# Biomass Gasification

- Chemical process in which any carbonaceous (solid or liquid) fuel is converted to gaseous fuel.


- Involves partial combustion of biomass.
- Product gases can be used to produce heat and energy and also fuels.
- Product gas: $H_2$, $H_2O$, CO, $CO_2$, $CH_4$, $N_2$ and impurities e.g. ash, tars, $H_2S$, HCl and alkali species.

# Biomass Gasification

- Chemical process in which any carbonaceous (solid or liquid) fuel is

Any problem in the gasification process?

The presence of corrosive species dictates the boundaries within which, e.g., superheaters and syngas coolers will operate.

- Product gas: $H_2$, $H_2O$, CO, $CO_2$, $CH_4$, $N_2$ and impurities e.g. ash, tars, $H_2S$, HCl and alkali species.

Corrosion studies in biomass/waste gasification is scarce!

Thus…

It is of great importance to increase our knowledge about this complex corrosion process.


2MWChalmers Gasifier


Wood Chips

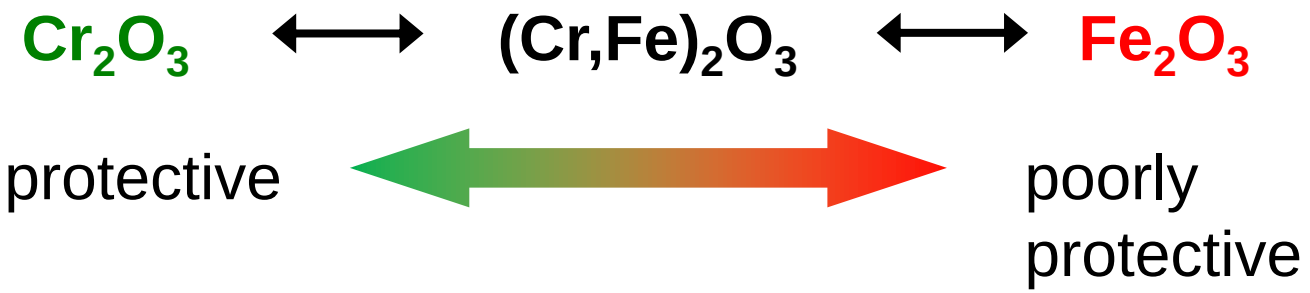
Exposure Matrix:

Samples: Stainless steel (304L) and low alloyed steel (T22)

- Temperature: 600 °C
- Time: 4 hours
- Complex environment: $H_2$, $H_2O$, CO, $CO_2$, HCl, $H_2S$, KCl, etc

# The properties of the protective oxide formed on FeCr alloys

The oxide formed on FeCr alloys consist of a corundum type solid solution, $(Cr, Fe)_2O_3$. The Cr/Fe ratio determines whether it is protective (as $Cr_2O_3$) or poorly protective (as $Fe_2O_3$).




However, the oxygen activity in an gasifier environment is typically in the order $10^{-25}$. **At 600 °C, $Fe_2O_3$ is not stable in this environment!**

# Hence, reactions that deplete the oxide in chromia tend to destroy the protective properties of the oxide!

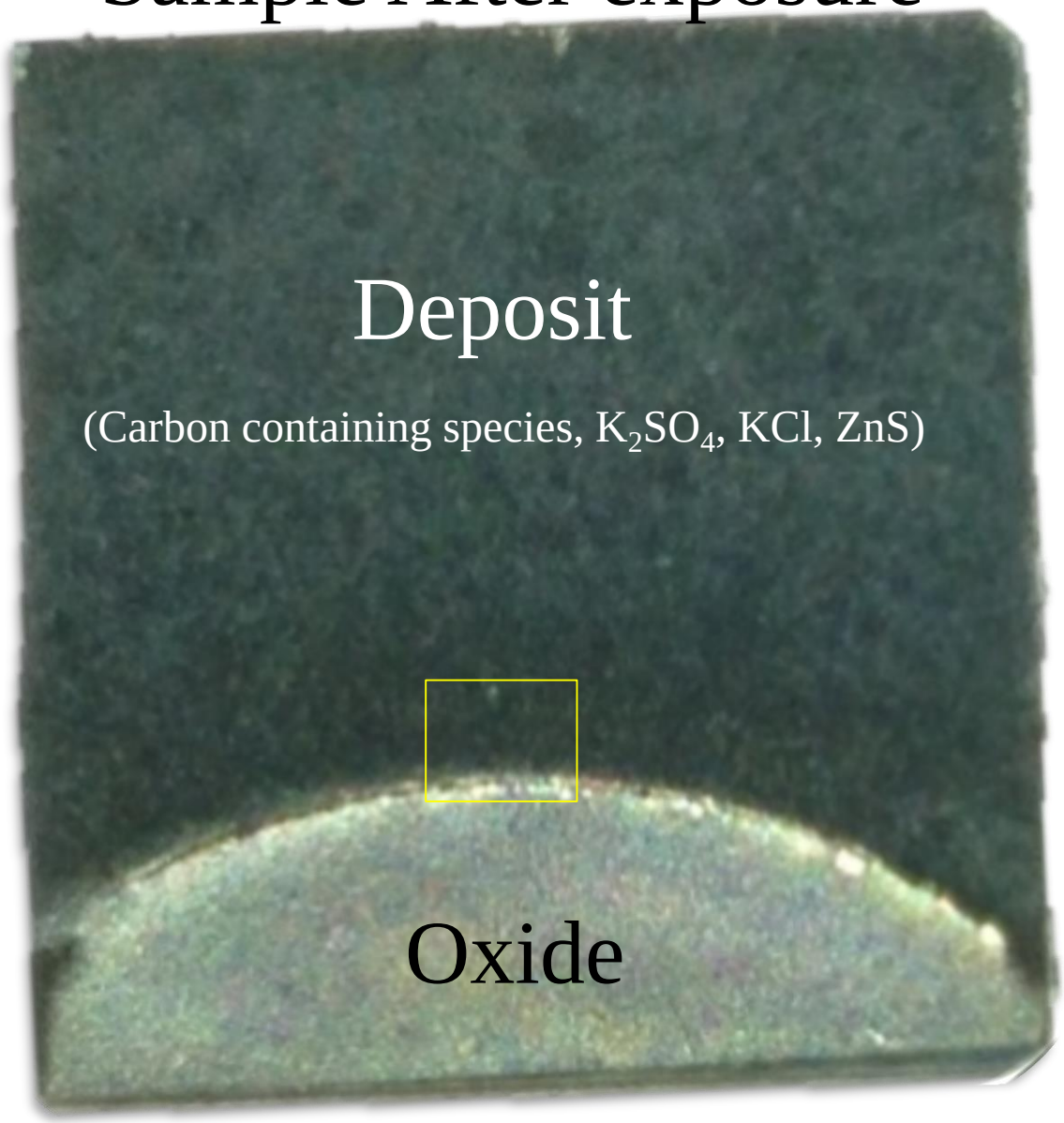
$$(Cr,Fe)_2O_3 \xrightarrow{O_2 + H_2O(g)} Fe_2O_3 + CrO_2(OH)_2(g)$$

**$O_2 + H_2O$** $p_{eq}(CrO_2(OH)_2)$: 0.15ppm (600°C, $pO_2$: 0.6bar, $pH_2O$: 0.40bar)

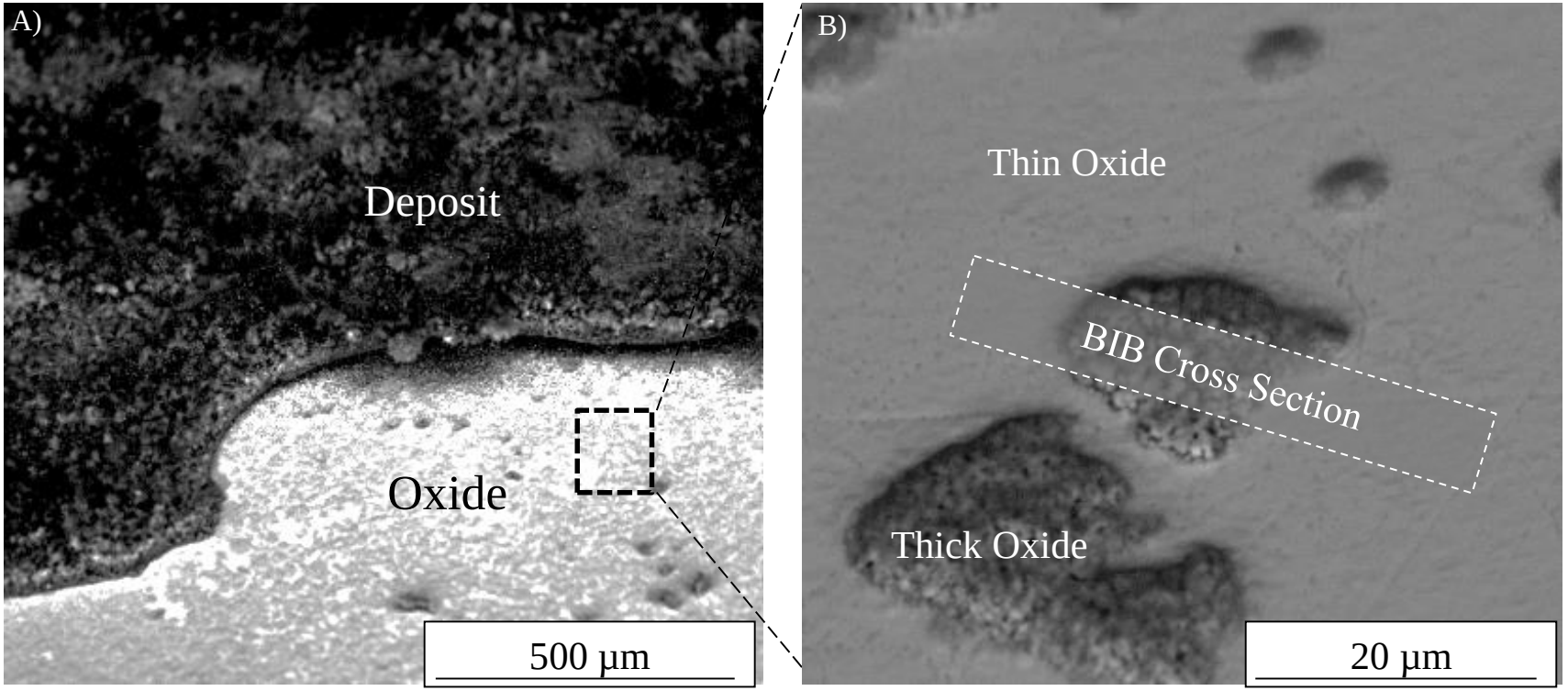
$$Cr_2O_3(s) + 2H_2O(g) + 1.5O_2(g) \rightarrow 2CrO_2(OH)_2(g)$$

Oxygen is needed!

