# Corrosion of FeCr alloys in Solid Oxide Fuel Cells

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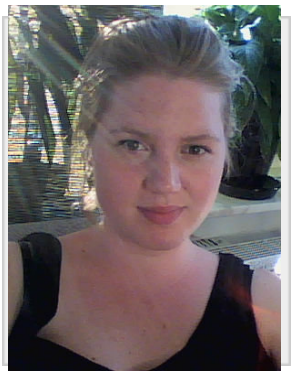
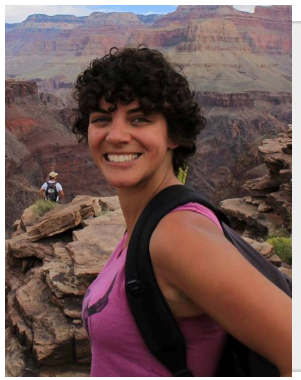


Maria Nikumaa



Claudia Göbel

# Project partners

SANDVIK

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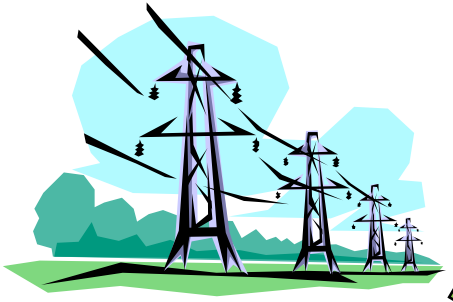
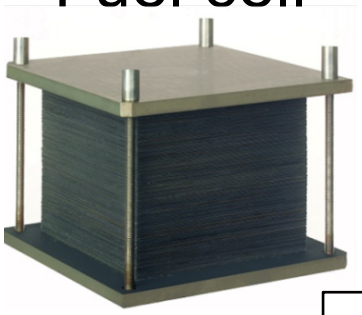
# Solid Oxide Fuel Cells



Fuel cell



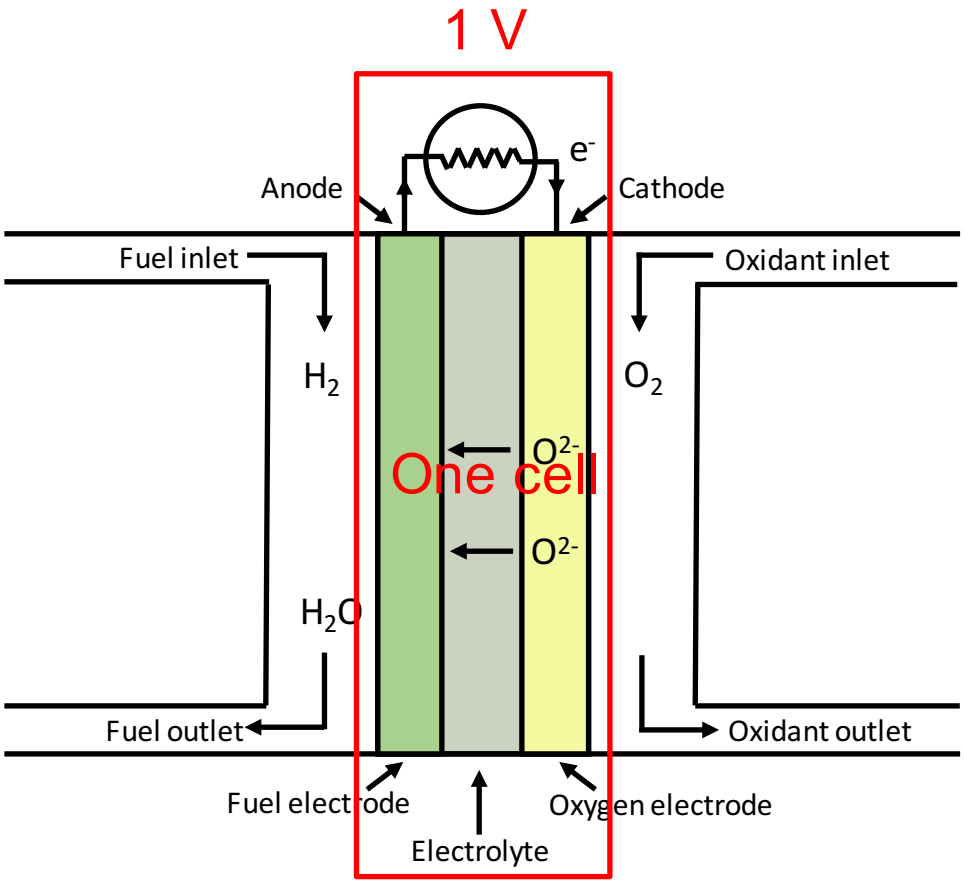
$(CO_2)$
$H_2O$
Electricity

$O_2$
$H_2$ ($CH_4$, CO, other)

Truck or RV
Auxiliary Power &
Range Extender (APU)

- Efficient power generation (60 el%)
- Fuel flexible
- Low emissions
- Scalable

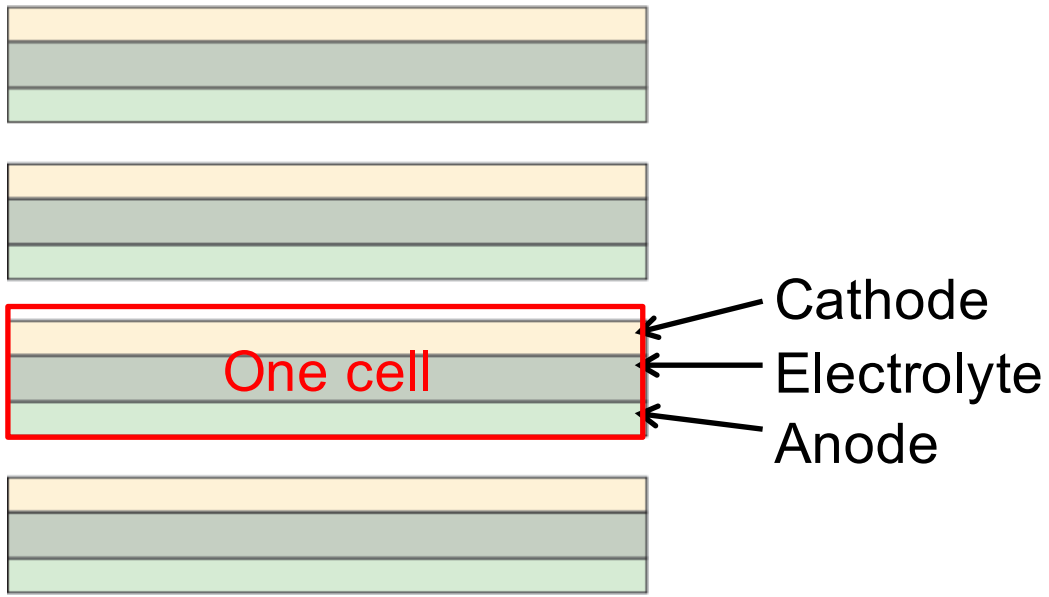
# Solid Oxide Fuel Cell



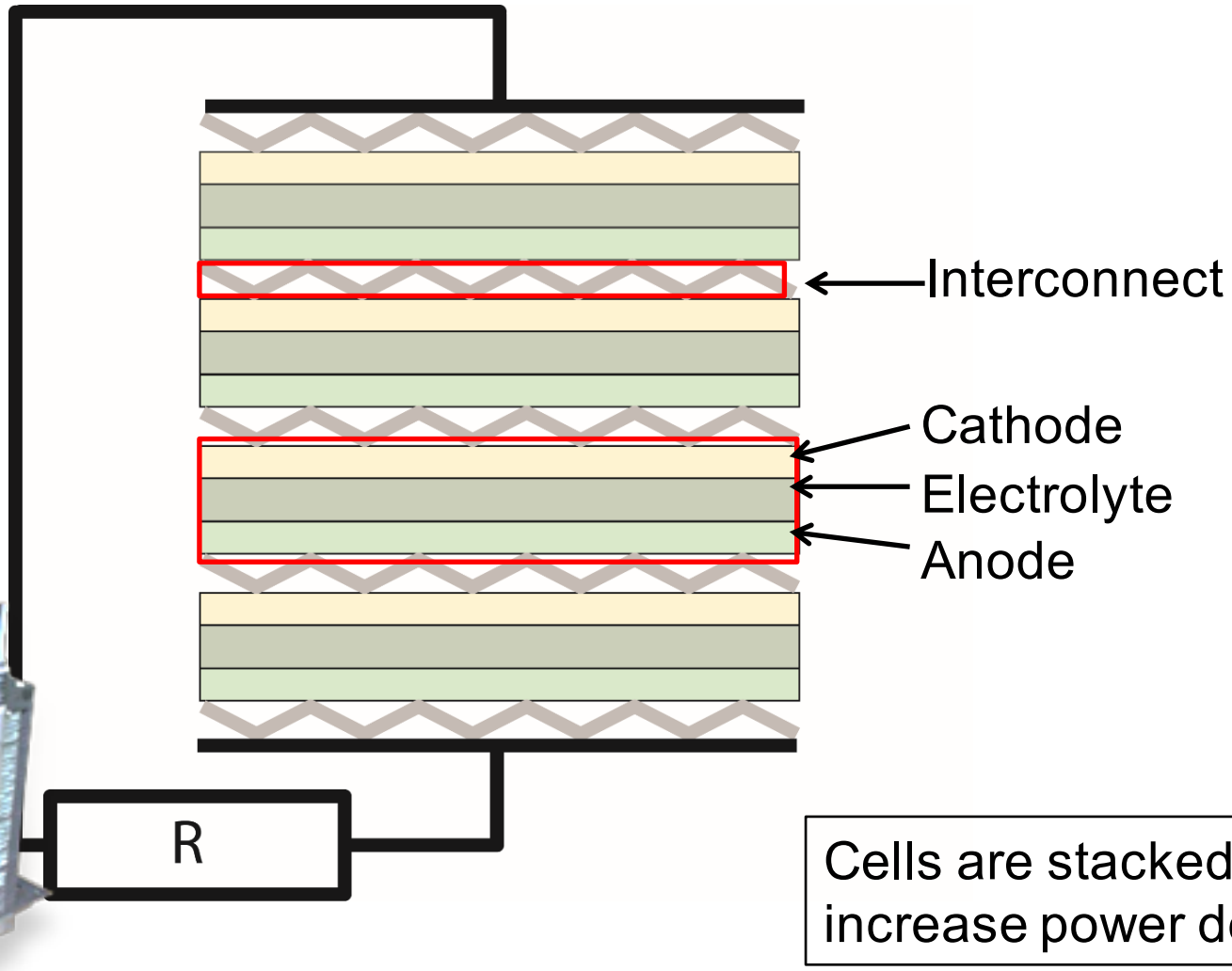

- Operating temperature: 500 – 900 °C
- Controlled reaction of hydrogen and oxygen
- Various fuels can be used
- Ceramic components

$$O_2 + 2H_2 \rightarrow 2H_2O + \text{el.}$$

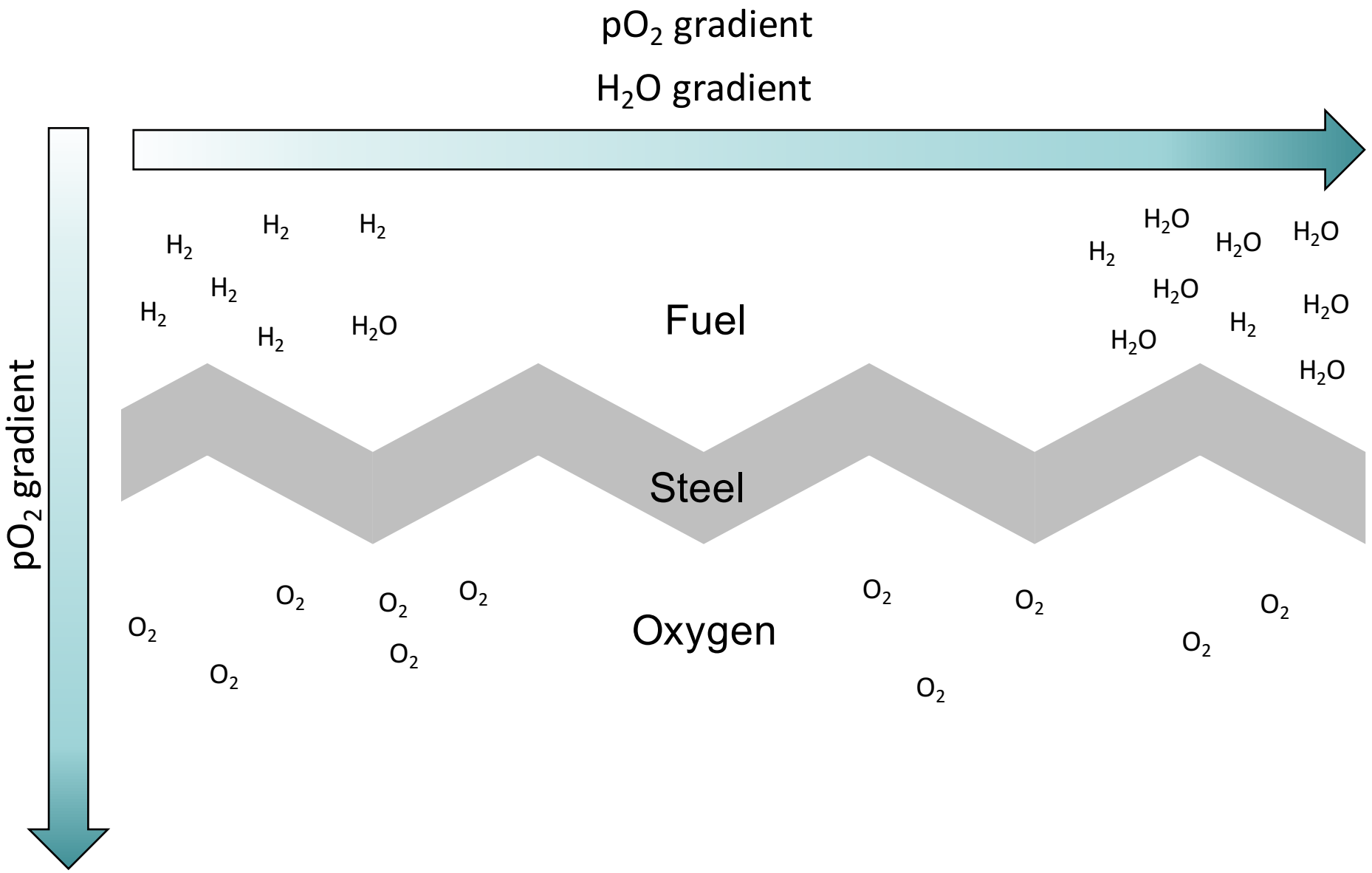
# Stacking of cells



# Stacking of cells

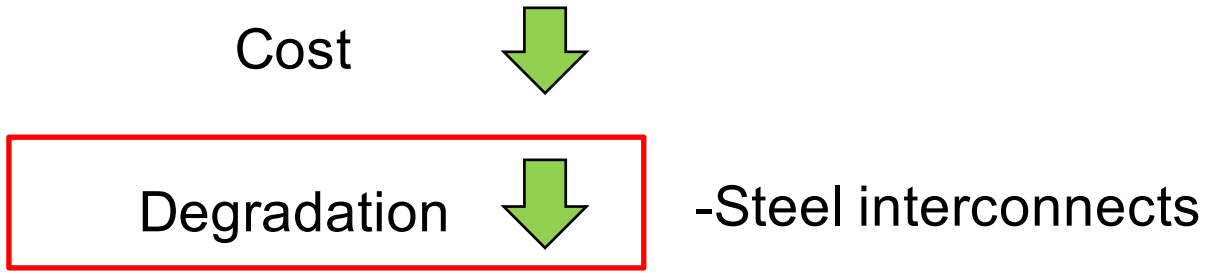



Cells are stacked to increase power density


$pO_2$ gradient
$H_2O$ gradient
$pO_2$ gradient
Fuel
Steel
Oxygen
$H_2$
$H_2O$
$O_2$

