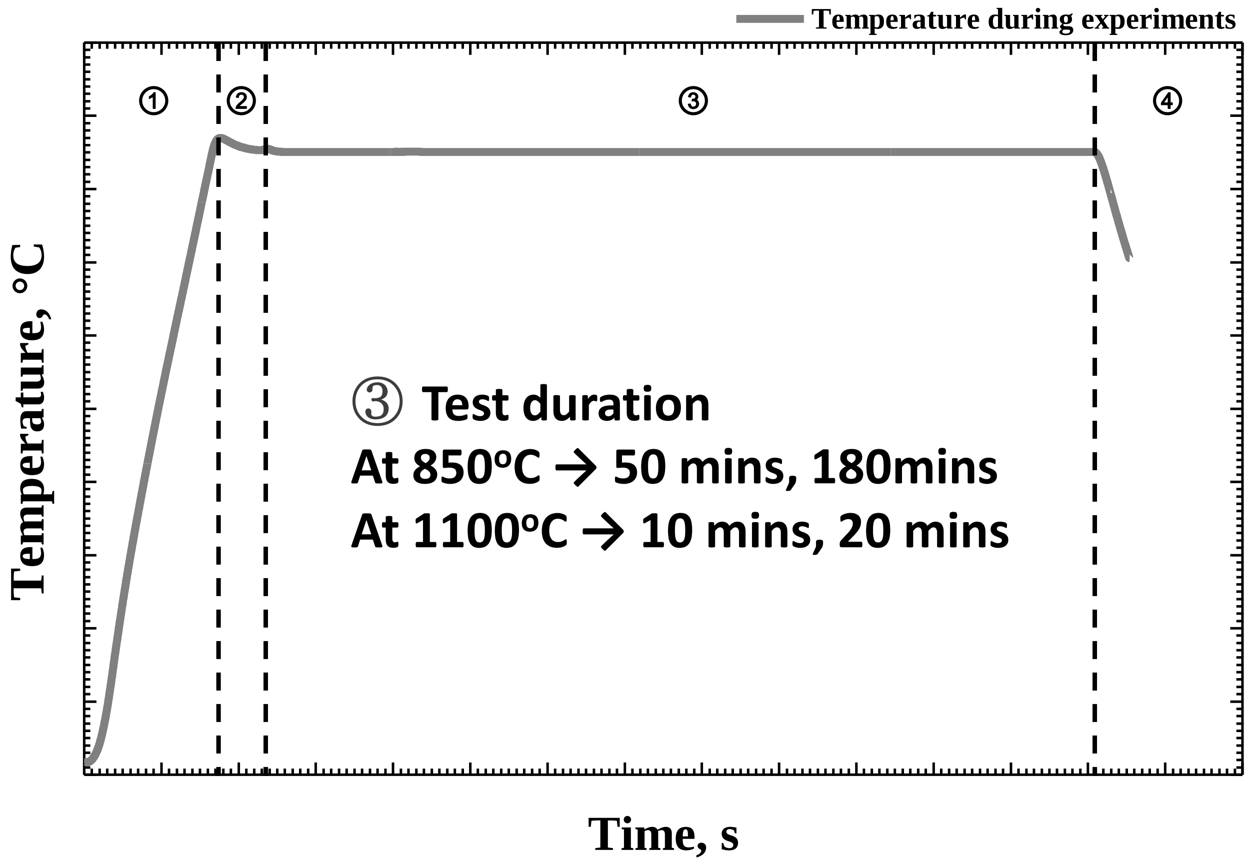


■ Macrophotography



■ Metallography (Optical microscopy)

# Experimental Procedure




① **Heating period**

**Furnace temperature 30 K/min. ↑ in argon**

② **Thermal stabilization phase**

**10 minutes thermal stabilization**

③ **Isothermal region**

**Oxidation begins with supply of air.**

④ **Cooling region**

**Air supply stopped.**

**Furnace temperature 30K/min. ↓ in argon**

# Test Matrices

## ☐ FA test series

| Temp. (°C) | ID | Air flow rate (l/h) | Ar flow rate (l/h) | Total flow rate (l/h) |
|---|---|---|---|---|
| 850°C and 1100°C | FA1 | 3 | 1 | 4 |
| | FA2 | 6 | 2 | 8 |
| | FA4 | 12 | 4 | 16 |
| | FA6 | 18 | 6 | 24 |
| | FA8 | 24 | 8 | 32 |
| | FA10 | 30 | 10 | 40 |

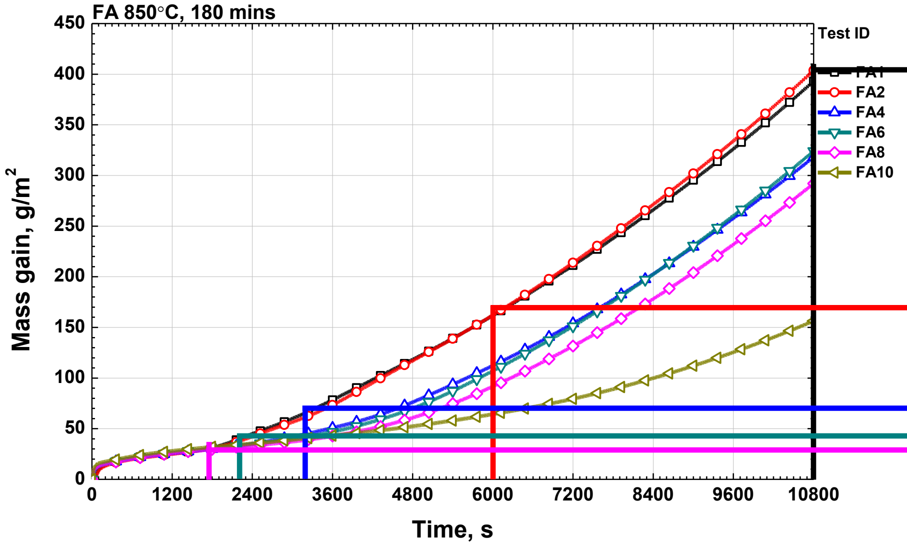
■ All experiments of FA test series were conducted under the constant partial pressure of air ($P_{O_2}$ = 15%)