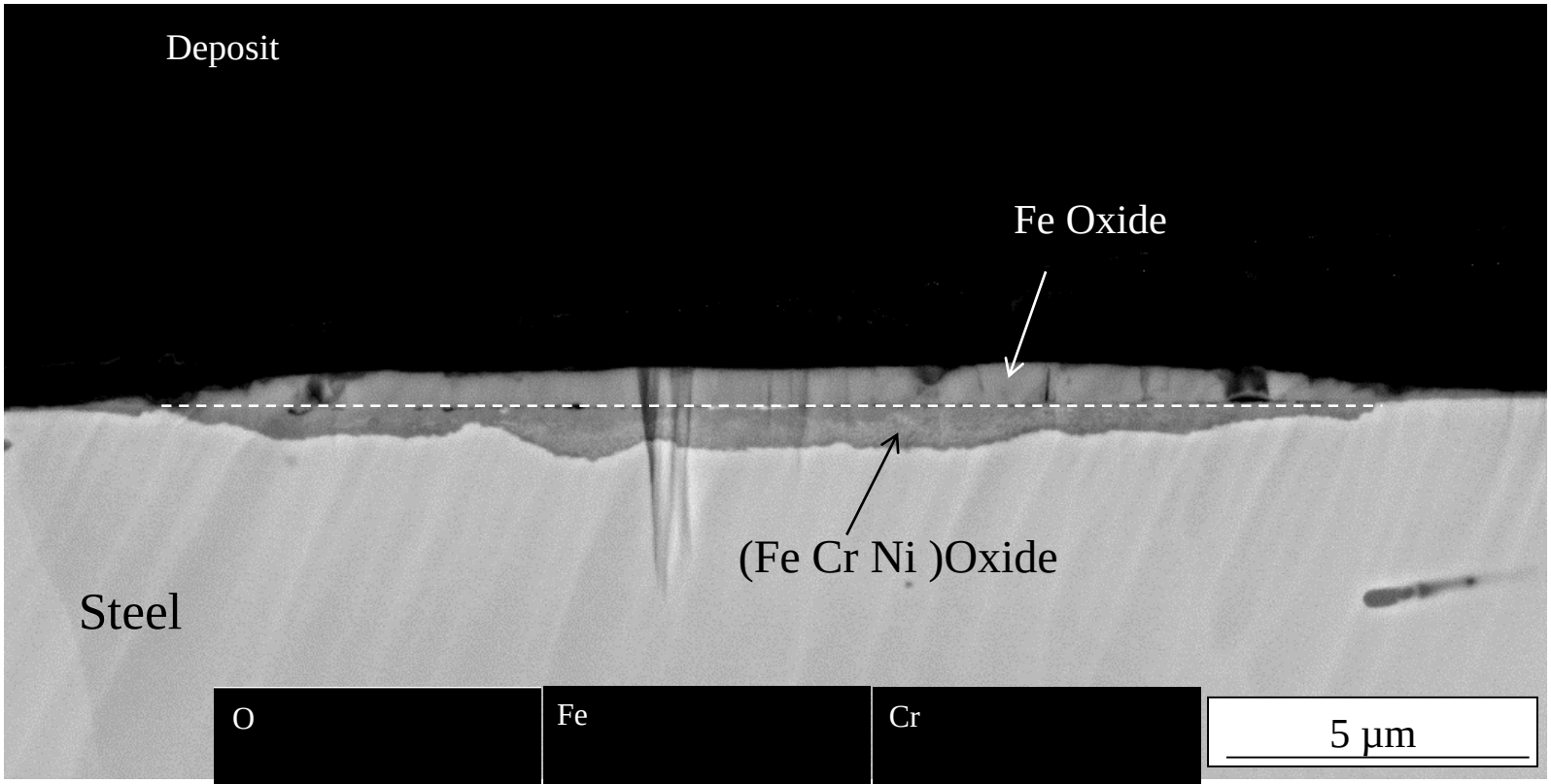
# Sample After exposure

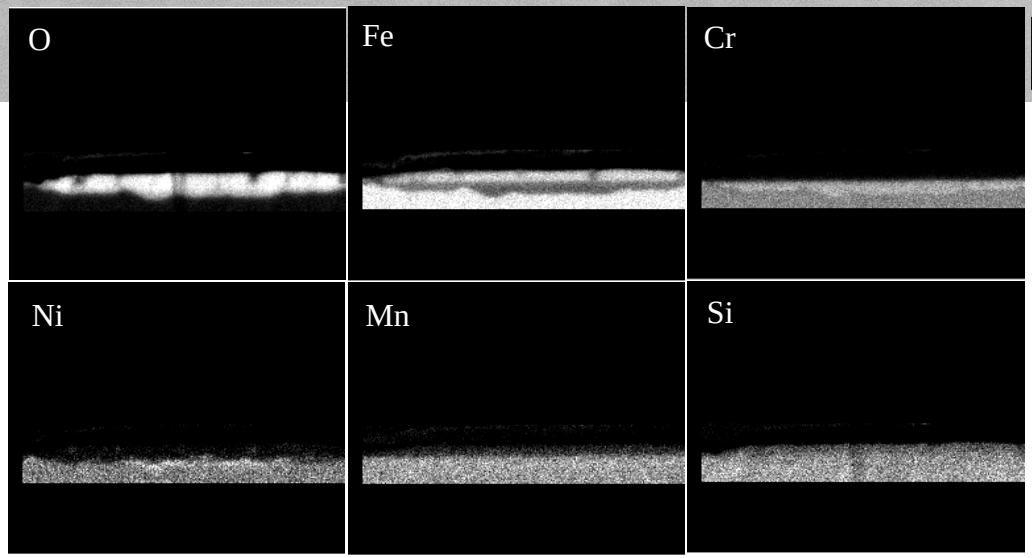


# 304L exposed for 4 hours at 600 ° C in the Chalmers gasifier

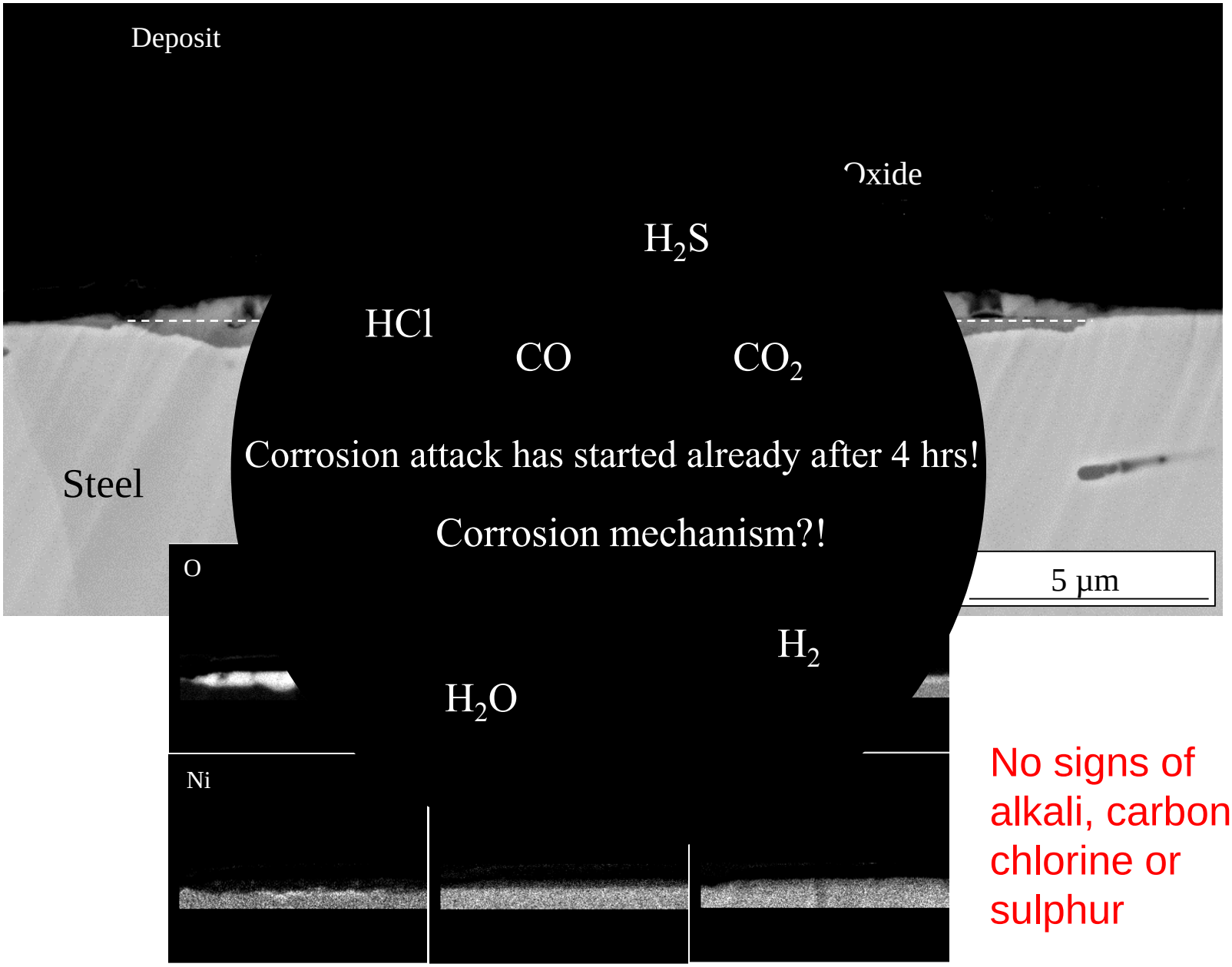



304L (bal% Fe,18% Cr, 10% Ni, 0.1% Mn)




No signs of alkali, carbon, chlorine or sulphur




No signs of alkali, carbon, chlorine or sulphur

# The properties of the protective oxide formed on FeCr alloys

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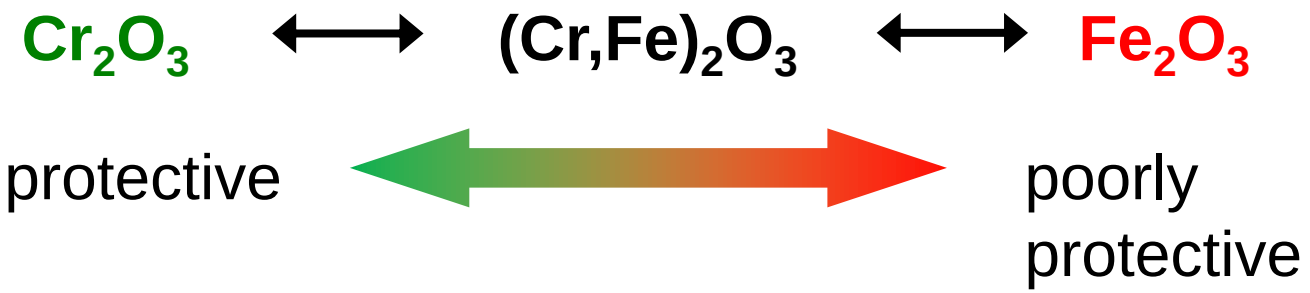



However, the oxygen activity in an gasifier environment is typically in the order $10^{-25}$. **At 600 °C, $Fe_2O_3$ is not stable in this environment!**

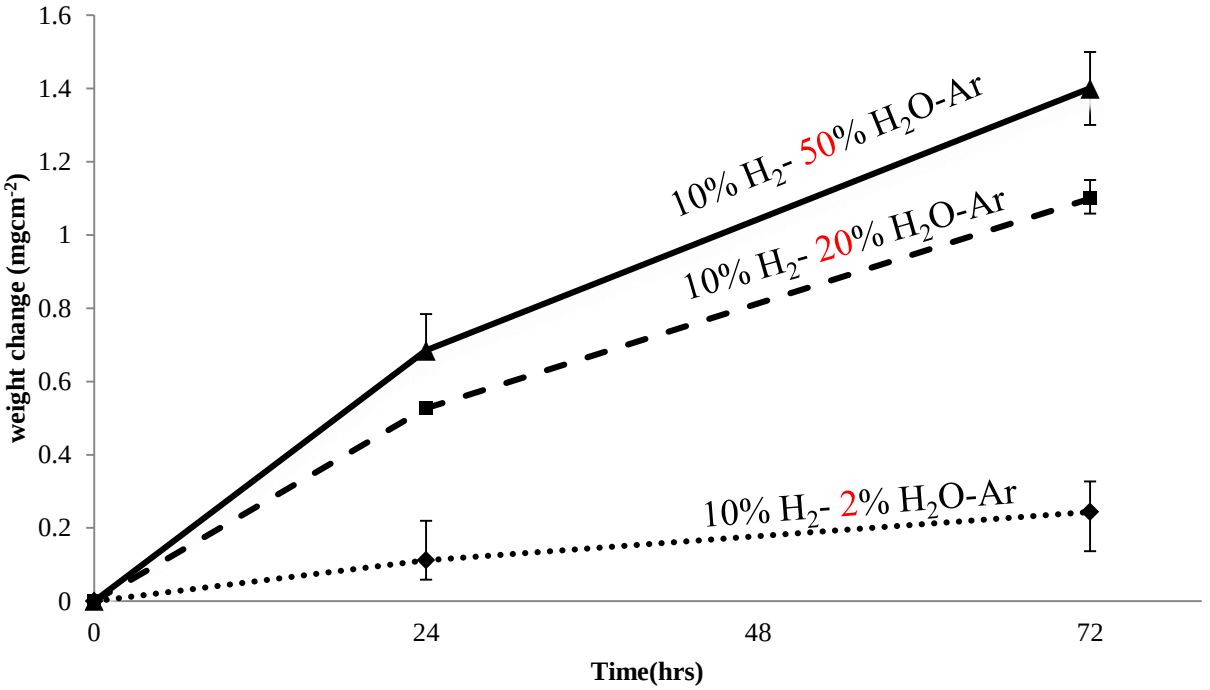
# Laboratory Studies

## Focusing on $H_2$-$H_2O$ environments

| Composition [wt%] | Cr | Mo | C | Mn | Si | Minor Add. | Fe | Ni |
|---|---|---|---|---|---|---|---|---|
| 304L(18/8) | 18.18 | 0.53 | 0.022 | 1.53 | 0.31 | Present | Bal. | 8.10 |

| | | |
|---|---|---|
| Dry oxygen/air | Cr-rich $(Fe_xCr_{1-x})_2O_3$ | Protective |
| Humid oxygen/air | Cr-depleted $(Fe_xCr_{1-x})_2O_3$ | Non-protective |
| $H_2$-$H_2O$ | ? | ? |

