



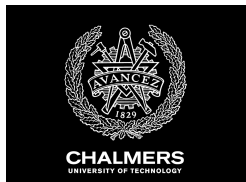
# High temperature materials for industrial processes

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Energy and Materials  
Chalmers Tekniska Högskolan

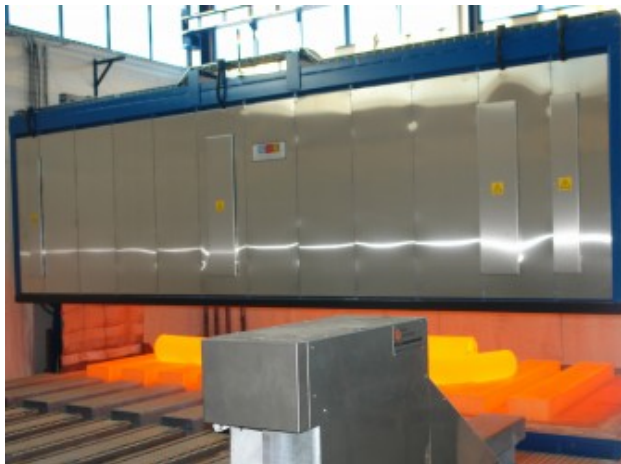
Applied Physics  
Chalmers Tekniska Högskolan

Chemical Science and Engineering  
Kungliga Tekniska Högskolan



## What is meant with industrial processes?

This project is dedicated to industrial processes which are running in **low oxygen** environments with other oxidants **instead** such as **carbon or nitrogen**.



### Furnaces for heat treatments under inert conditions

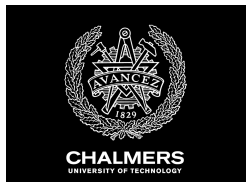
- ,inert' conditions  $N_2/H_2$
- high temperature 900-1200°C

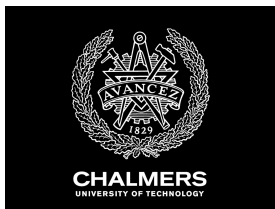


### Pre-reformer for fuel cell stacks

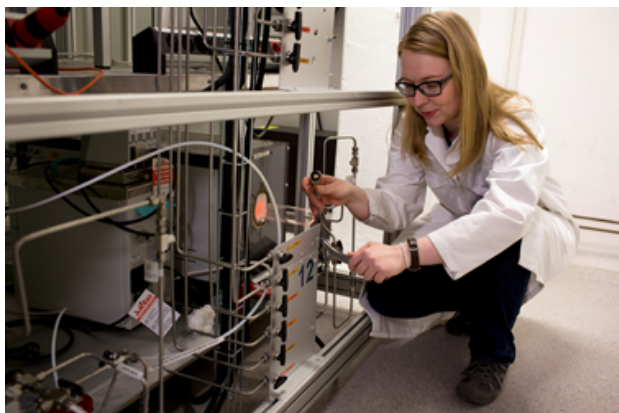
- syngas production in the pre-reformer ( $CO/H_2/H_2O$ )
- high temperature (600-900°C)

|                                 |                                                                                                                                                                                                                                              |
|---------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>Project leader:</i>          | Jan-Erik Svensson, CTH                                                                                                                                                                                                                       |
| <i>Participating companies:</i> | <b>Sandvik Heating Technology (SHT)</b><br><b>Sandvik Materials Technology (SMT)</b><br><b>Powercell</b><br><b>Entech</b>                                                                                                                    |
| <i>Research organizations:</i>  | Chalmers, KTH                                                                                                                                                                                                                                |
| <i>Senior researchers:</i>      | JE Svensson, CTH, B Jönsson, SHT/ CTH, M Halvarsson, CTH, LG Johansson, CTH, K Hellström CTH, I Panas, CTH, P Szakalos, KTH                                                                                                                  |
| <i>Post Doc:</i>                | C Geers, CTH; Gustav Sundell                                                                                                                                                                                                                 |
| <i>PhD students:</i>            | N Mortazawi, CTH, M Lindgren, CTH                                                                                                                                                                                                            |
| <i>Company personal:</i>        | B. Jönsson, SHT, D. Chandrasekaran, SHT, E. Ström, SHT, M. Lundberg SMT, P. Ekdunge, Powercell, J. Jyrinki, Entech                                                                                                                           |
| <i>Project group:</i>           | B. Jönsson, SHT, D. Chandrasekaran, SHT, E. Ström, SHT<br>M. Lundberg SMT, L. Kylhammar, Powercell, J. Jyrinki, Entech,<br>JE Svensson, CTH, B Jönsson, SHT/CTH, M. Halvarsson, CTH,<br>LG Johansson, CTH, K. Hellström CTH P. Szakalos, KTH |





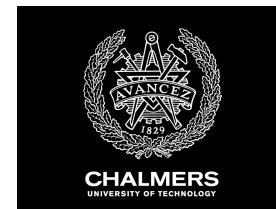
High temperature exposures in low oxygen activity environments



Theoretical Chemistry - DFT



High temperature exposures in low oxygen activity environments



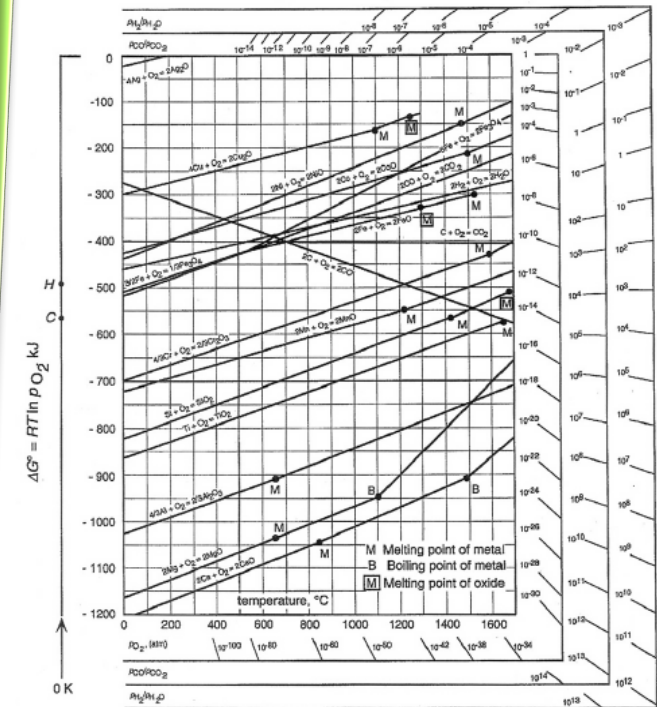
State-of-the-art microscopy





With decreasing  
oxygen  
availability...

... the demand  
for a reliable  
oxide former  
increases  
significantly...



... while the availability of  
oxide formers decreases.