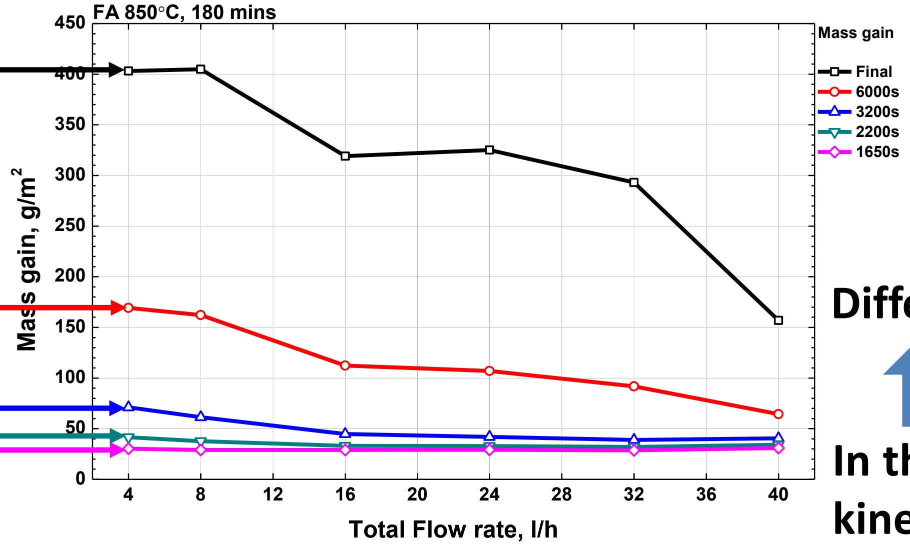
## ☐ APP test series

| Temp. (°C) | ID | Air Flow rate (l/h) | Ar Flow rate (l/h) | $P_{O2}$ (%) |
|---|---|---|---|---|
| 850°C and 1100°C | A03PP1 | 3 (case of lower air flow rate) | 1 | 15.0 |
| | A03PP2 | | 2 | 12.0 |
| | A03PP4 | | 4 | 8.6 |
| | A03PP6 | | 6 | 6.7 |
| | A03PP8 | | 8 | 5.5 |
| | A03PP10 | | 10 | 4.6 |
| | A18PP1 | 18 (case of higher air flow rate) | 1 | 18.9 |
| | A18PP2 | | 2 | 18.0 |
| | A18PP4 | | 4 | 16.4 |
| | A18PP6 | | 6 | 15.0 |
| | A18PP8 | | 8 | 13.8 |
| | A18PP10 | | 10 | 12.9 |