# Sustainable = economically viable?

SOFC technology faces two major challenges:




Commercialization of SOFC

# Material challenges for metallic SOFC interconnects

- Corrosion
- Chromium evaporation
- Degradation of electronic conductivity

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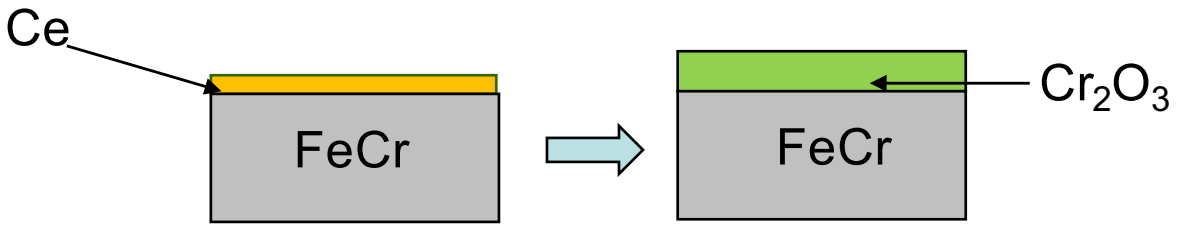
# Precoated steel concept

- PVD coatings
- Roll to Roll process
- Production line
- High capacity
- 800mm width
- Multilayered coatings

# Solving corrosion

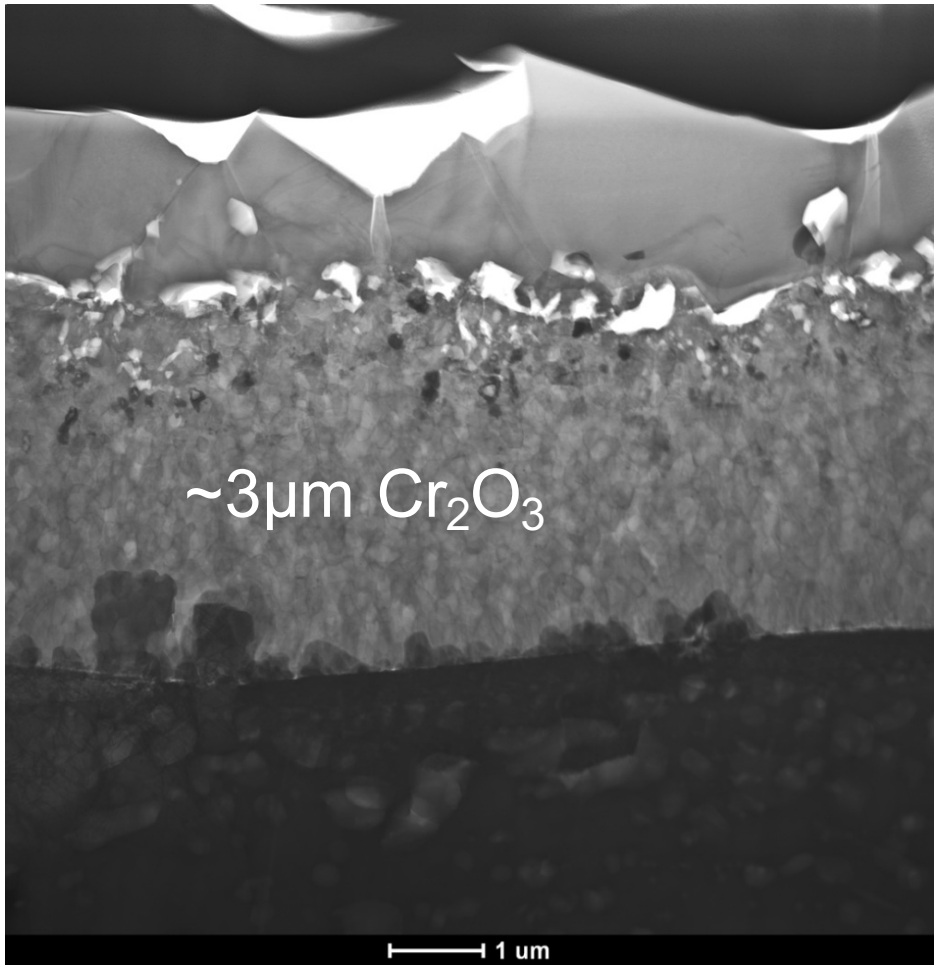
- Adding reactive element coating by PVD