Focus in this project:

- ☐ Parameters that control nitridation
- ☐ Parameters that control carburization
- ☐ Support first principle project and solar project

## Materials

- Kanthal APMT™
- Kanthal AF
- Nikrothal® 80
- Nikrothal 45 OC
- Nikrothal PM 58
- Model alloys

## Exposure

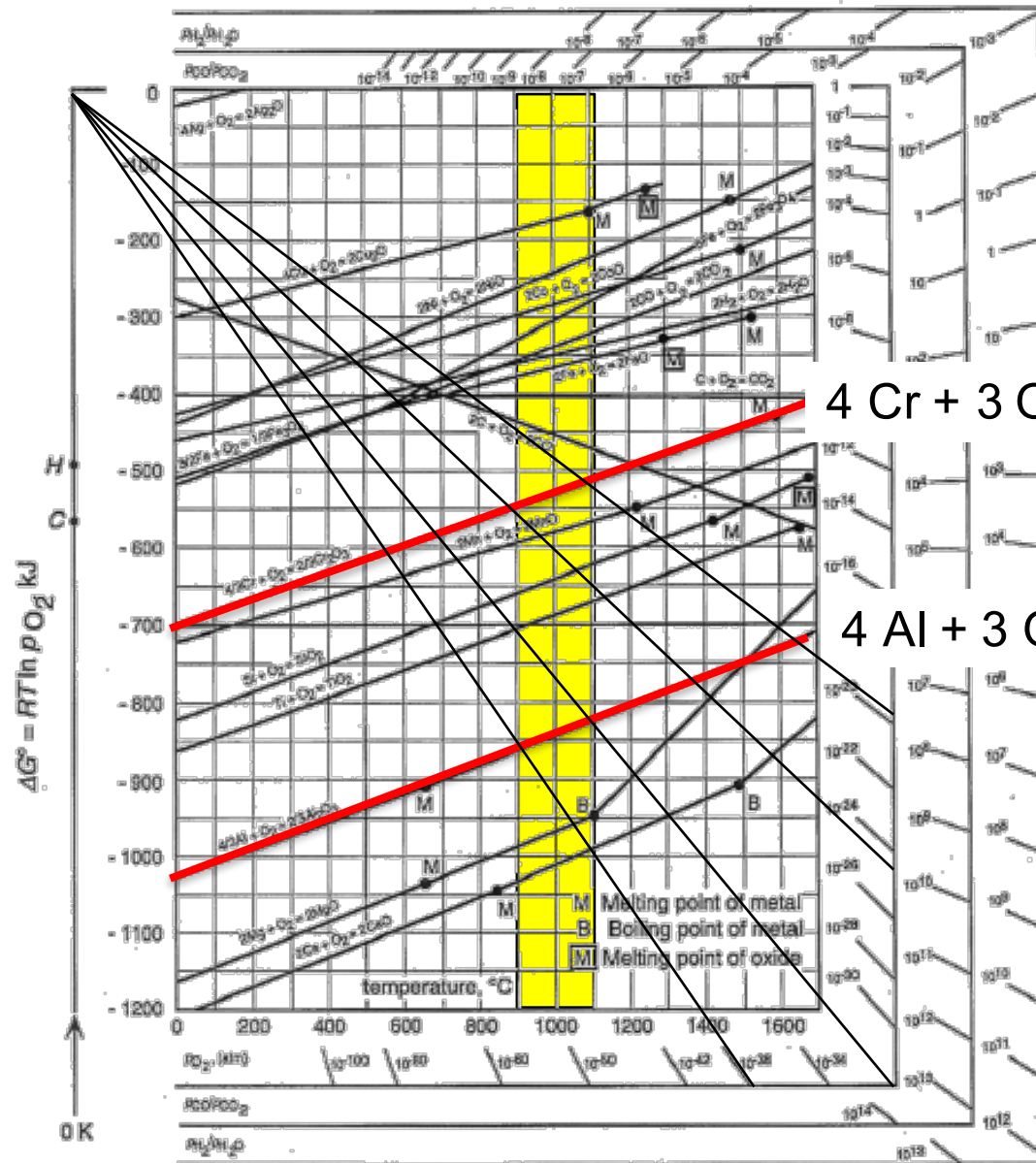
- Stage one:
  - **N<sub>2</sub>-H<sub>2</sub> (dry)**
  - N<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O
  - Ar-H<sub>2</sub>-H<sub>2</sub>O
- Stage two:
  - CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, (C<sub>x</sub>H<sub>y</sub>)

## Parameters

- 900-1100°C
- Variations of dew points
- 1 day – 1 month
- Preparation effects (grinding, polishing)
- cycling

Year of nitrogen – 2015  
detailed

Year of carbon – 2016  
preview

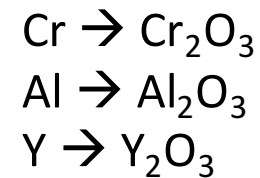


## Materials

- alumina former
- Kanthal APMT
- Kanthal AF
- Kanthal PM 58

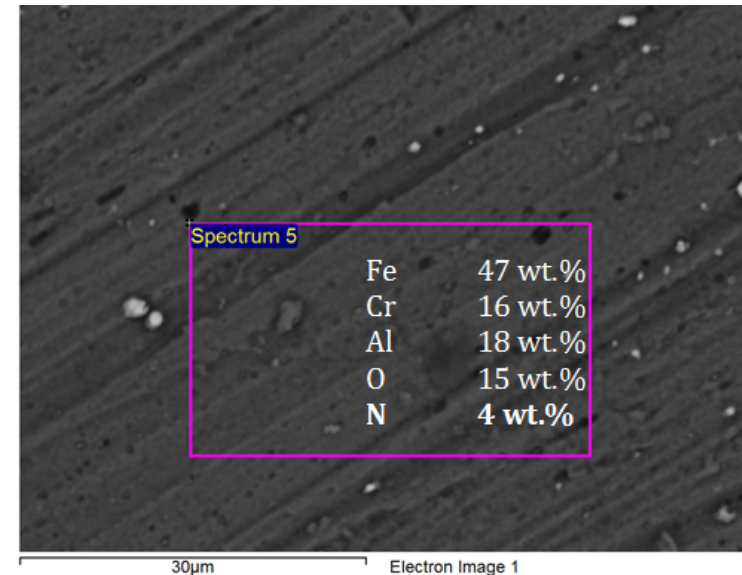
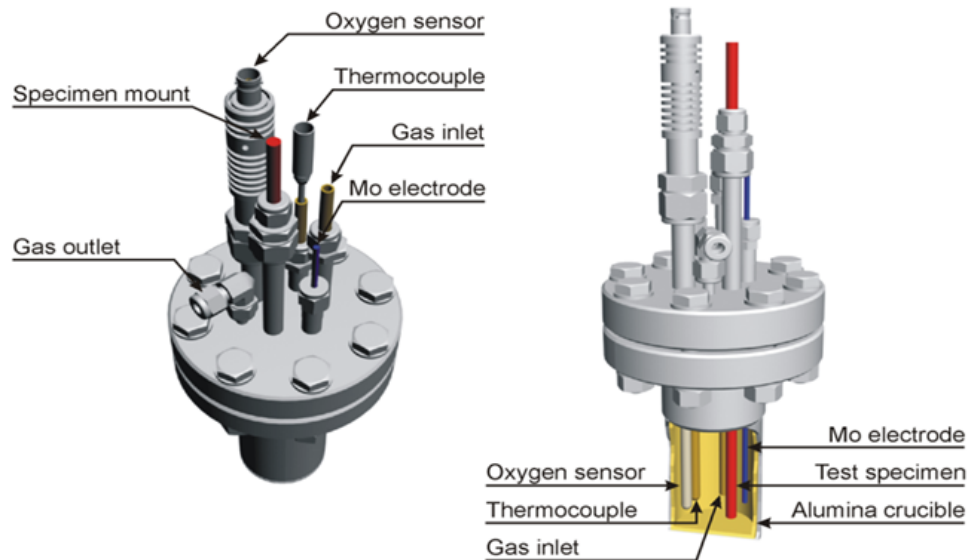
- chromia former
- Nikrothal 80
- Nikrothal 45 OC

For 900°C:



$p_{O_2} = 10^{-24}$  bar  
 $p_{O_2} = 10^{-38}$  bar  
 $p_{O_2} = 10^{-46}$  bar

# Real-time *in situ* oxidation monitoring



Schematic drawings of the equipment used for all tests included in the HTC IP project and SEM top view SEM analysis of Kanthal AF exposed for 31 days at 700° C.

