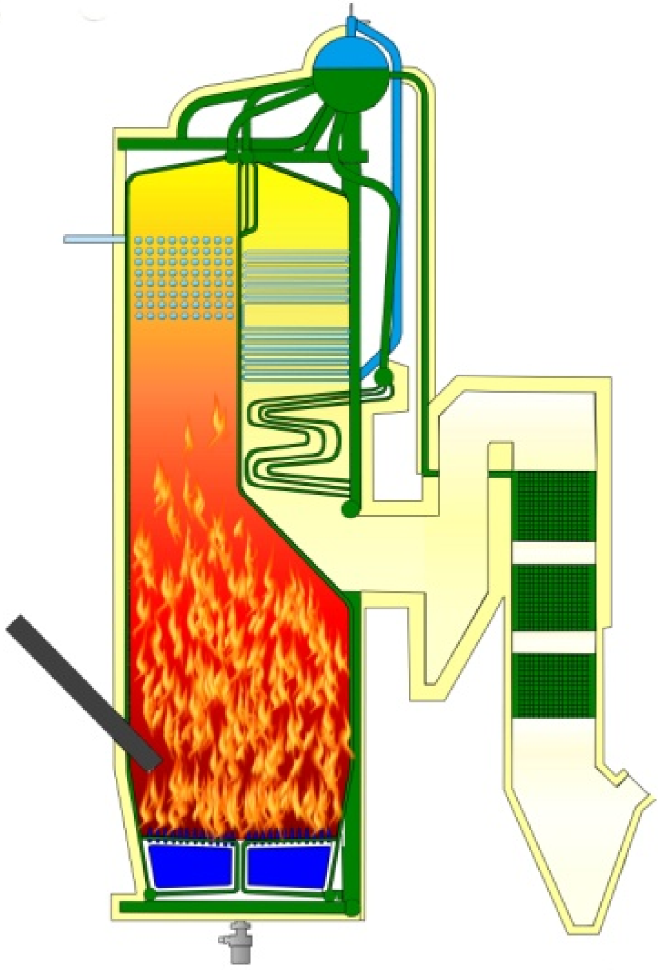
The effect of Cr and Si on corrosion properties of FeCrAl model alloys in KCl-rich environments at low temperatures (600° C)

Johan Eklund

Background

- Renewable energy – Substitute fossil fuels
- Biomass and waste
  - Corrosive environment
    - Superheater
  - Higher steam temperature
    - Higher electrical efficiency

→ Need for more corrosion resistant materials



Materials

Compound tubes

Low alloyed steels

Ferritic steels

FeCrAl alloys

Corrosion problems

Stainless steels

Nickel based alloys

Austenitic steels

Coatings

More than 3500 different steel grades exists today…

CONSORTIUM MATERIALS TECHNOLOGY

The High-Temperature Corrosion Center

Potential for using FeCrAl alloys in combustion environment

Why does FeCrAl alloys have potential?

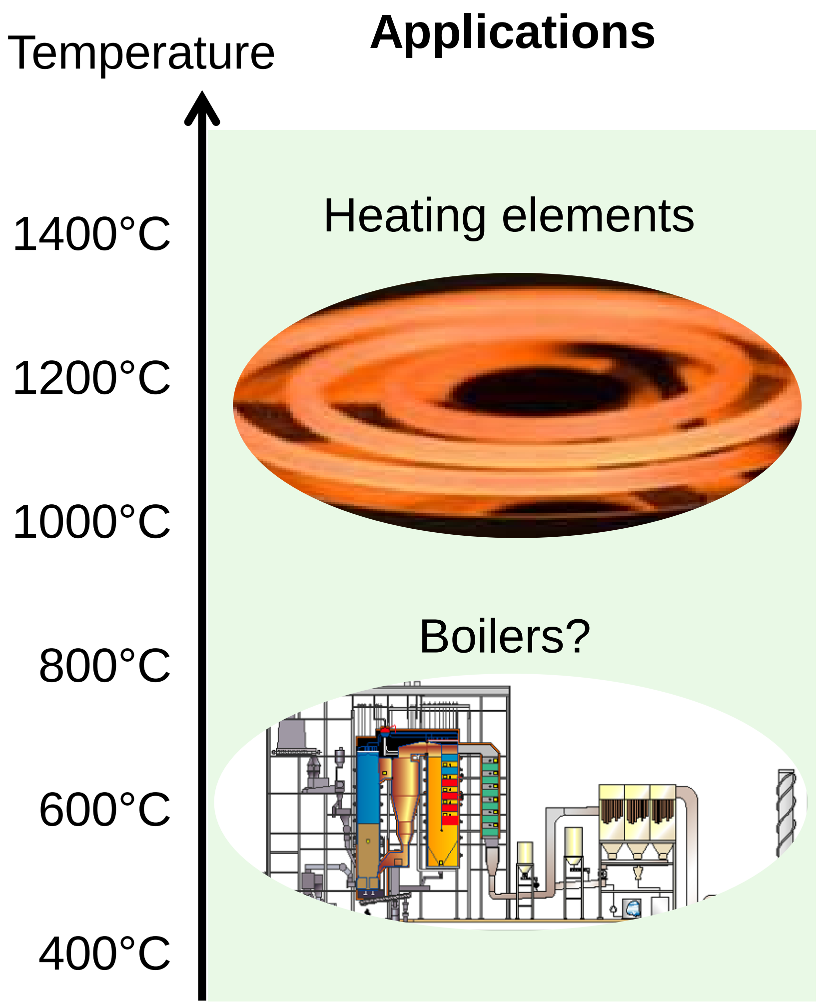
- Highly stochiometric
- Low defect concentration
- Thermodynamically stable
- α-Al_2O_3 does not suffer from evaporation
- α-Al_2O_3 does not form chromates

Improved oxidation resistance

α-Al_2O_3
SiO_2
Cr_2O_3
α-Fe_2O_3

NiO
CoO
FeO

Challenges with FeCrAl alloys

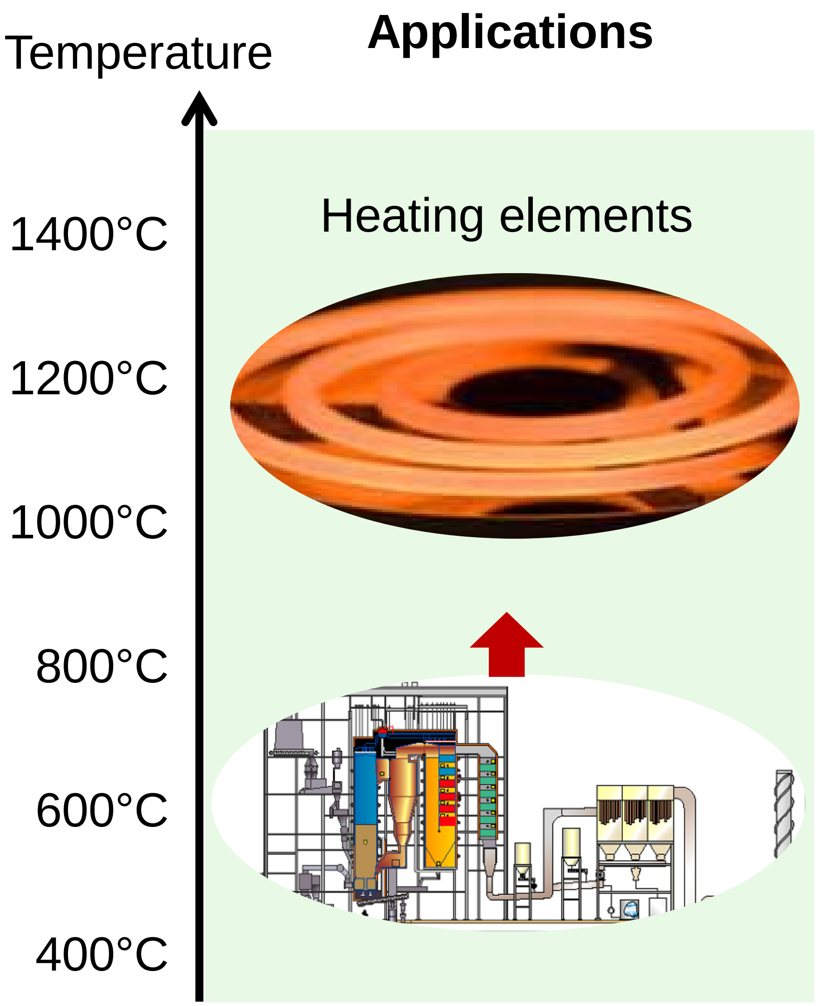


An α-alumina scale forms at temperatures above ~900 °C that protects the alloy

At lower Temperatures

- Metastable forms of alumina may form
- How protective are metastable alumina's?