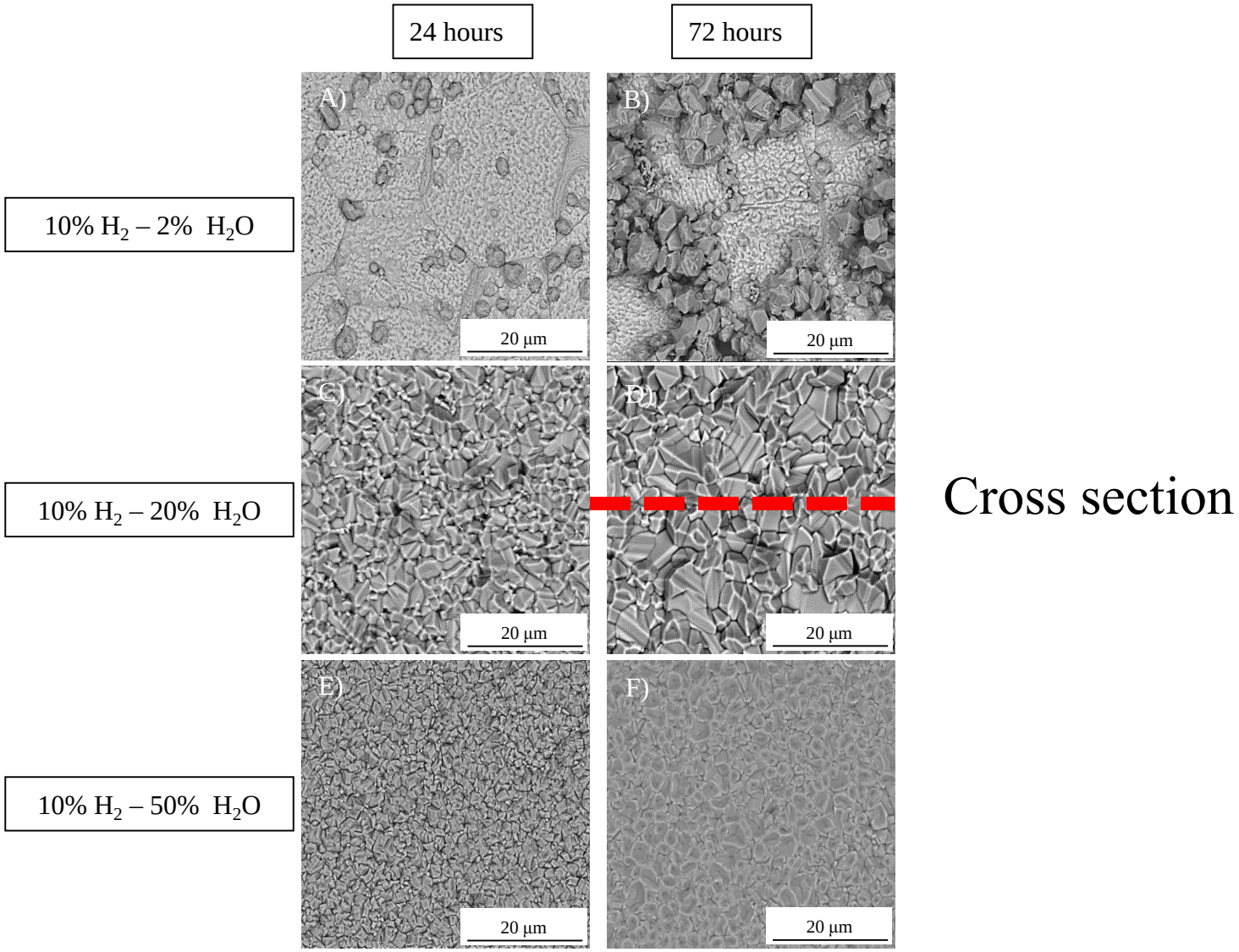
# Laboratory exposures in low $pO_2$



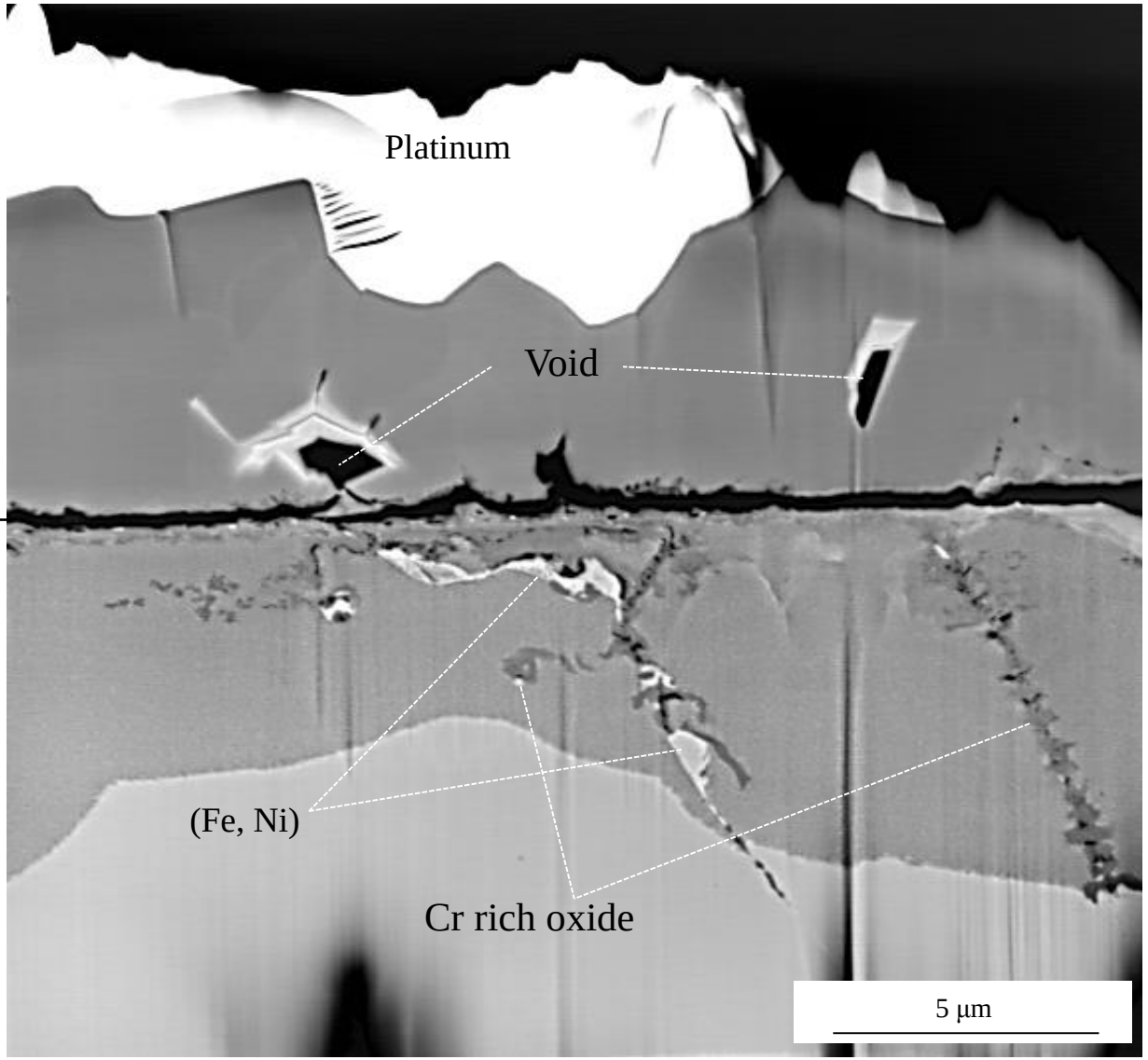

| Exposure | $H_2$ (volume %) | $H_2O$ (volume %) | Calculated a($O_2$) |
|---|---|---|---|
| **1** | 10 | 2 | $5*10^{-26}$ |
| **2** | 10 | 20 | $5*10^{-24}$ |
| **3** | 10 | 50 | $3*10^{-23}$ |

- 304L exposed to 10% $H_2$- X% $H_2O$-Ar at 600 $^oC$ for 24 and 72 hours.

# Laboratory exposures in low $pO_2$



# Laboratory exposures in low $pO_2$



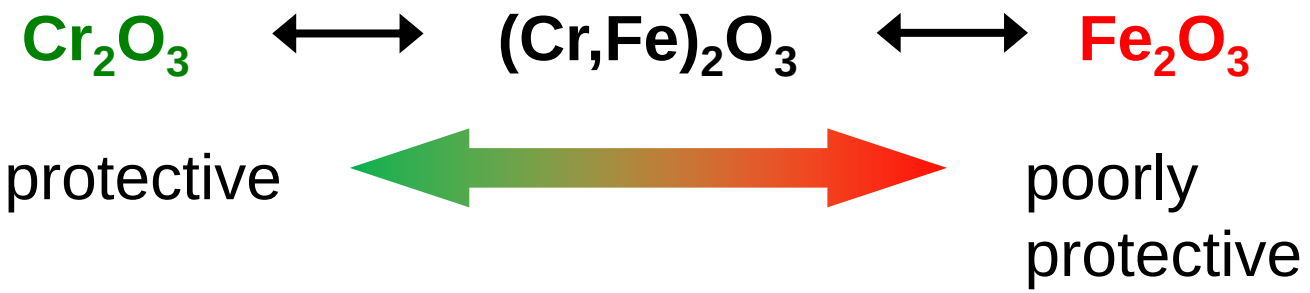

$Fe_3O_4$

Reaction zone (RZ):
$(Fe,Cr)_3O_4$ and Fe,Ni metal

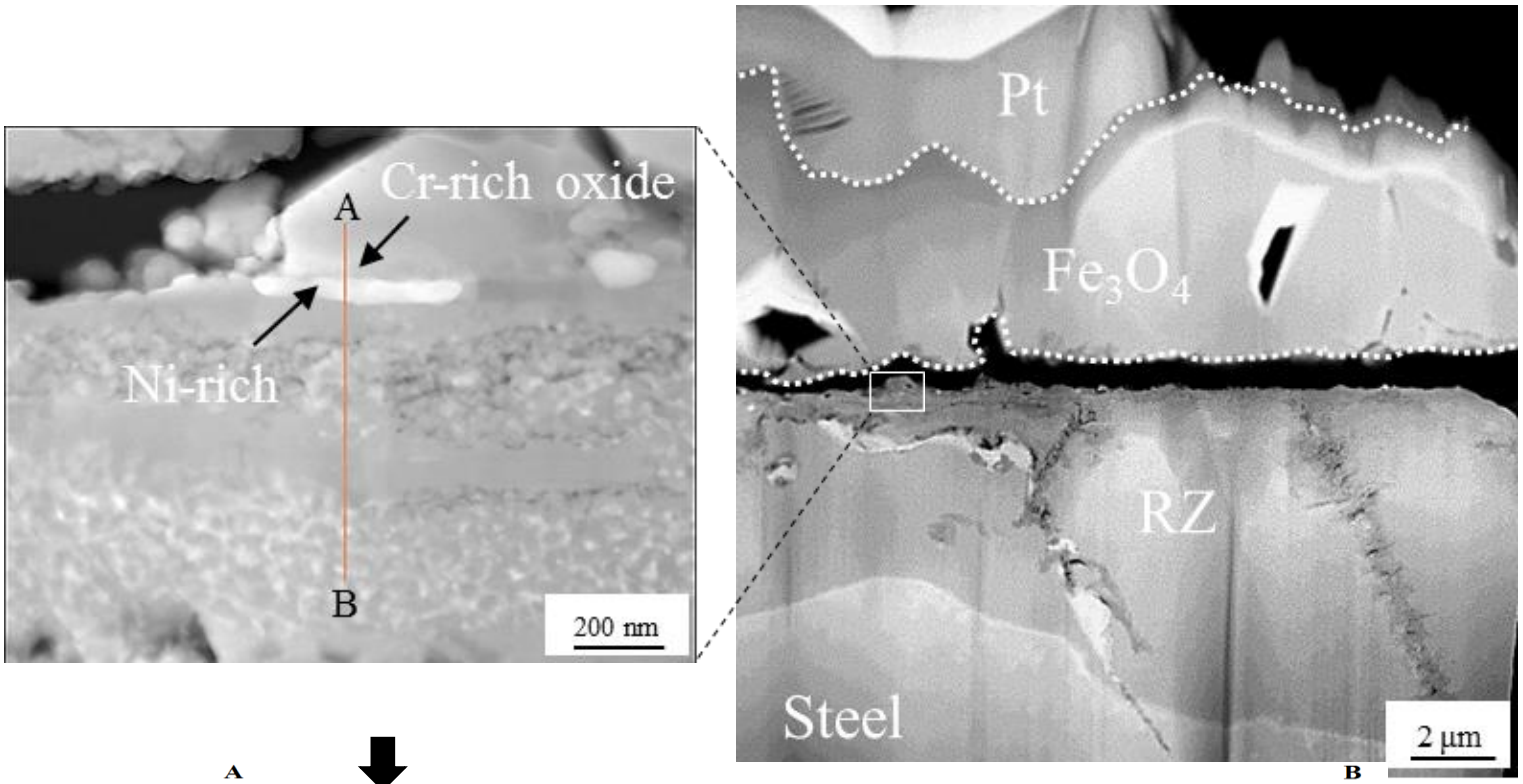
Steel

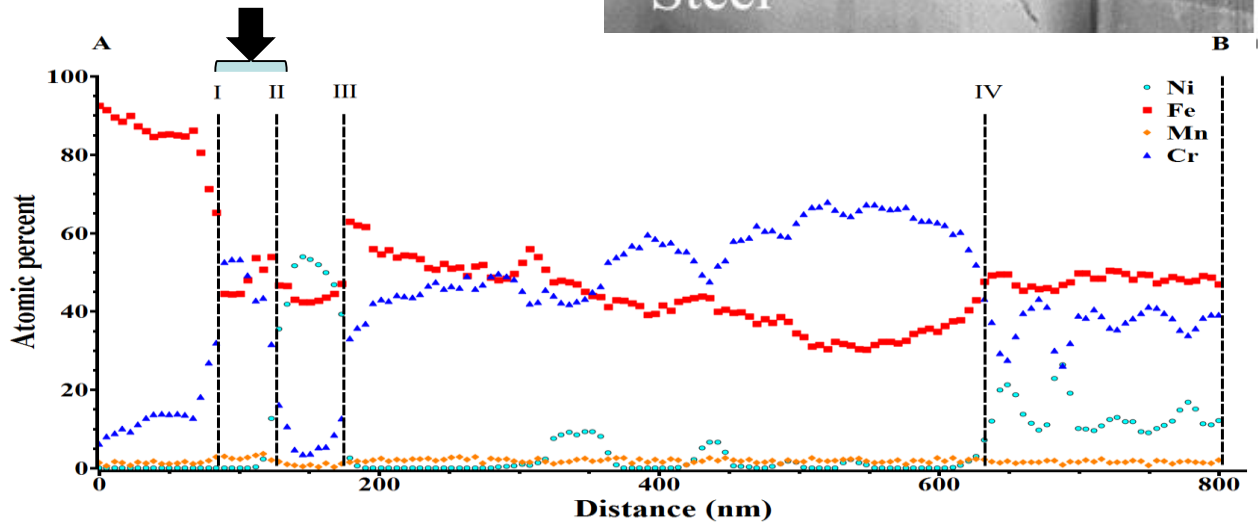
# The properties of the protective oxide formed on FeCr alloys

The oxide formed on FeCr alloys consist of a corundum type solid solution, $(Cr, Fe)_2O_3$. The Cr/Fe ratio determines whether it is protective (as $Cr_2O_3$) or poorly protective (as $Fe_2O_3$).