# Results of FA test Series (850°C/1100°C)

## ☐ FA test series at 850°C

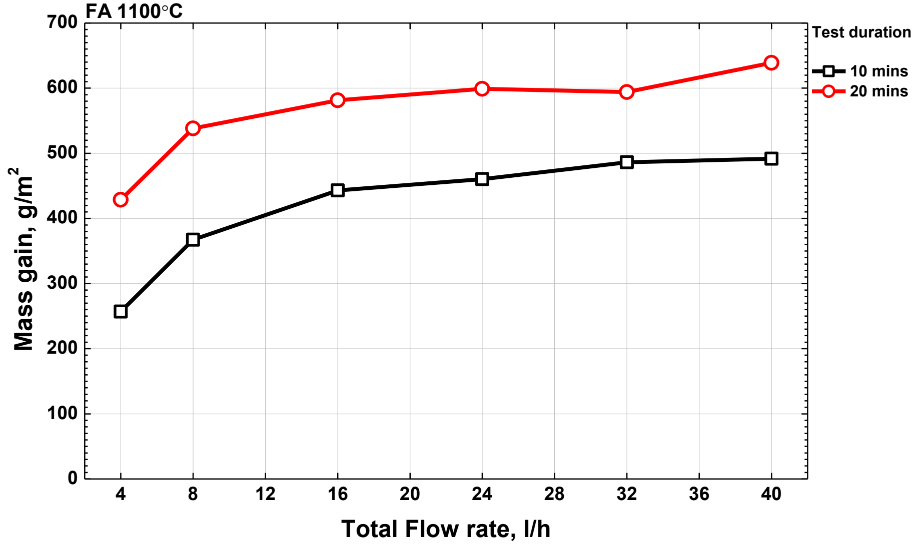



Different oxidation kinetics

In the beginning, similar oxidation kinetics

## ☐ FA test series at 1100°C



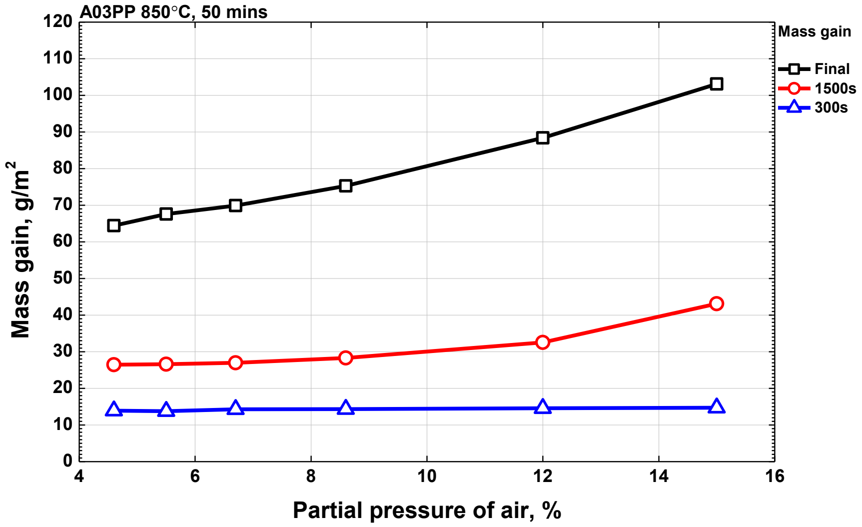

■ At 850°C, an oxidation kinetics increased <u>as total flow rate decreased</u>

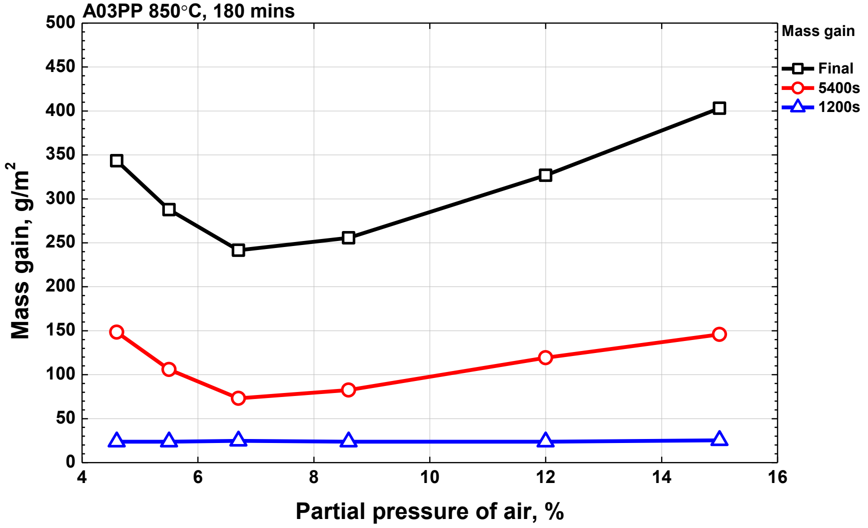
■ Breakaway and post-breakaway oxidation kinetics was affected by flow rate

■ At 1100°C, an oxidation kinetics increased <u>as total flow rate increased</u>

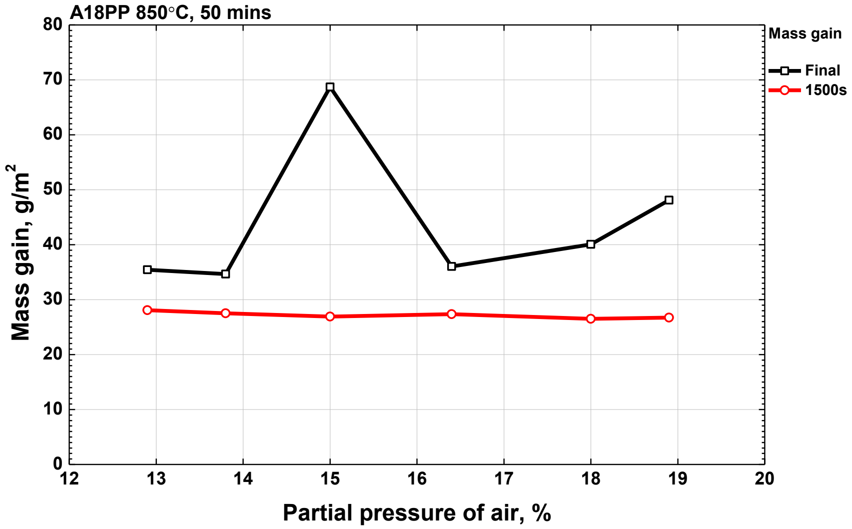
# Results of APP test Series (850°C)

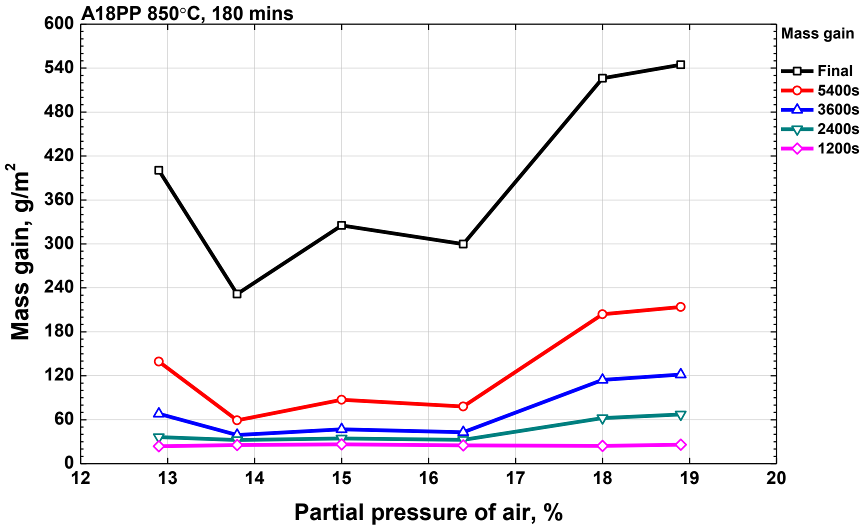
□ Low air flow rate (3 l/h)




□ High air flow rate (18 l/h)



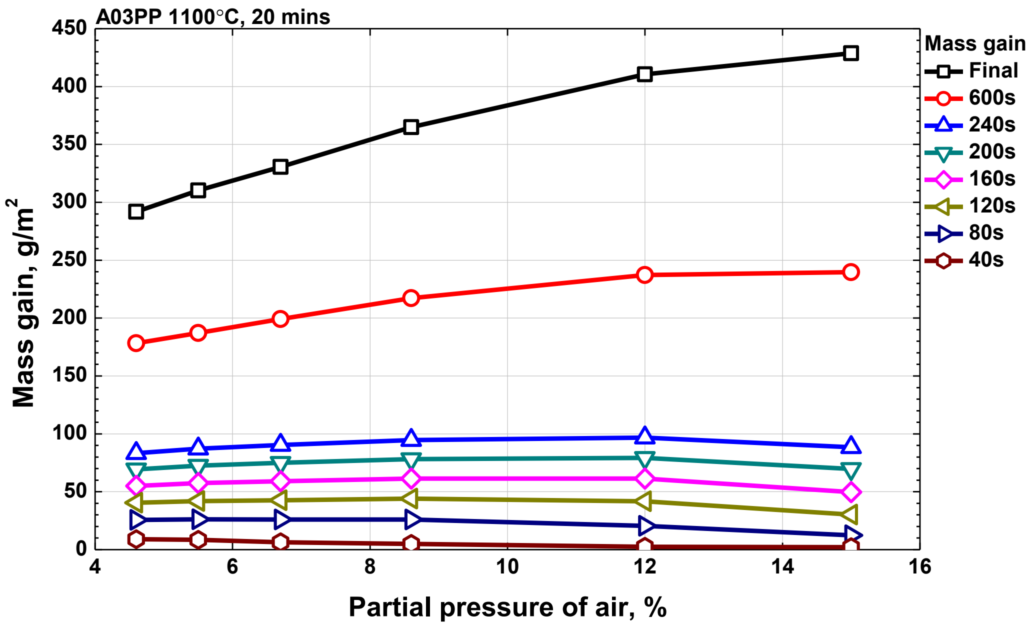




■ In the beginning, oxidation kinetics of samples was similar regardless of the partial pressure of air