- Temperature is too low to cause well observable nitridation





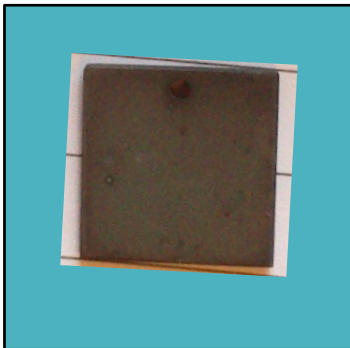
0hrs

Evaluation conditions are:

- 900°C
- N<sub>2</sub> – 5%H<sub>2</sub>
- 100 ml/min



24hrs



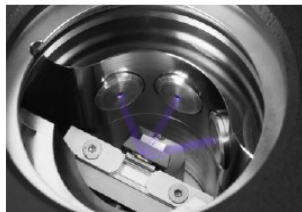
168hrs

## *Cross sectional sample preparation*

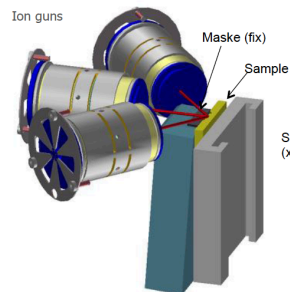
### **BIB (Broad Ion Beam)**



Argon Ion Beam

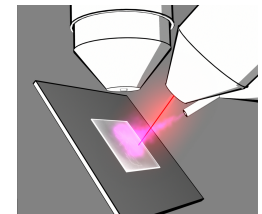


Triple Ion Beam Milling System

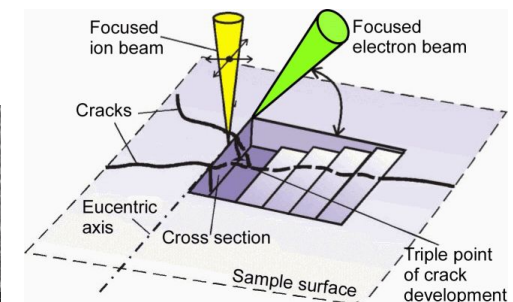
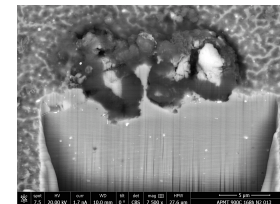


To produce large cross-sectioned surface ( $> 4 \times 1 \text{ mm}$ )

### **FIB (Focused Ion beam)**



Gallium Ion Beam



For more selective and site-specific cross-section (around  $30 \times 50 \mu\text{m}$ )