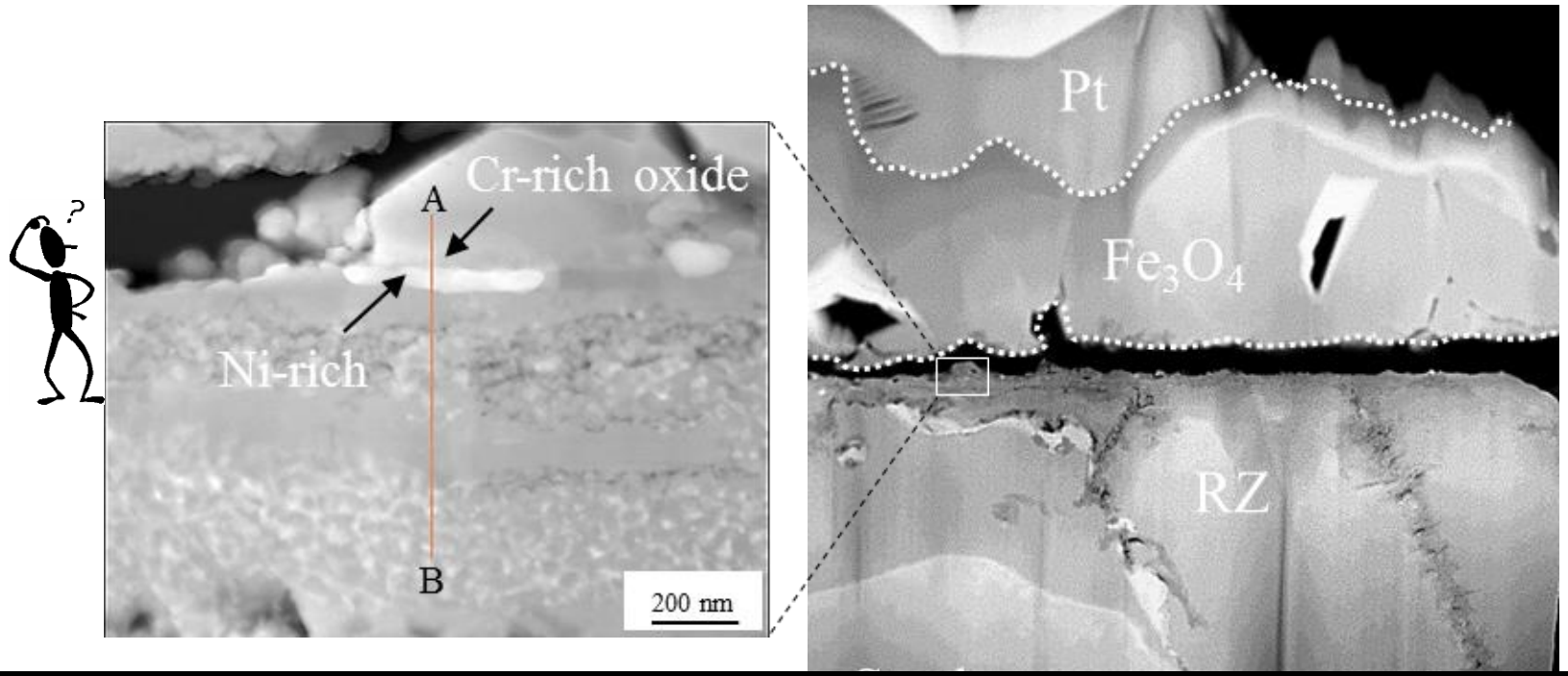



However, the oxygen activity in an gasifier environment is typically in the order $10^{-25}$. **At 600 °C, $Fe_2O_3$ is not stable in this environment!**



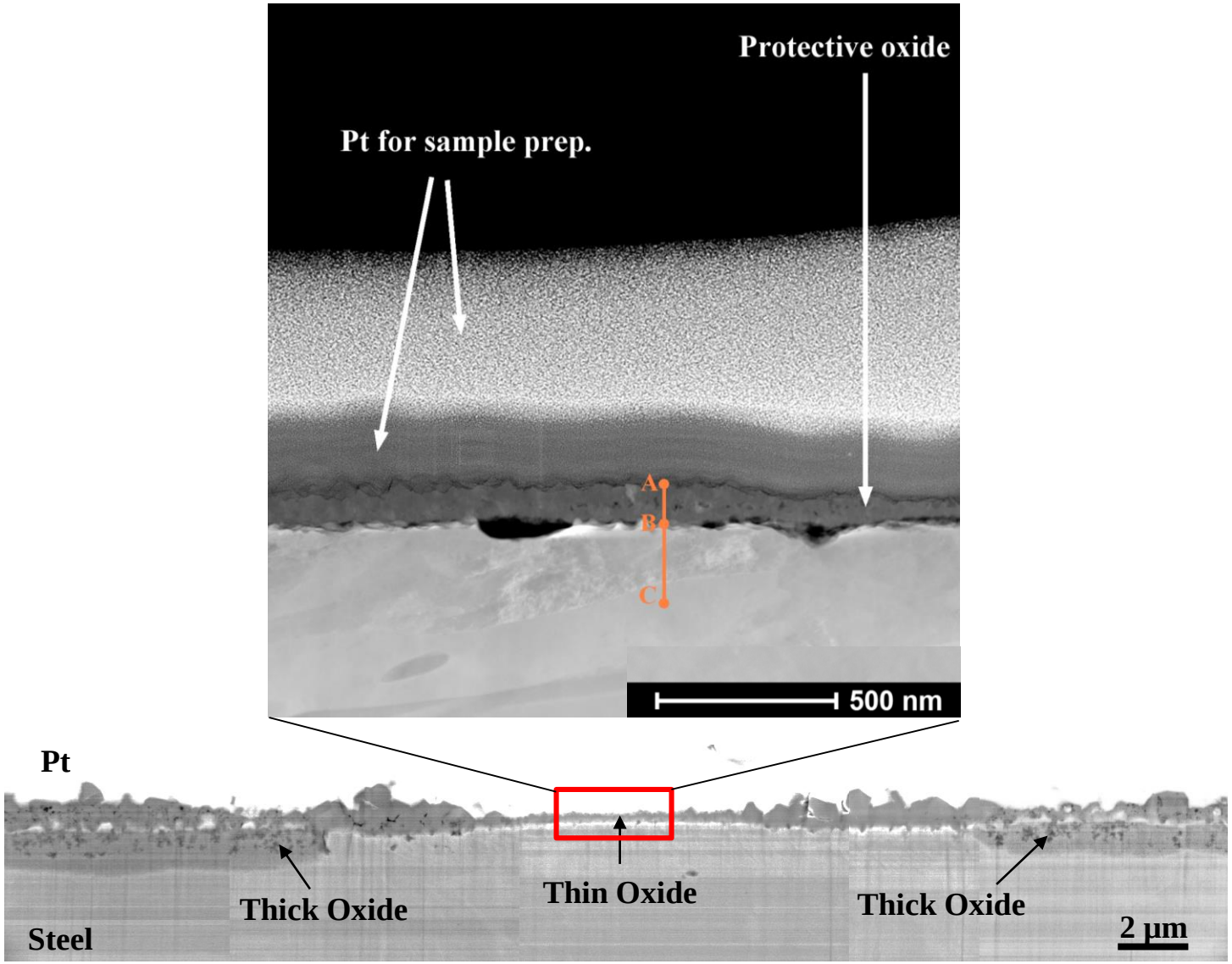

- STEM/HAADF cross section image of 304L exposed to 10 % $H_2$- 20% $H_2O$-Ar at 600 °C for **72 hours.**



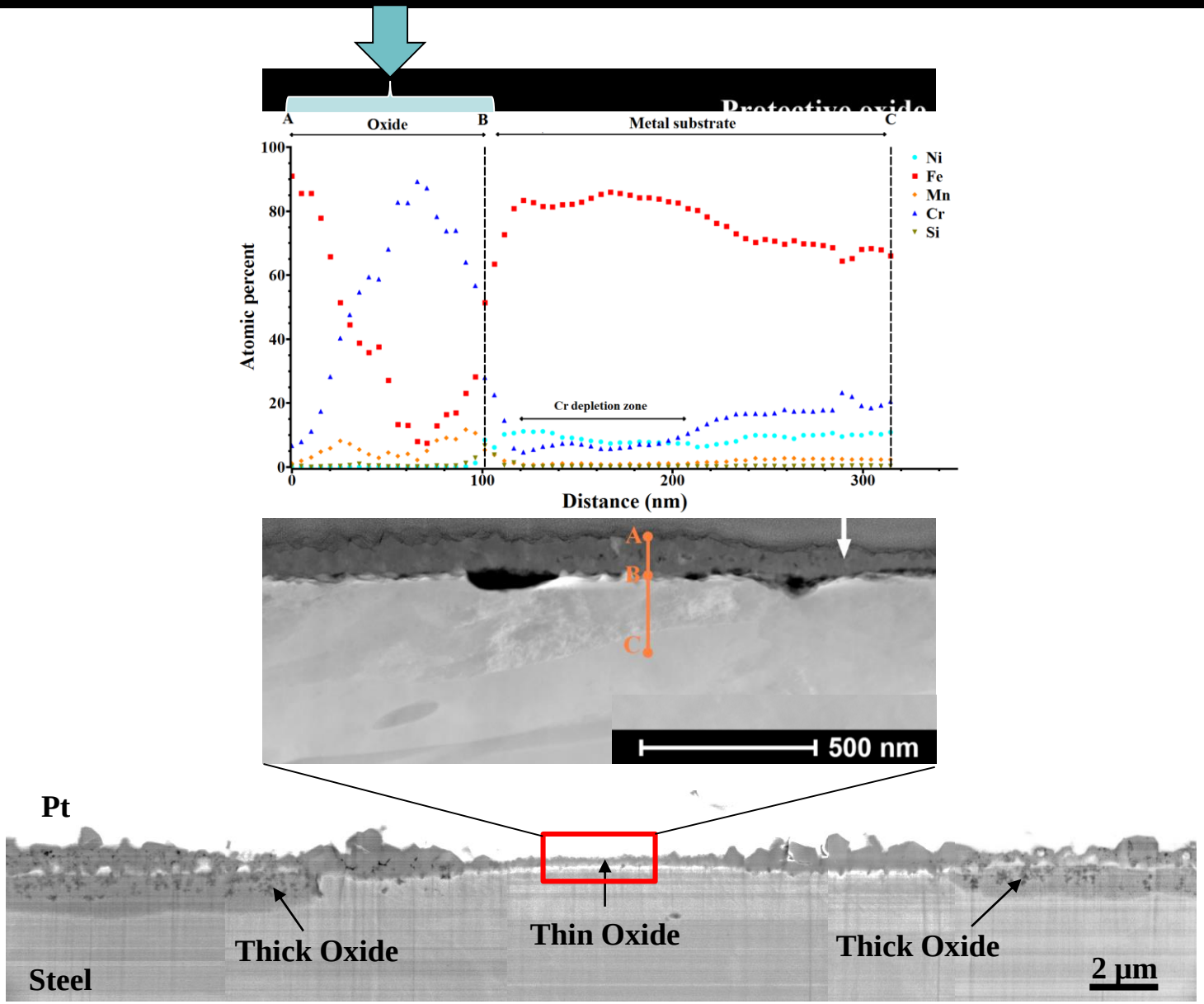

Is it the remnant of initially formed Cr-rich oxide?

Need to perform a shorter exposure!

- STEM/HAADF cross section image of 304L exposed to 10 % $H_2$- 20% $H_2O$-Ar at 600 $^oC$ for **72 hours.**




- STEM/BSE image of 304L exposed to 10 % $H_2$- 20% $H_2O$-Ar at 600 °C for **1 hour.**




- STEM/BSE image of 304L exposed to 10 % $H_2$- 20% $H_2O$-Ar at 600 °C for **1 hour.**

# Cr evaporation in presence of $H_2O$ at **high** $a(O_2)$

But

Negligible at **low** $a(O_2)$!