Potential with FeCrAl alloys



An α-alumina scale forms at temperatures above ~900 °C that protects the alloy

- Replace steels in existing materials
- Higher boiler temperatures

FeCrAl alloys for combustion environments

FeCrAl alloys are potential materials for biomass and waste fired environments

Develop new FeCrAl alloys for biomass and waste fired environments

Existing FeCrAl alloys are optimized for higher temperatures

In close collaboration with Sandvik

Research direction
-FeCrAl

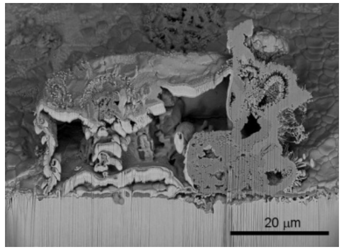
Model FeCrAl alloys – tailor made for biomass and waste fired boilers
- excellent oxidation resistance, good weldability and workability

- Investigate effect of Cr content
  - ✓ For better weldability and less chromate formation
- Investigate effect of Al content
  - ✓ For better weldability, workability and corrosion resistance
- Investigate effect of other elements content
  - ✓ For increased corrosion resistance

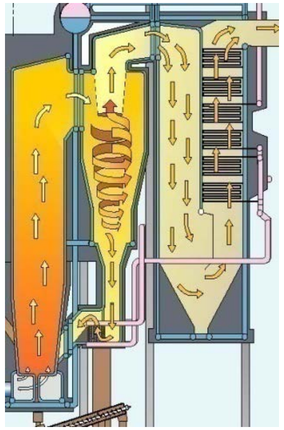
Research strategy – a two pronged approach

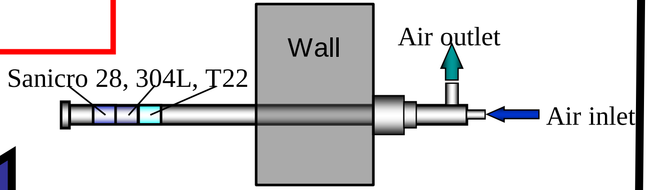
Fundamental research

Corrosion mechanisms



Fundamental understanding of the corrosion process in boilers





Effects of corrosion

Applied research

Laboratory studies

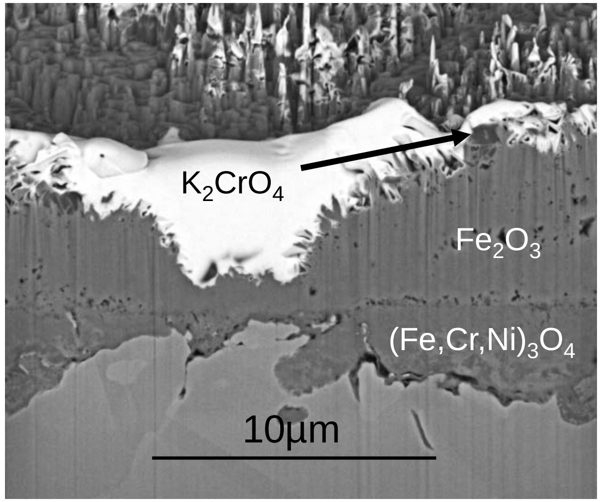
Field studies

Research approach - Laboratory

Before

X °C, x h
1,0 mg KCl/cm^2

After



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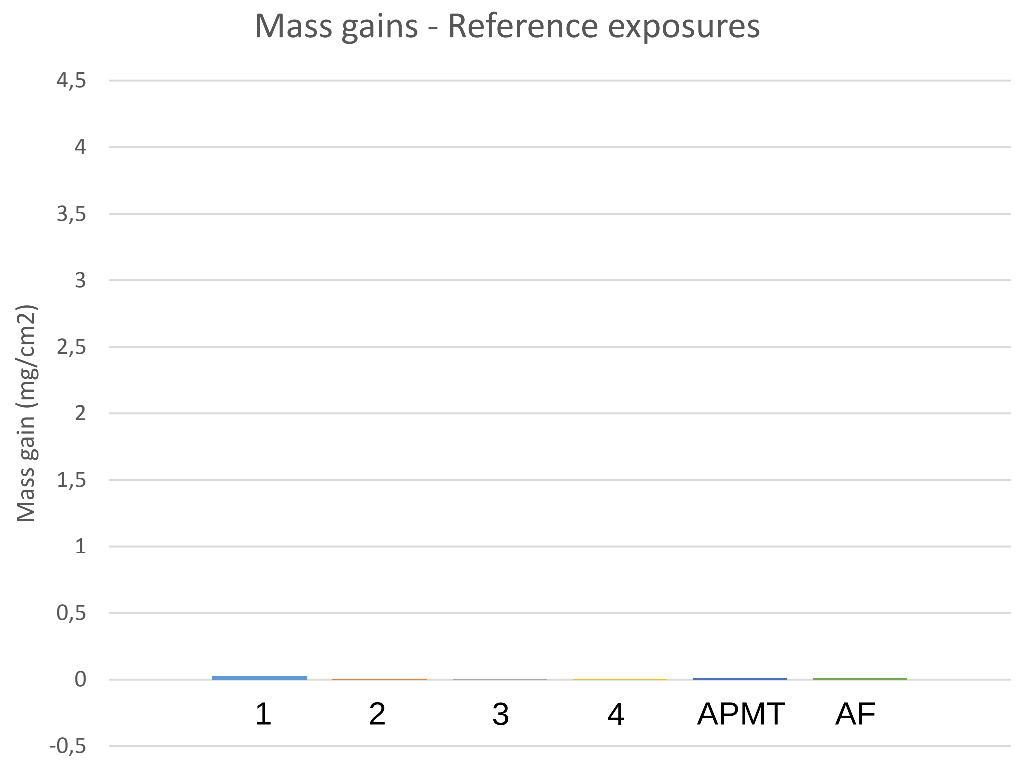
Effect of Chromium – Exposure matrix

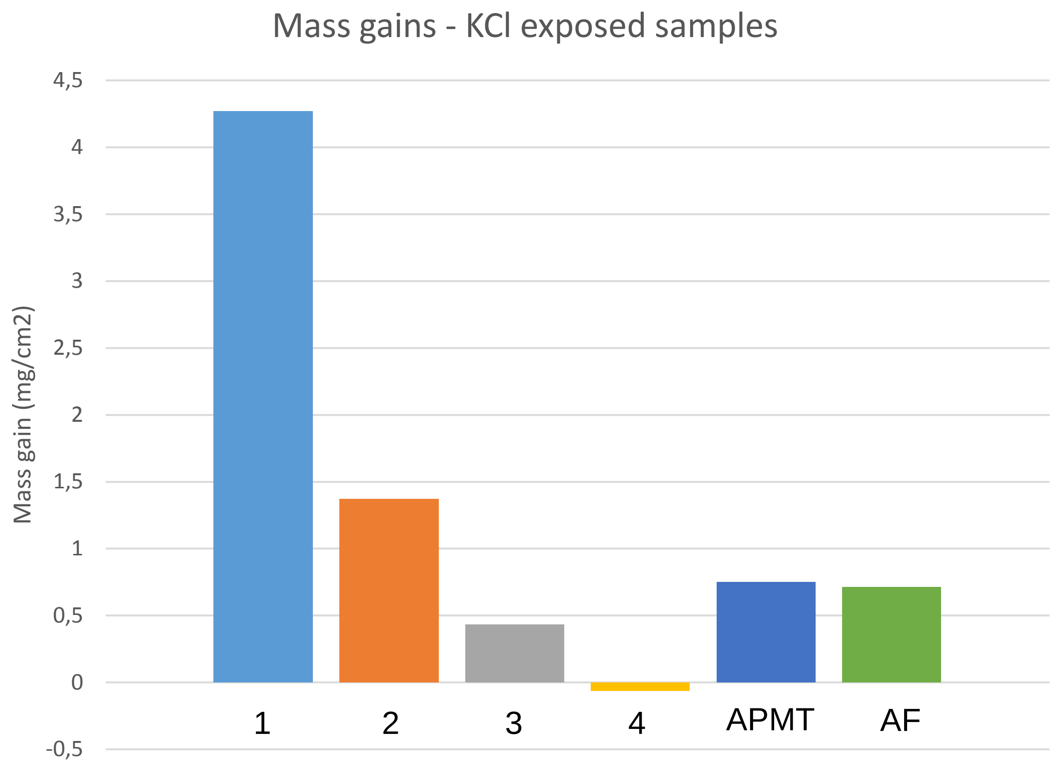
Alloy	Cr	Al	Other elements
1	5	3	Fe, Si, C, N, Zr
2	10	3	
3	15	3	
4	20	3	