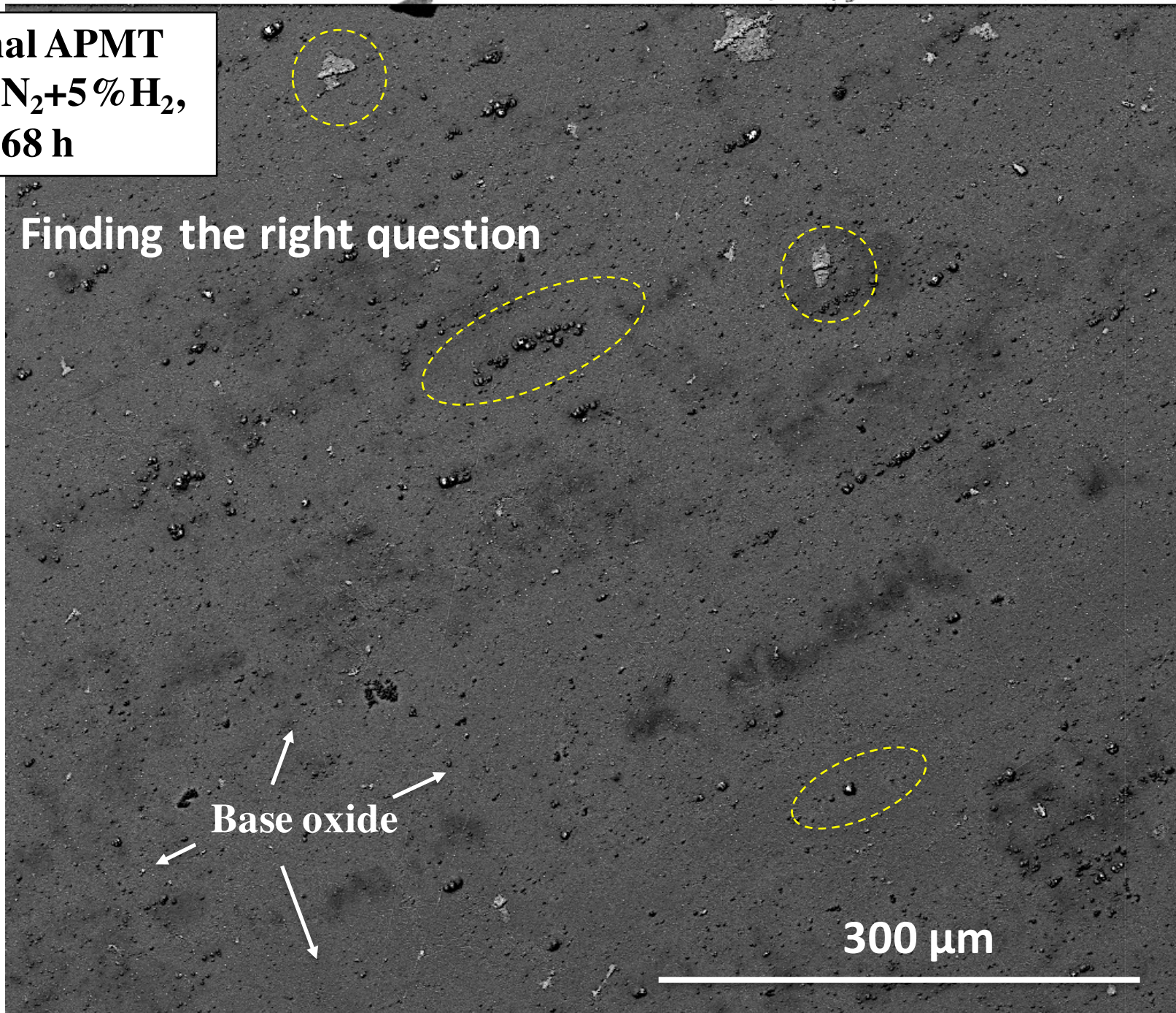


**Kanthal APMT**  
**900°C, N<sub>2</sub>+5% H<sub>2</sub>,**  
**168 h**

**Finding the right question**

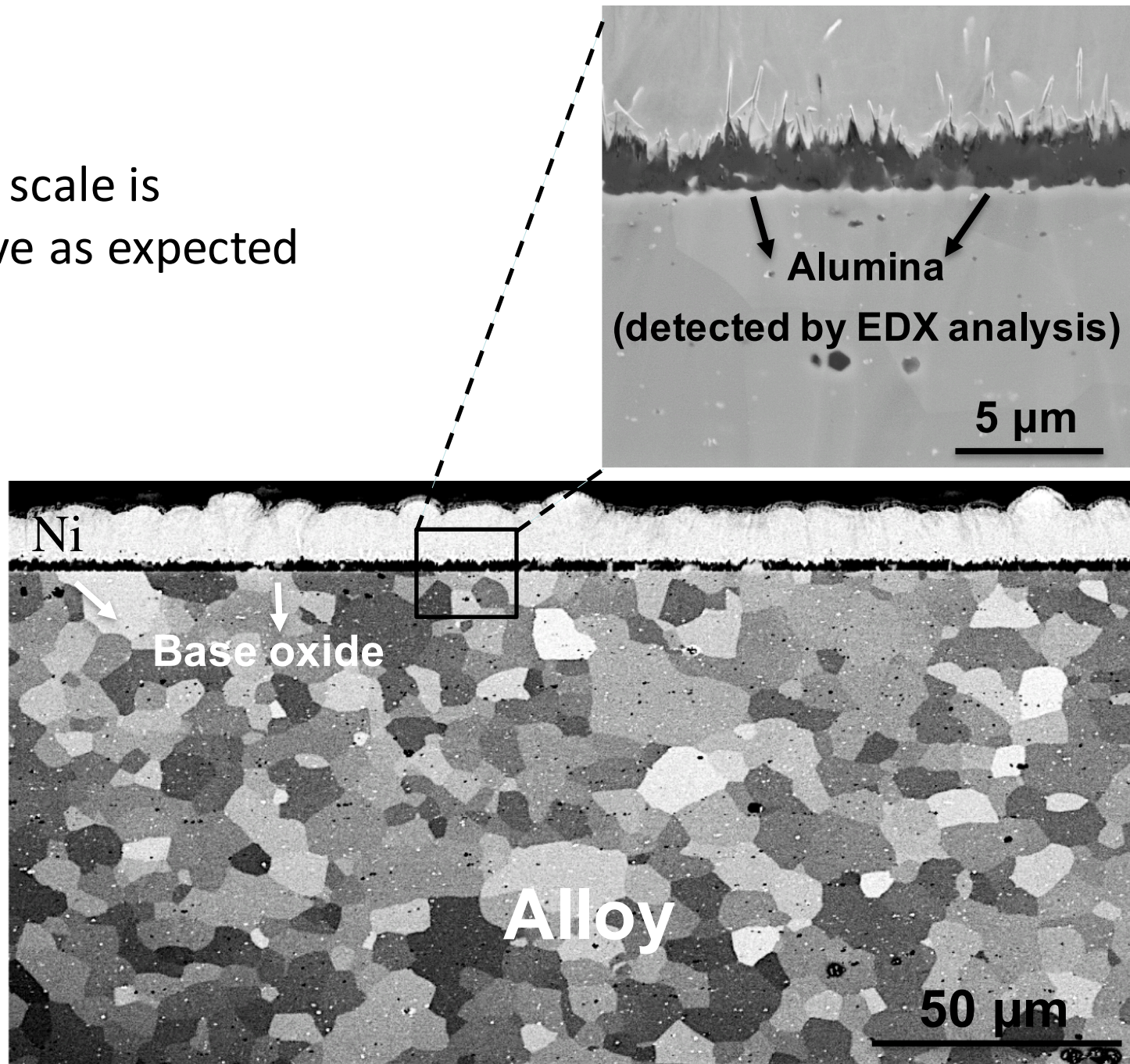
**Base oxide**

**300 μm**

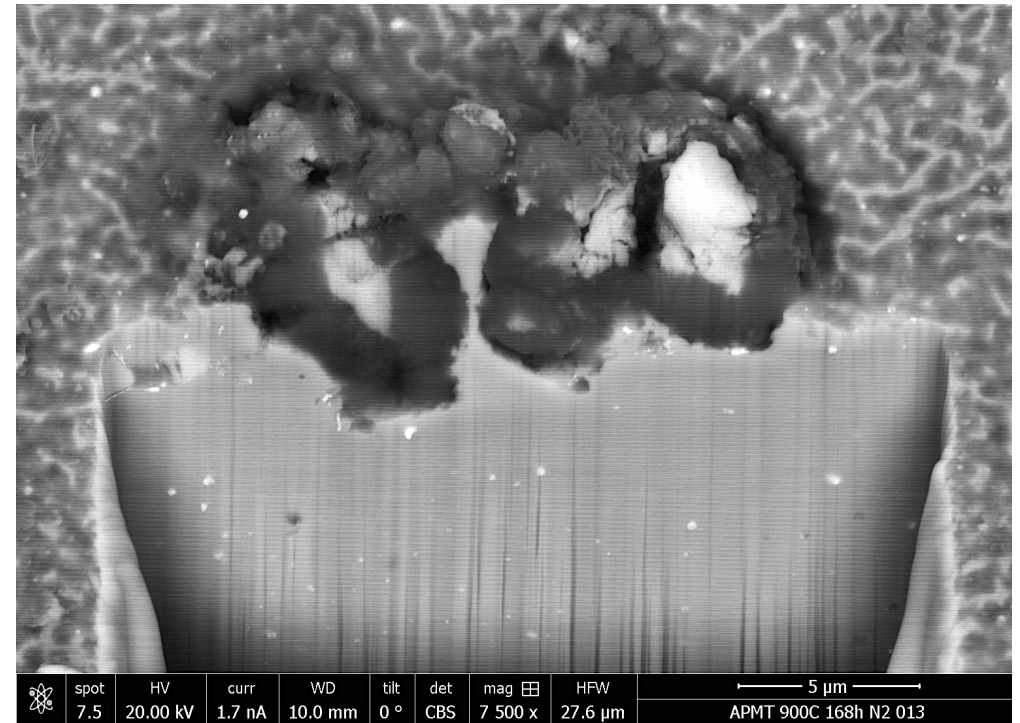
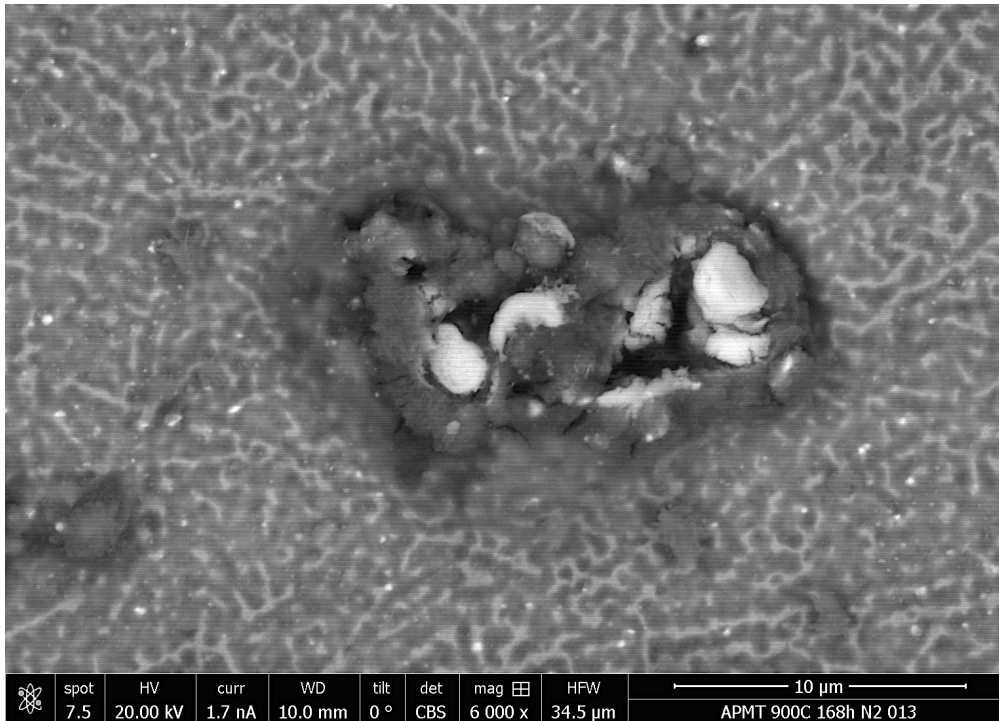