Dry oxygen/air — Cr-rich $(Fe_xCr_{1-x})_2O_3$ — Protective

$H_2$-$H_2O$ — Cr-rich $(Fe_xCr_{1-x})_2O_3$ — Non-protective

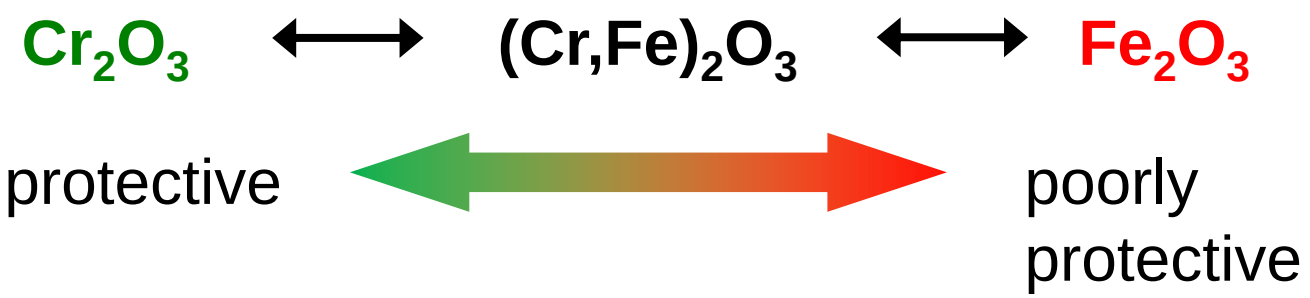
$Cr_2O_3$ ⟷ $(Cr,Fe)_2O_3$ ⟷ $Fe_2O_3$

protective ⟷ poorly protective

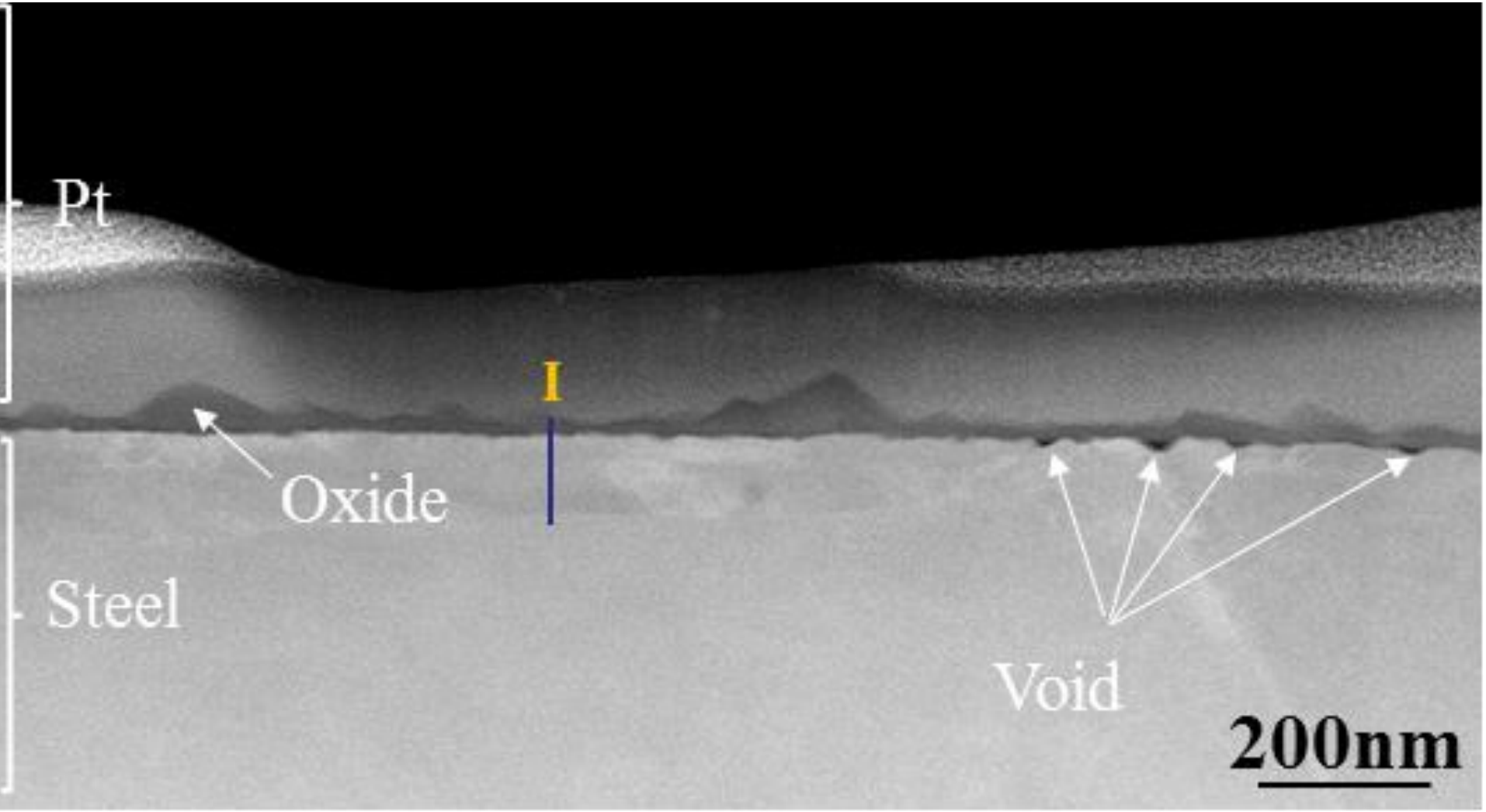
Cr evaporation in presence of $H_2O$ at **high** ***a(O$_2$)***

But

We are missing something…

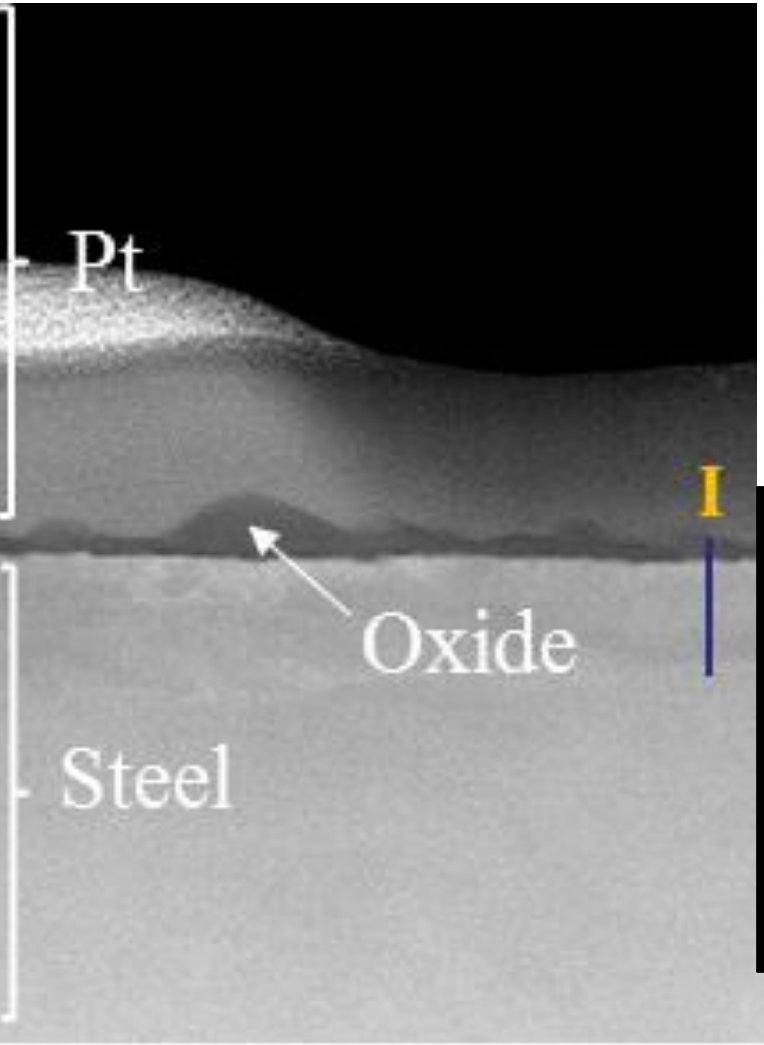


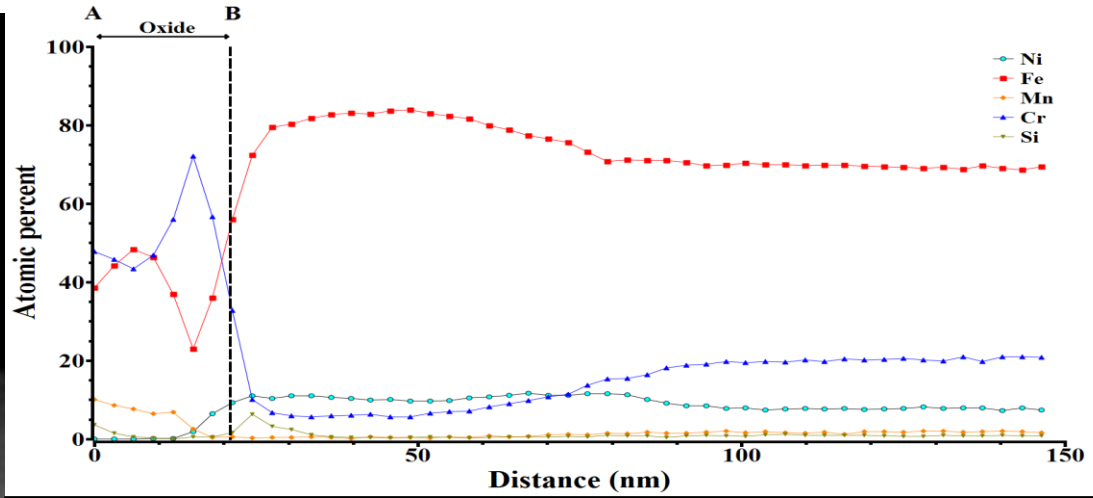
Dry oxygen/air  Cr-rich $(Fe_xCr_{1-x})_2O_3$  Protective




- STEM/BSE image of 304L exposed to 5 % $O_2$- $N_2$ at 600 °C for 24 hour.