Sample	Temperature (°C)	Time(h)	Environment
Reference	600	168	5% O_2 + 20% H_2O + 75% N_2
With KCl	600	168	5% O_2 + 20% H_2O + 75% N_2 +1.0 mg/cm^2 KCl

Mass gains after exposures



Increased Cr content



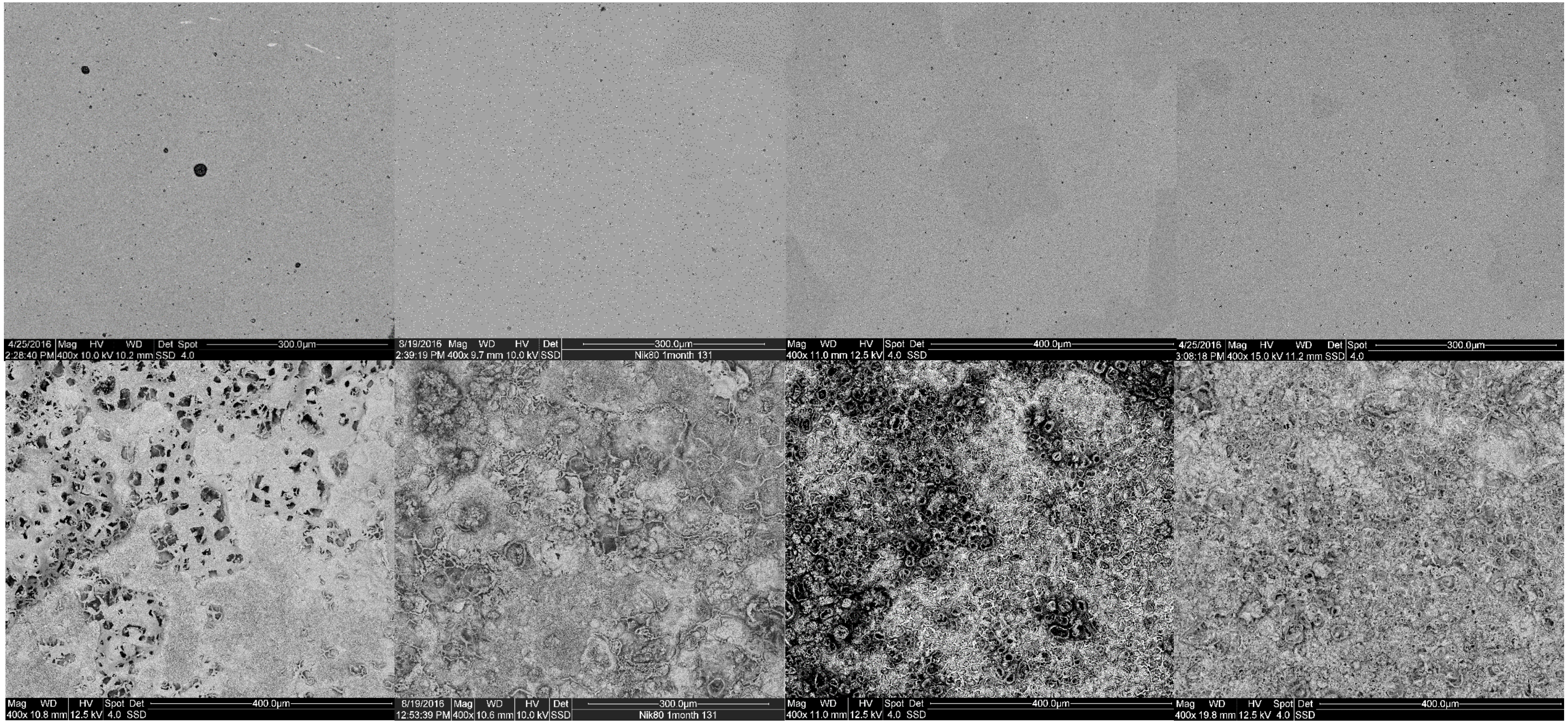
Increased Cr content

SEM Analysis

- Plan view
  - Reference samples
  - KCl exposed samples
  - EDX
- Cross section
  - KCl exposed samples
  - EDX