  - Promotes chromia formation
  - Decreases oxidation speed

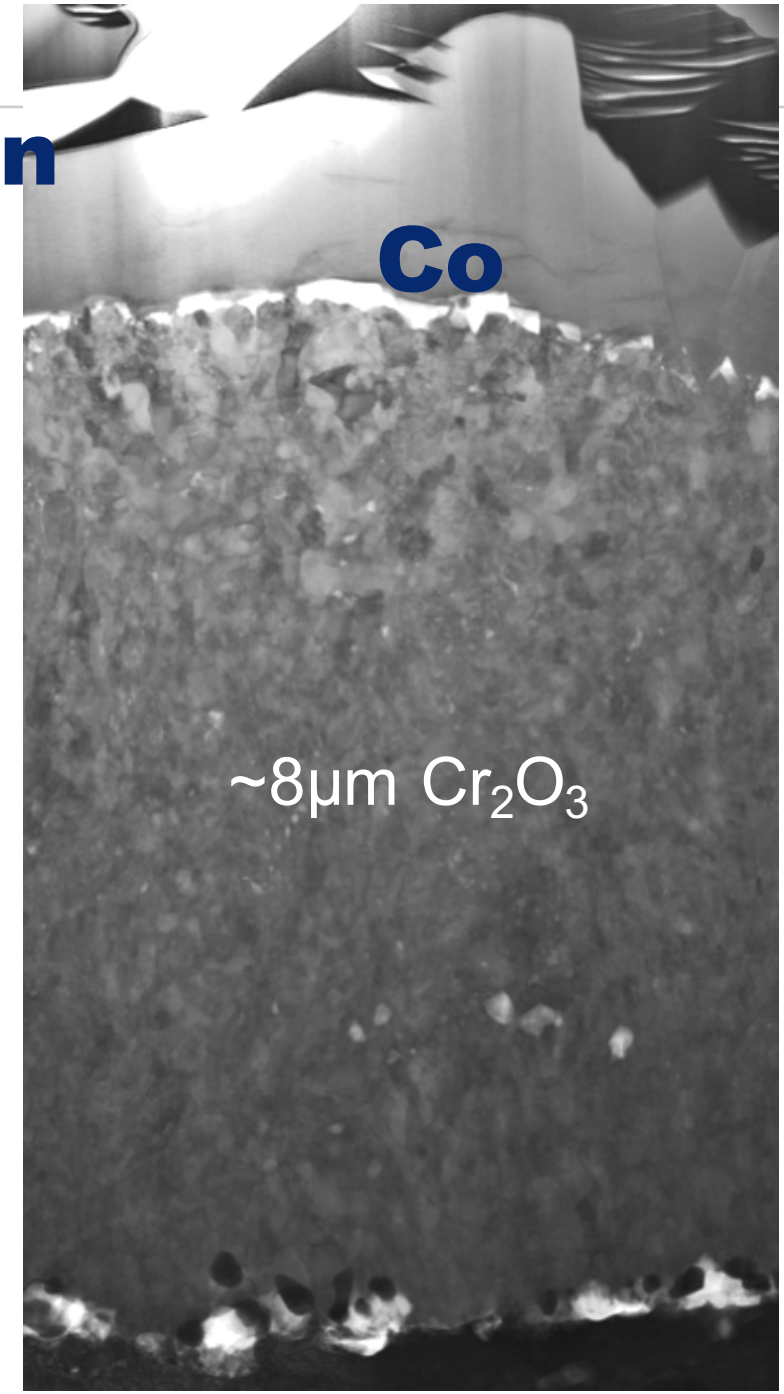


# Comparison

## Co/Ce




## Co

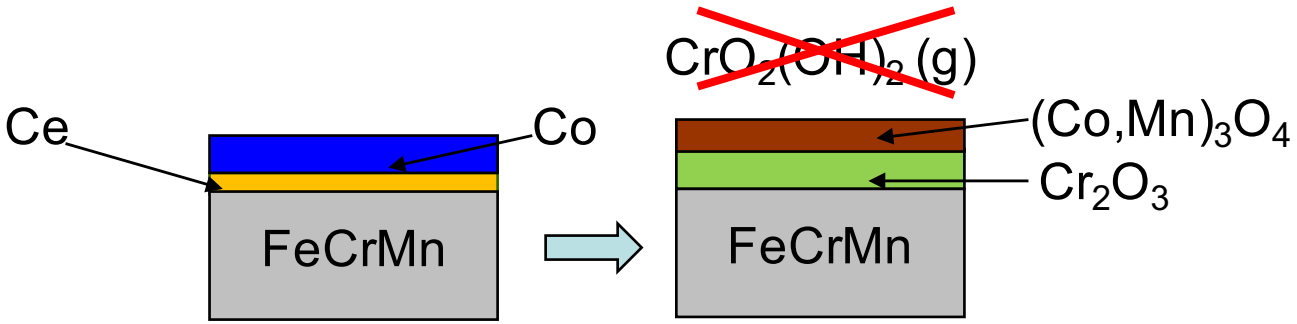



Ce slows down the growth of the $Cr_2O_3$ layer

# Solving chromium evaporation

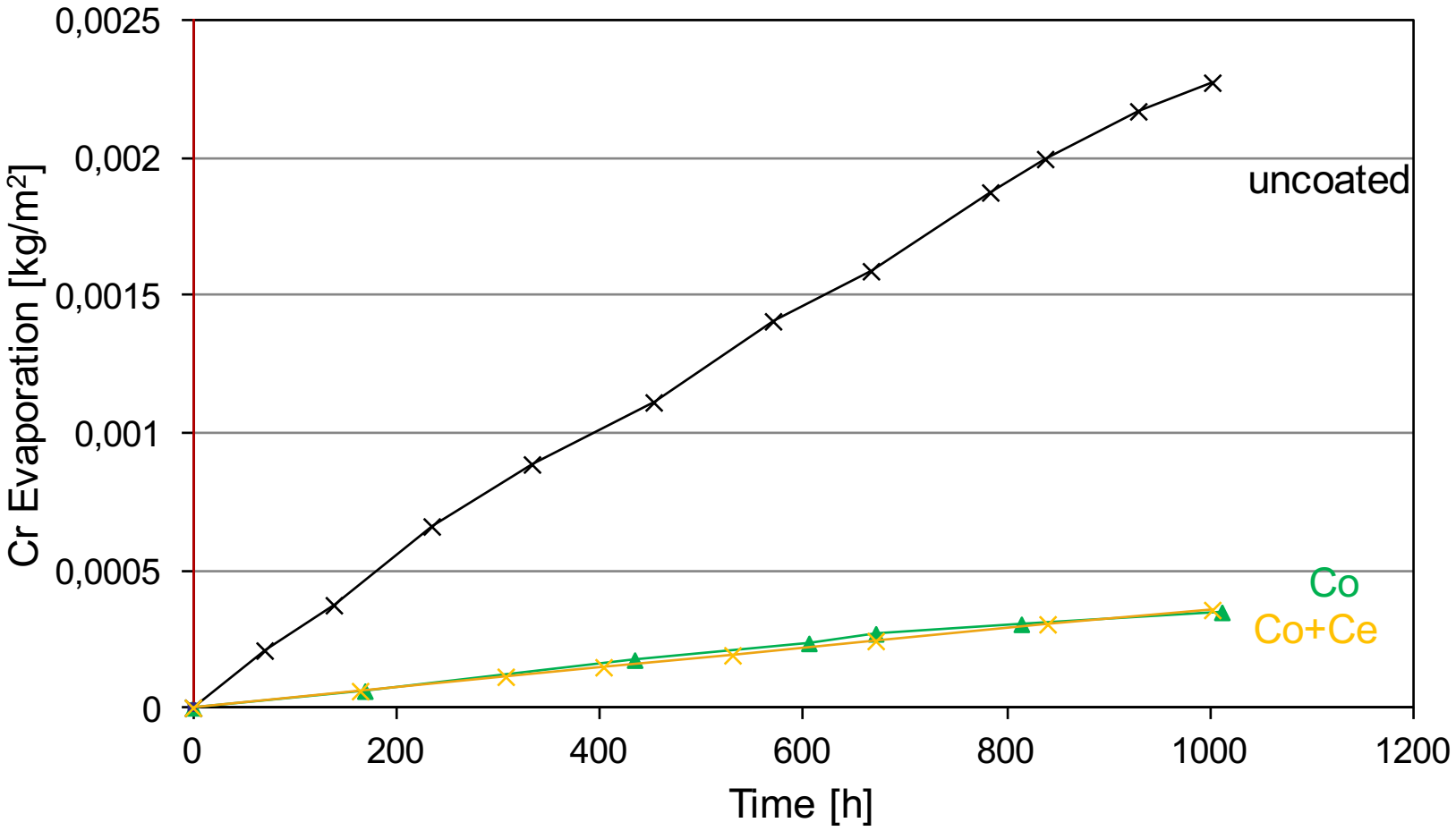
- Adding metallic Co coating by PVD

  - Oxidizes to Co-Mn-spinel
  - Low Cr activity



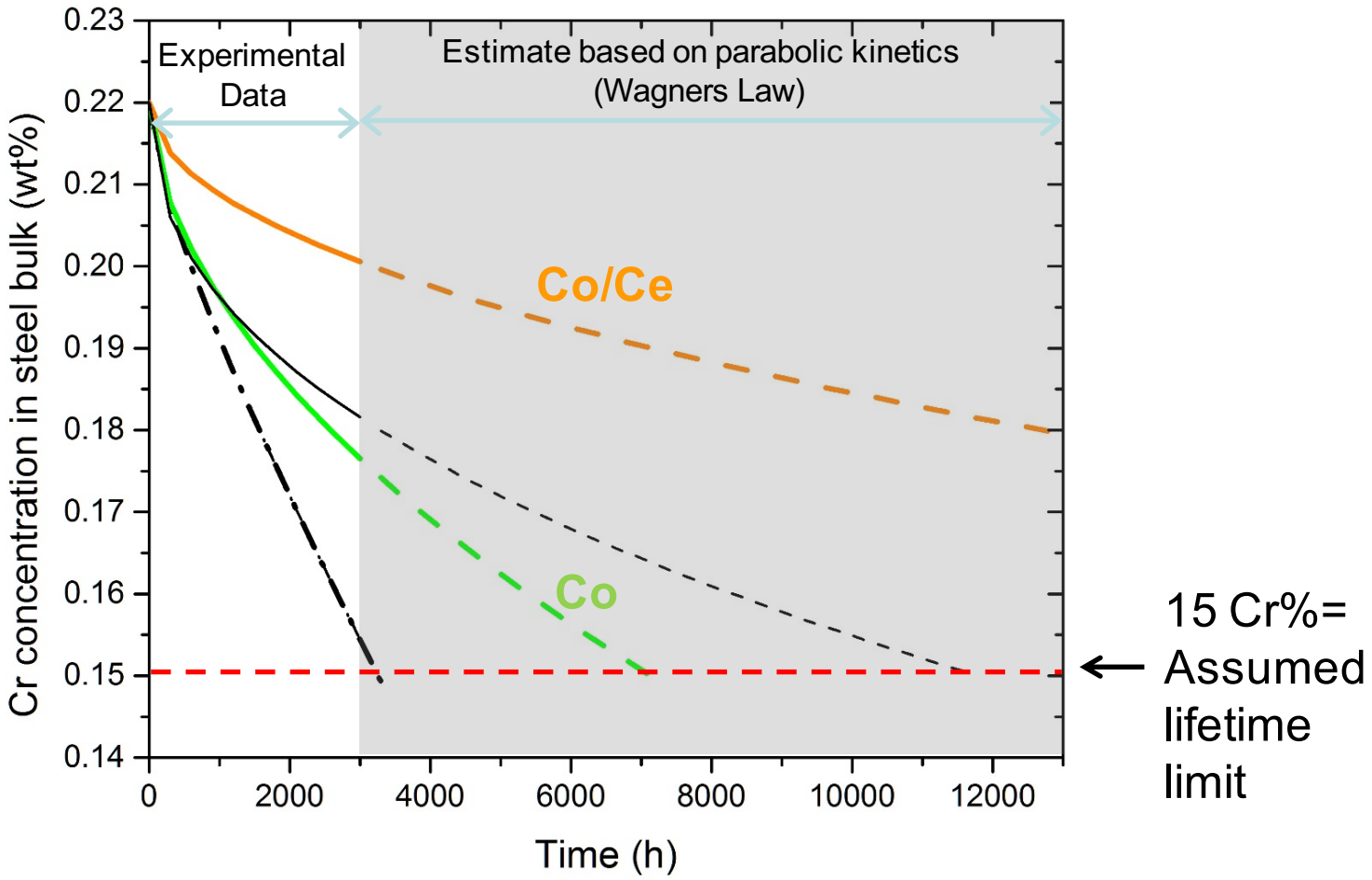
# Cr Evaporation

## (850°C in air + 3% $H_2O$)



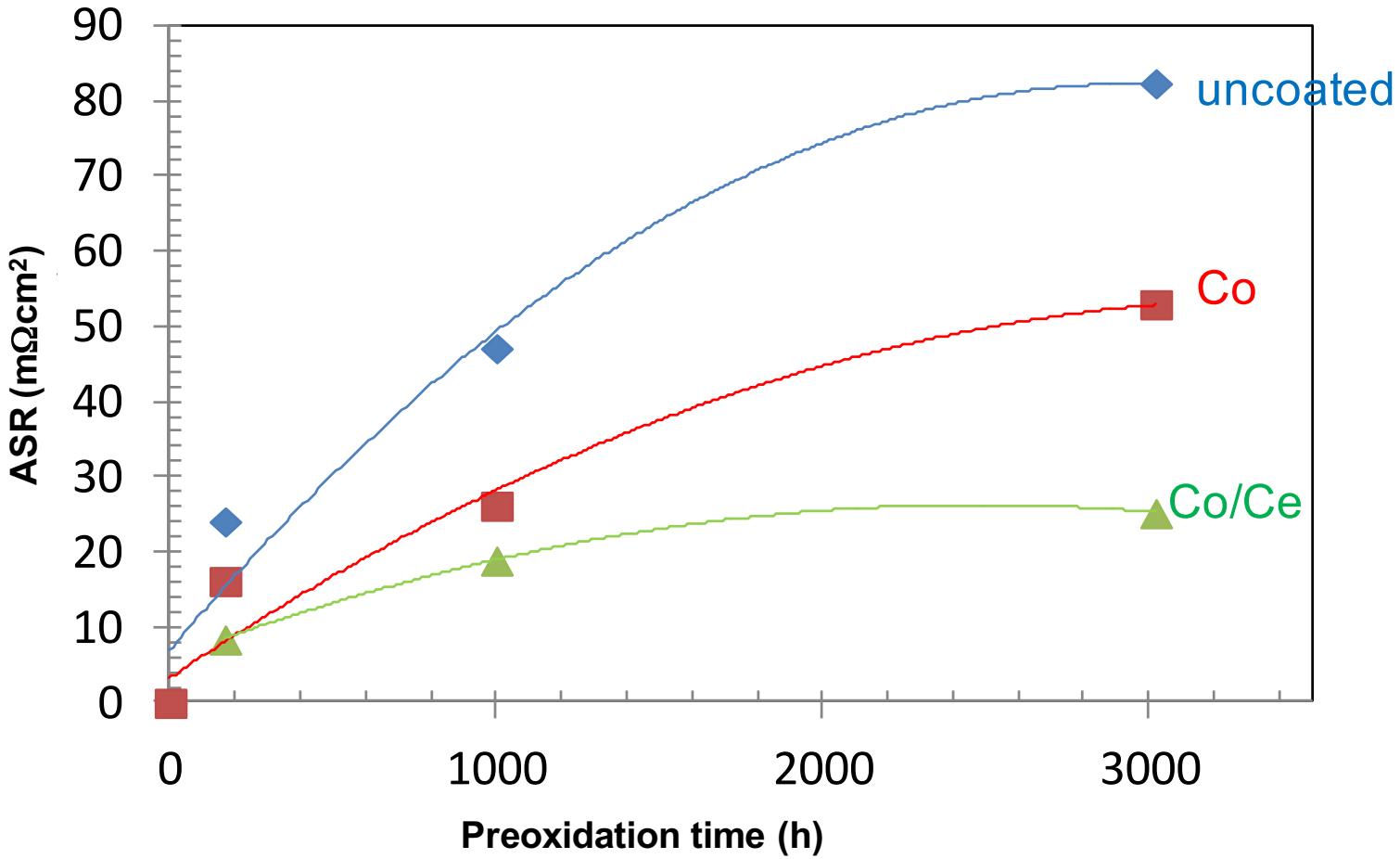

Co+Ce coating as good as Co coating

# Lifetime estimate - Calculated remaining Cr



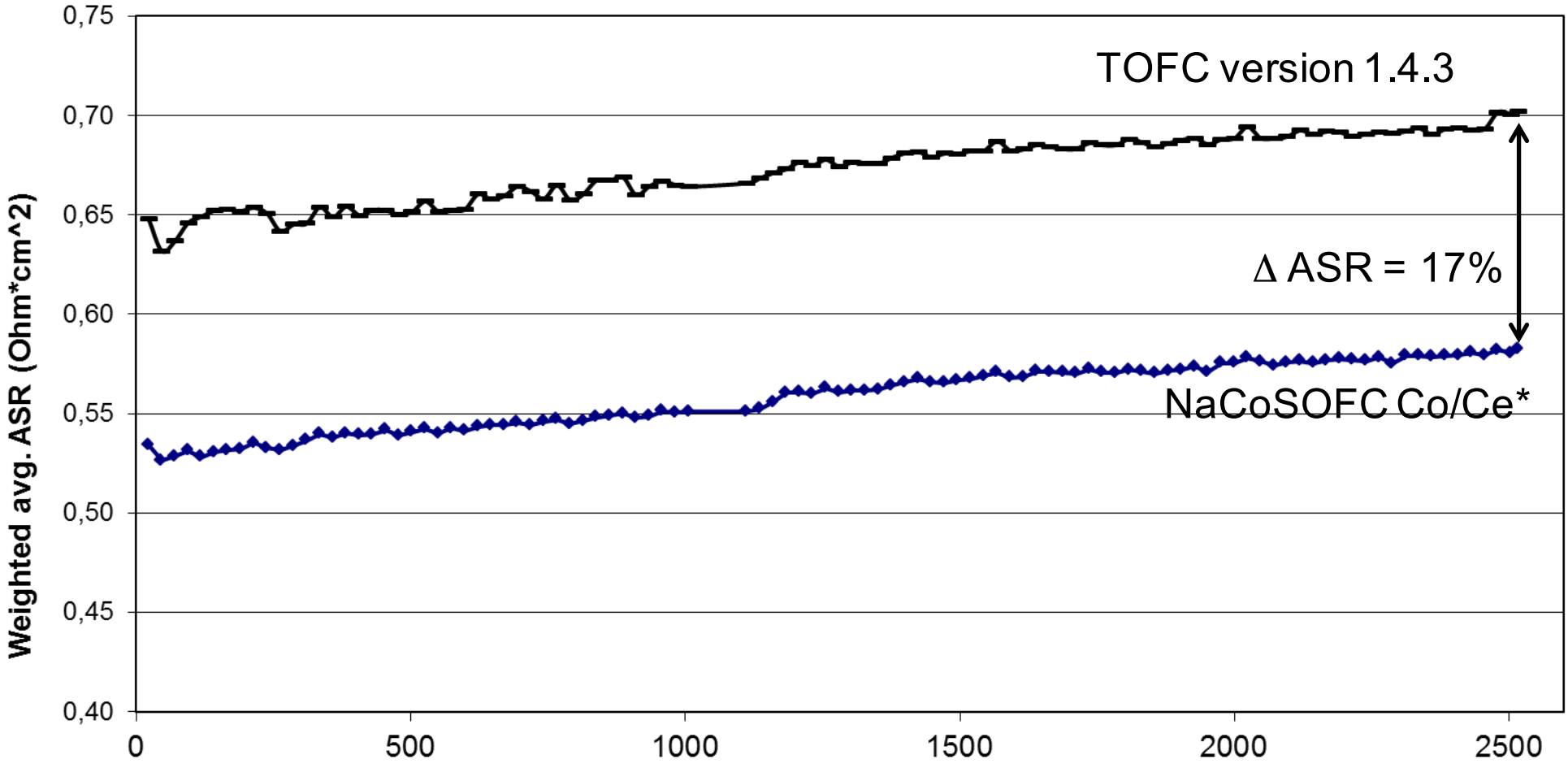
# ASR characterization

**@ Department of Chemistry, University of Oslo FERMiO**



# 2500h Stack Test

**@ 700°C, 20A**




TOPSOE FUEL CELL

*640nm/10nm Co/CePVD postcoated

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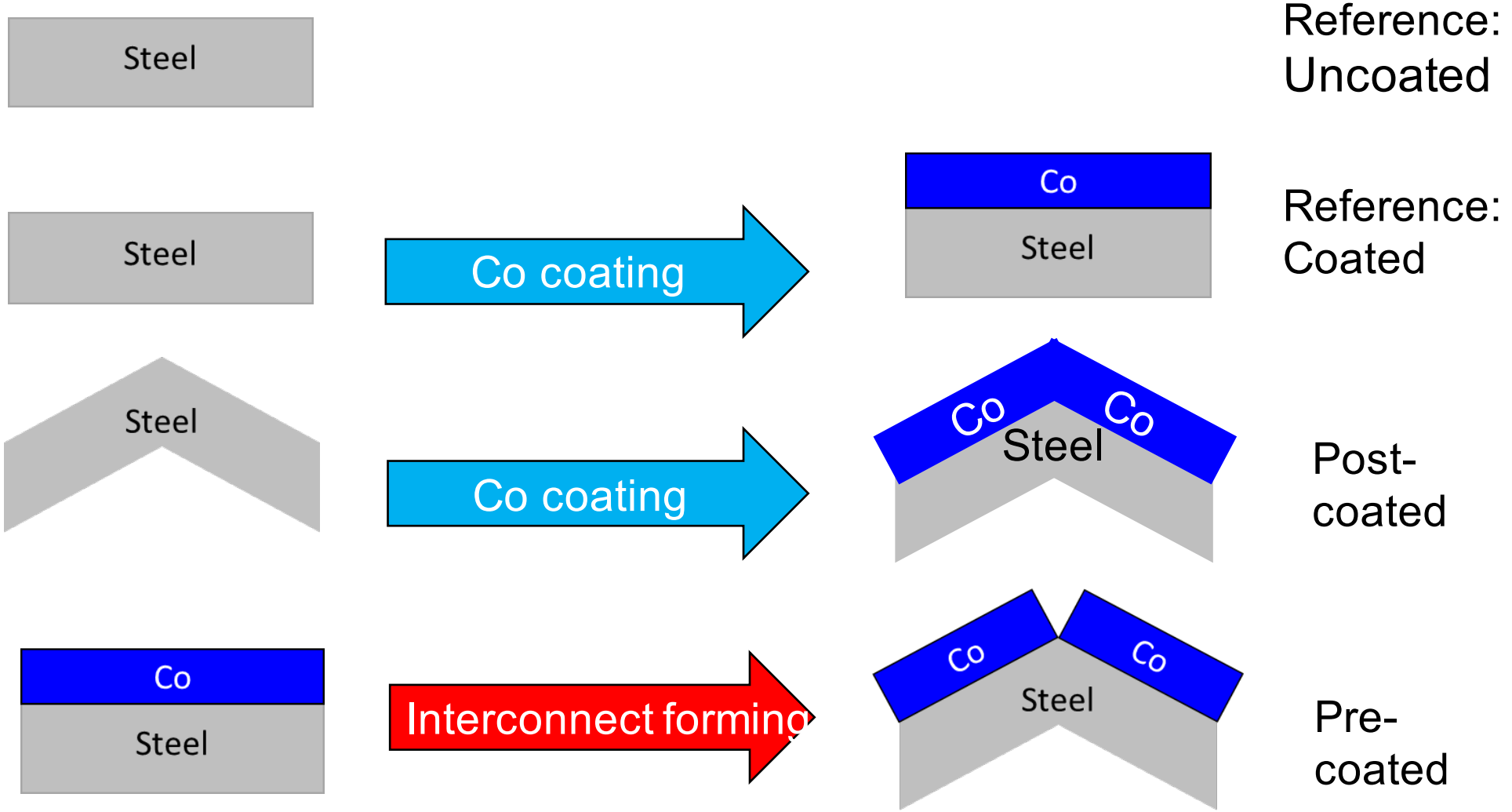
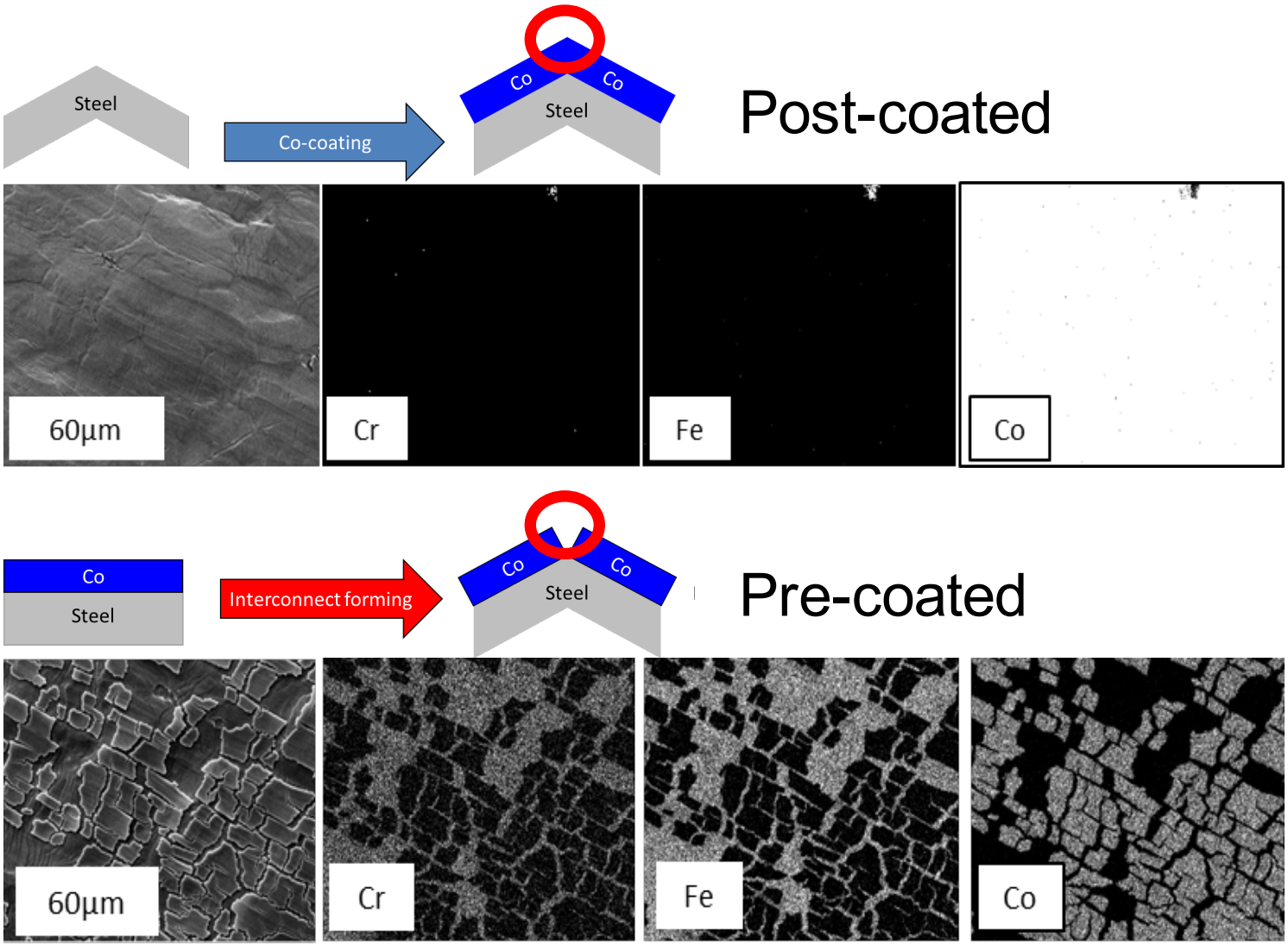
# Effect of deformation


Increased Cr vaporization?