Dry oxygen/air  Cr-rich $(Fe_xCr_{1-x})_2O_3$  Protective




Cr-rich Oxide

Oxide thickness: ≈ 10 nm

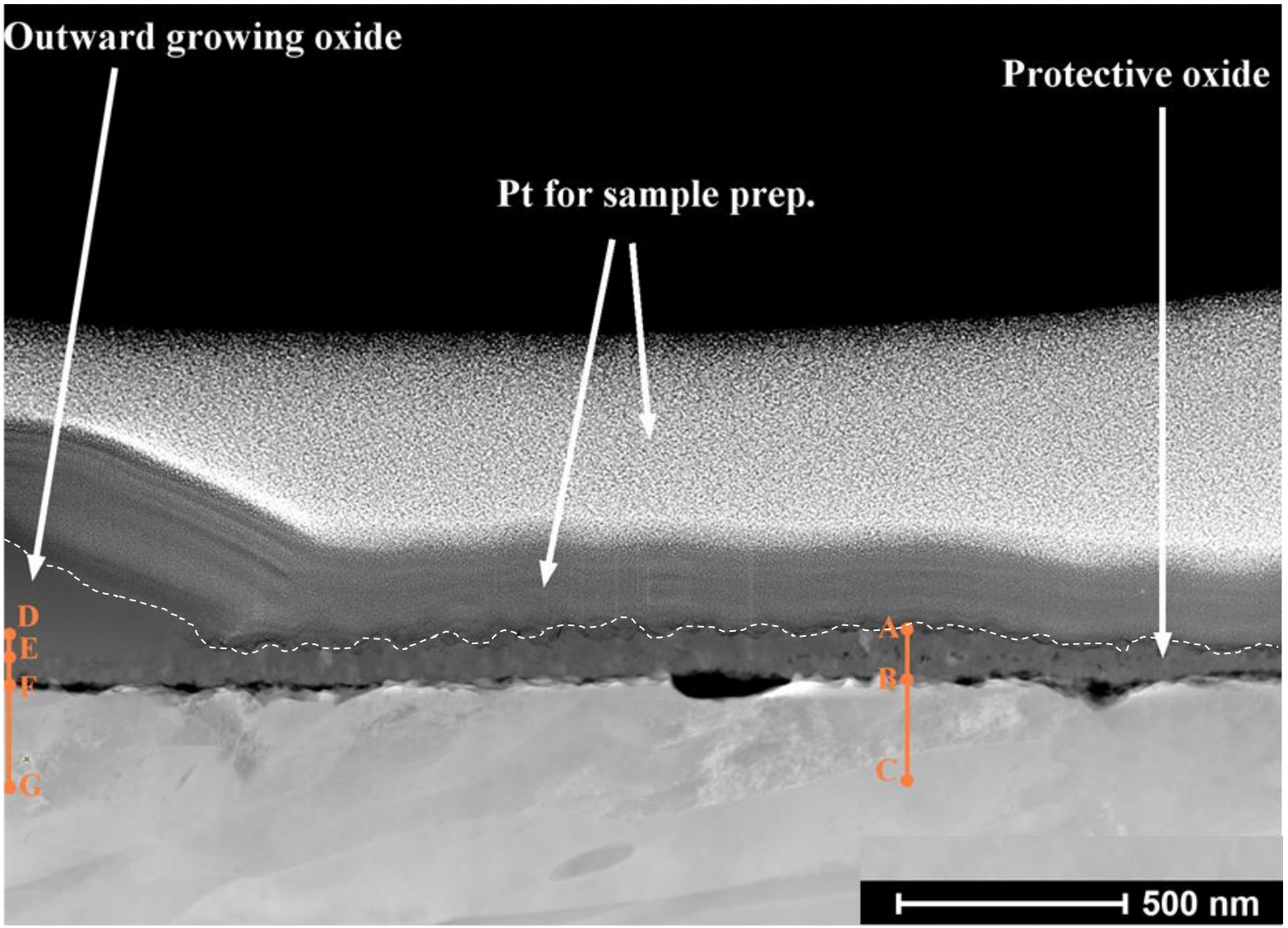
Cr level (oxide): ≈ 70 cat.%

Alloy

Cr level in depletion zone: ≈ 6 atm.%

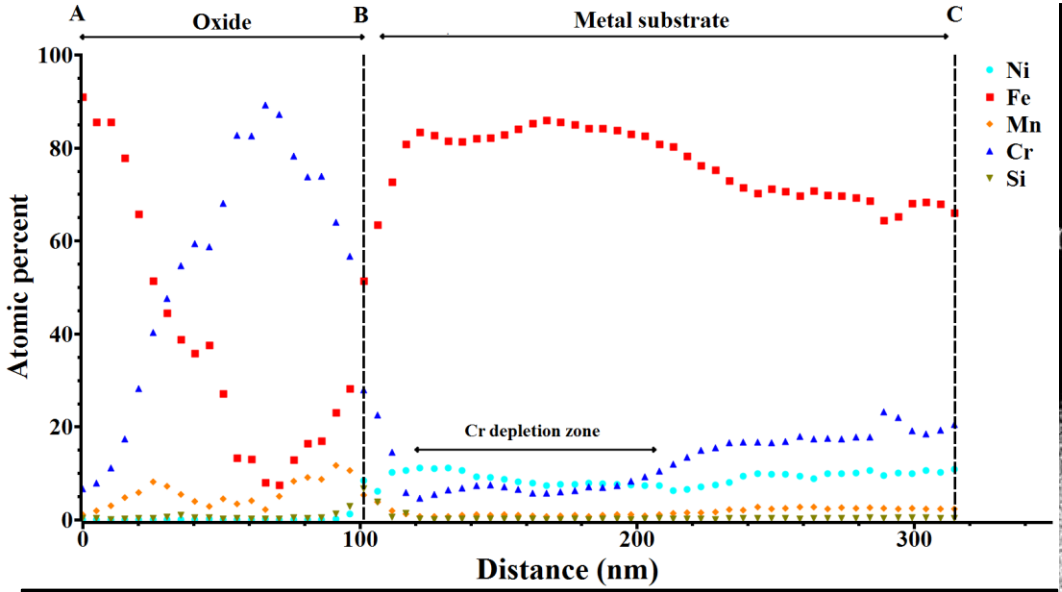
- STEM/BSE image of 304L exposed to 5 % $O_2$- $N_2$ at 600 °C for 24 hour.

$H_2$-$H_2O$ Cr-rich $(Fe_xCr_{1-x})_2O_3$

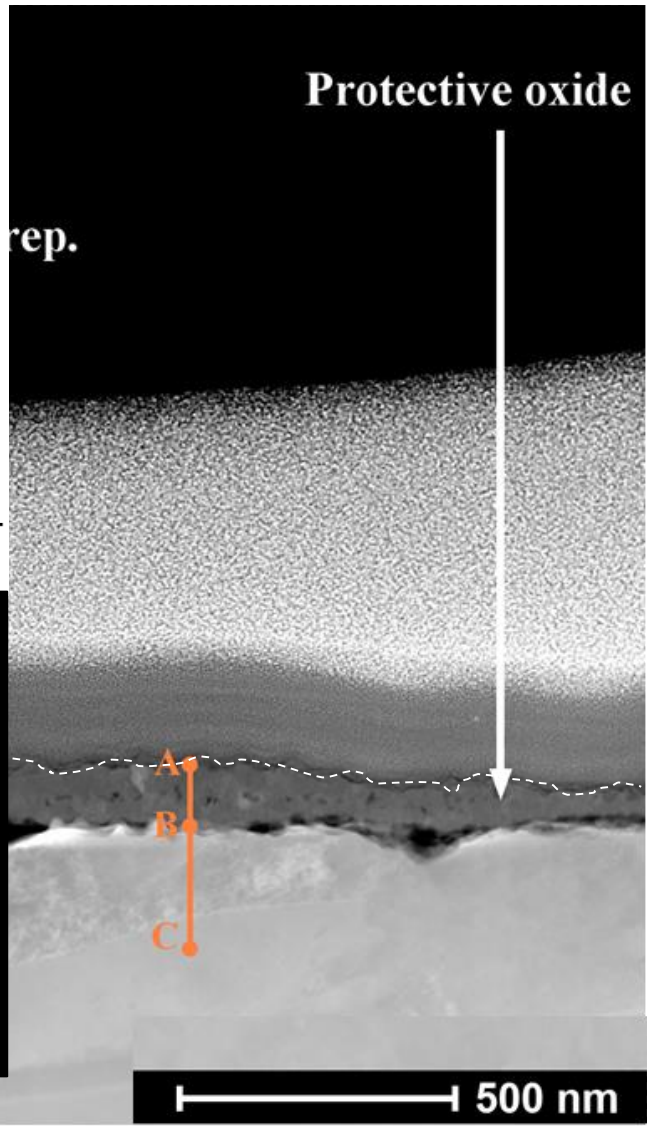



- STEM/BSE image of 304L exposed to 10 % $H_2$- 20% $H_2O$ at 600 °C for 1 hour.

# $H_2$-$H_2O$




# Cr-rich $(Fe_xCr_{1-x})_2O_3$




## Cr-rich Oxide

Oxide thickness: ≈ 60 nm

Cr level (oxide): ≈ 95 cat.%

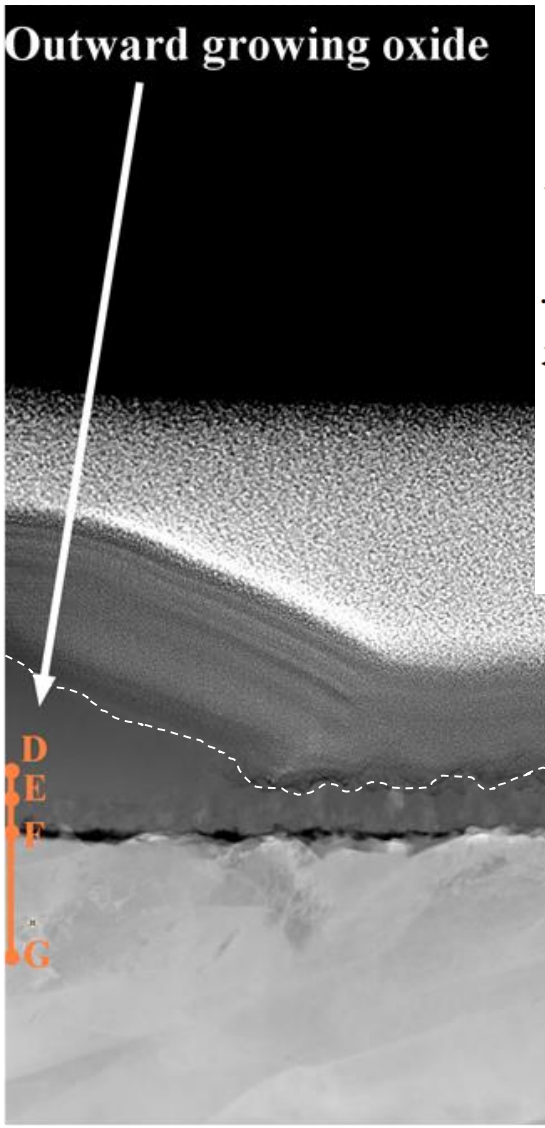
## Alloy

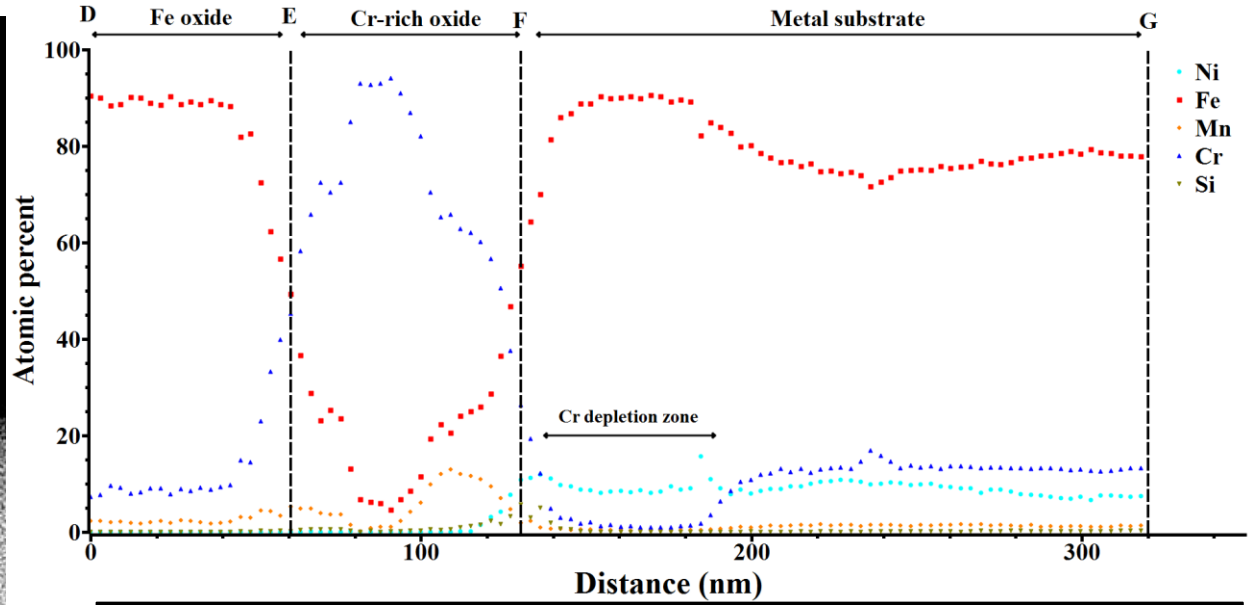
Cr level in depletion zone: ≈ 6 atm.%

- STEM/BSE image of 304L exposed to 10 % $H_2$- 20% $H_2O$ at 600 °C for 1 hour.

# $H_2$-$H_2O$

# Cr-rich $(Fe_xCr_{1-x})_2O_3$




Cr-rich Oxide

Oxide thickness: ≈ 60 nm

Cr level (oxide): ≈ 95 cat.%

Alloy

Cr level in depletion zone: ≈ 2 atm.%

500 nm

- STEM/BSE image of 304L exposed to 10 % $H_2$- 20% $H_2O$ at 600 °C for 1 hour.

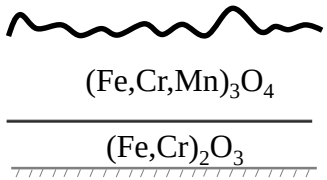
## $H_2$-$H_2O$ compare to dry oxygen:

- The base oxide is almost pure chromia. ➡ Faster oxidation rate than $(Fe_xCr_{1-x})_2O_3$
- The base oxide is thicker.
- Significant Cr-depletion zone exists at the oxide/alloy interface.

This can describe the breakaway oxidation mechanism!

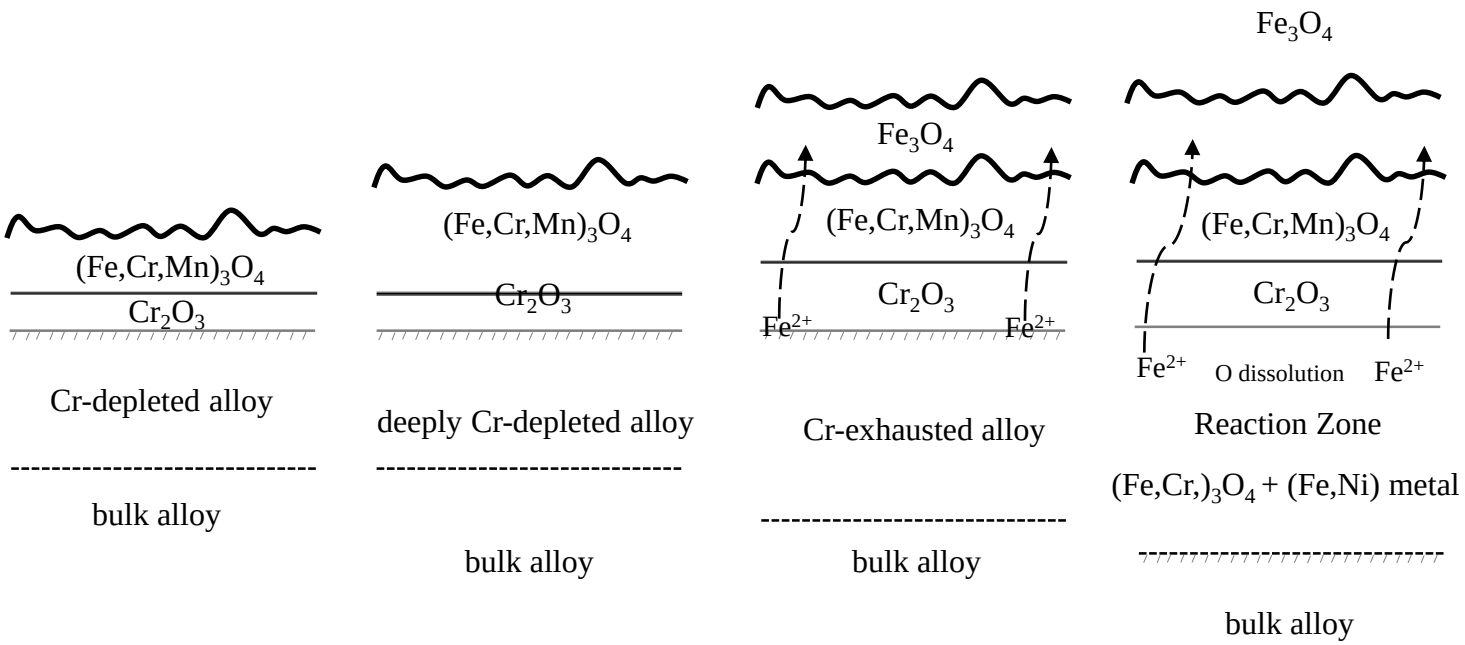
# *Exposing to $O_2$ + $N_2$ at 600 ˚C*

**a)**



# *Exposing to $H_2$-$H_2O$ at 600 °C*

**b)** ***Stage I*** **c)** ***Stage II*** **d)** ***Stage III*** **e)** ***Stage IV***



Perfect!
Now we have the breakaway oxidation mechanism!