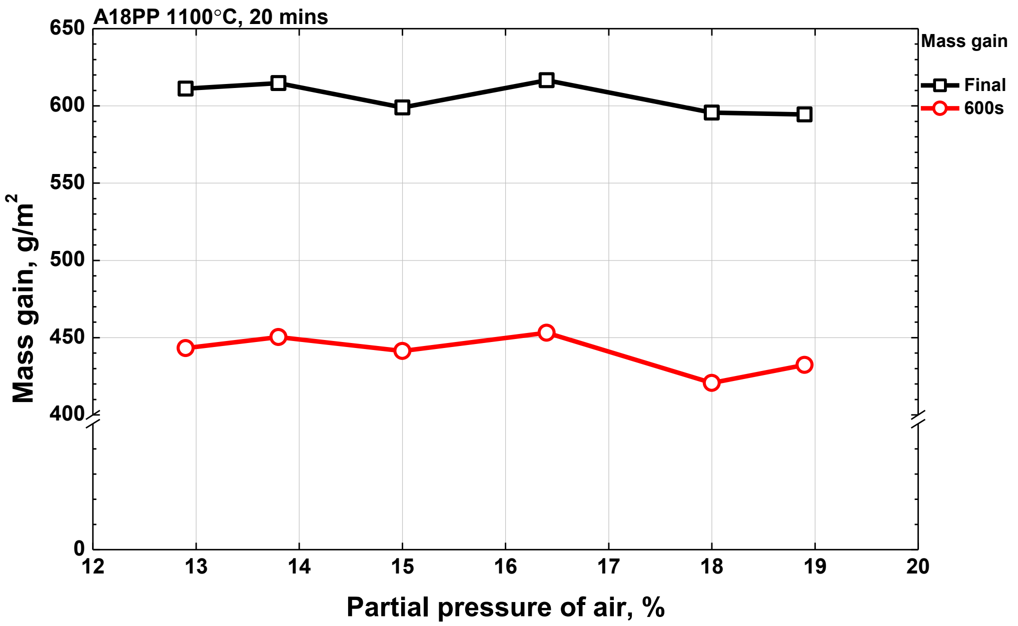
■ Different mass gain was observed at the final state of tests

# Results of APP test Series (1100ºC)

☐ Low air flow rate (3 l/h)




☐ High air flow rate (18 l/h)




- At low air flow rate (3 l/h), an oxidation kinetics increased by increasing partial pressure of oxygen
- At high air flow rate (18 l/h), an oxidation kinetics was not significantly affected by partial pressure of oxygen
- It might be that an effect of partial pressure of air decreased as flow rate increased

# Comparison with Oxidation in Steam/Nitrogen Mixture

□ Optimization of flow rate of steam

■ For example, FA1 (Air) matches with FS1 (Steam)

| | FA1 | FS1 |
|---|---|---|
| Composition | $O_2$ 0.6 l/h<br>$N_2$ 2.4 l/h<br>Ar 1 l/h | $H_2O$ 1 g/h (≒ 1.2 l/h)<br>$N_2$ 1.8 l/h<br>Ar 1 l/h |

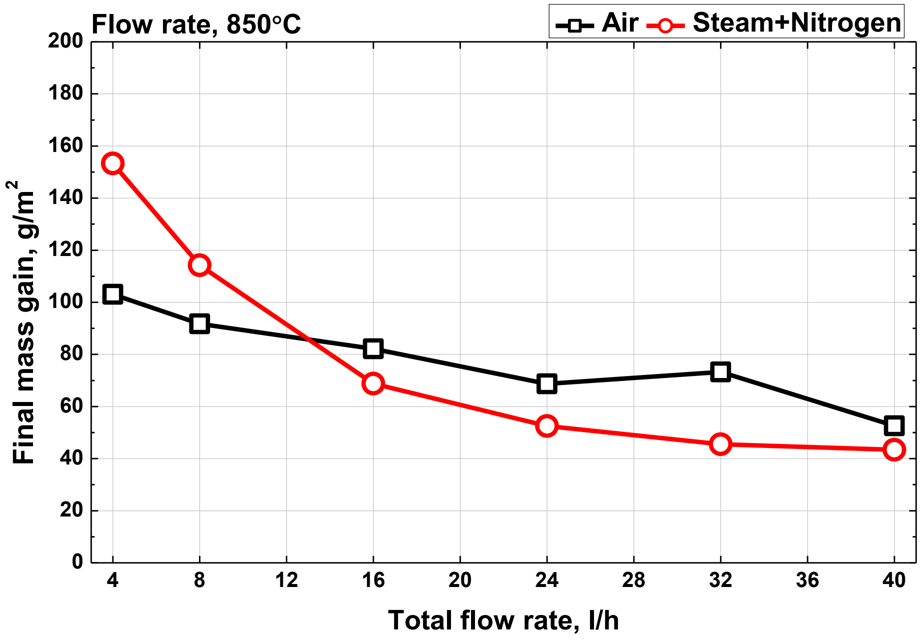
■ In composition of FA1 and FS1, amount of oxygen is same

■ Test matrix of oxidation in steam/nitrogen mixture is same with oxidation in air