# Materials investigated

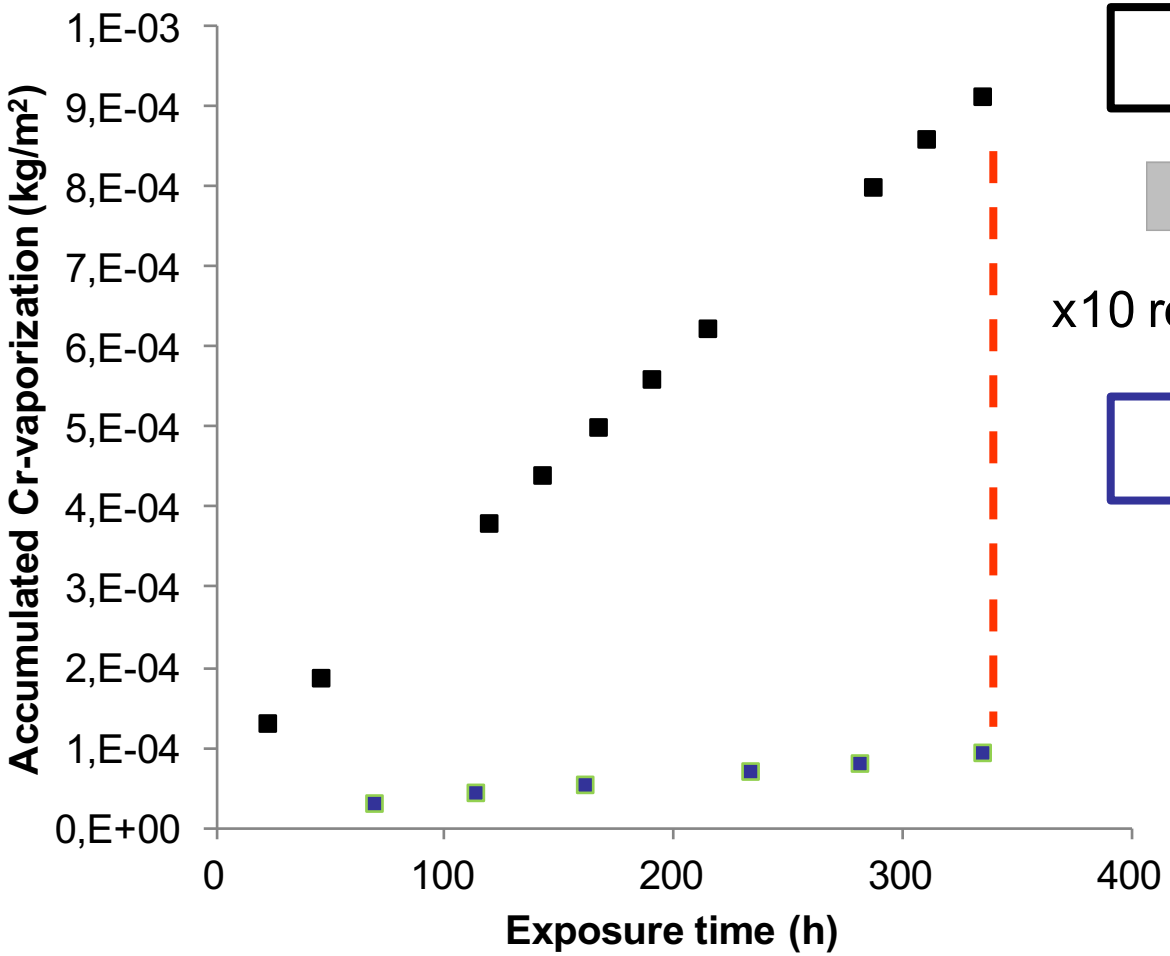


# Before exposure

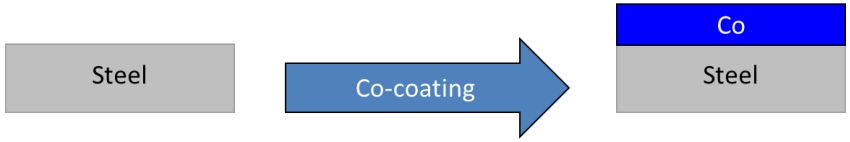


# Cr vaporization

## Air, 850 °C




Uncoated and undeformed

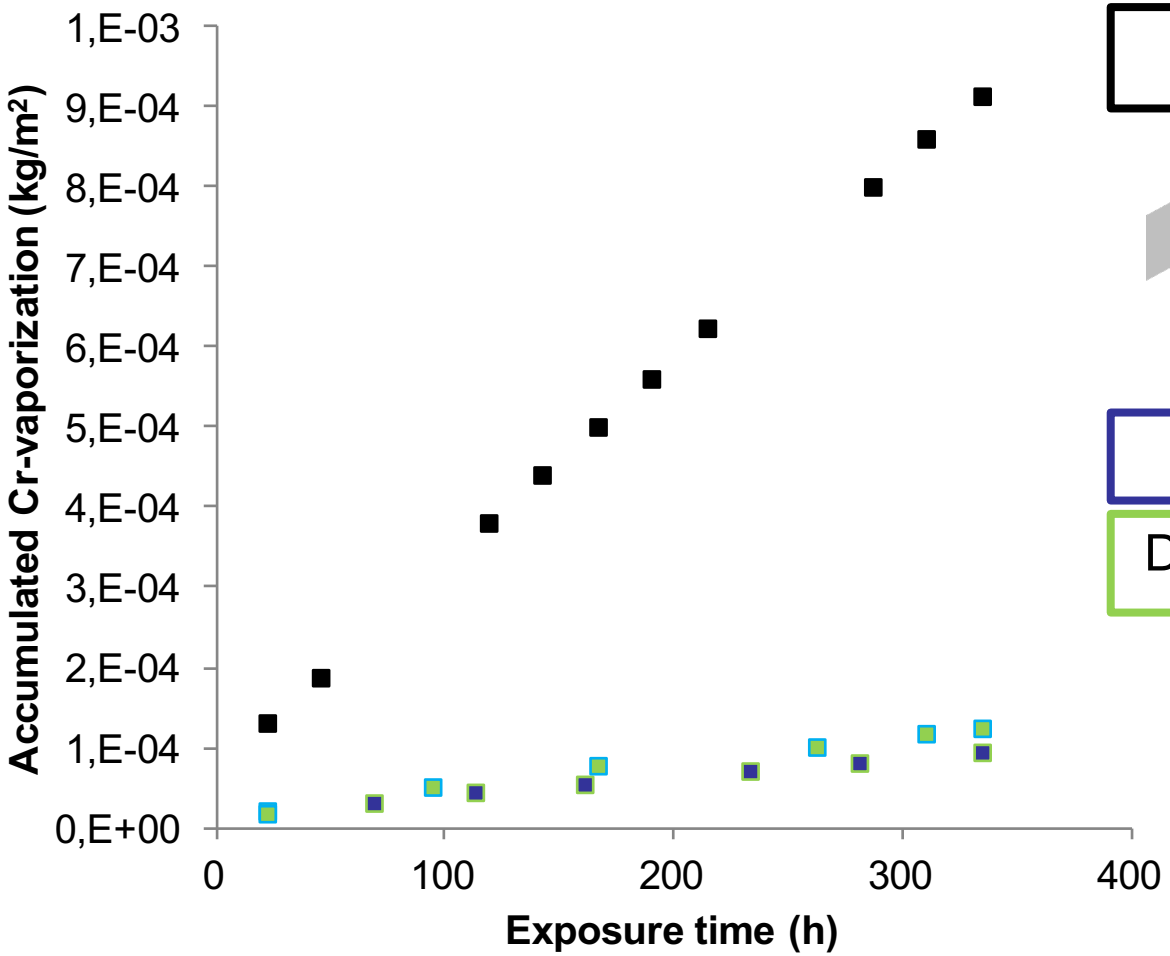



x10 reduction

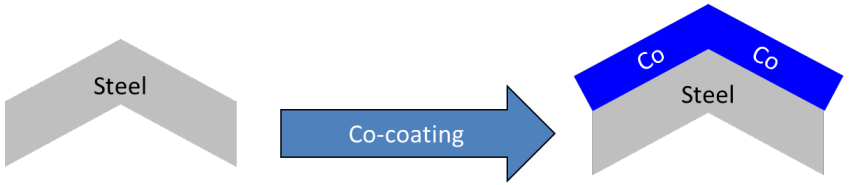
Undeformed (600nm Co)

# Cr vaporization

## Air, 850 °C




Uncoated and undeformed

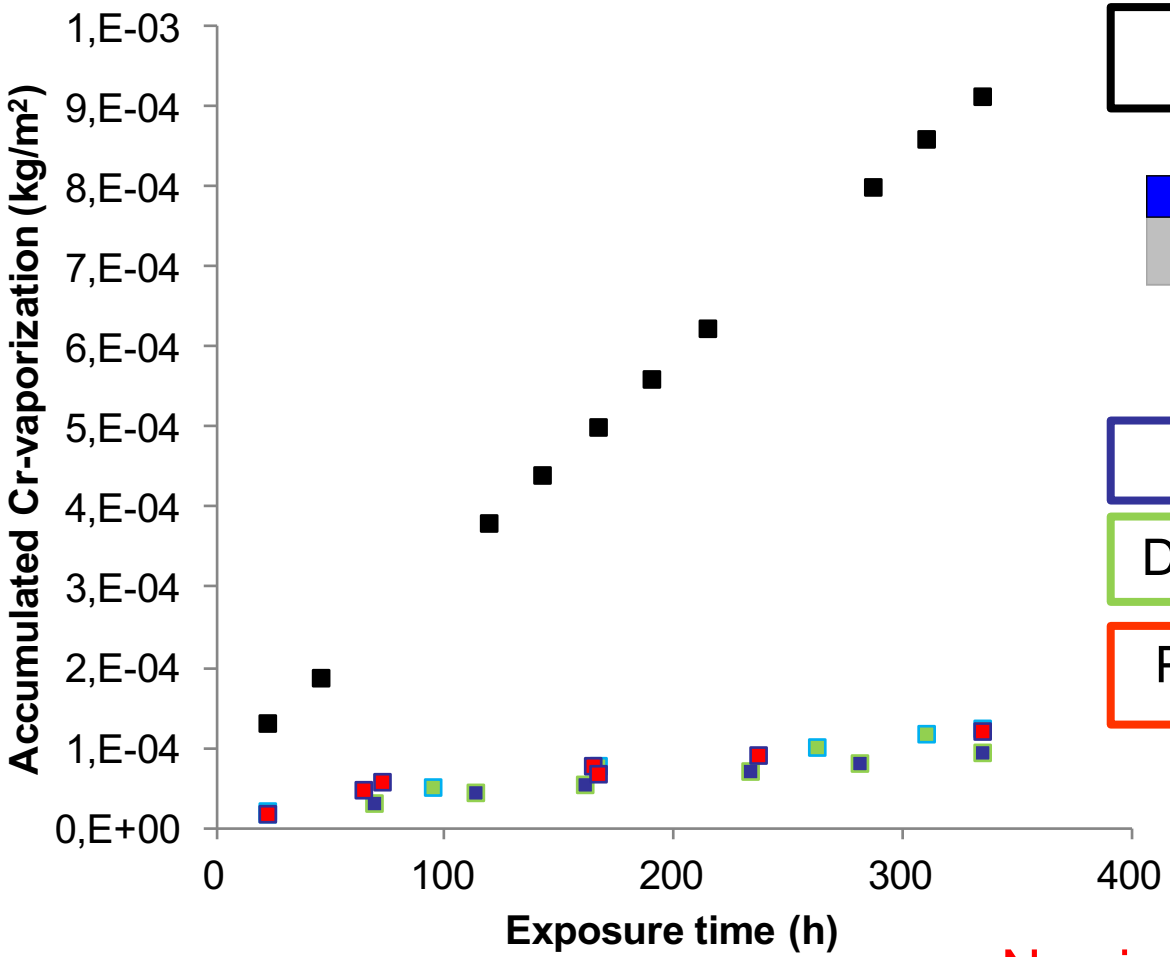



Undeformed (600nm Co)

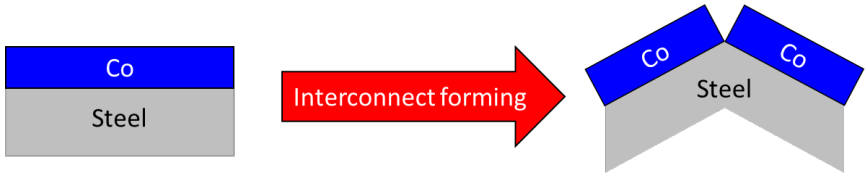
Deformed + post-coated (600nm Co)

# Cr vaporization

## Air, 850 °C




Uncoated and undeformed

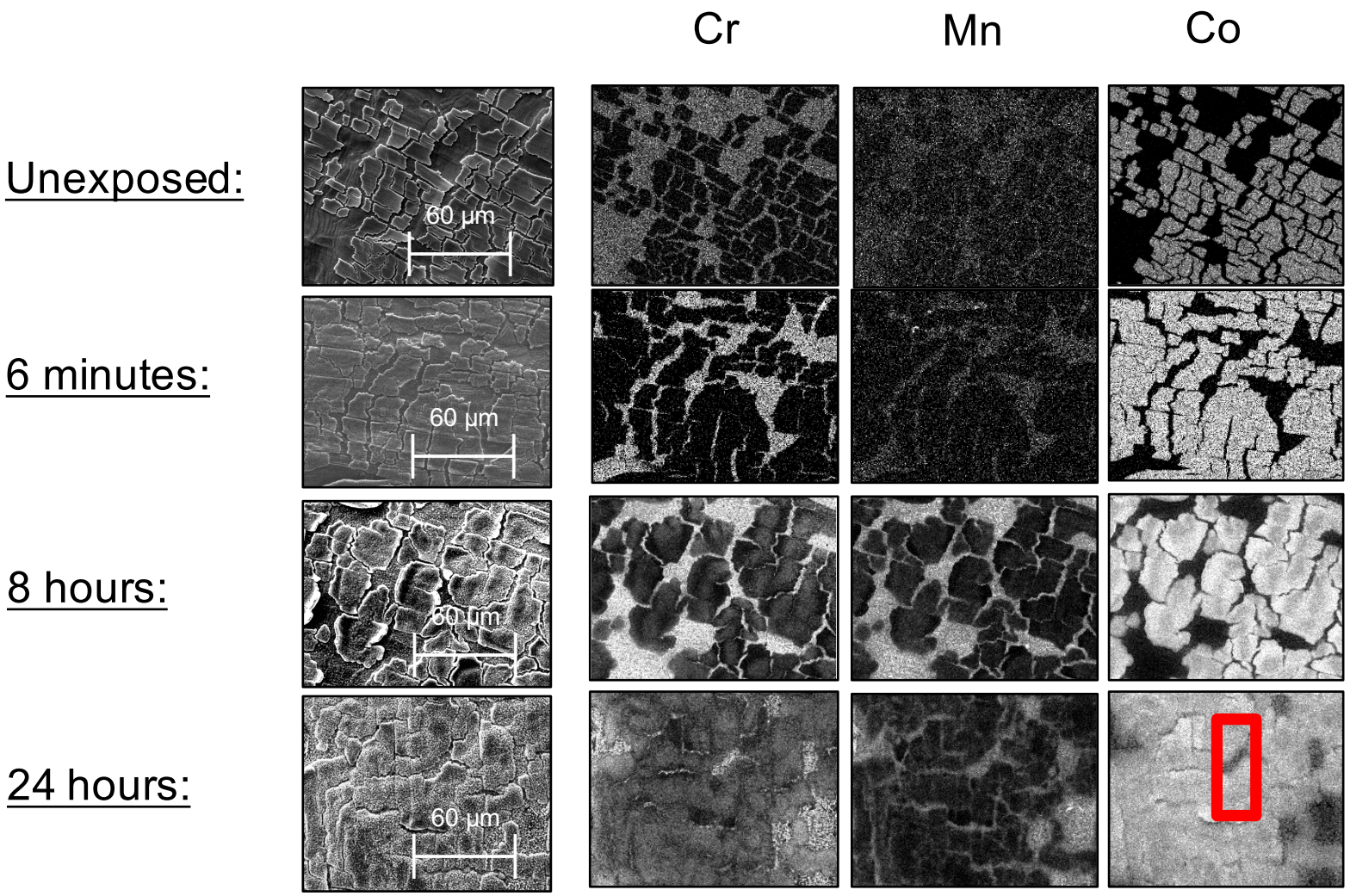



Undeformed (600nm Co)