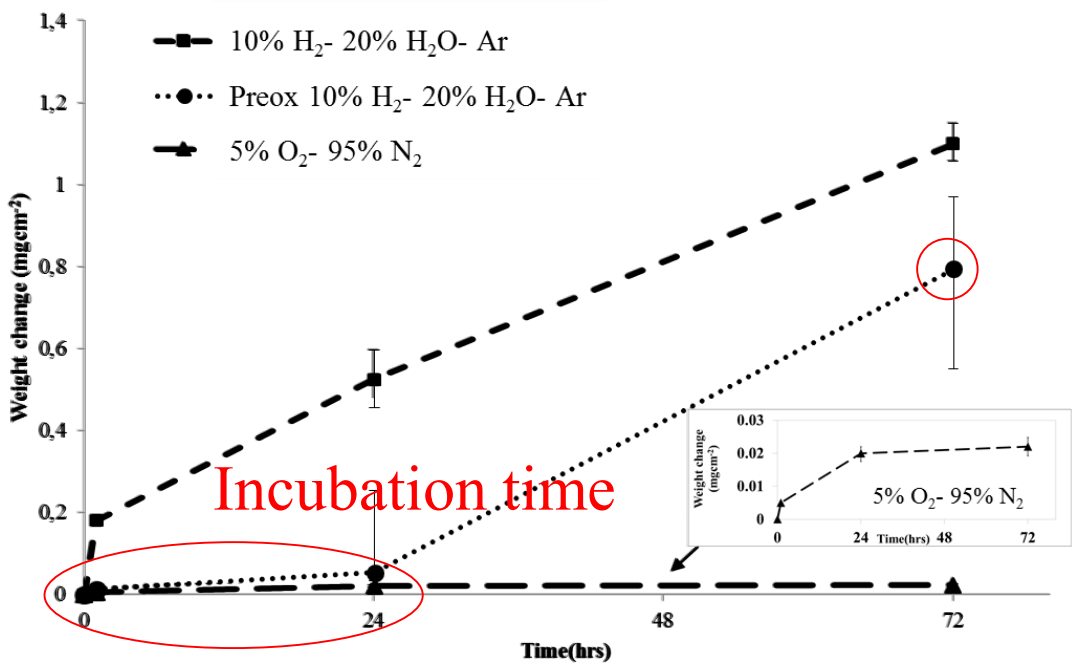
But
The last puzzle of the mechanism:
why do we form pure chromia, instead of $(Fe_xCr_{1-x})_2O_3$, in $H_2$-$H_2O$?

If sample is pre-oxidized in $O_2 + N_2$ first

i.e. forming Cr-rich $(Fe_xCr_{1-X})_2O_3$

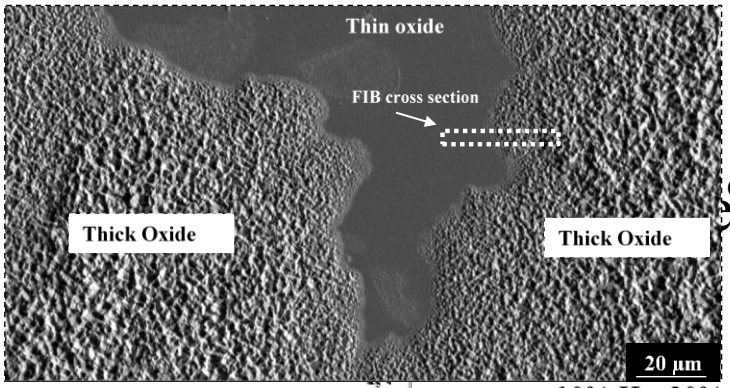
then

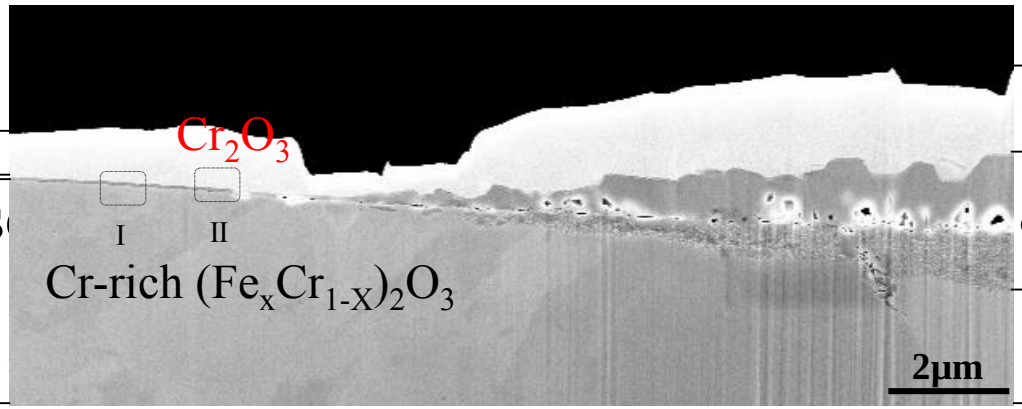
exposed to $H_2$-$H_2O$

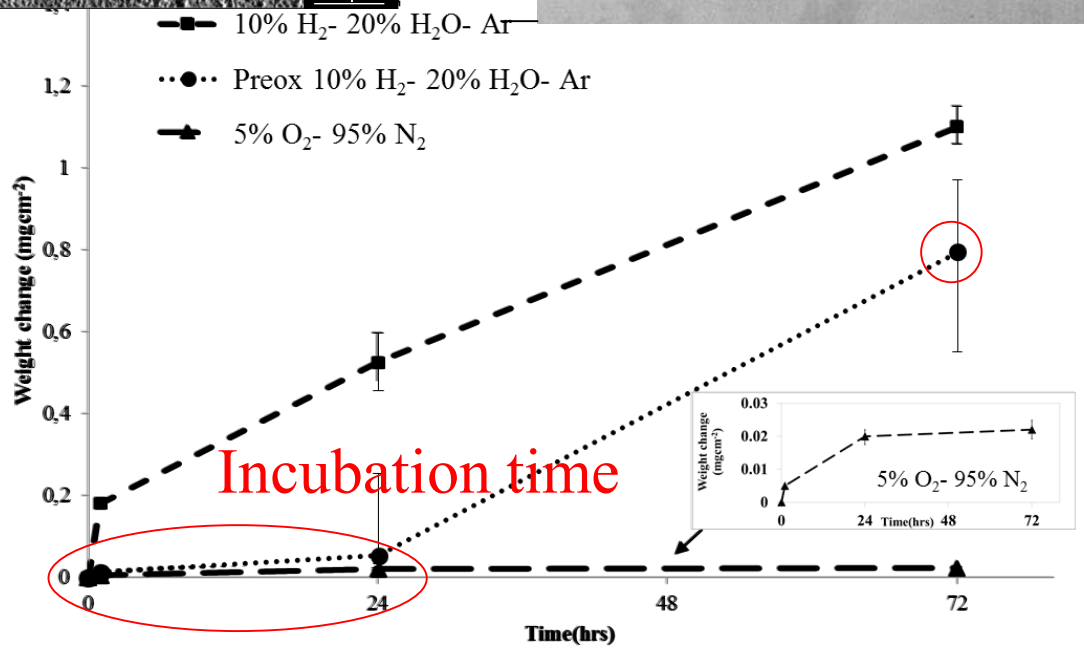


# If sample is pre-oxidized in $O_2 + N_2$ first

## i.e. forming Cr-rich $(Fe_xCr_{1-X})_2O_3$



# Three main points:

- When as-polished sample exposed to $H_2$-$H_2O$ $Cr_2O_3$
- When pre-oxidized sample exposed to $H_2$-$H_2O$

  $(Fe_xCr_{1-x})_2O_3$ Replaced by $Cr_2O_3$

Why?