Increased Cr content

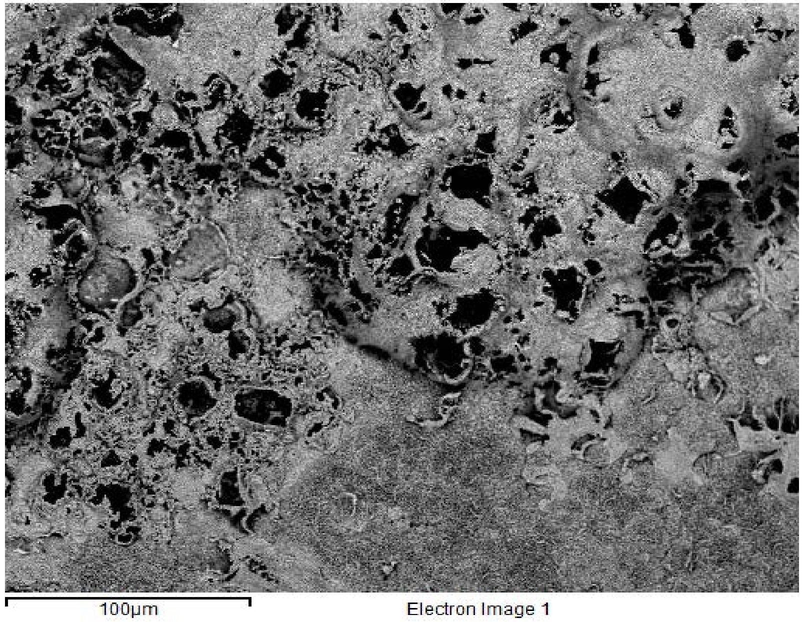
5% 10% 15% 20%

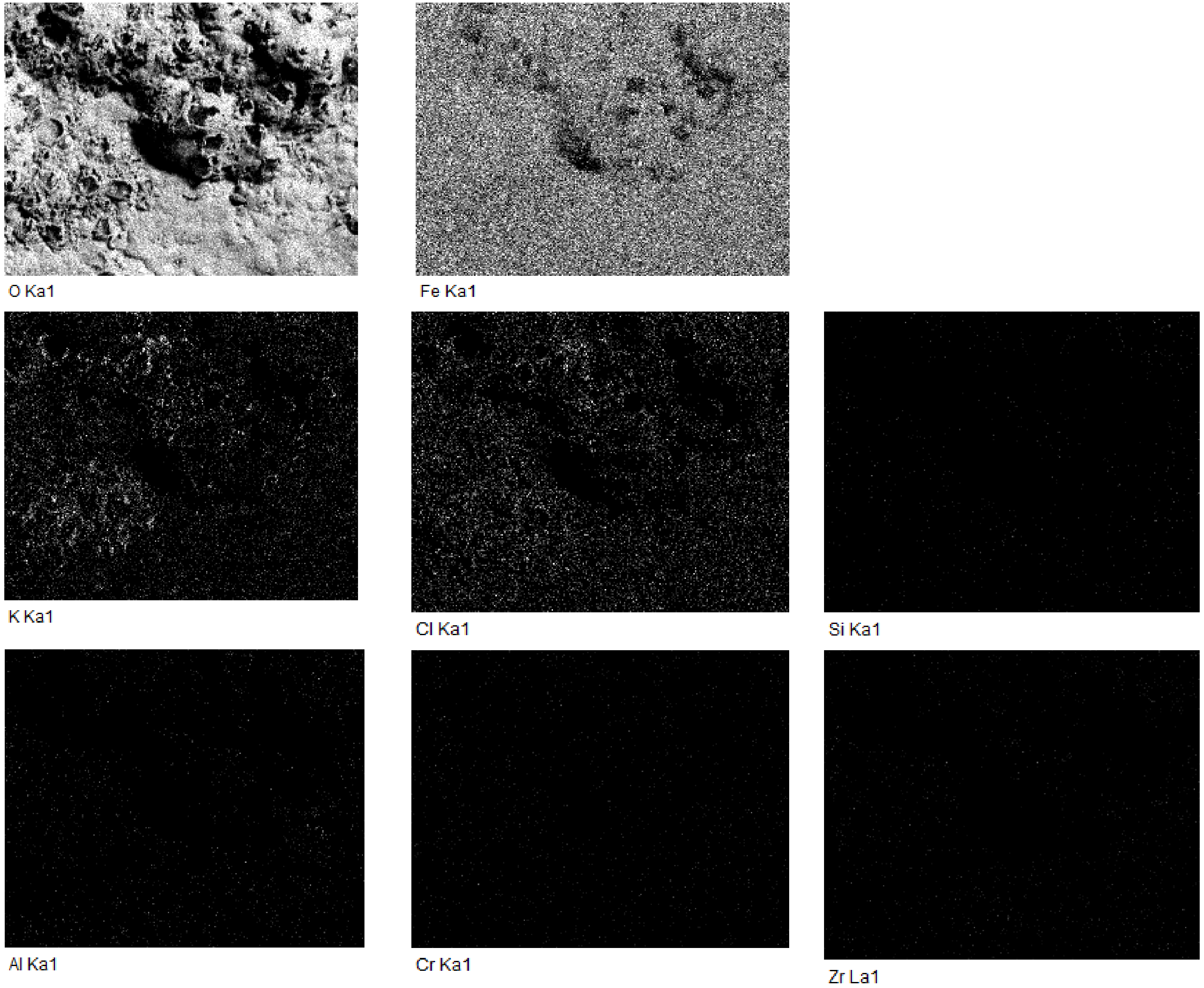


← Reference

← With KCl

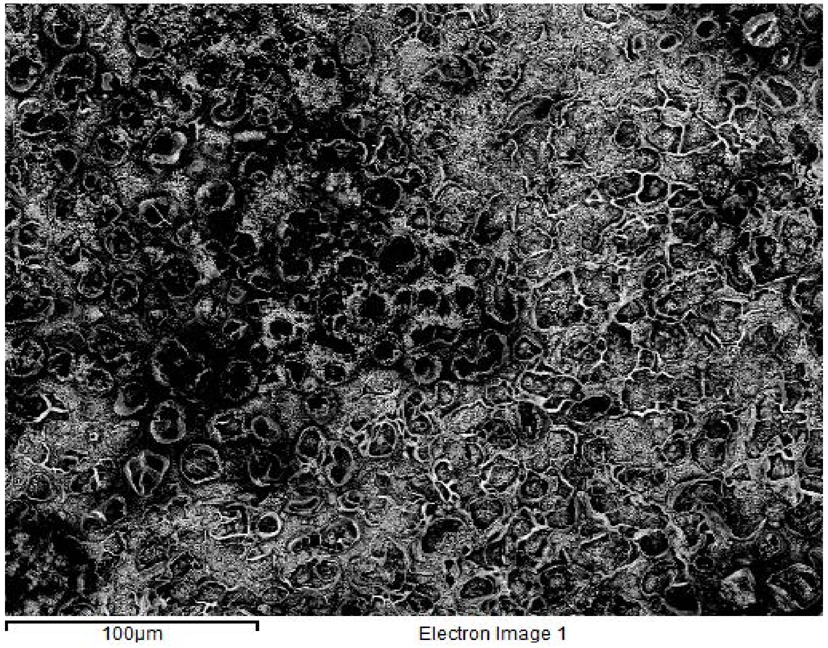
Alloy 1
(5% Cr)

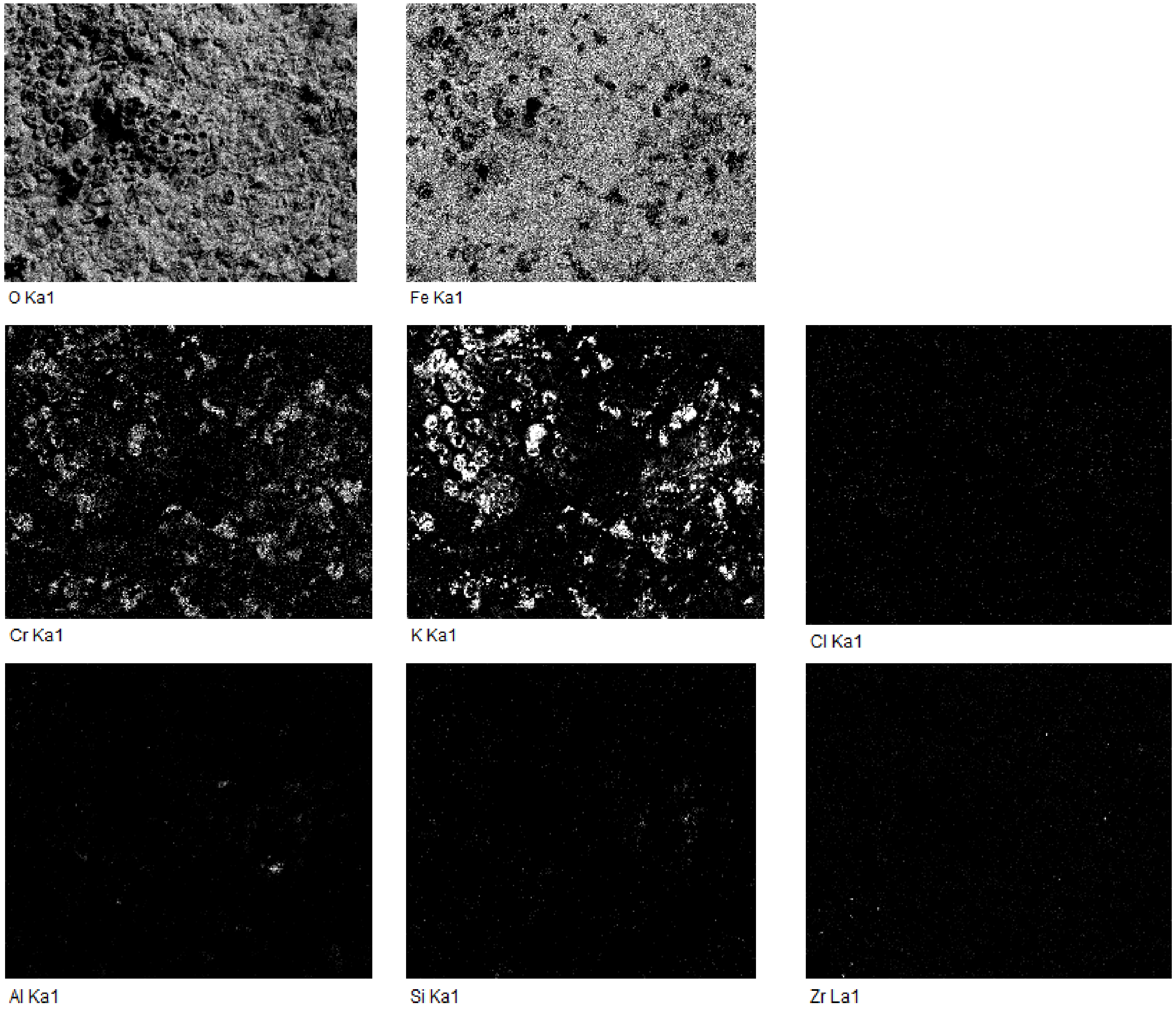




Pure iron oxide on the surface

Alloy 3 (15% Cr)



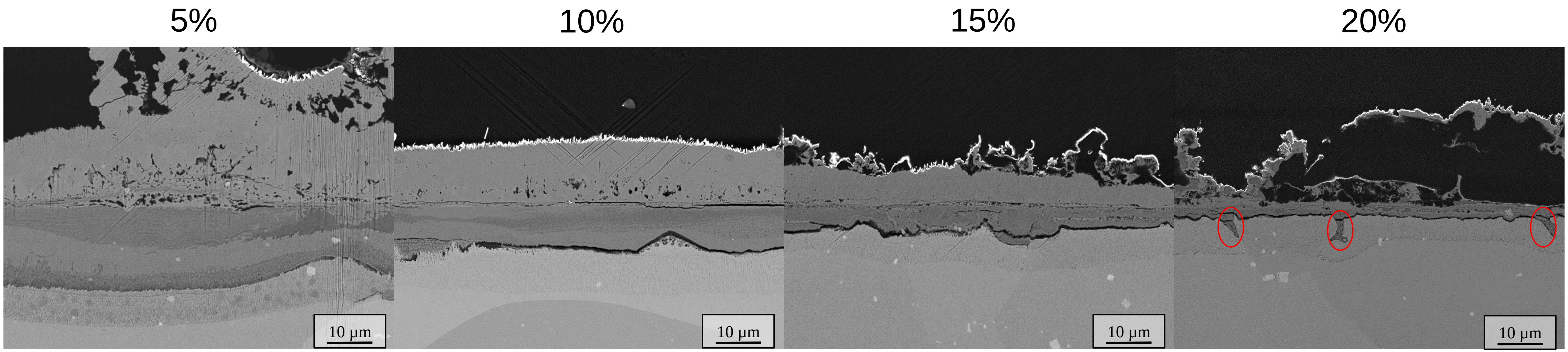


Formation of K_2CrO_4 on the surface

SEM Analysis

- ~~Plan view~~
  - ~~Reference samples~~
  - ~~KCl exposed samples~~
  - ~~EDX~~
- Cross section
  - KCl exposed samples
  - EDX