Deformed + Post-coated (600nm Co)

Pre-coated + Deformed (600nm Co)

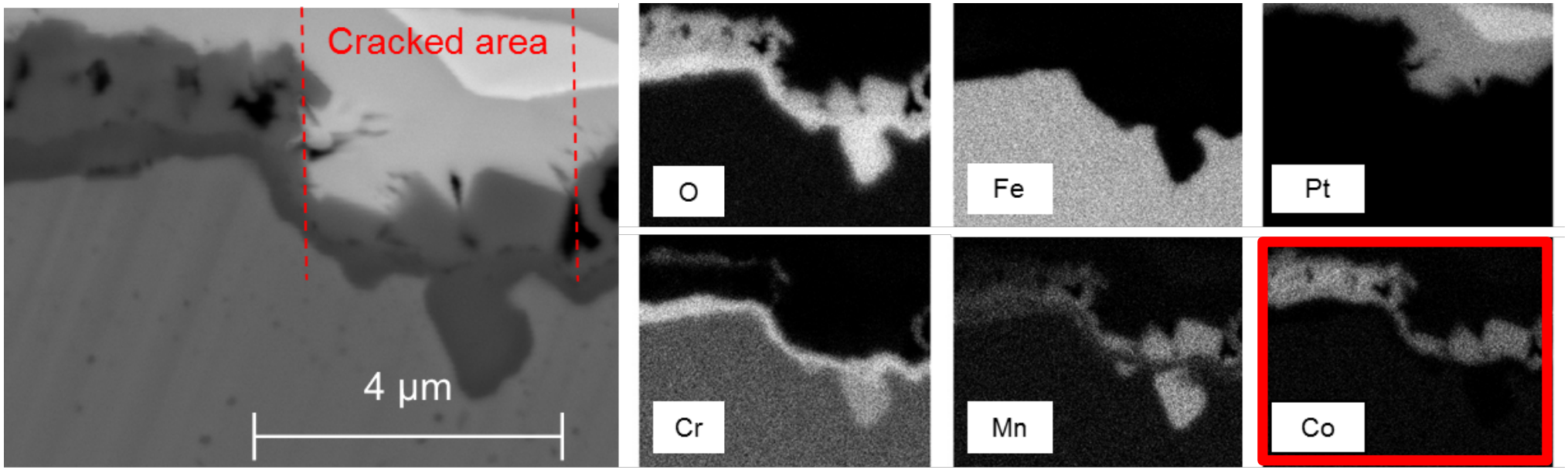
No signs of increased Cr-vaporization after mechanical deformation/stamping




Mn enrichment within the cracked area

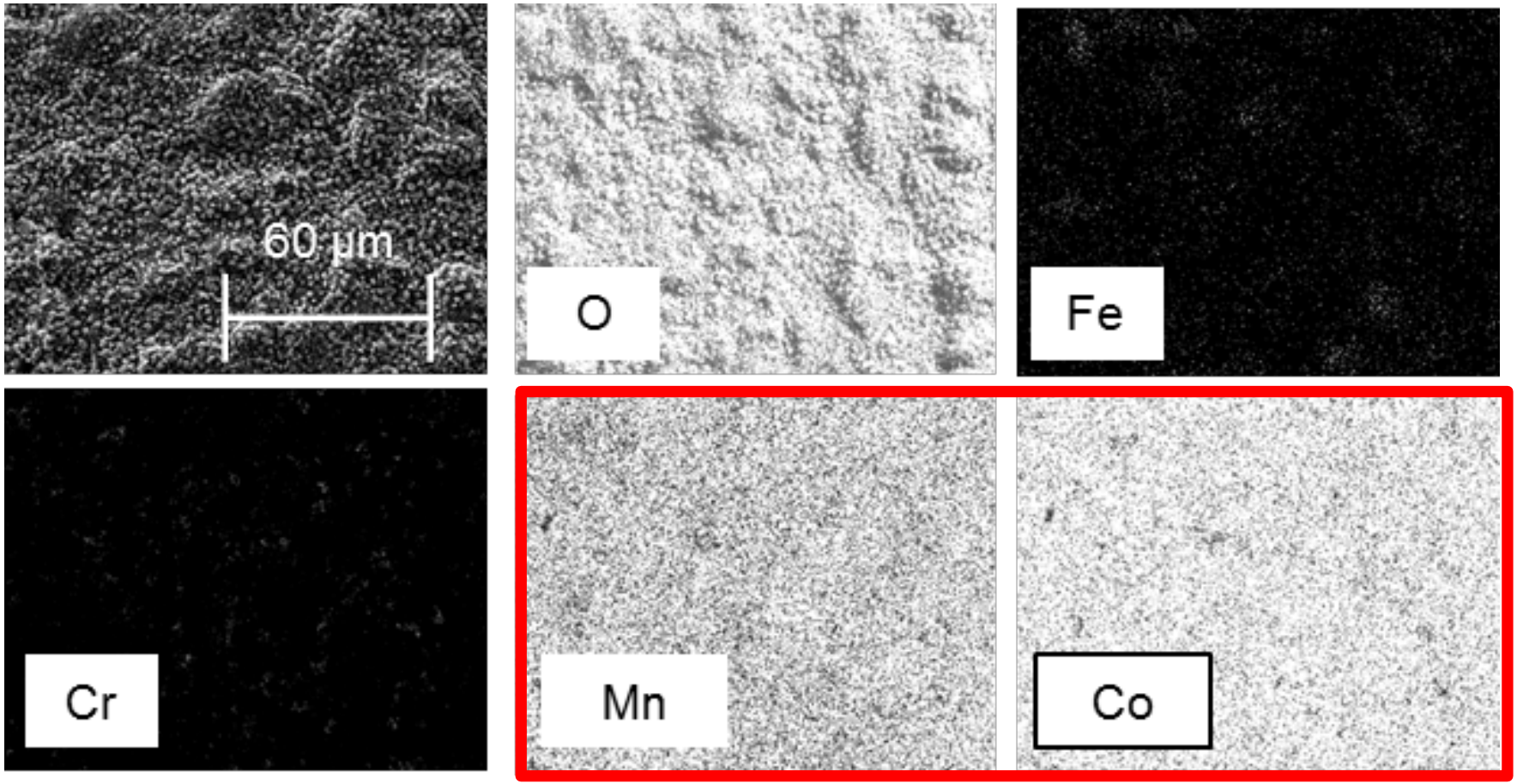
More homogenues Cr, Mn and Co signal after 24 h

## 24 h (Air, 850 ºC):




Thin Co-rich layer within the cracked area
Growth of $(Co,Mn)_3O_4$ crystals within cracked area