Alumina scale is  
protective as expected

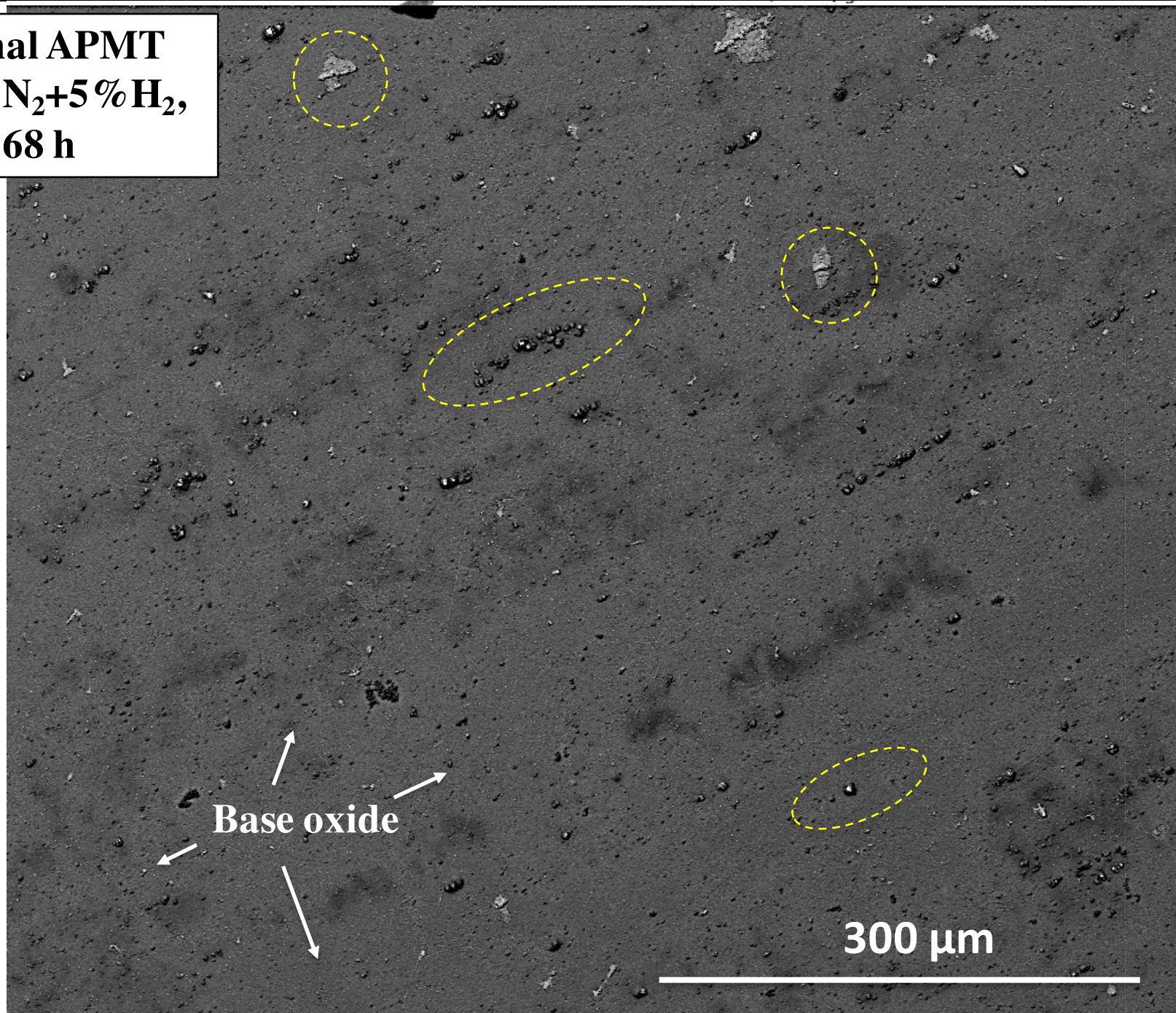


Most crack-like structure was found in connection with RE-particles -  
however, the alumina scale underneath was even more pronounced.