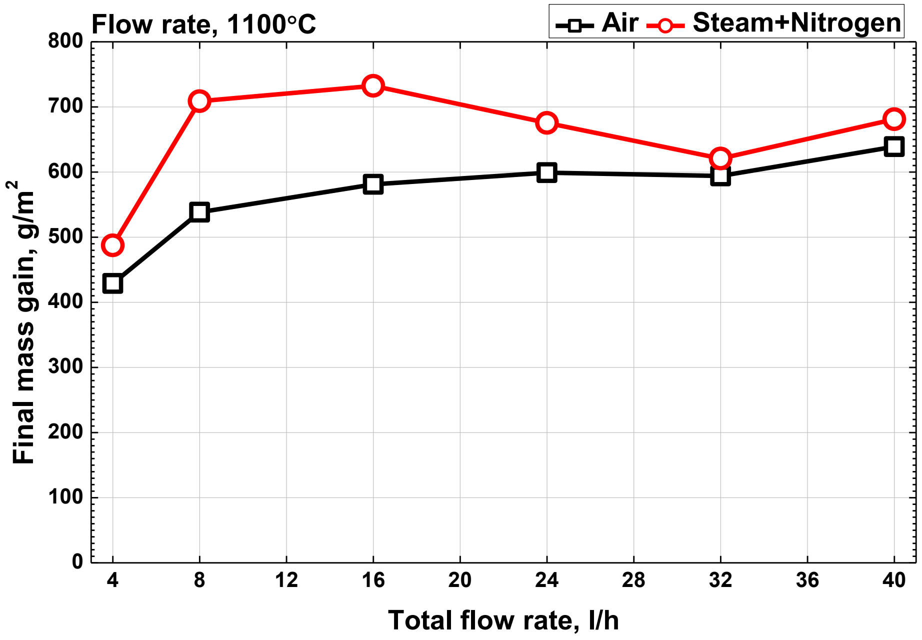
# Comparison with Oxidation in Steam/Nitrogen Mixture

## □ Effect of flow rate (850ºC, 1100ºC)

### □ Result at 850ºC



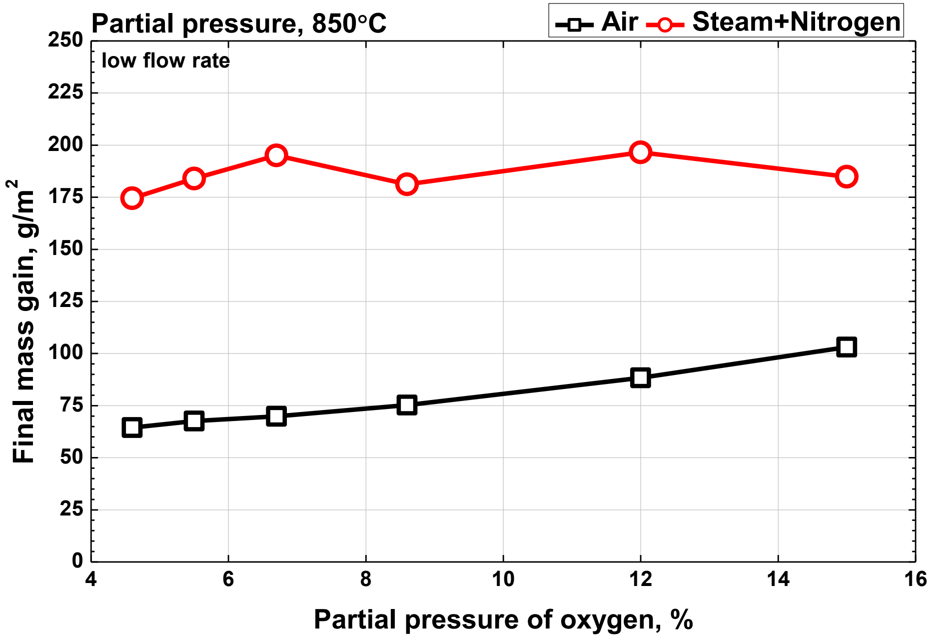

### □ Result at 1100ºC



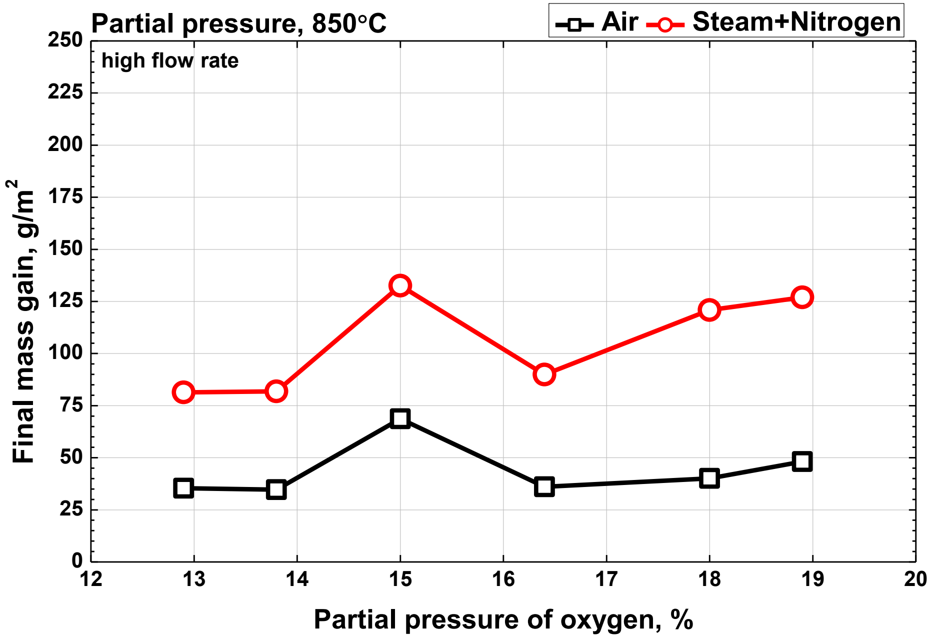
# Comparison with Oxidation in Steam/Nitrogen Mixture

☐ Effect of partial pressure of oxygen at 850°C

☐ Lower flow rate (3 l/h)