## 336 h (Air, 850 ºC):



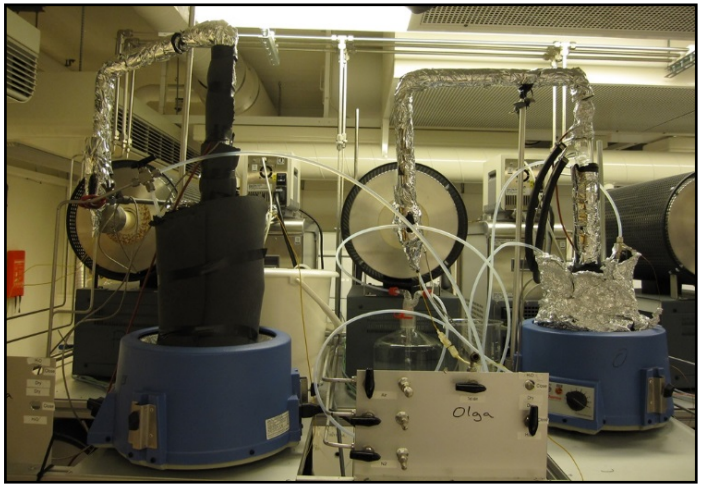

Surface homogenously covered by an oxide rich in Co and Mn

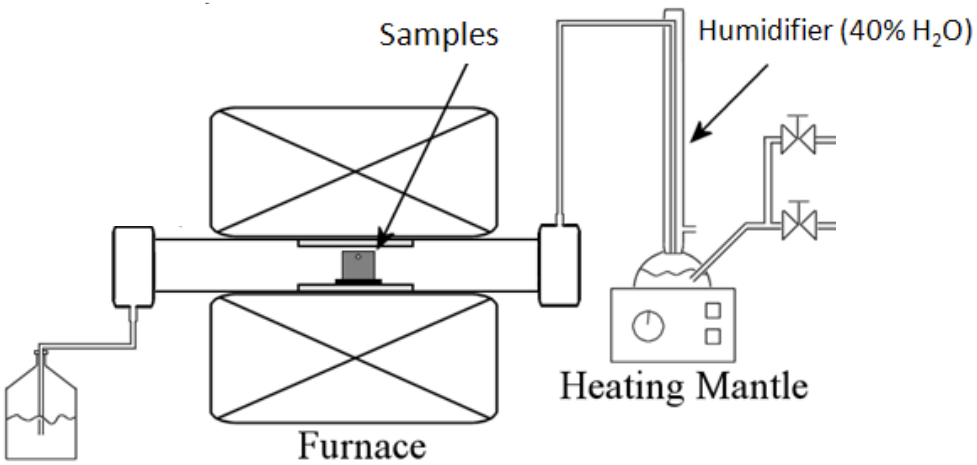
# Fuel side exposures

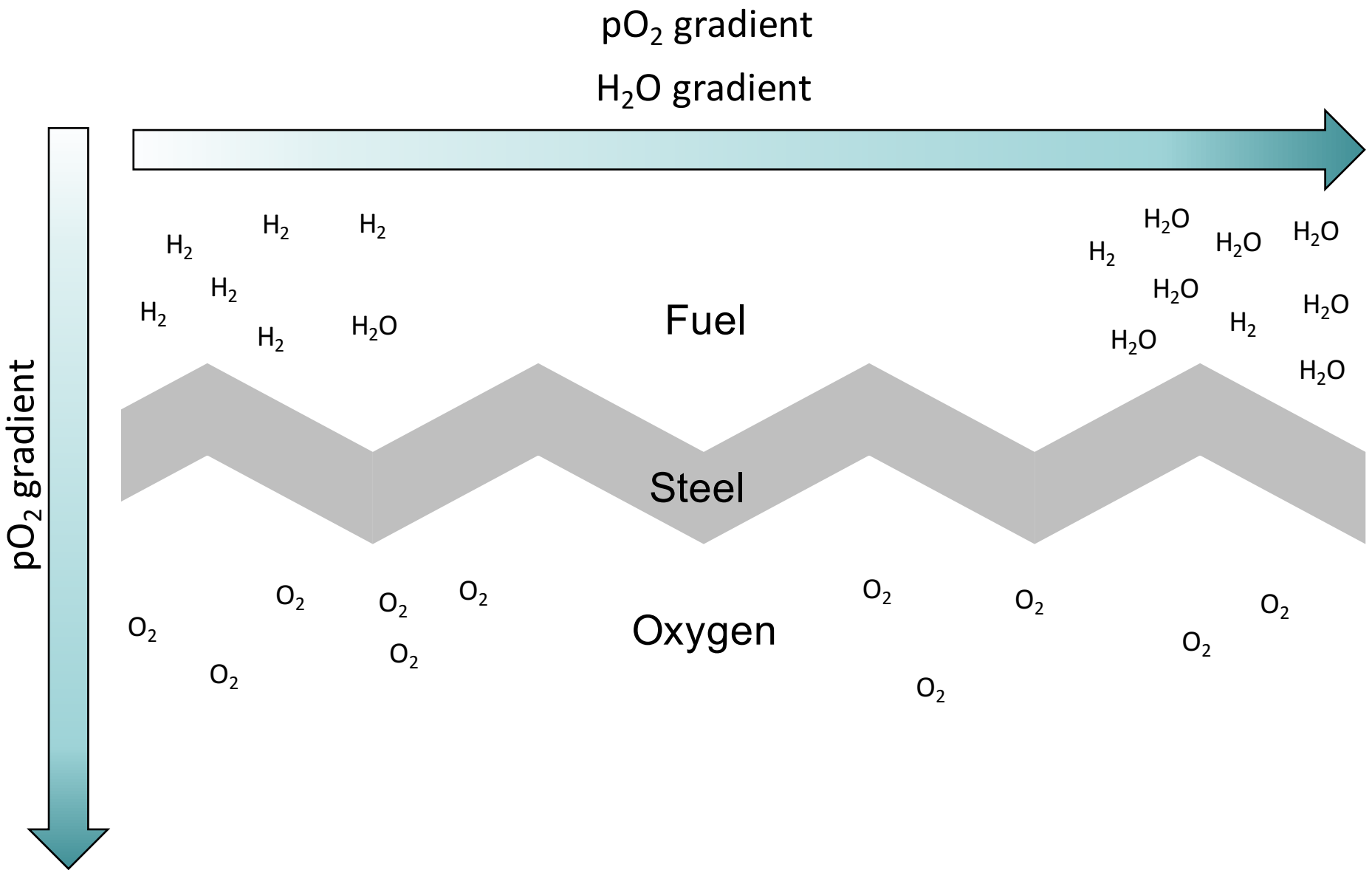
Temperature: 850 °C

Atmosphere: Ar – 3% $H_2$ – 40% $H_2O$: $pO_2 = 10^{-15}$

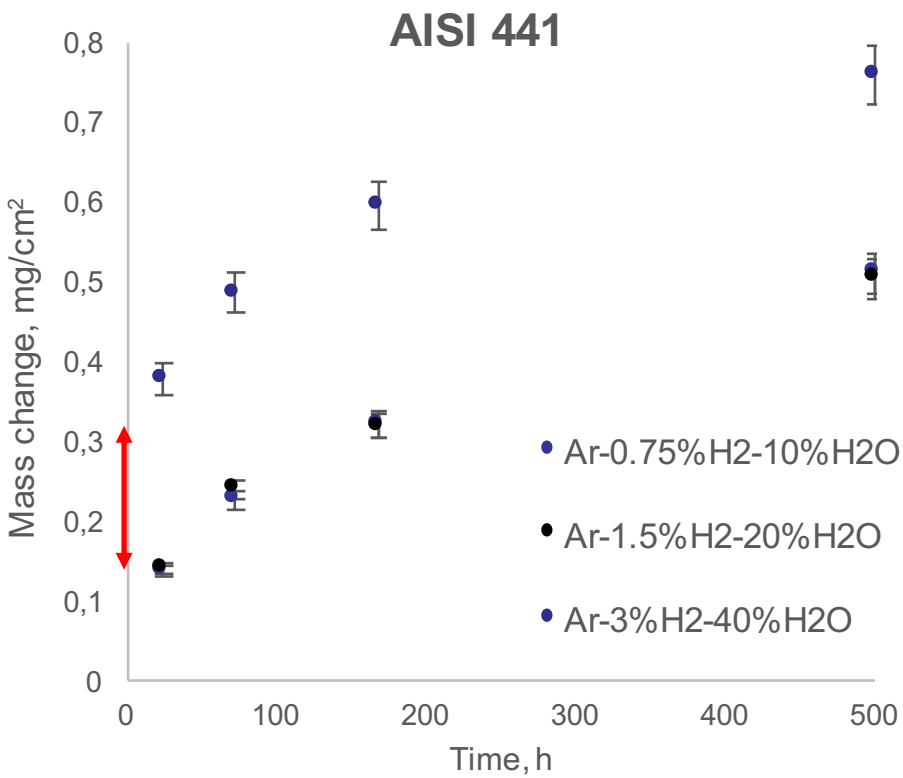
Sample size: 15 x15 x 0.2 mm

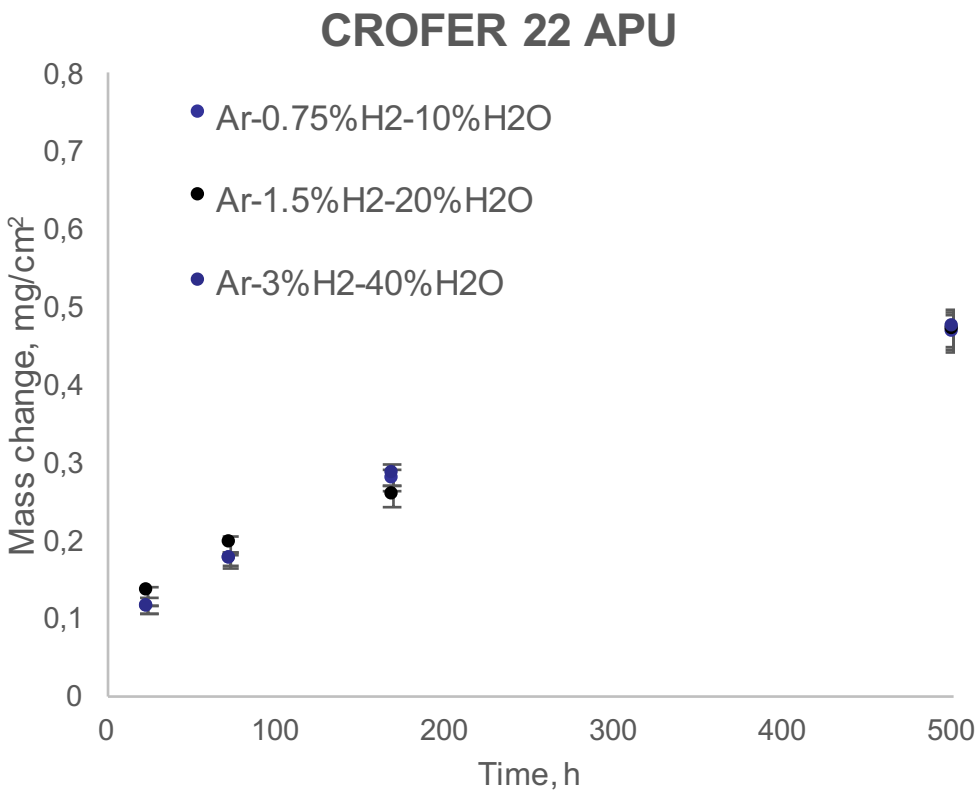




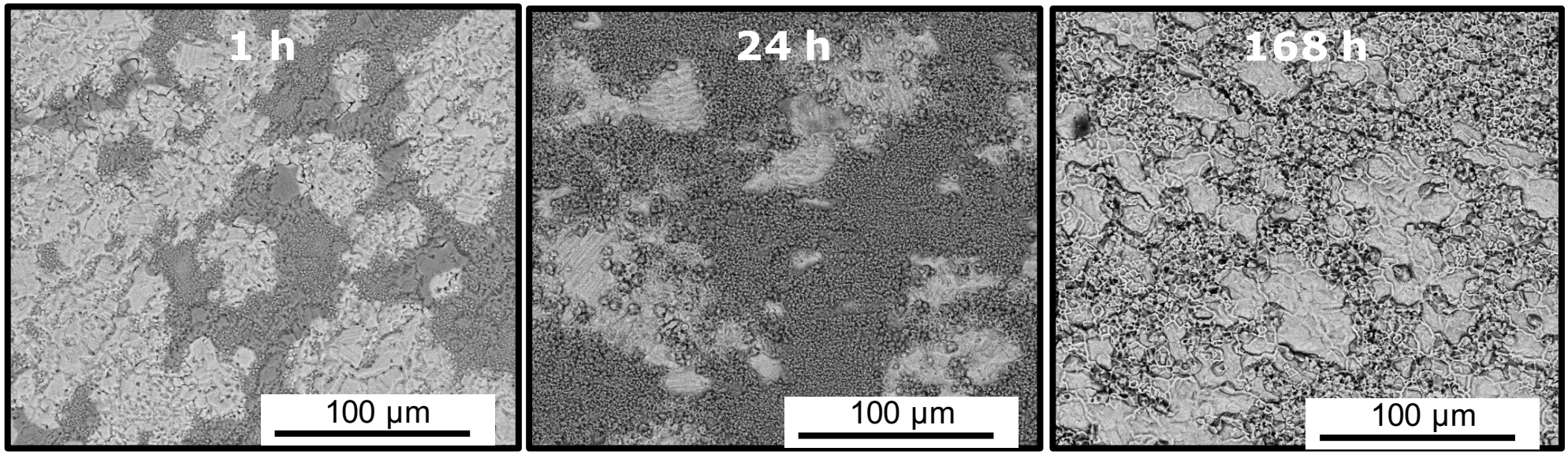

$pO_2$ gradient
$H_2O$ gradient
$pO_2$ gradient
Fuel
Steel
Oxygen
$H_2$
$H_2O$
$O_2$

# Absolute humidity

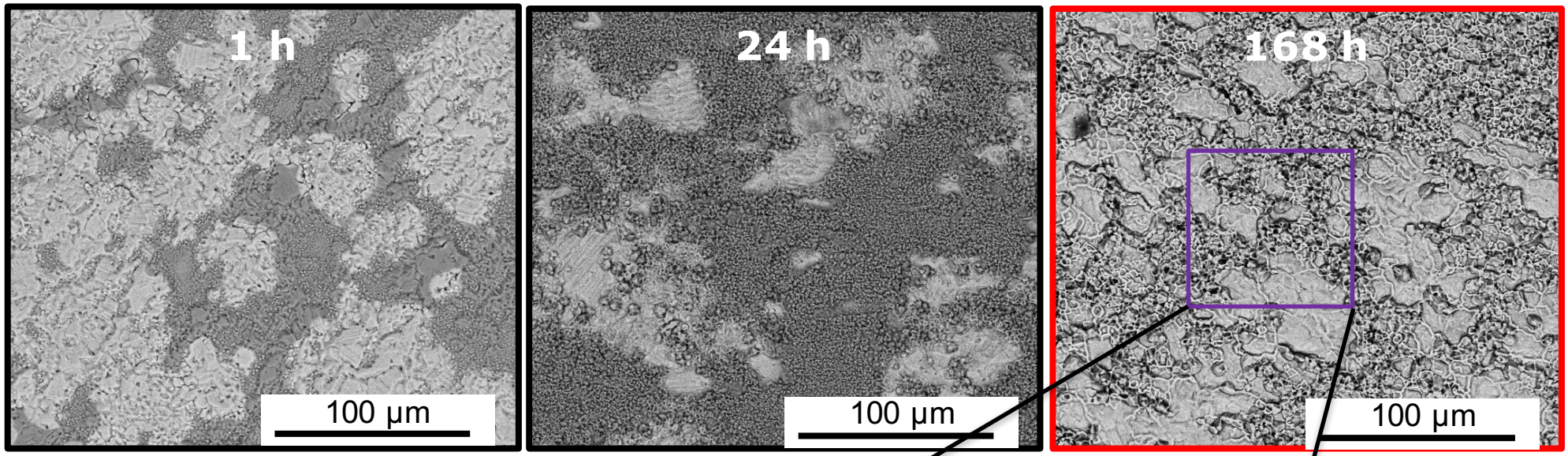


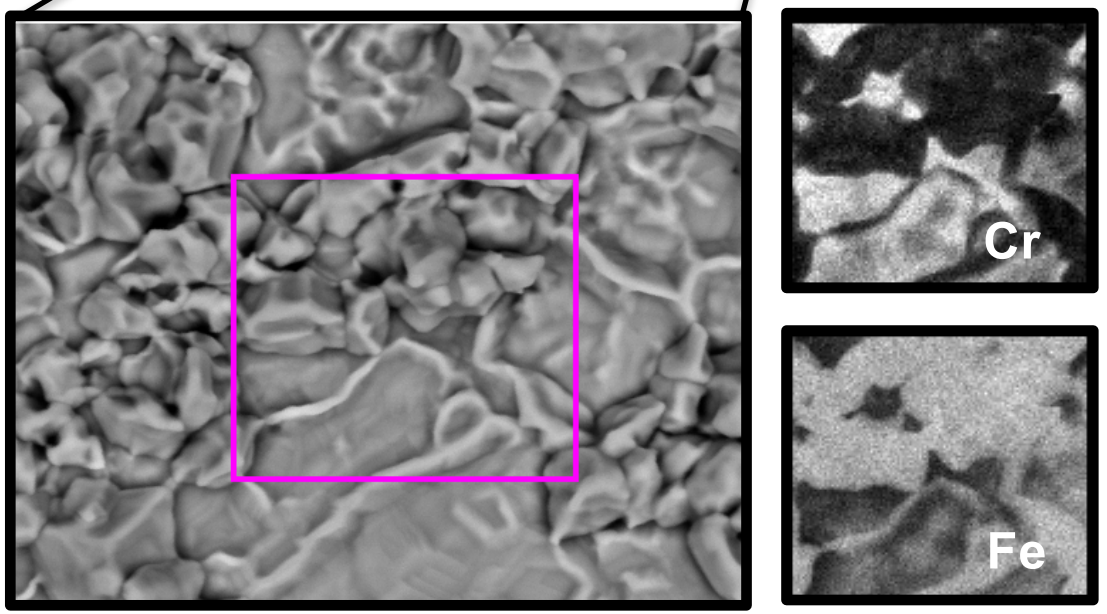

- Similar oxidation rate up to 20 % $H_2O$
- Rapid initial oxidation of 441 at 40 % $H_2O$
- Humidity more important than $pO_2$