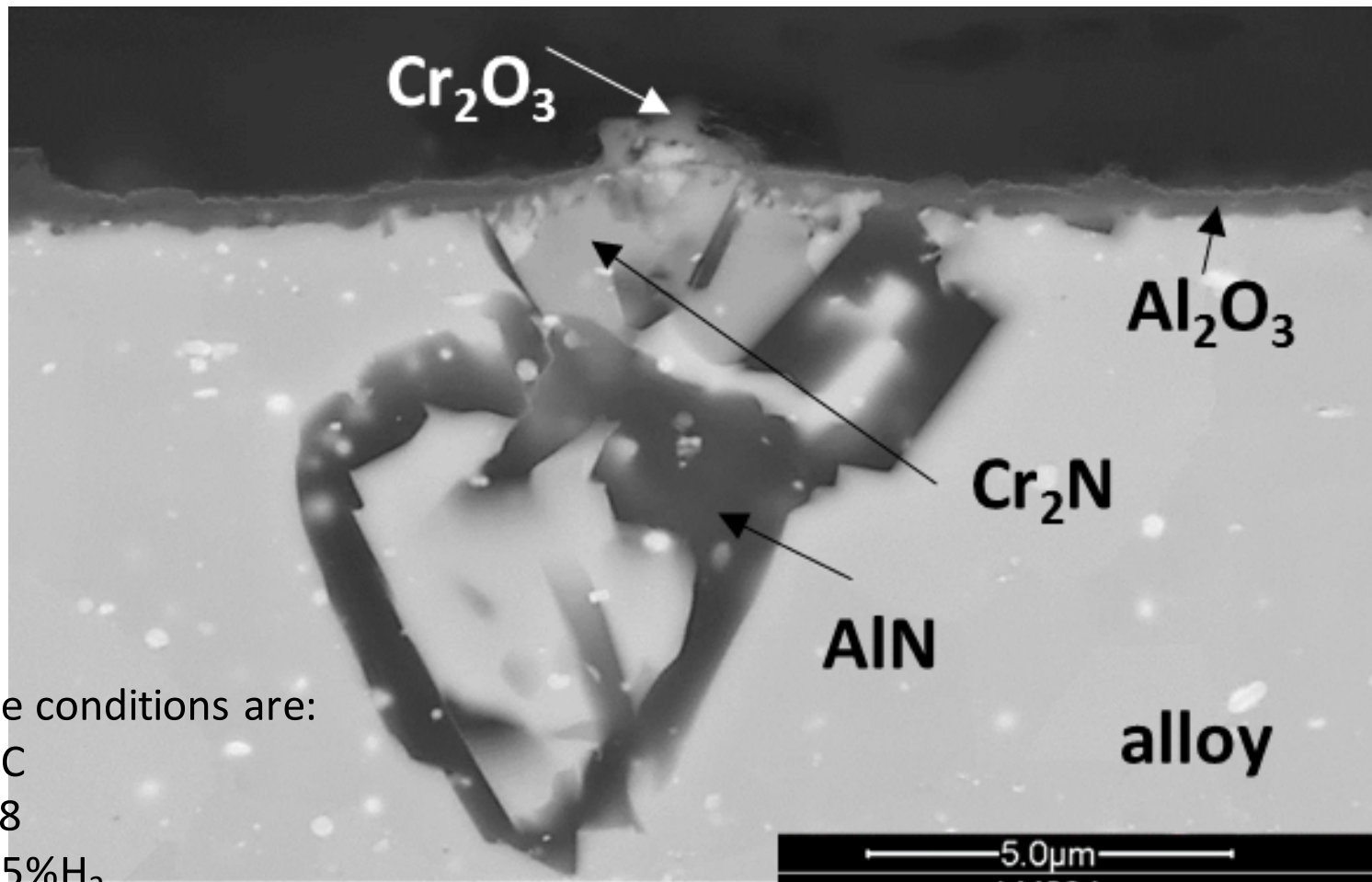


**Kanthal APMT**  
**900°C, N<sub>2</sub>+5% H<sub>2</sub>,**  
**168 h**





## BIB cross section through one chromia island

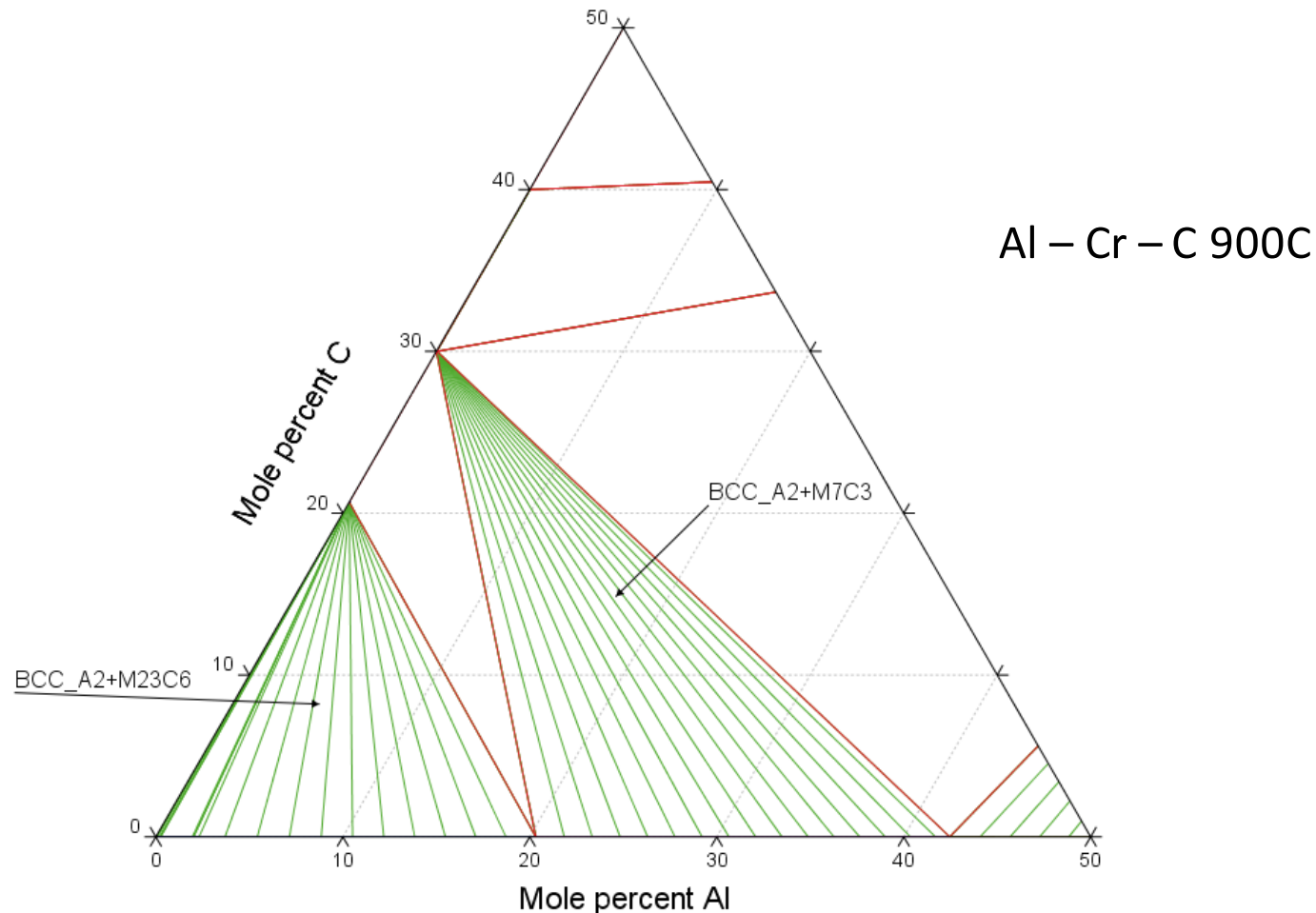


Exposure conditions are:

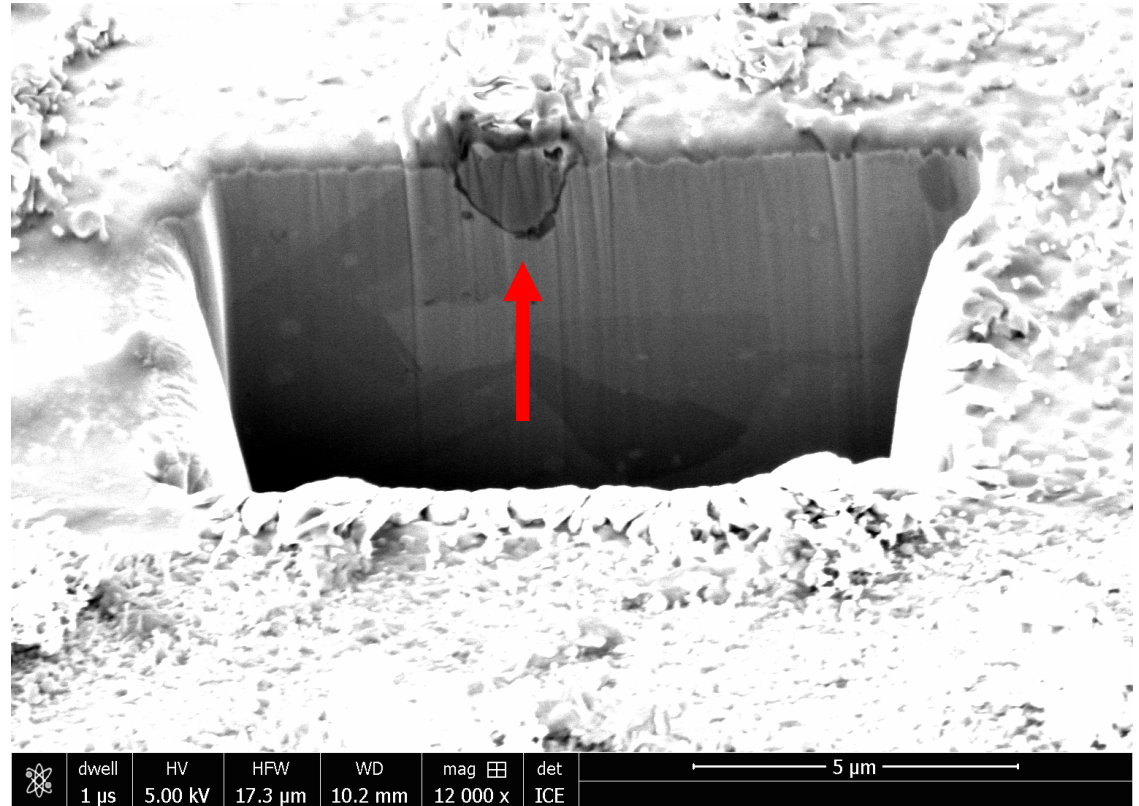
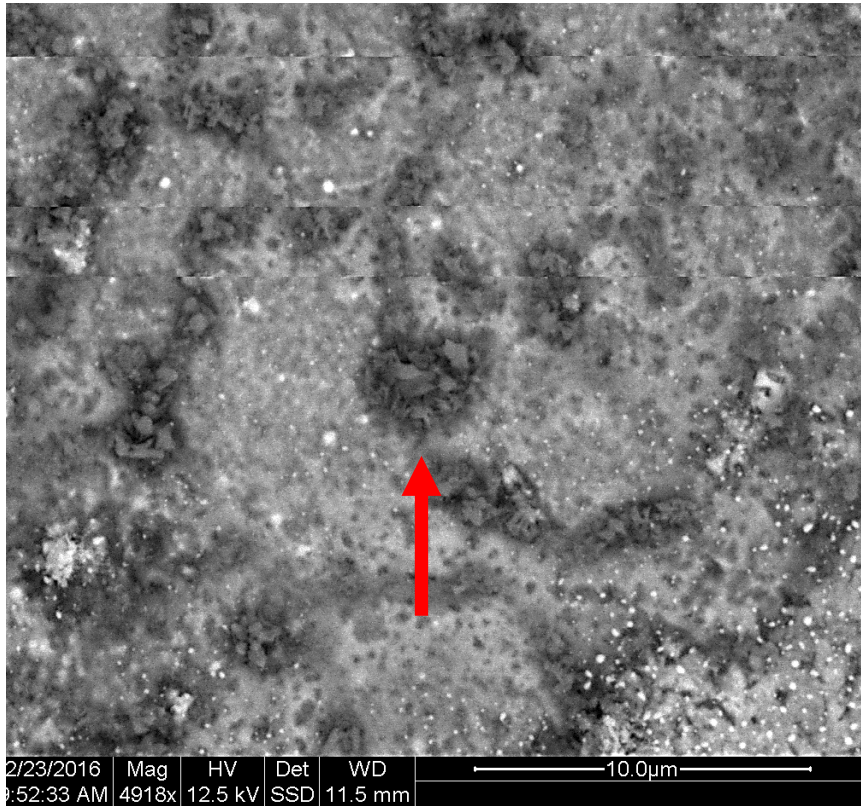
- 900°C
- PM58
- $\text{N}_2 - 5\%\text{H}_2$
- 100 ml/min