Increased Cr content

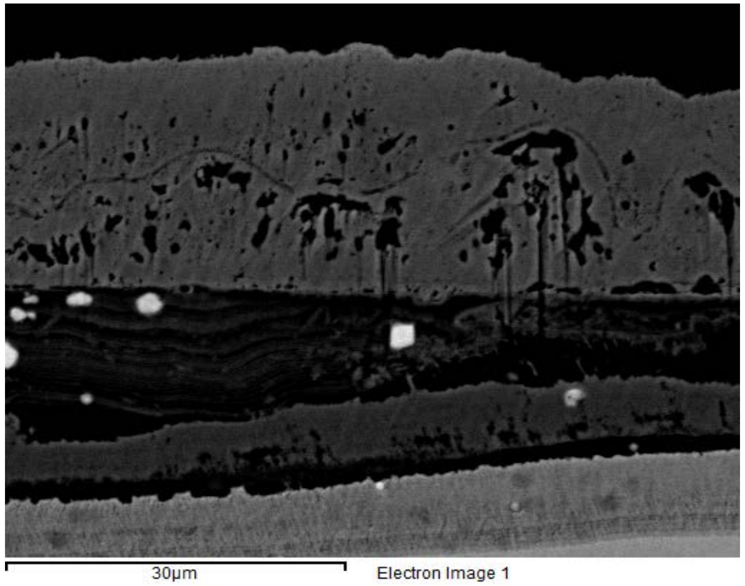


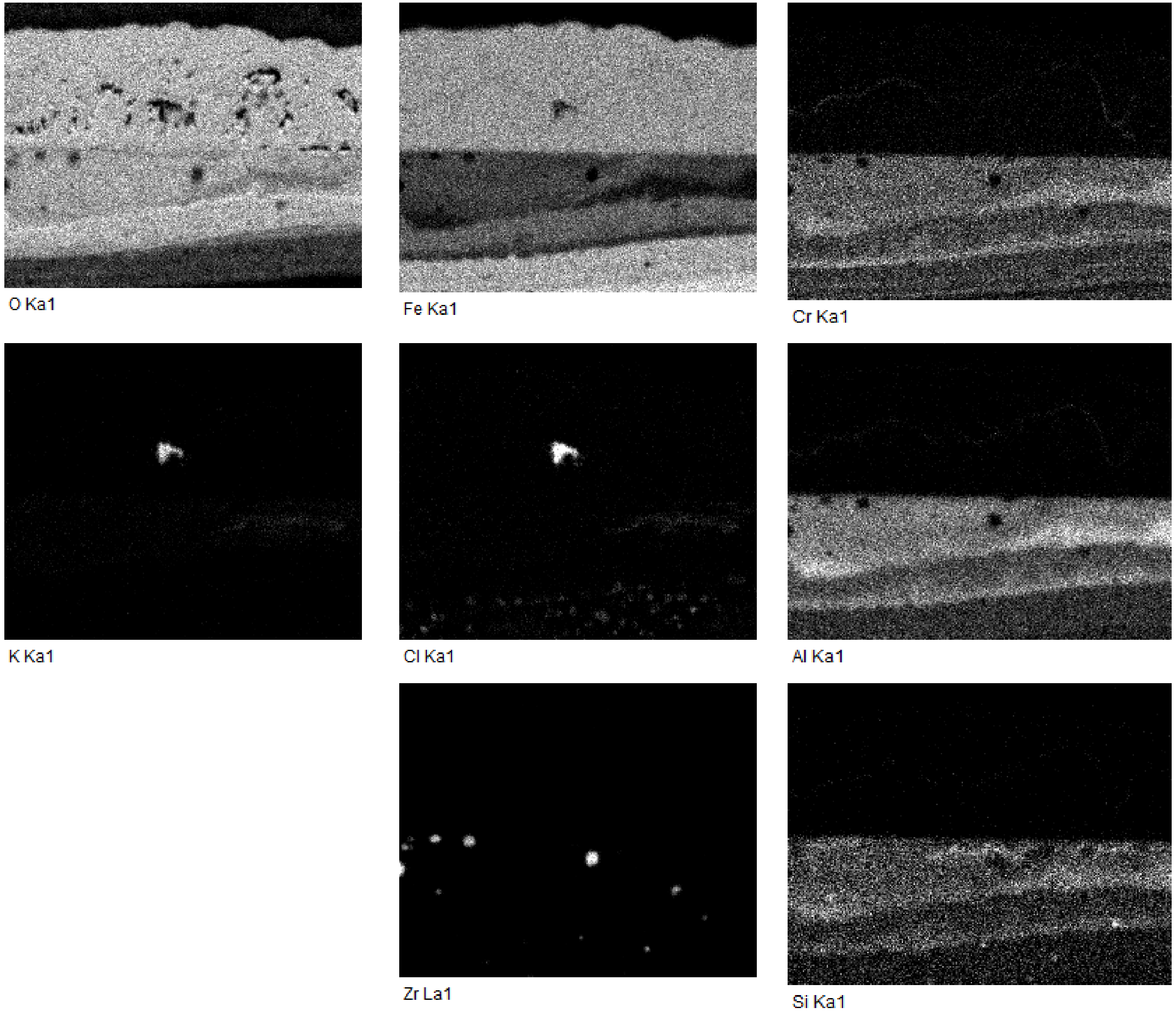
- Great beneficial effect of Cr on corrosion properties
  - Decreased oxide thickness

But:

- Increased formation of K_2CrO_4
- Grain boundary attack

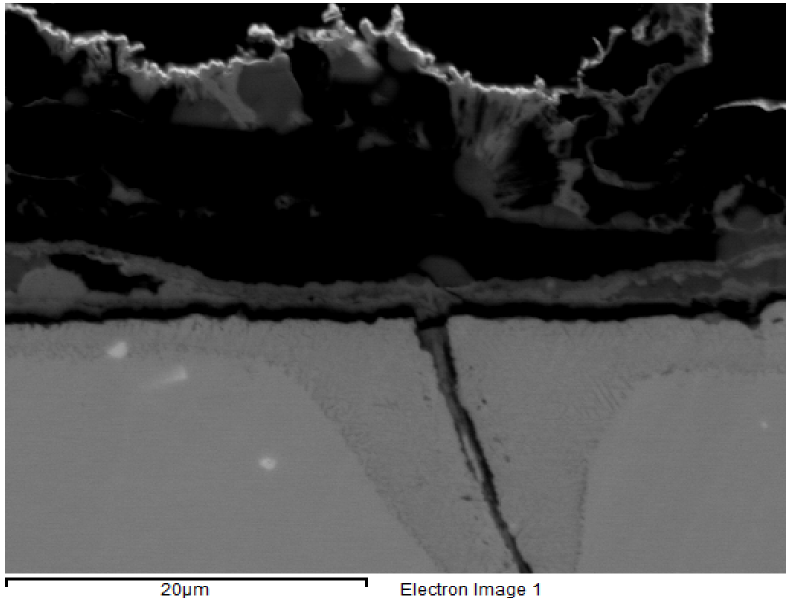
Alloy 1 (5% Cr)