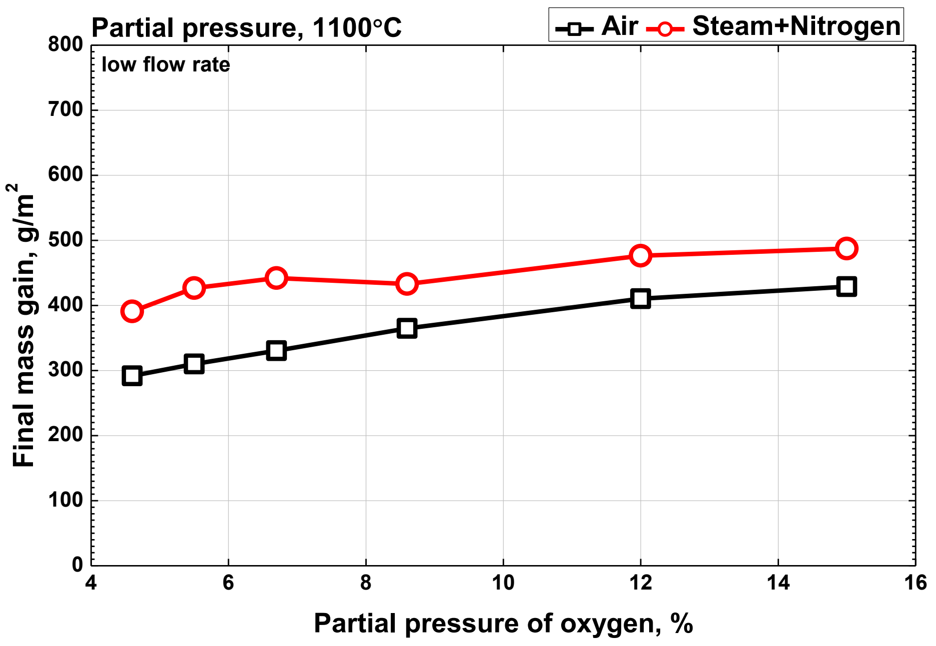

☐ Higher flow rate (18 l/h)



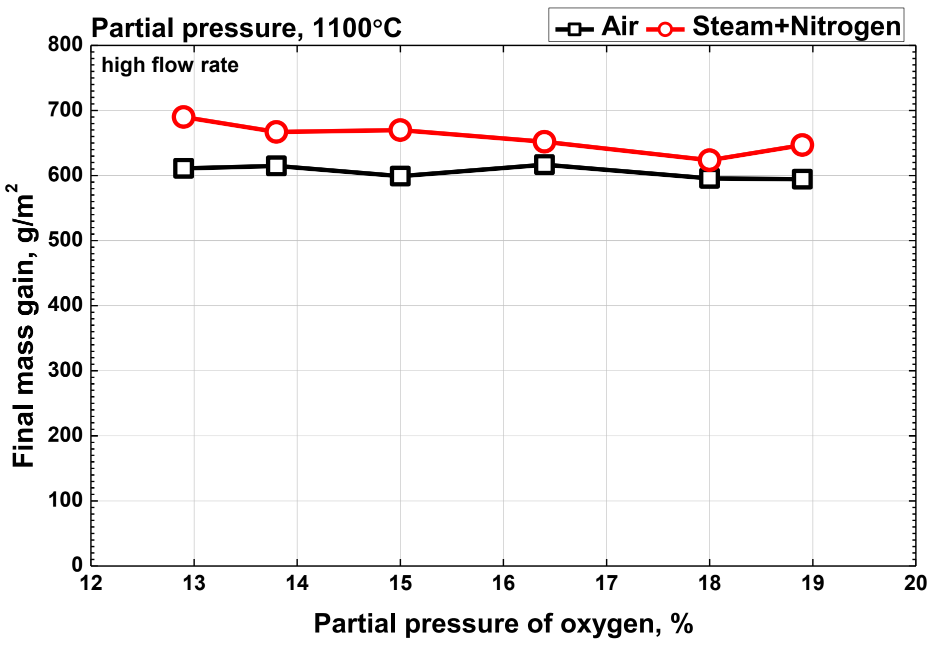
# Comparison with Oxidation in Steam/Nitrogen Mixture