What could be the source for the chromia island

- Cracks in the alumina scale
- Phases in the alloy with limited solubility of aluminium



## Carbides as possible chromia island source

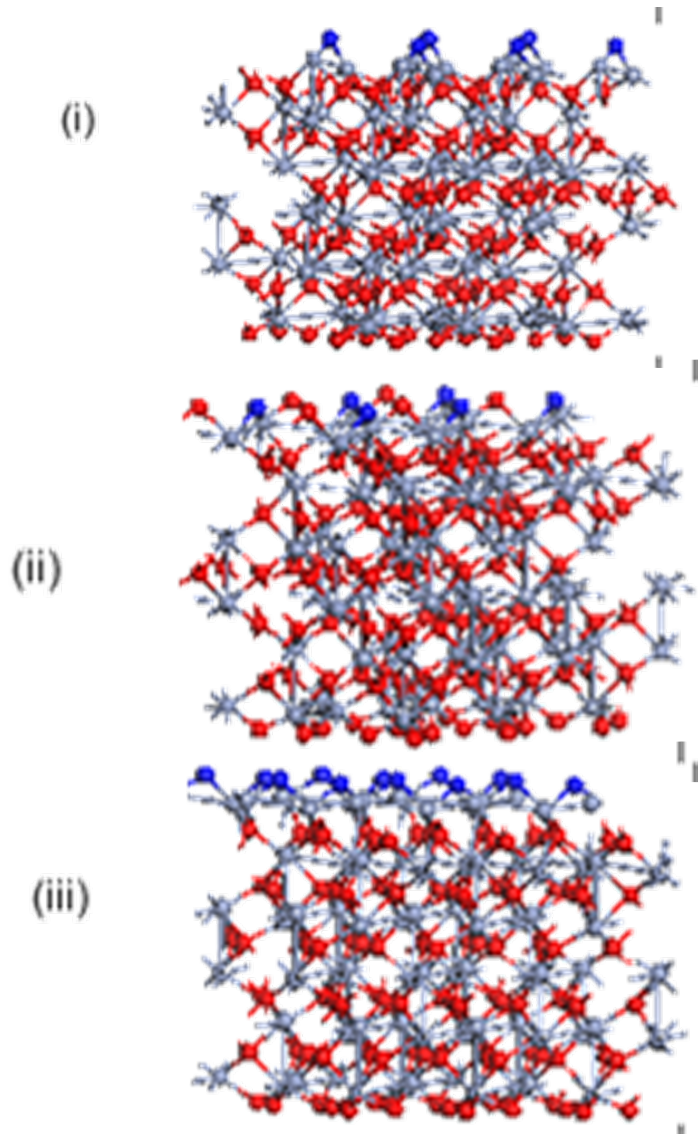


Exposure conditions are:

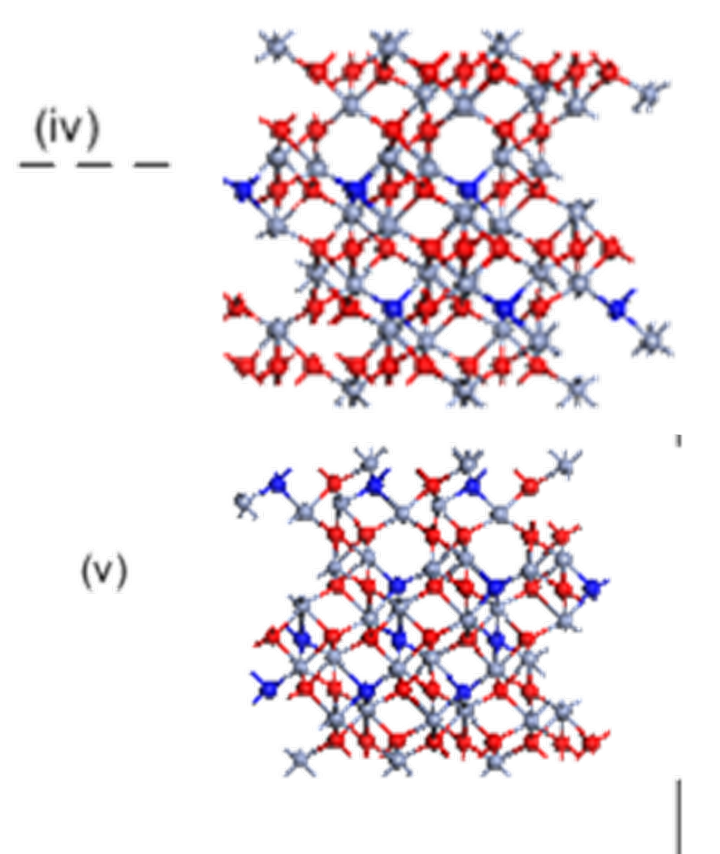
- 900°C
- PM58
- N<sub>2</sub> – 5%H<sub>2</sub>
- 100 ml/min