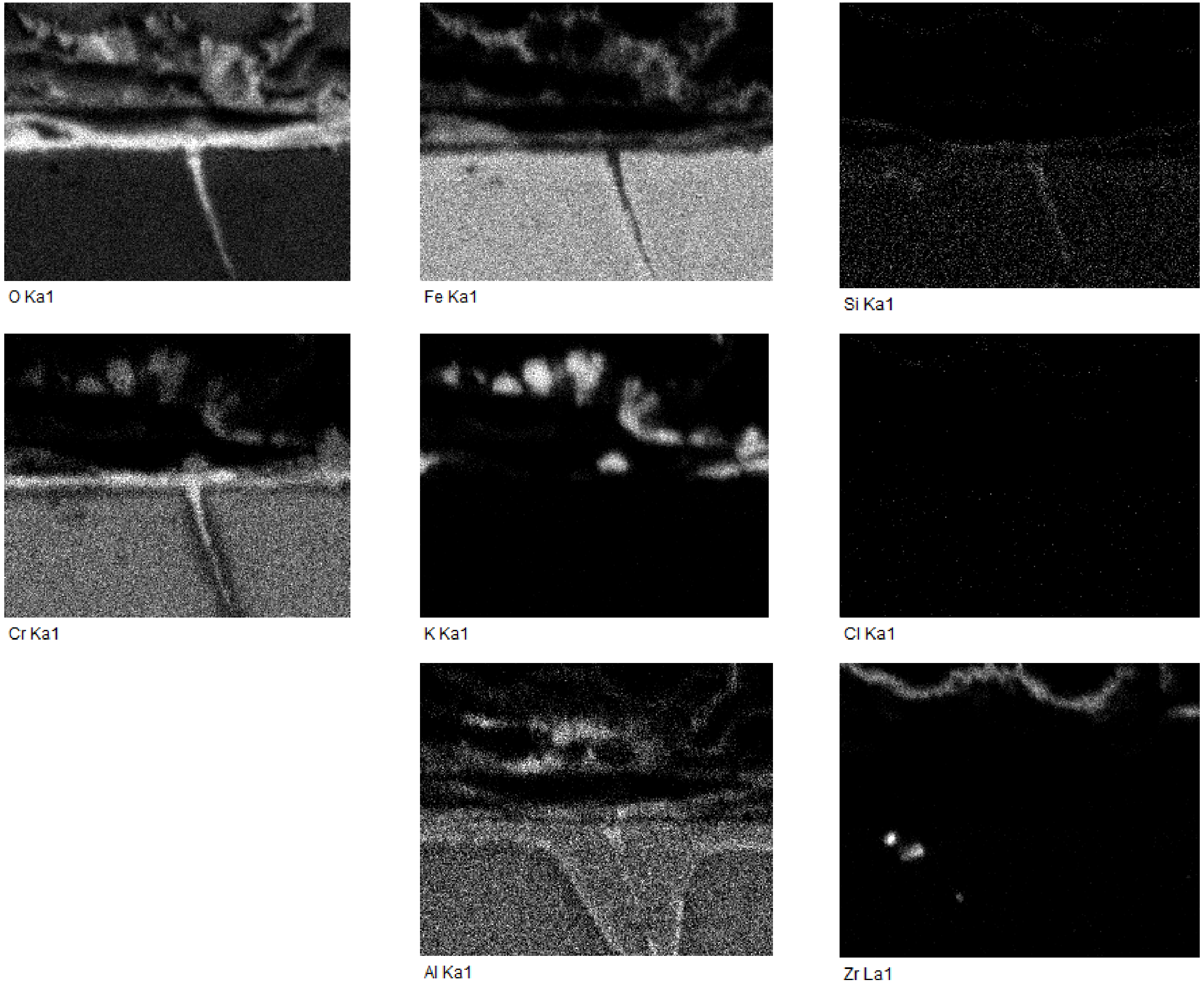




- Outward growing oxide (Fe rich)
- Inward growing oxide (Fe, Cr, Al-spinel)

Alloy 4 (20% Cr)





- Cr-rich oxide ”spike”

Conclusions

- Great beneficial effect of Cr on corrosion resistance
  - Decrease in mass gain
  - Decrease in oxide thickness

But:

- Increased formation of K_2CrO_4
- More prone to grain boundary attack

Better understanding of the initiation of corrosion attack needed

Future work:

- Thermogravimetric in-situ exposures
  - 24 -72 hours
- Microscopy
  - Cross section of reference samples
  - More advanced microscopy (TEM)

Research direction
-FeCrAl

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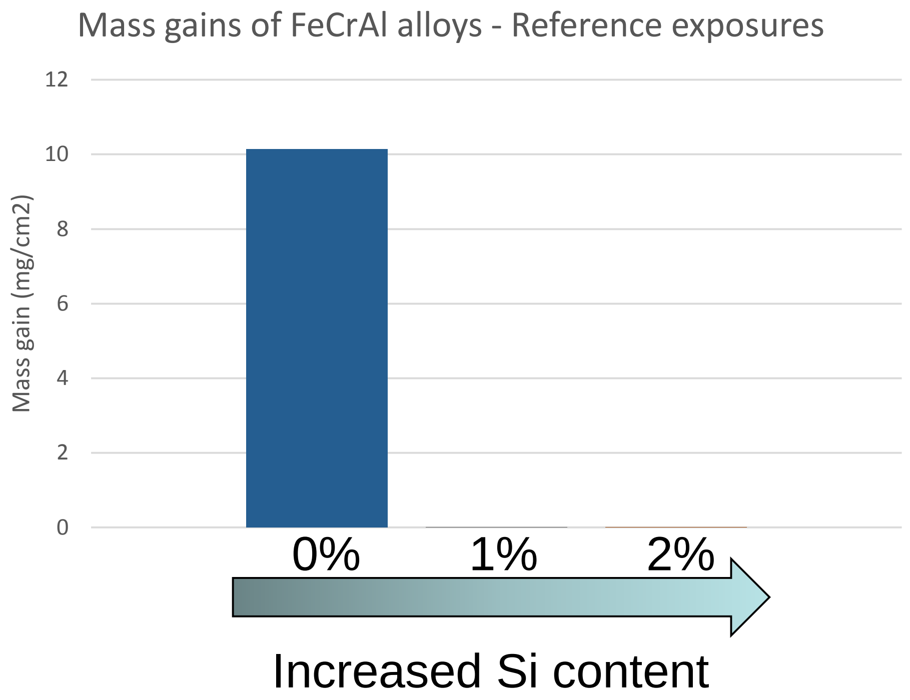
- Investigate effect of Al content
  - ✓ For better weldability, workability and corrosion resistance

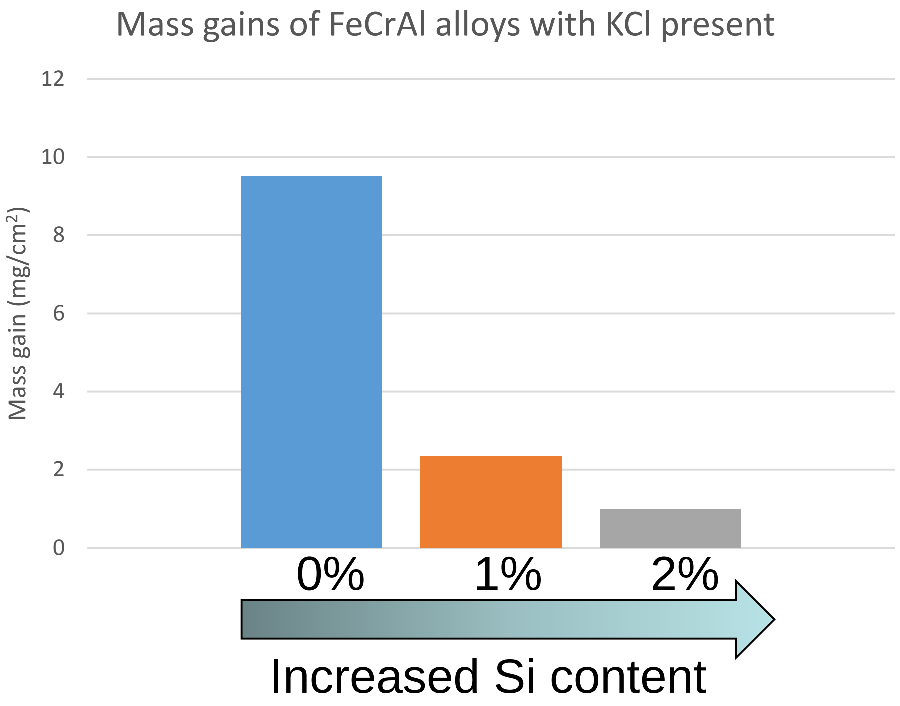
- Investigate effect of other elements content
  - ✓ For increased corrosion resistance

Effect of Silicon – Exposure Matrix

Alloy	Cr	Al	Si	Other elements
1	10	4	0	Fe, C, N, Zr
2	10	4	1	
3	10	4	2	

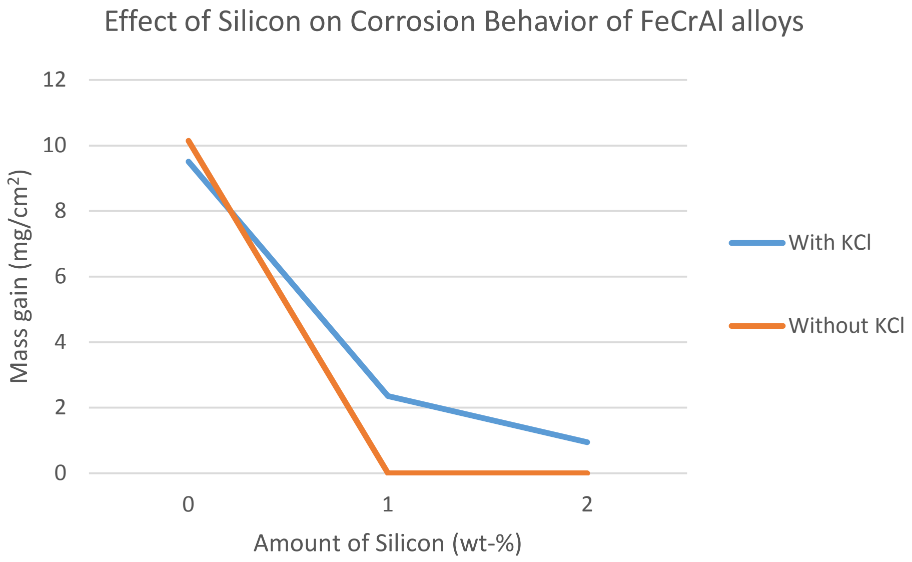
Sample	Temperature (°C)	Time(h)	Environment
Reference	600	168	5% O_2 + 20% H_2O + 75% N_2
With KCl	600	168	5% O_2 + 20% H_2O + 75% N_2 +1,0 mg/cm^2 KCl