- Incubation time for pre-oxidized sample before breakaway oxidation

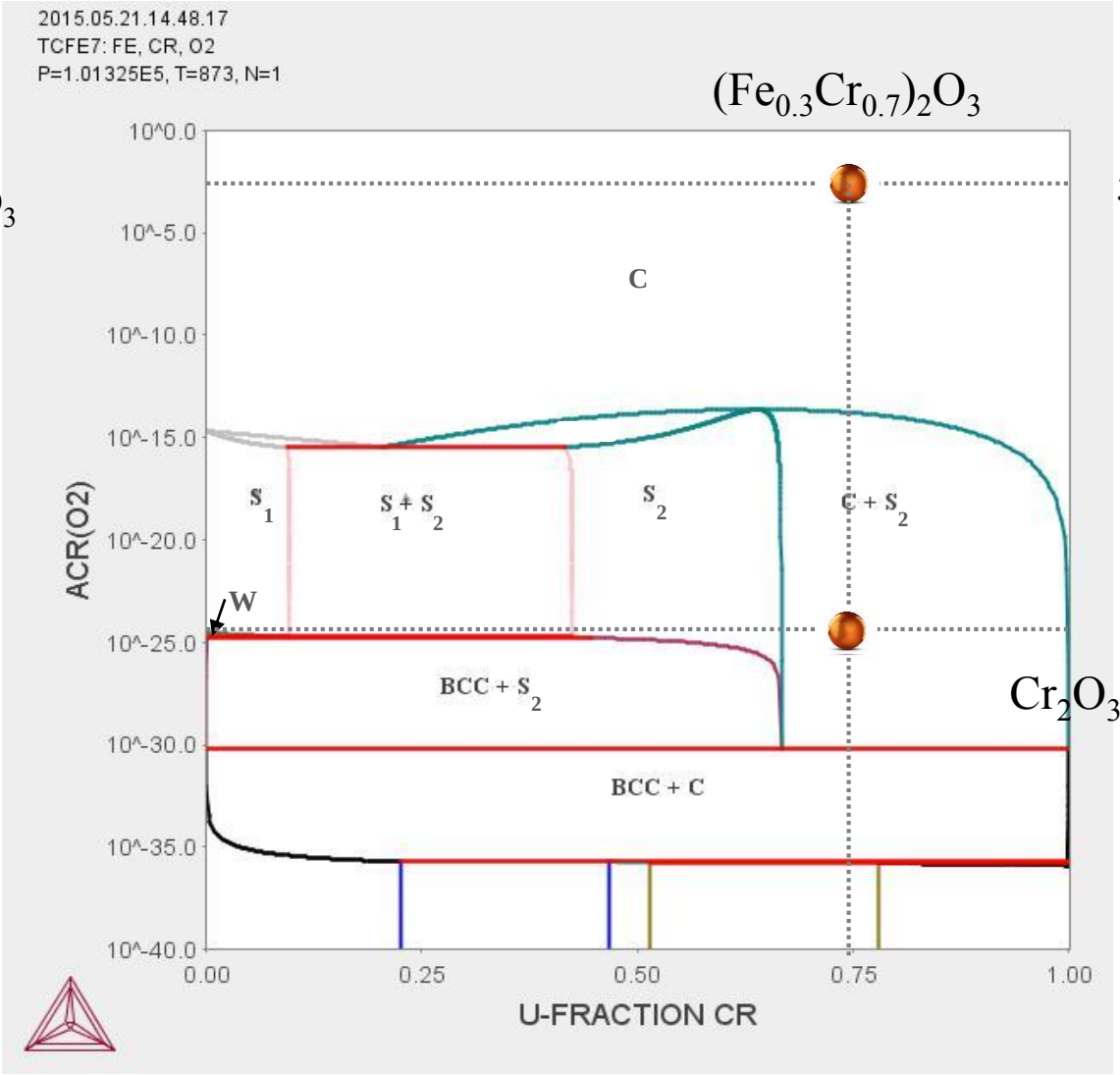
C = corundum-type $M_2O_3$

$S_1 = Fe_{3-x}Cr_xO_4$

$S_2 = FeCr_{2-x}Fe_xO_4$

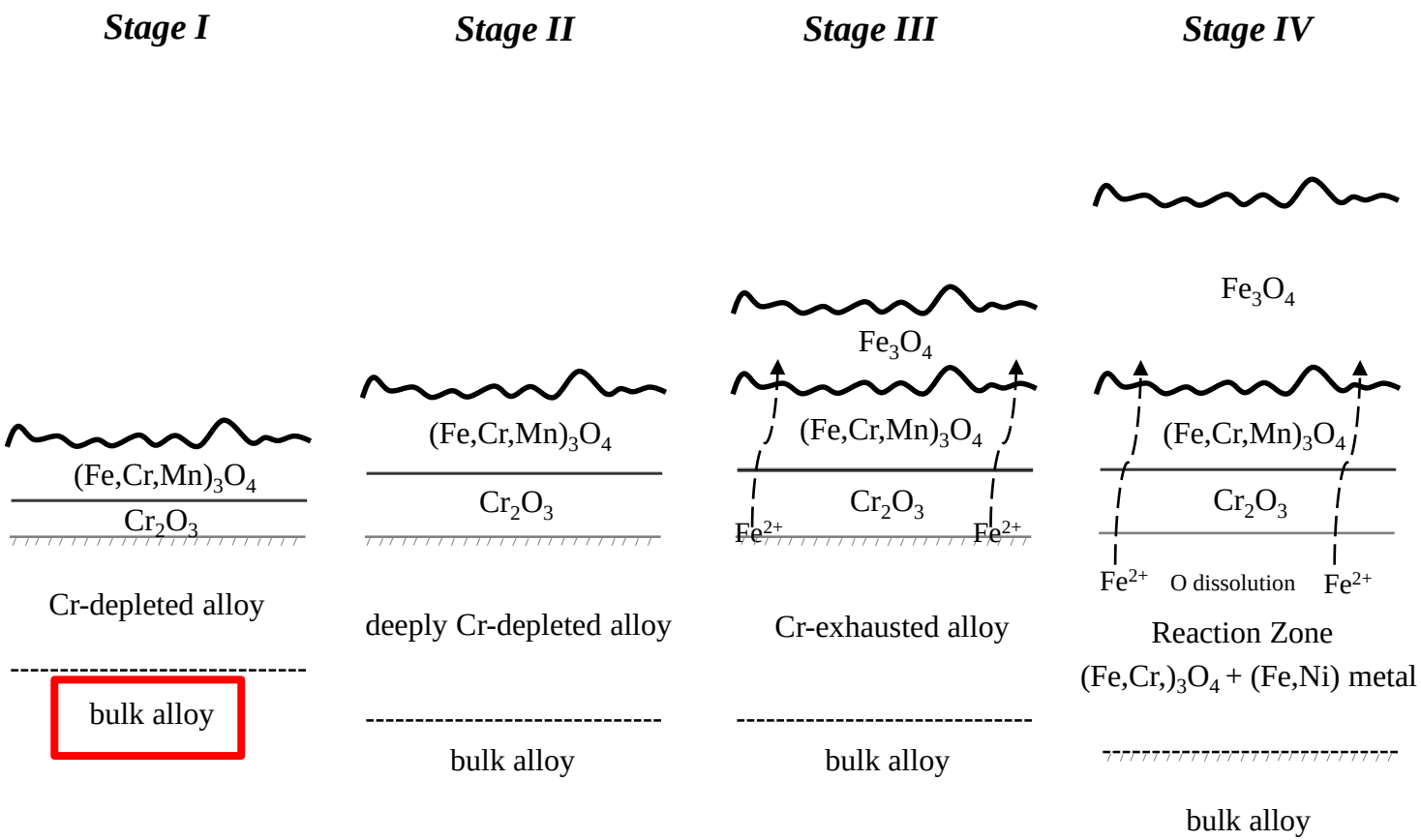
W= $Fe_{1-x}O$

BCC = ferrite-structured metal




Stable phases in the Fe-Cr-O system at 600 ºC as a function of oxygen activity and mole fraction of Cr calculated using the THERMO-CALC.

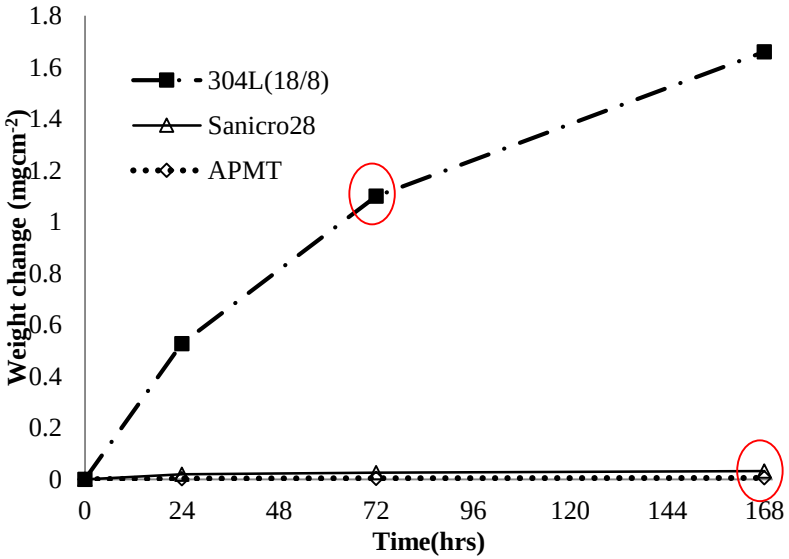
# *Breakaway oxidation in $H_2$-$H_2O$ at 600 °C*



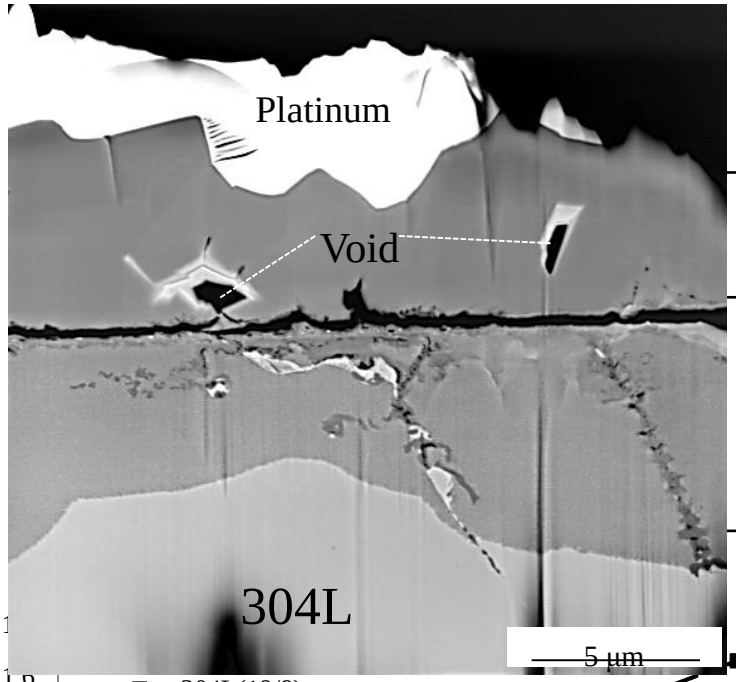

What if the alloy has enough Cr-reservoir?

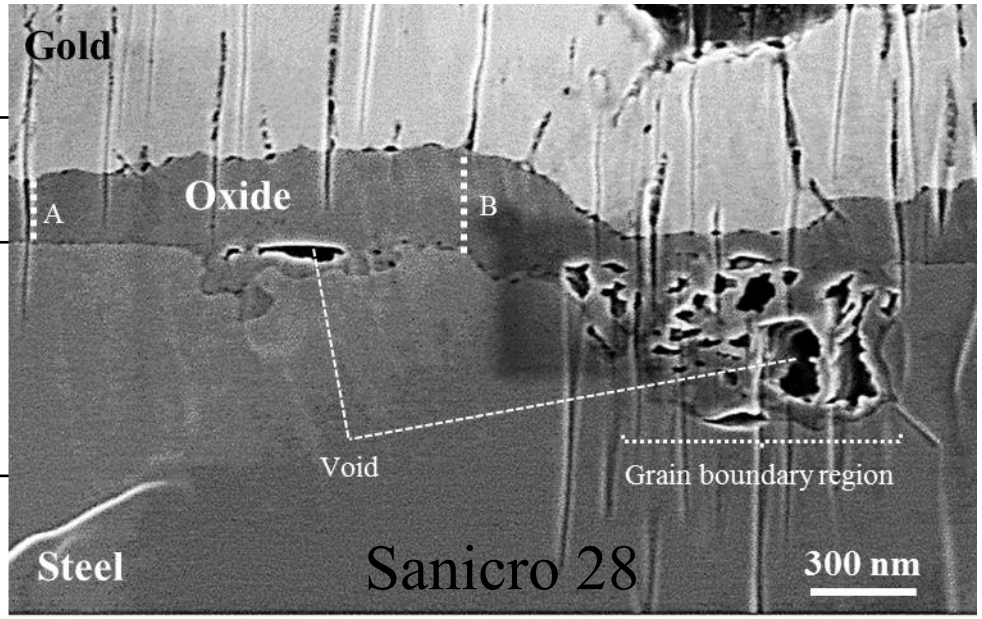
# Mitigate corrosion by improved materials

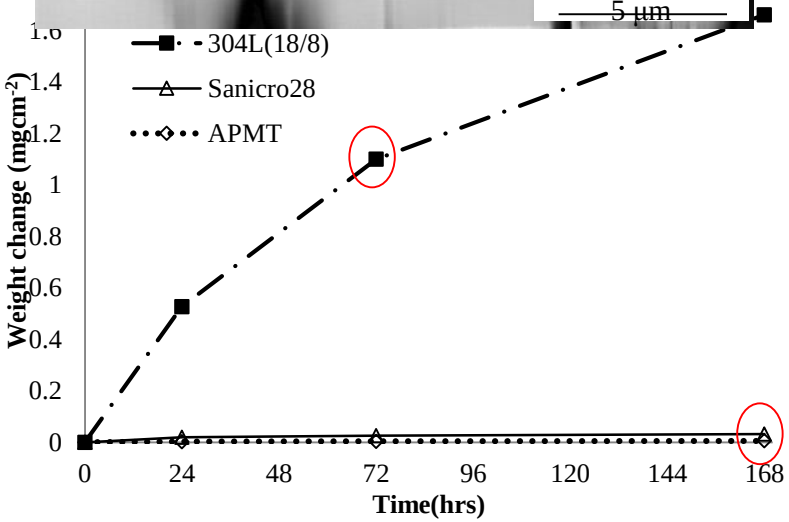
| Composition [wt%] | Cr | Al | Mo | C | Mn | Si | Minor Add. | Fe | Ni |
|---|---|---|---|---|---|---|---|---|---|
| 304L(18/8) | 18.18 | - | 0.53 | 0.022 | 1.53 | 0.31 | Present | Bal. | 8.10 |
| Sanicro 28 | 27 | - | 3.5 | 0.02 | 2 | 0.7 | Cu | Bal. | 31 |
| Kanthal APMT | 22 | 5 | 3 | ≤0.05 | ≤0.4 | ≤0.7 | Present | Bal. | - |

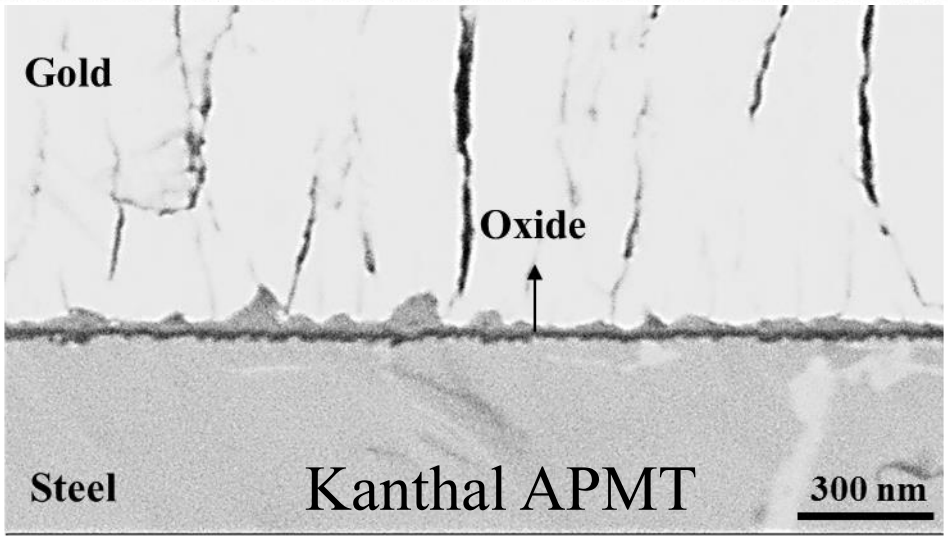


# Mitigate corrosion by improved materials



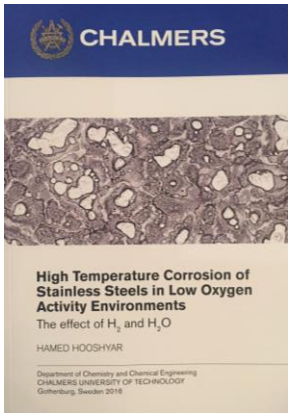



# Summary

- Low oxygen activity environments can cause (marginal) chromia forming steels to go into breakaway oxidation
  - This is due to a Cr exhausted alloy beneath the oxide leading to iron oxidation
- More highly alloyed stainless steels and alumina formers exhibit more protective behaviour in this environment.
- Important to point out that this has been a fundamental study focusing on the corrosion mechanism in low oxygen activity environment containing $H_2$ and $H_2O$

$CO$, $CO_2$, $CH_4$, $H_2S$, HCl, KCl etc may still cause corrosion!!




**Hamed Hooshyar Doctoral Thesis Defense**
Friday 18 March at 13.00 at Chalmers

"High Temperature Corrosion of Stainless Steels in Low Oxygen Activity Environments -The effect of $H_2$ and $H_2O$"

- ***Paper I*** Field study in Chalmers Gasifier
- ***Paper II*** Process investigation
- ***Paper III*** General effects of $H_2$ and $H_2O$
- ***Paper IV*** Mechanistic study of corrosion in presence of $H_2O$ at low $a(O_2)$
- ***Paper V*** Propagation after breakaway oxidation
- ***Paper VI*** Oxidation behavior of other alloys
- ***Paper VII*** Influence of $a(O_2)$ on the base oxide