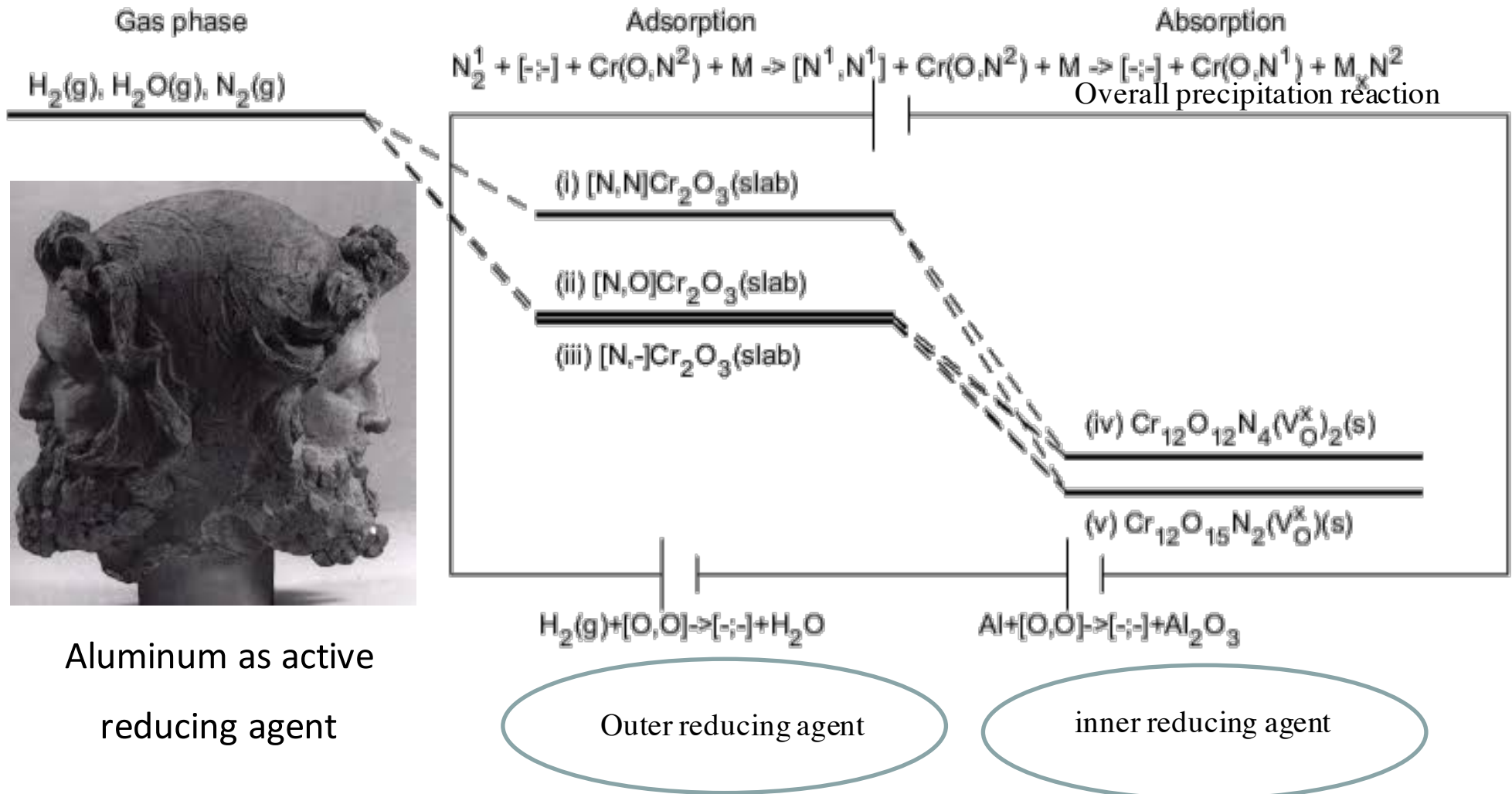
## Oxide surface calculations



## Oxide bulk calculations



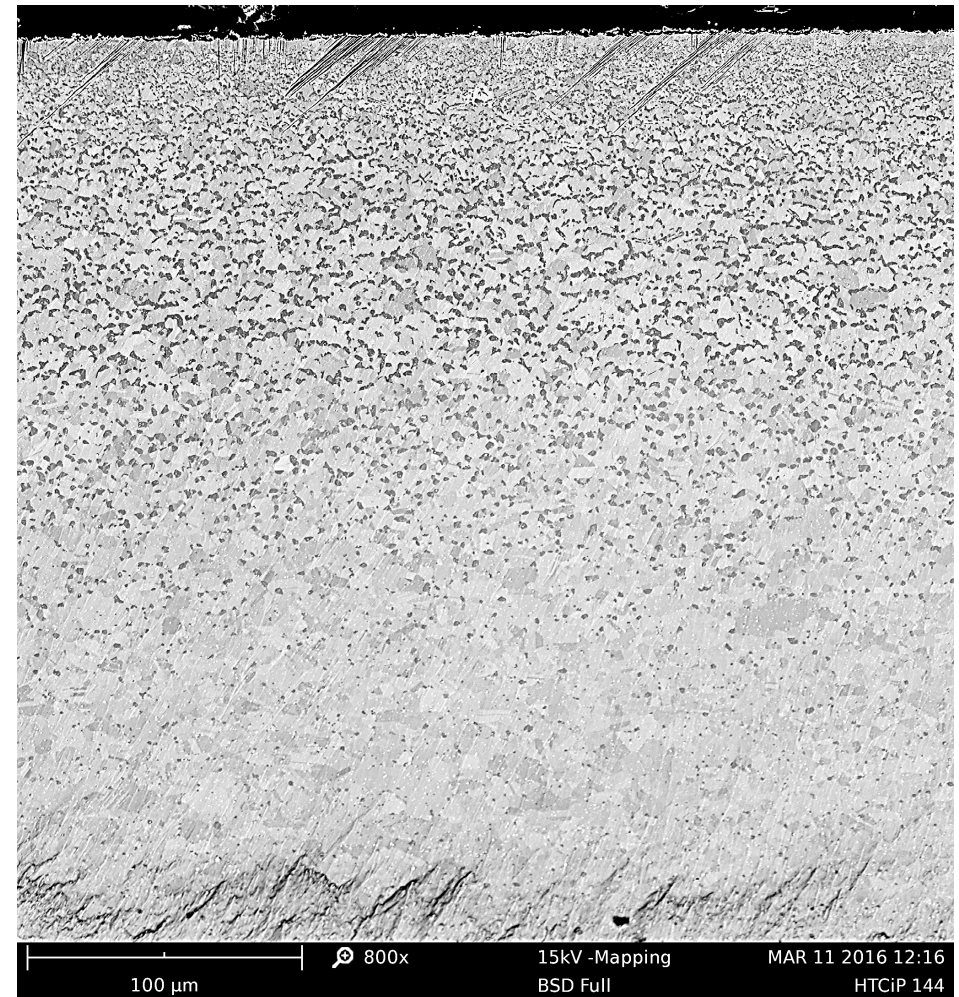
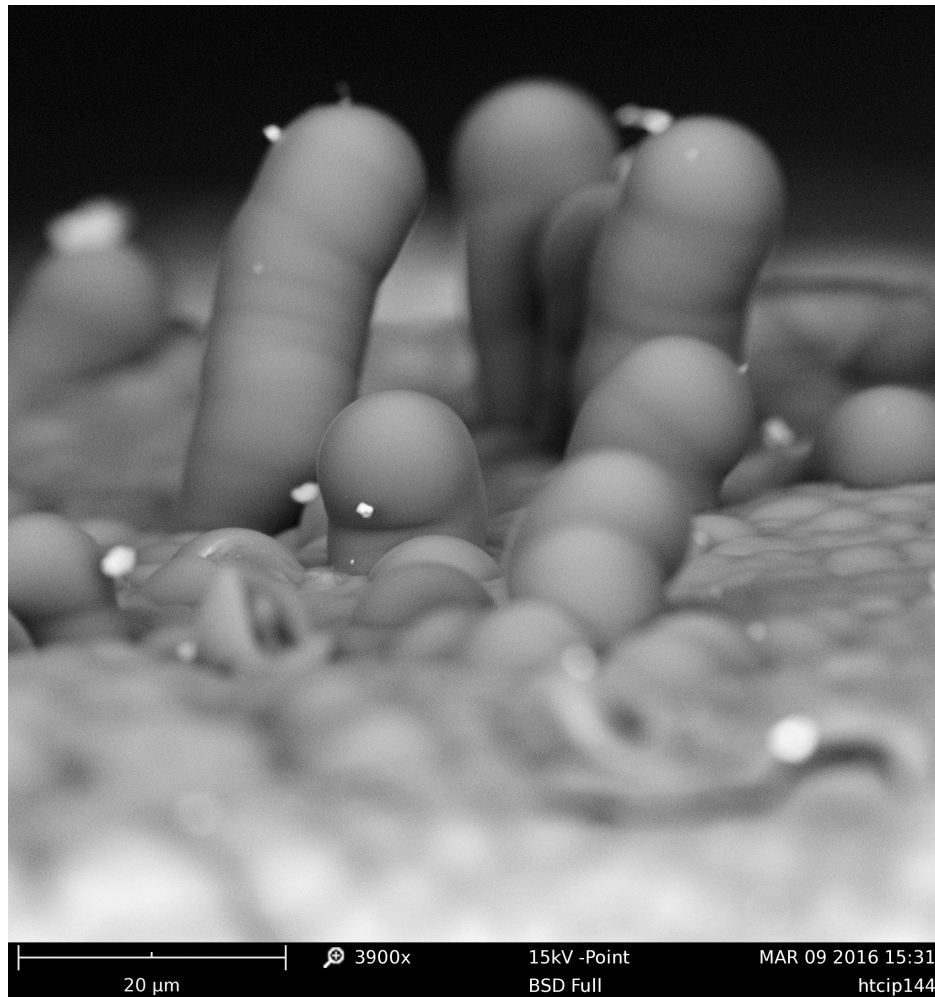
Variation of the nitrogen content



There are two drivers for oxygen depletion from the chromia scale, one is the reducing hydrogen at the oxide/gas interface and the other much stronger one is aluminum at the chromia/alloy interface.



Carbon year has started - A preview:







## Summary

In the case of nitridation, the way of entry towards the alloy has yet been identified as secondary oxide species in the oxide scale, here chromia embedded in alumina.

Reducing conditions allow the formation of metastable oxy-nitrides which present as one of the possible diffusion paths.

DFT techniques allow this insight which would otherwise not be detectable via microscopy.

Carburisation mechanisms will be approached in the same manner.

**Thank you for your attention.**