Without KCl present:

- Large decrease in mass gain upon addition of Si
- Formation of protective oxide when adding Si

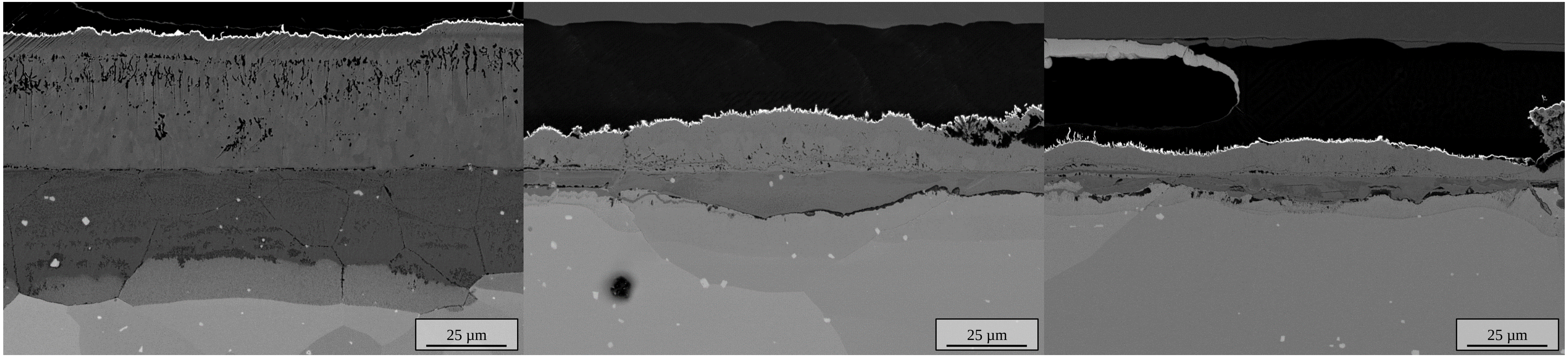


With KCl present:

- Large decrease in mass gain upon addition of Si
- Breakaway oxidation in all cases
  - Forms more protective oxide with addition of Si