☐ **Effect of partial pressure of oxygen at 1100°C**

☐ **Lower flow rate (3 l/h)**



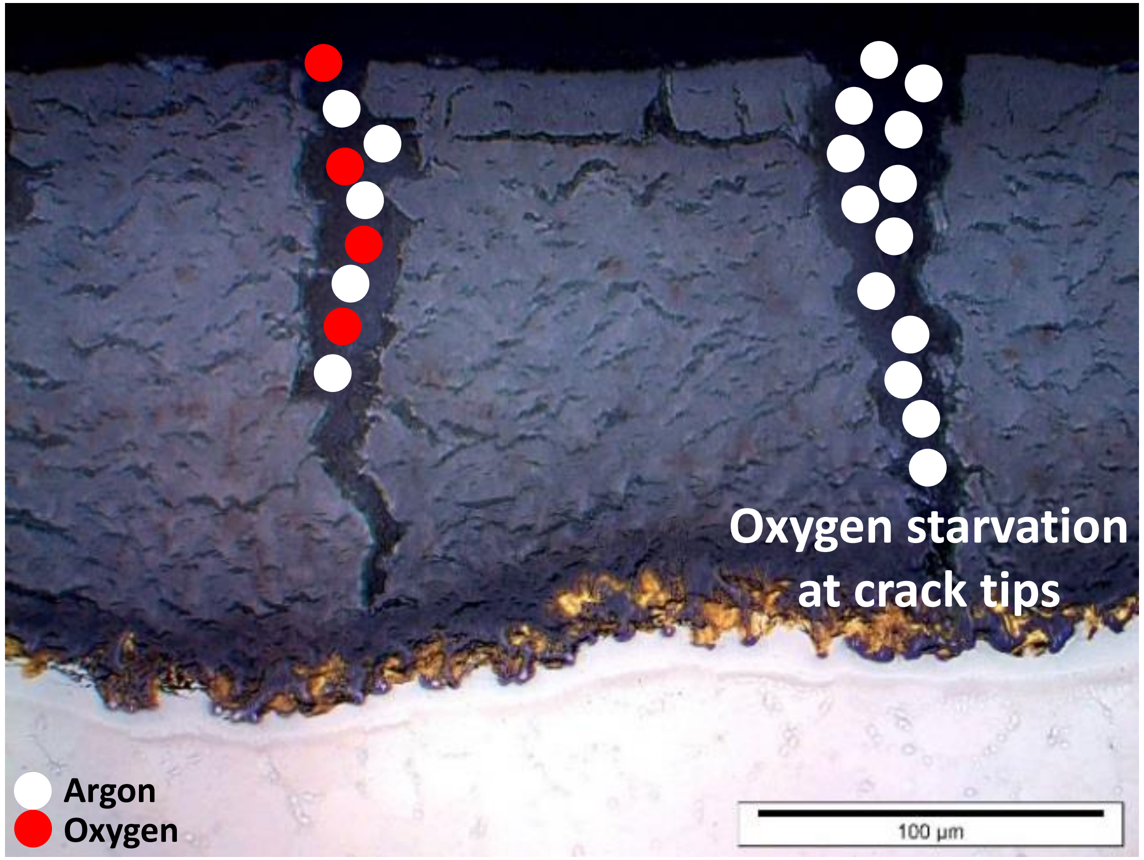

☐ **Higher flow rate (18 l/h)**



# Problem Statement: Oxide Structure

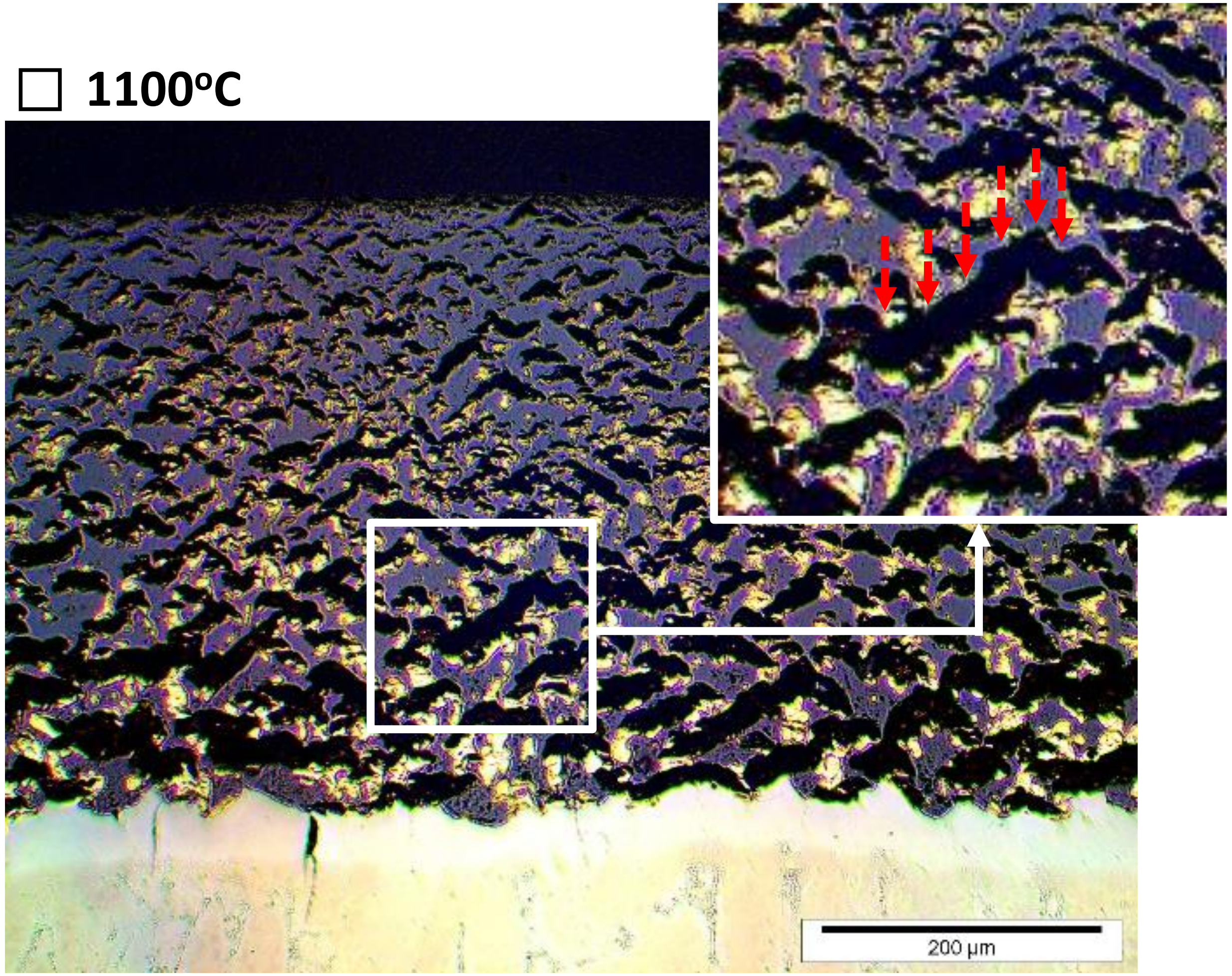
☐ **Difference of oxide structure**

☐ **850°C**



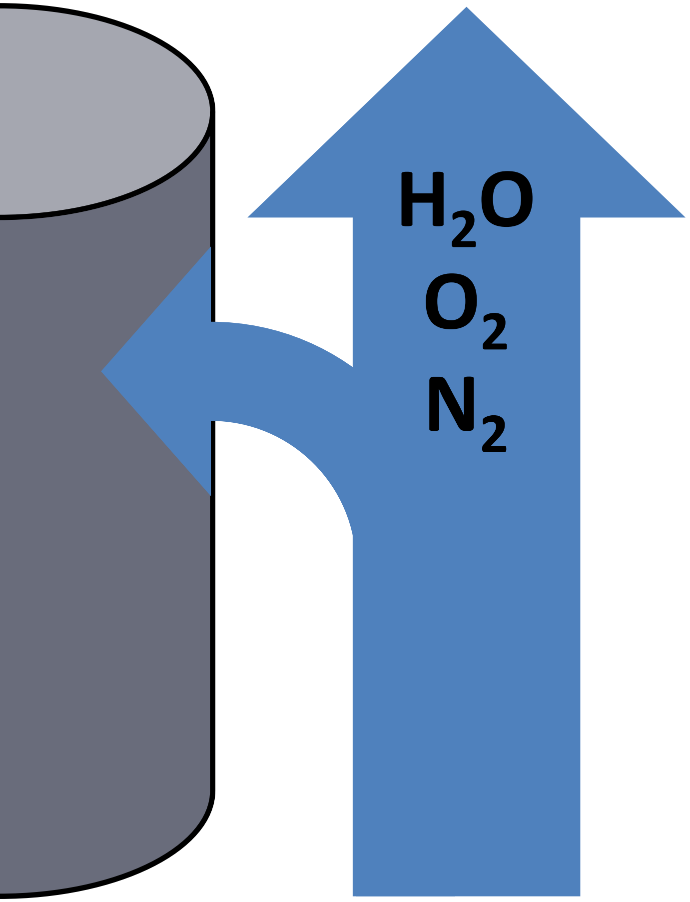

■ oxygen starvation by inert gas (in steam, hydrogen) at radial crack tip (gas-phase diffusion)