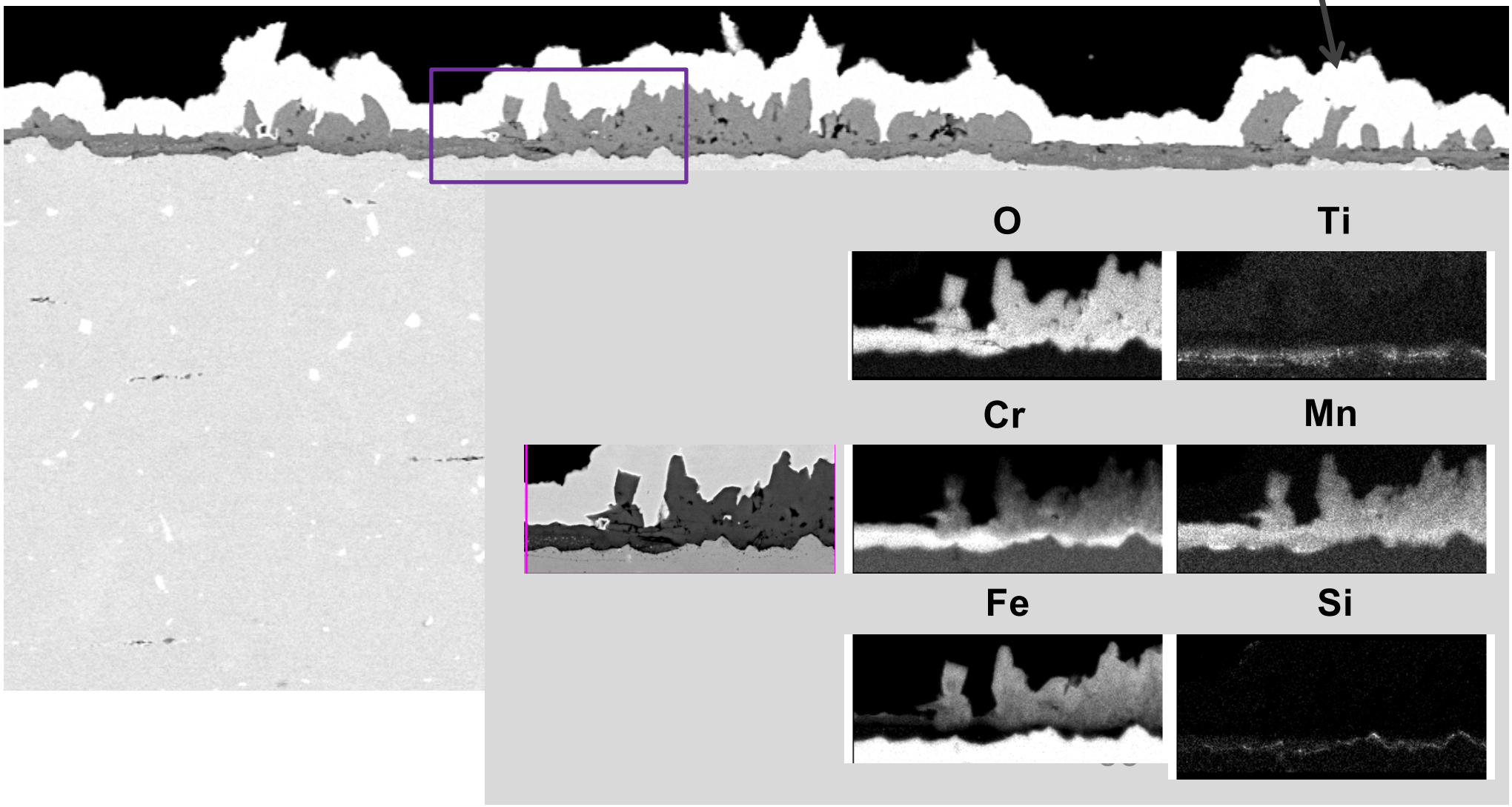

AISI 441



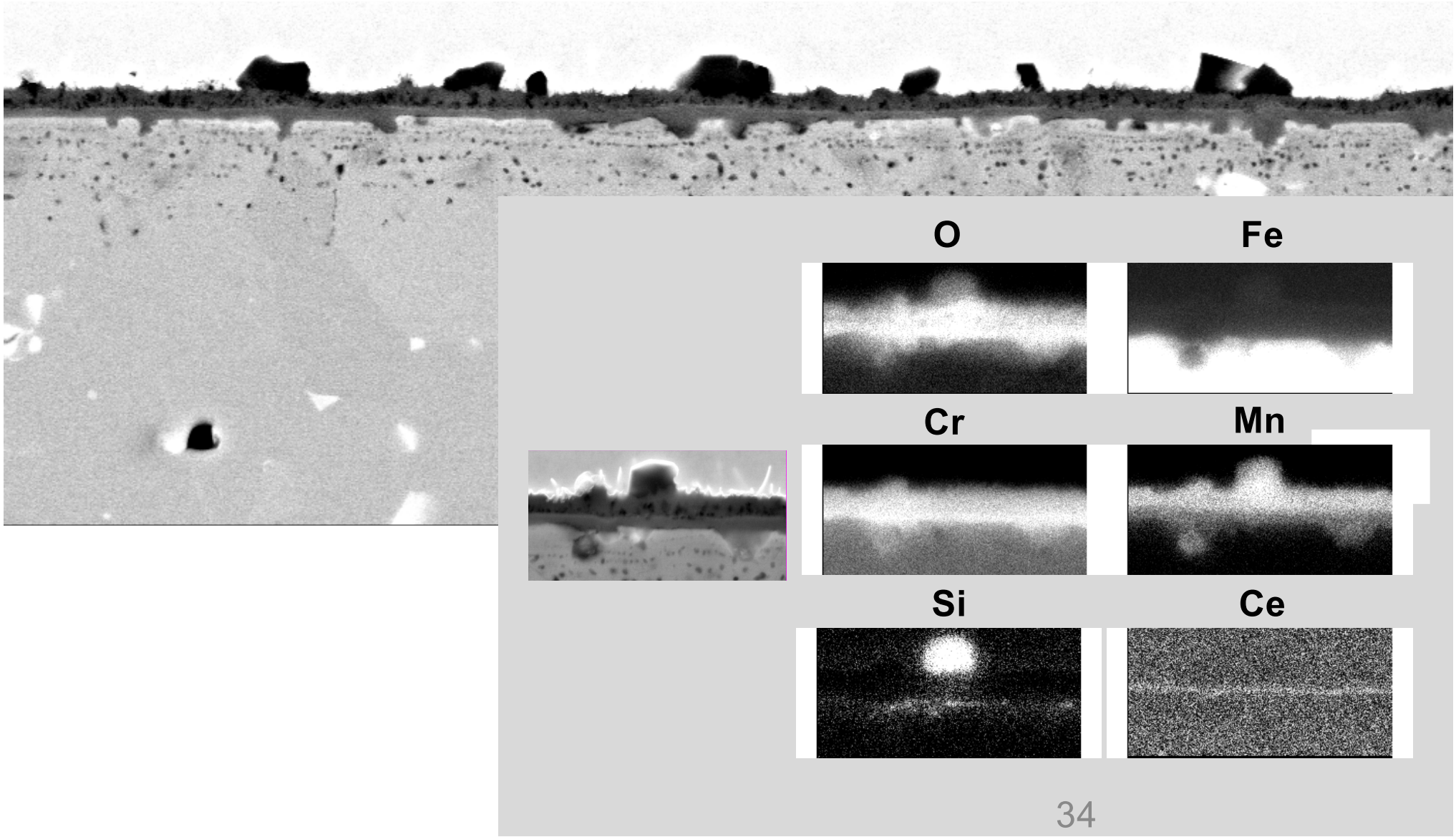

- Iron oxide competing reaction – fast oxidation



# AISI 441 - 500 h



# AISI 441 Ce - 168 h



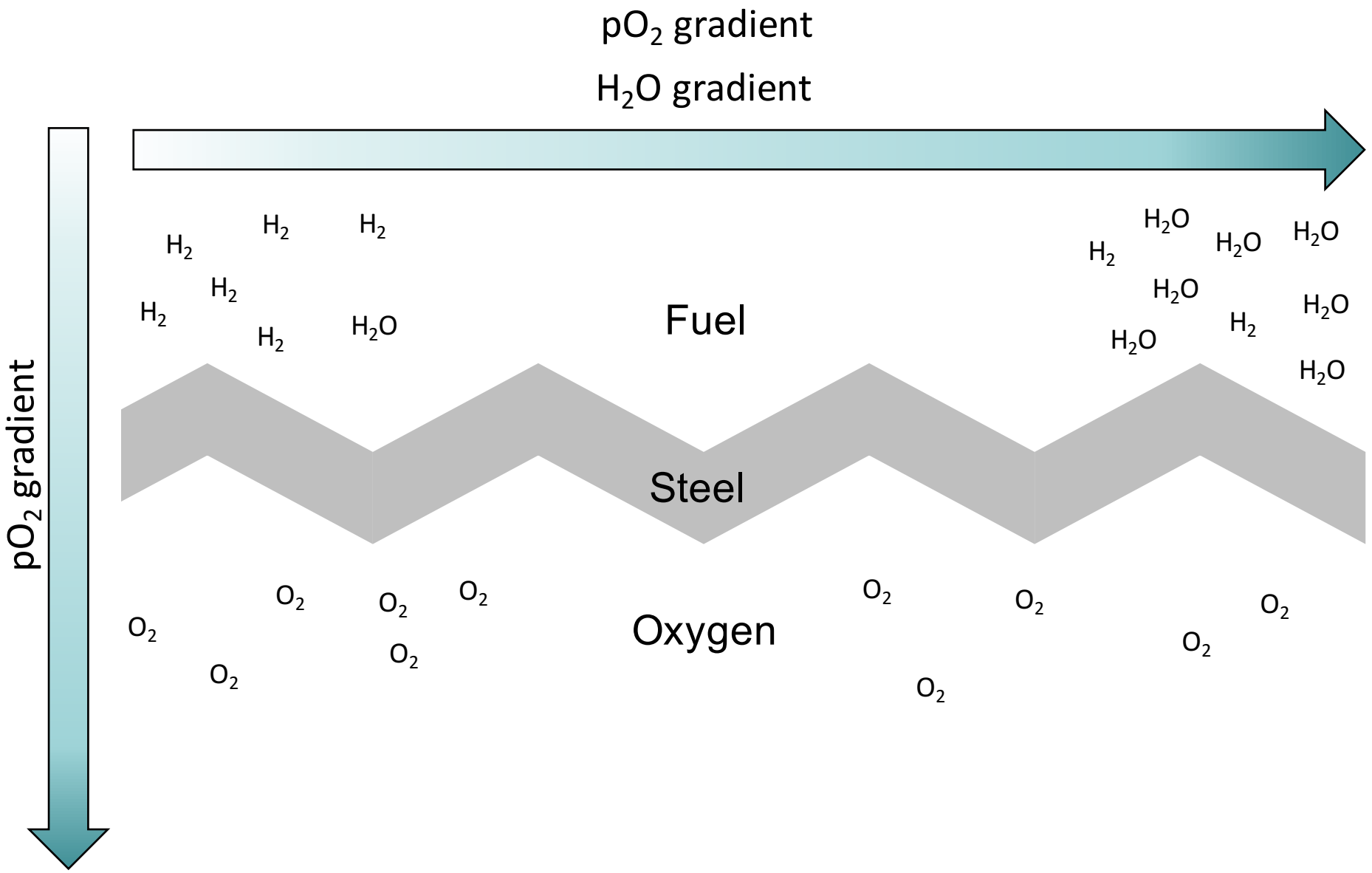
# Dual atmosphere

Do ferritic steels corrode differently in a dual atmosphere?

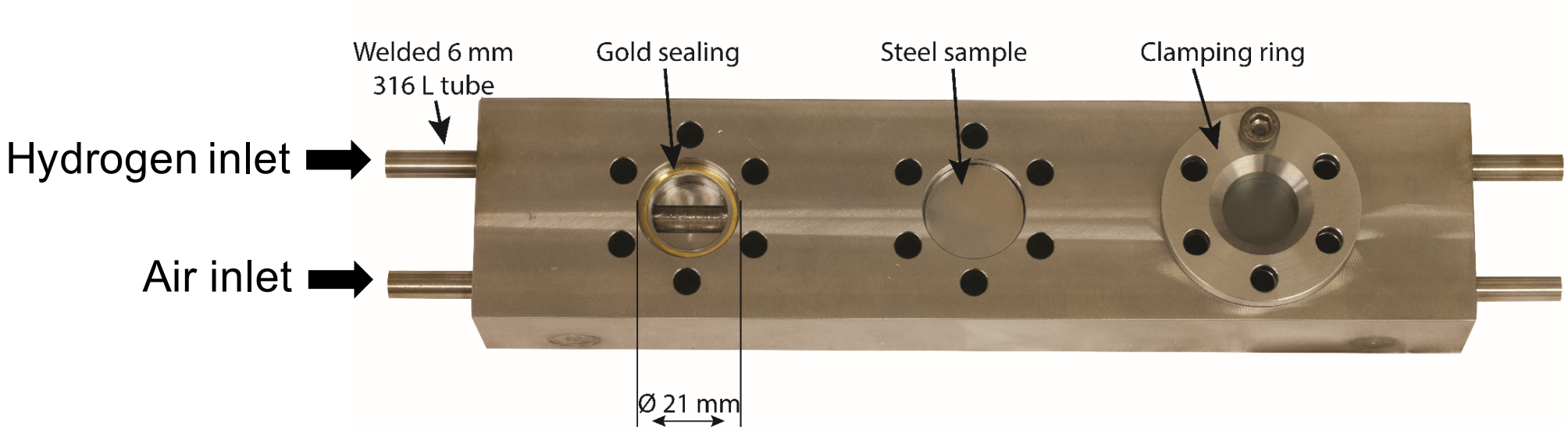
Motivation:

- Closer to reality exposure

- Reduced SOFC operating temperature


$pO_2$ gradient
$H_2O$ gradient
$pO_2$ gradient
Fuel
Steel
Oxygen
$H_2$
$H_2O$
$O_2$

# Experimental




3x reference samples


3x dual samples


- Pre-oxidation 3 h at 800 °C
- 1000 h exposure (up to 3000 h)
- 600 °C
- High flow rate air + 3 % $H_2O$

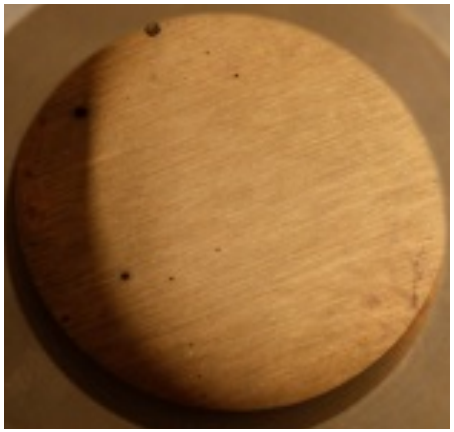
| Material | Fe | Cr | C | Mn | Si | W/Mo | Nb | Ti | RE |
|---|---|---|---|---|---|---|---|---|---|
| AISI 441 | Bal. | 17.8 | 0.012 | 0.26 | 0.55 | no | 0.48 | 0.14 | no |