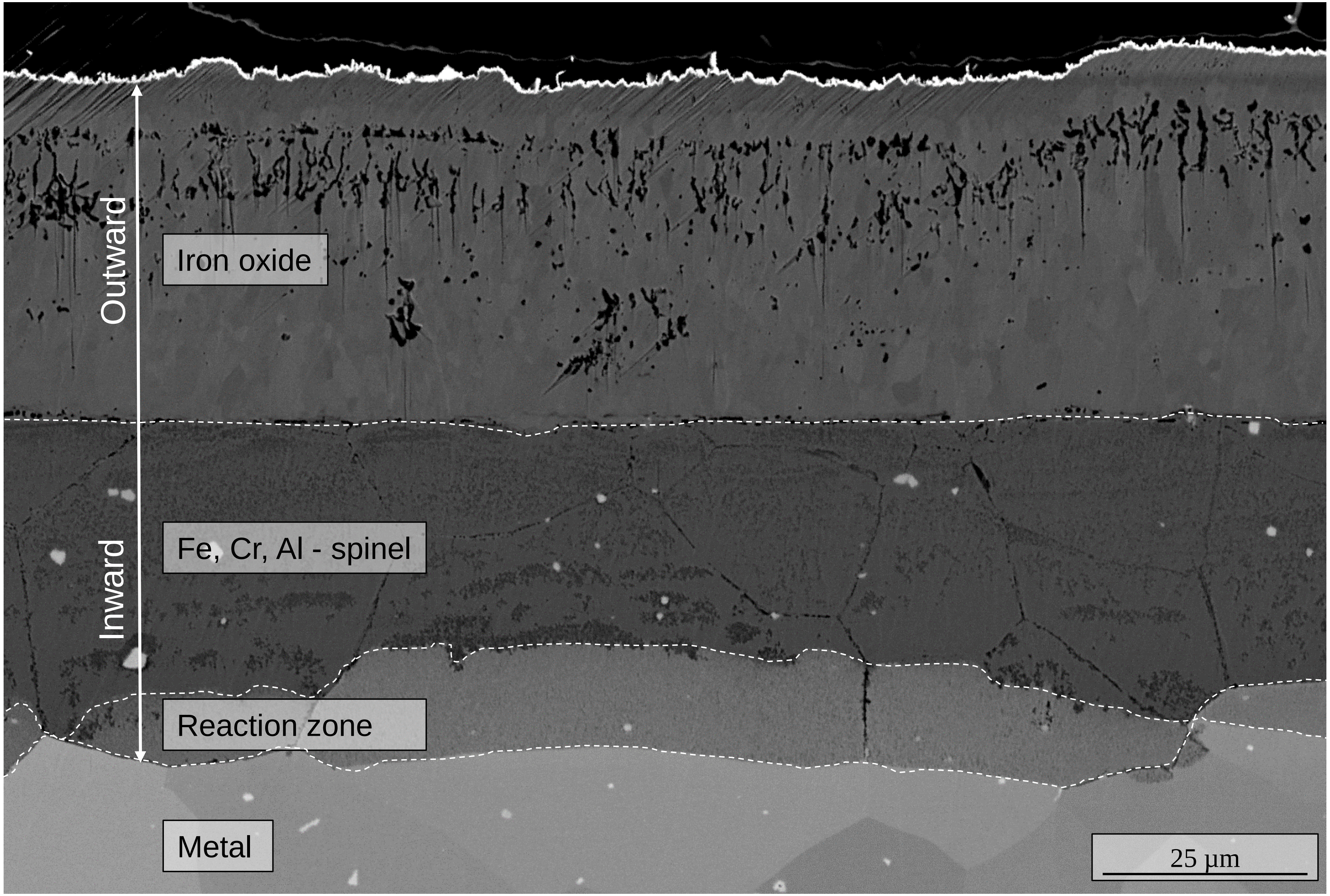
Increased Si content

0% 1% 2%

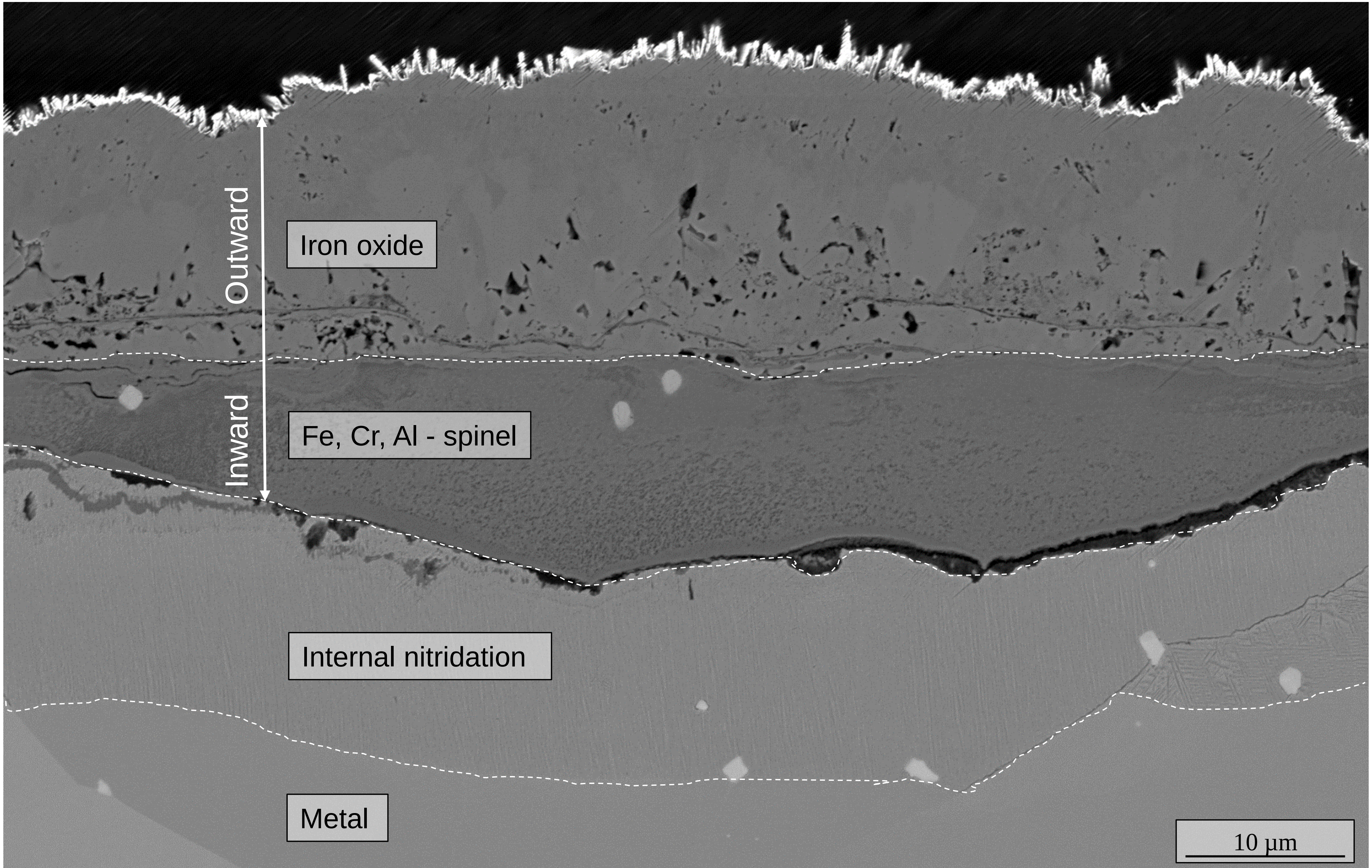


- Observed oxide thickness correlates well with measured mass gains
  - Large decrease in oxide thickness upon addition of Si

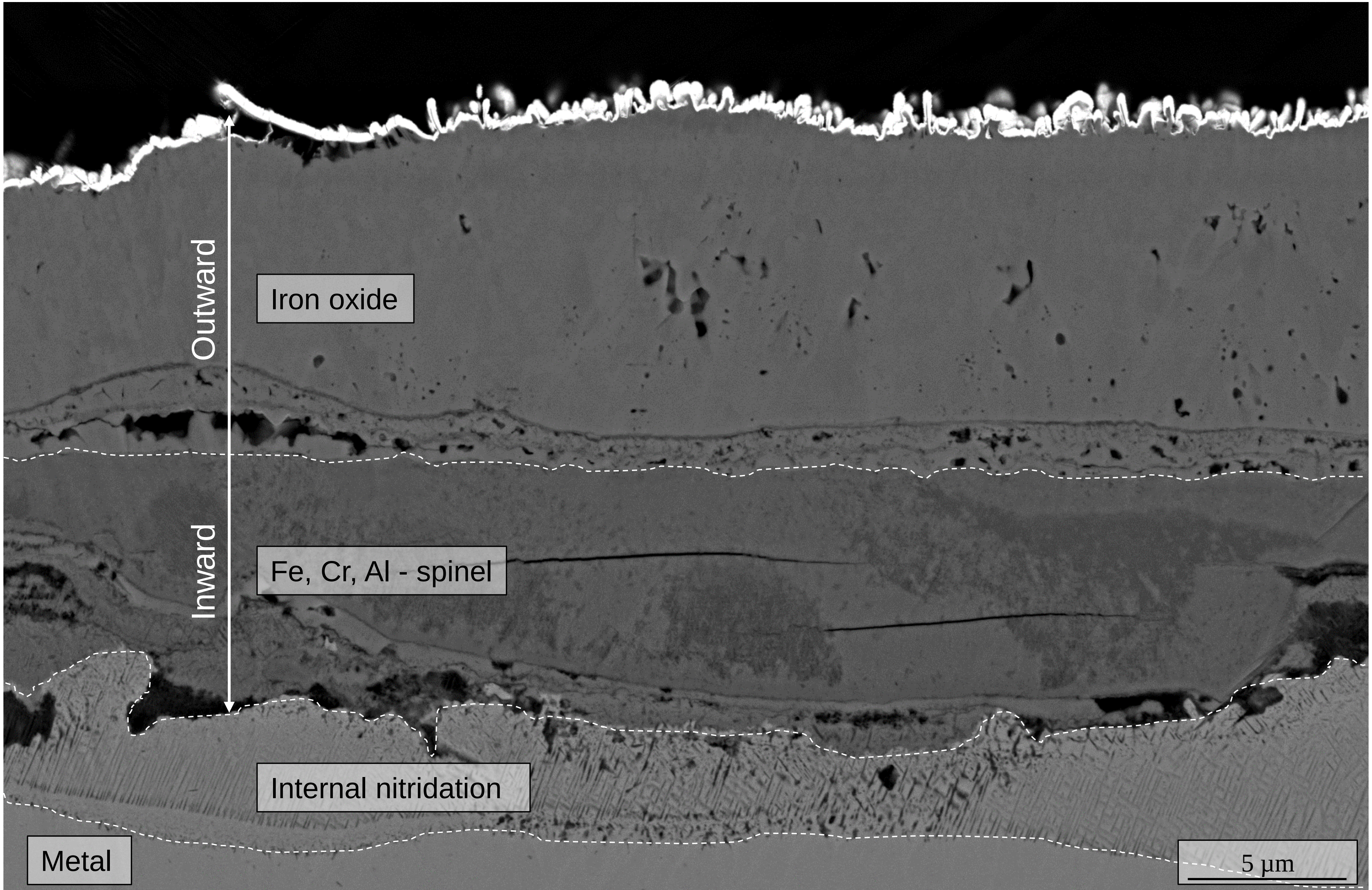
0% Si


Outward
Inward
Iron oxide
Fe, Cr, Al - spinel
Reaction zone
Metal
25 µm

1% Si

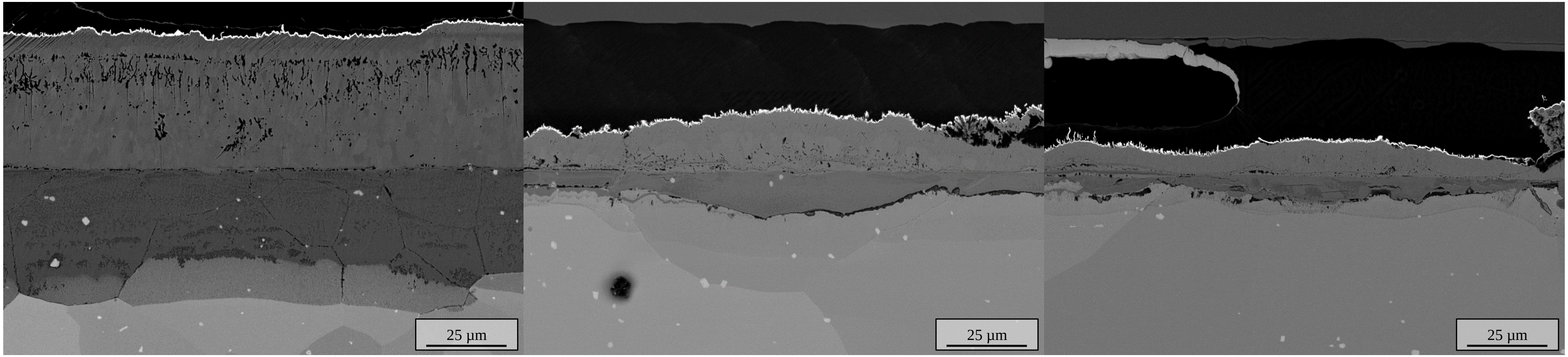

Outward
Inward
Iron oxide
Fe, Cr, Al - spinel
Internal nitridation
Metal
10 µm

2% Si


Outward
Inward
Iron oxide
Fe, Cr, Al - spinel
Internal nitridation
Metal
5 µm

Increased Si content

0% 1% 2%



- Observed oxide thickness correlates well with measured mass gains
  - Large decrease in oxide thickness upon addition of Si

However:

- No visible formation of SiO_2
- No significant accumulation of Si

Very interesting effect

But:

The role of Si still not fully understood

Conclusions

- Addition of Si shows **great beneficial effects** on corrosion resistance

- The role of Si on the corrosion resistance is unclear
    - No visible formation of SiO_2 layer
    - No visible accumulation of Si

- Investigation of initiation kinetics needed

Future work

- Thermogravimetric in situ exposures
  - Investigate the initiation kinetics
- More advanced microscopy
  - Study the oxides in more detail
  - Study the protective oxides of the reference samples

Thank you for your attention!