☐ **1100°C**



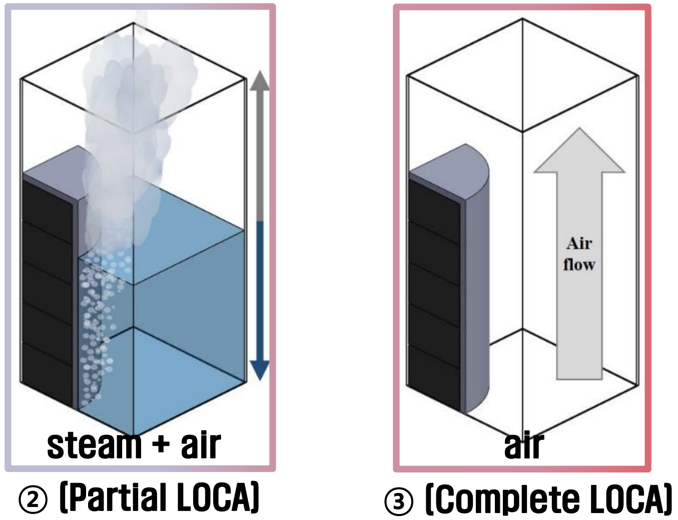

■ Oxygen diffusion path could be blocked by circumferential cracks (solid-state diffusion)

# Applicability of Test Results for Accident Management

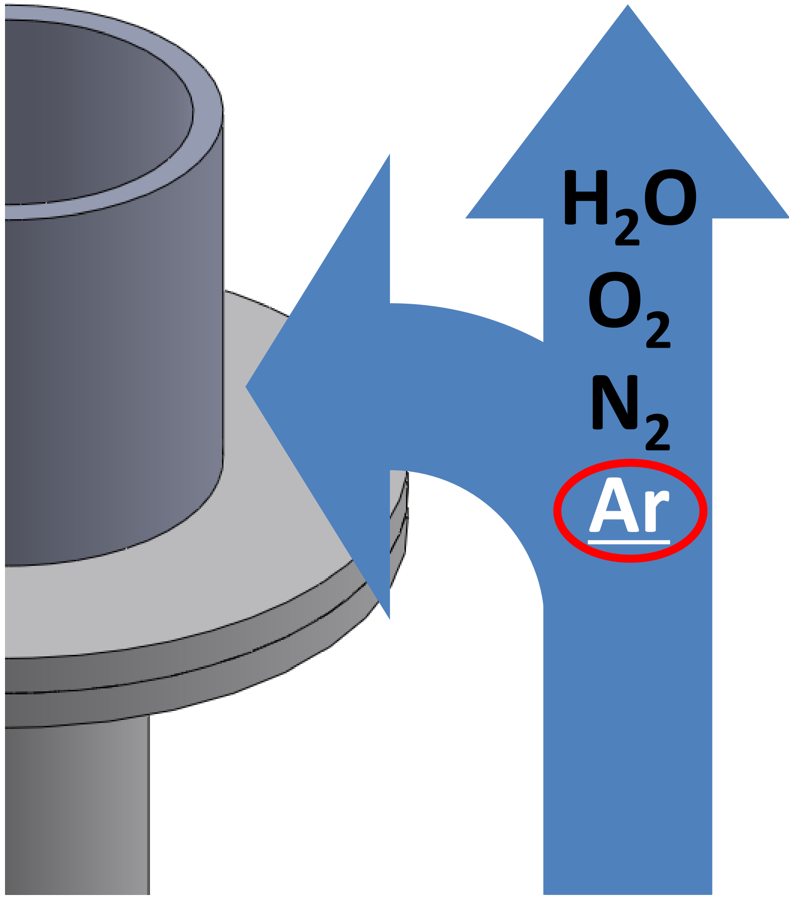



■ Cladding surface

**Difference of oxide structure**
**Scale**
**Breakaway**
**Composition of atmosphere**
**……**




■ Accident scenario




■ Zry-4 sample in furnace

# Summary

- An effect of flow rate (Constant partial pressure of oxygen; 15%)
  - At 850$^{o}$C, the oxidation kinetics increased by decreasing total flow rate
  - At 1100$^{o}$C, the oxidation kinetics increased by increasing total flow rate
- An effect of partial pressure (Constant flow rate of air; 3 l/h & 18 l/h)
  - At 850$^{o}$C, clear trend was not reproduced. It might be due to stochastic property of breakaway phenomenon
  - At 1100$^{o}$C and 3 l/h case, the oxidation kinetics increased by increasing partial pressure of air
  - At 1100$^{o}$C and 18 l/h case, the effect of partial pressure was not significant
- Breakaway phenomenon occurred at 850$^{o}$C
  - At initial phase of experiment, oxidation kinetics of samples were similar
  - The oxidation kinetics of samples showed difference by going through breakaway
- Comparison with oxidation tests in steam + nitrogen mixed atmosphere
  - Generally, the mass gain of samples oxidized in steam + nitrogen was higher
  - Further analysis is necessary

# Further Plan

- ☐ Additional experiment – extended criteria of test parameter
  - ■ Temperature: 850°C, 1100°C
  - ■ Flow rate: 4l/h – 40l/h
  - ■ Partial pressure: low flow rate (4.6 – 15.0%), high flow rate (12.9 – 18.9%)
  - ■ Scale of specimen: 10 mm length Zry-4 cladding segments
  - ■ Material: Zircaloy-4
- ☐ Quantitative analysis using various spectroscopy
- ☐ Comparison with test results of oxidation in steam/nitrogen mixed atmosphere

# Acknowledgement

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**Most of all, I want to thanks to Sanggil Park (ACT Co., Ltd), Martin Steinbrueck and Mirco Grosse (KIT). They are very cooperative and kind. I also want to thanks to Joon, my colleague in the laboratory.**

# Thank you for your attention