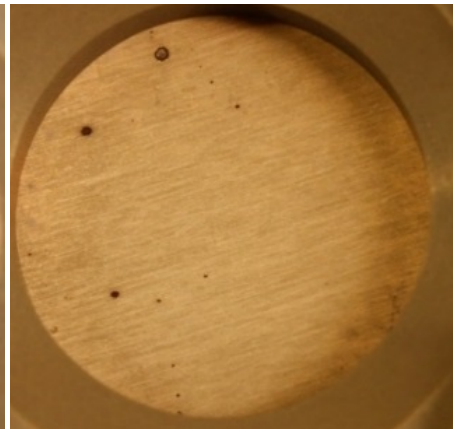
# Visual inspection of air sides

Single atmosphere

600 °C

Dual atmosphere



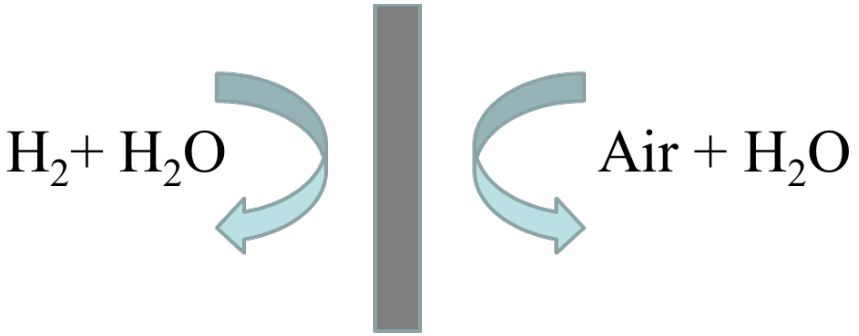


1000 h

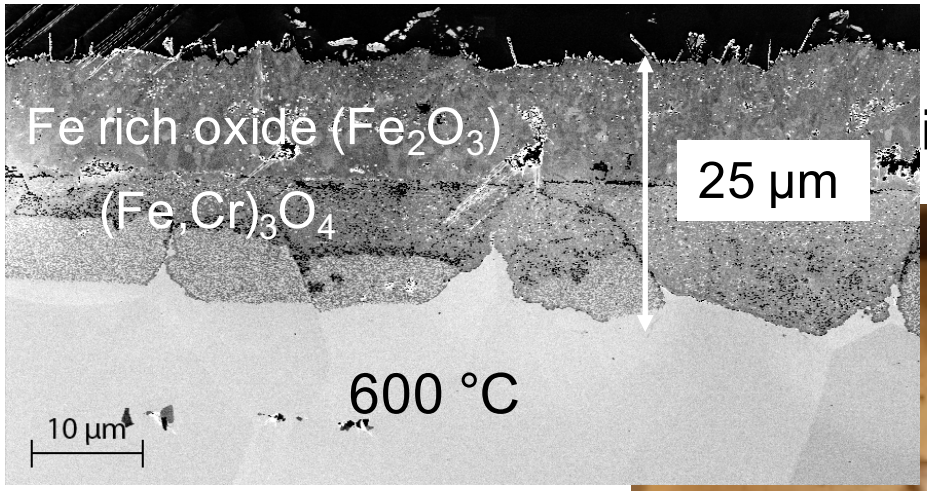
3000 h

1000 h

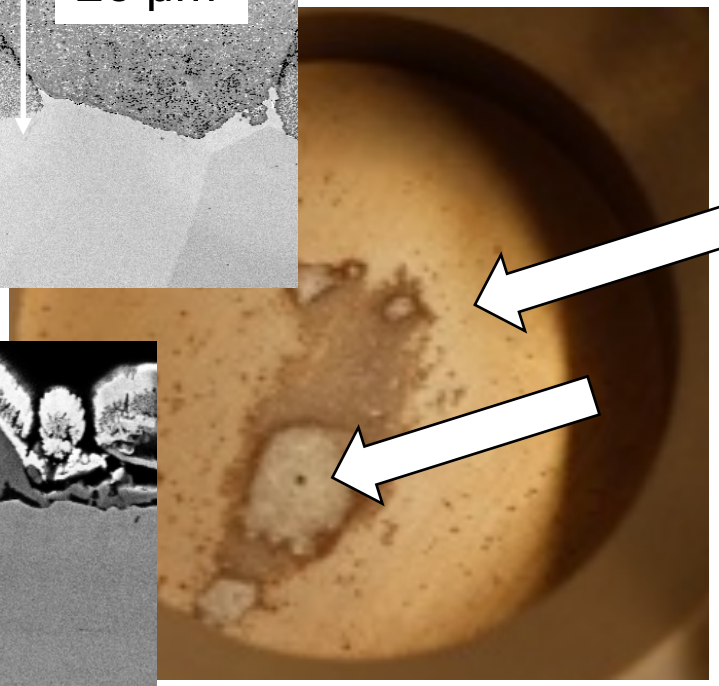
3000 h

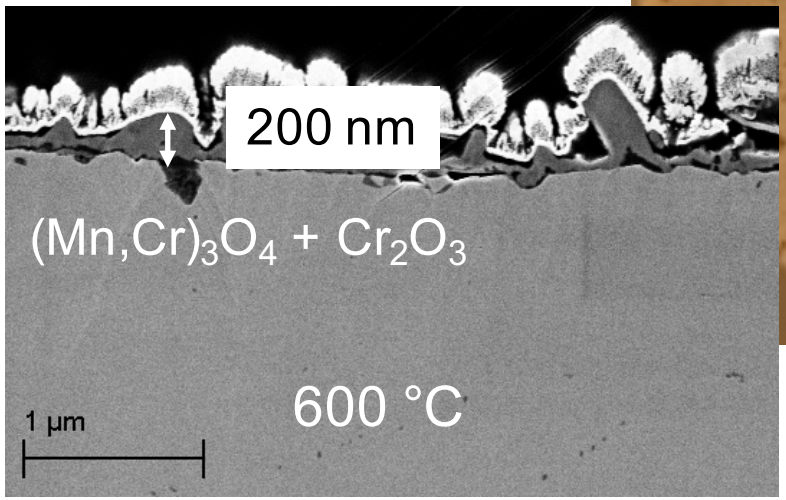


# Oxide scale morphology




ir side

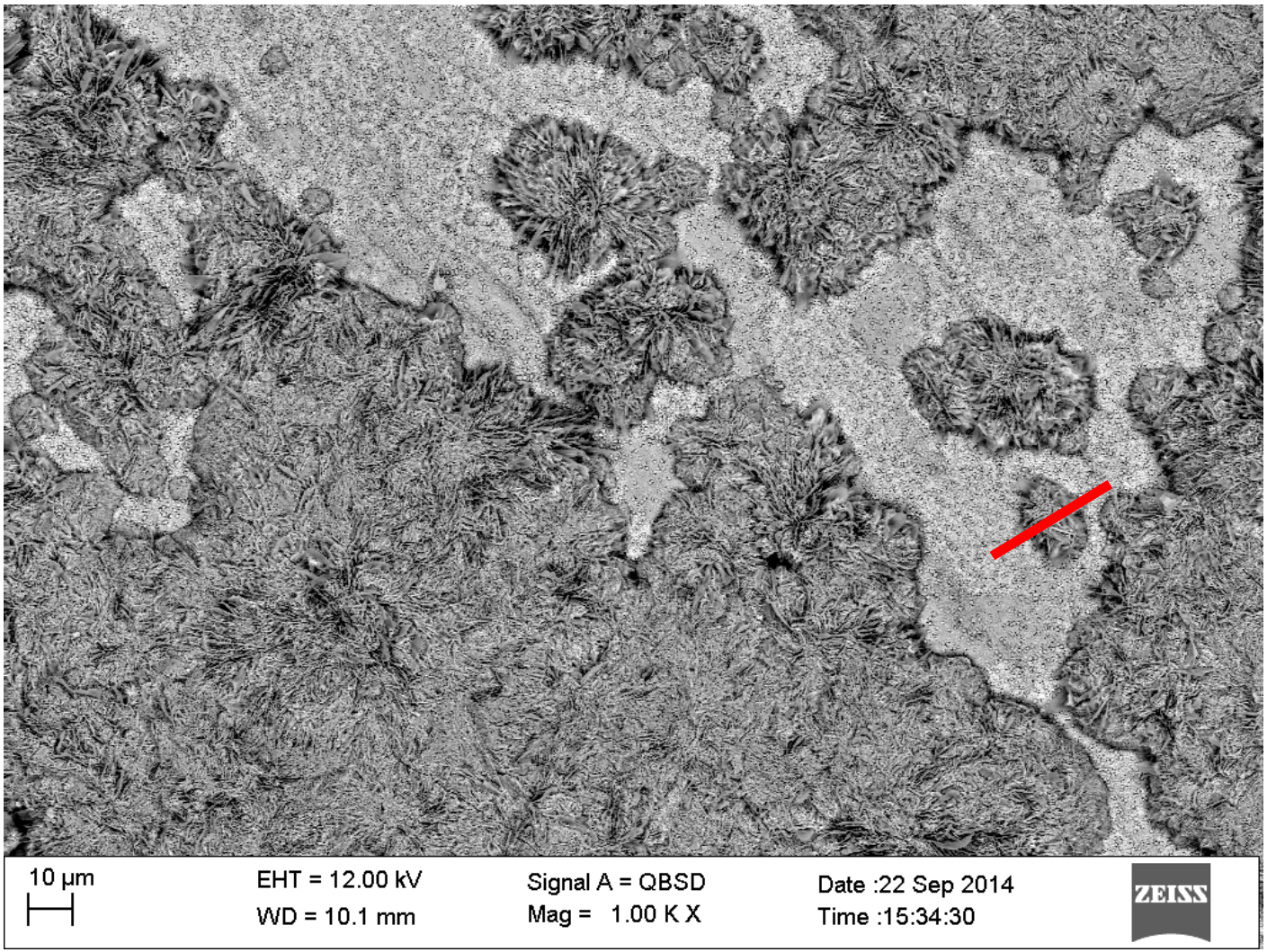




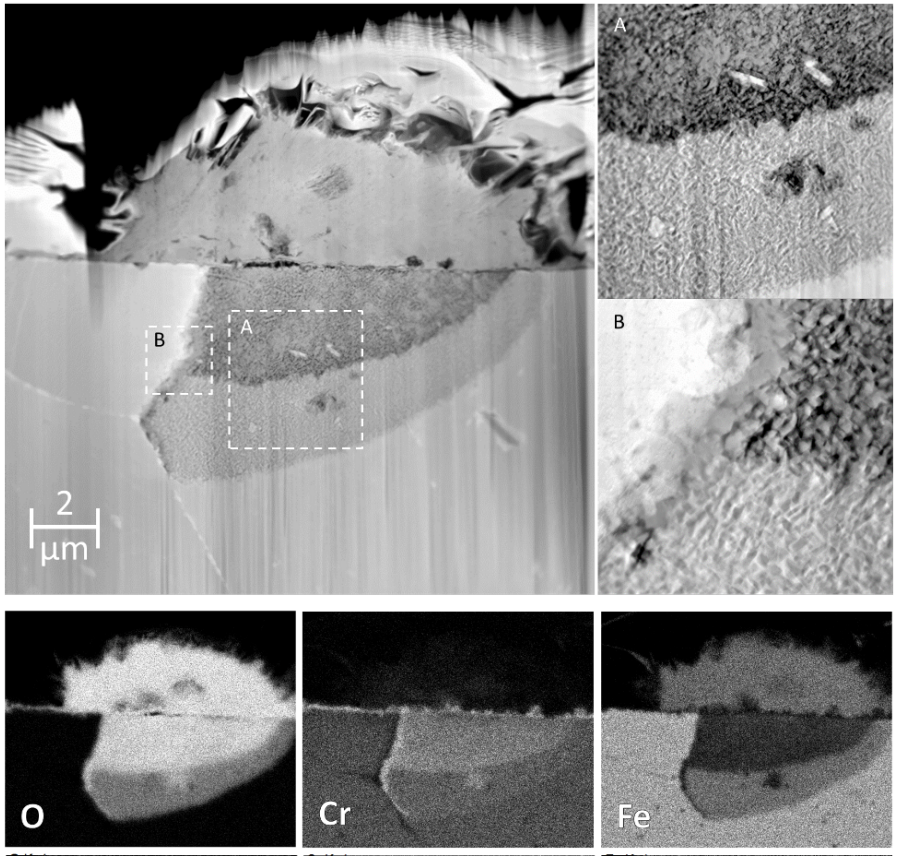

600 °C
Dual atm

# 600 °C early oxidation

Surface of air side 1000 h



# Initiation of breakaway

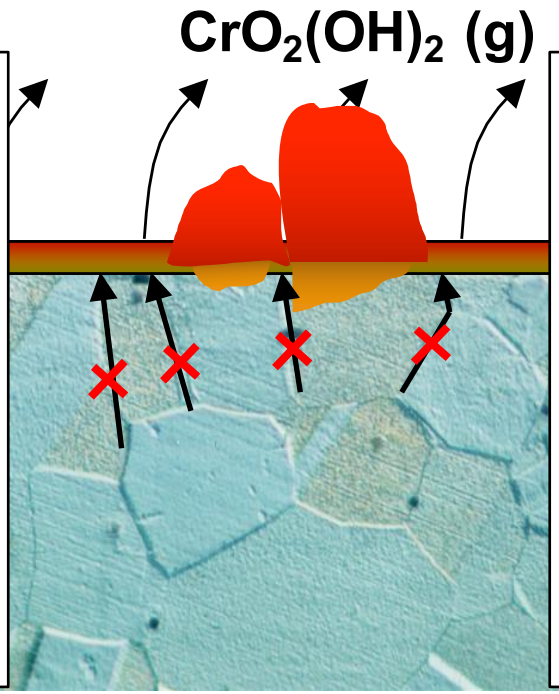



600 °C, dual atm, 1000 h

- Outward growing hematite $Fe_2O_3$
- Inward growing spinel $(Fe,Cr)_3O_4$
- Inner reaction zone, miscibility gap Fe-Cr-O
- Remnants of inital $Cr_2O_3$
- Enrichment of Cr in alloy grain boundary

# Mechanism for H induced breakaway

1. H increases the diffusion through the oxide scale[2]
2. Oxidation of Cr faster than supply
3. Non-protective Fe rich oxide is formed




1. The presence of hydrogen favors internal oxidation[1]
2. Cr re-supply impeded due to immobilization
3. Non-protective Fe rich oxide is formed

Condition to maintain a protective scale:

$$n_{Cr}(\text{Oxidation}) + n_{Cr}(\text{Evaporation}) < n_{Cr}(\text{Re-supply})$$

1. E. Essuman, et al. Oxid. Met., Vol 69, 2008
2. Z. Yang, et al. J. Electrochem. Soc. Vol 151, 2004

# $CO/CO_2$

- Crofer APU 0.3 mm
- 700 ° C
- 50/50 $CO/CO_2$ (200 ml/min each)
- Discontinous exposure

- Three sets of samples:
  - Uncoated
  - Preoxidized in air 24 h 800 ° C
  - 10 nm Ce coated

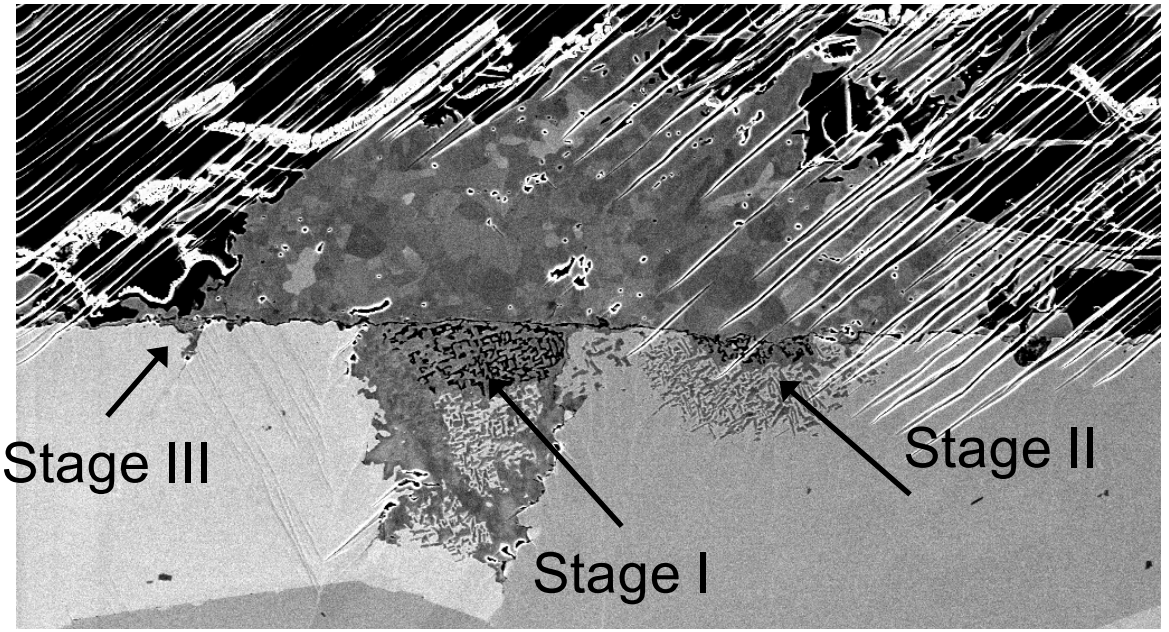
| T | 700 | 750 | 800 |
|---|---|---|---|
| CO/CO2 | 30/70 | 30/70 | 30/70 |
| CO/CO2 | 40/60 | 40/60 | 40/60 |
| CO/CO2 | 50/50 | 50/50 | 50/50 |

# Summary

- PVD coatings
  - Reduce corrosion
  - Reduce chromium evaporation
  - Reduce electrical resistance
- Self-healing of pre-coated interconnects
- New challenges
  - High humidity
  - Dual atmosphere effect
  - CO containing atmospheres

# extras

# Propagation

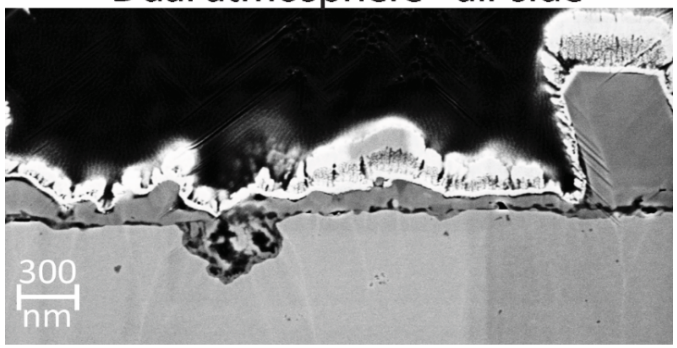



Dual atm, 600 °C, 1000 h

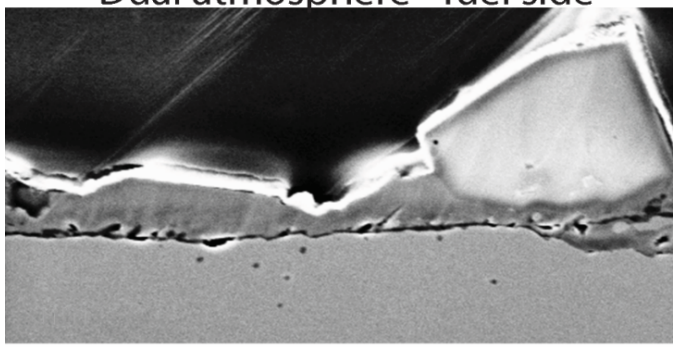
Fe rich crater spills over to neighbouring oxide scale and dilutes the Cr rich protective oxide.

# Protective scales

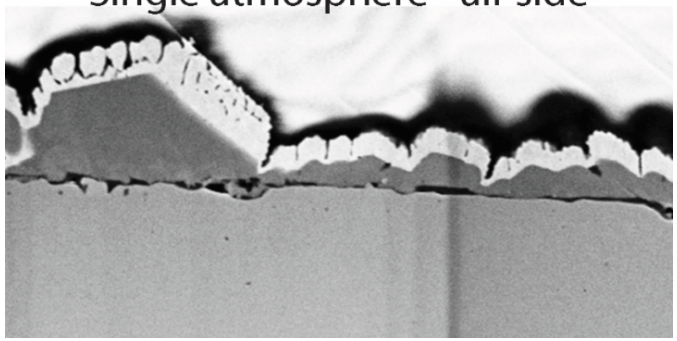
Dual atmosphere - air side



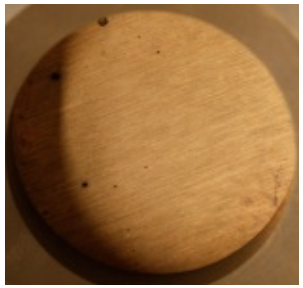
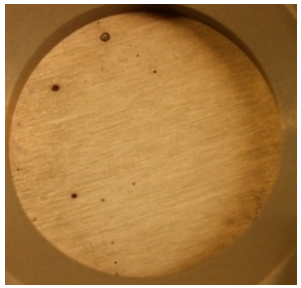
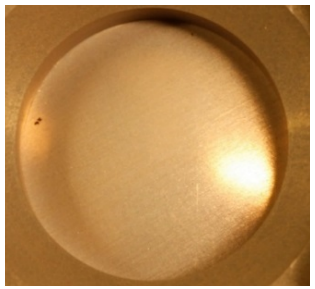
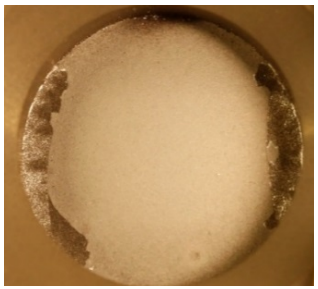

Dual atmosphere - fuel side



Single atmosphere - air side



# Preoxidation

| | Single atmosphere | | Dual atmosphere | |
|---|---|---|---|---|
| 600 °C |  |  |  |  |
| | 1000 h | 3000 h | 1000 h | 3000 h |
| |  | |  | |
| | 2000 h | | 2000 h | |

- Even more severe for non-preoxidized samples