# Effect of Ageing Temperature on Localised Corrosion and Atmospheric Stress Corrosion Cracking of 15-5PH Stainless Steel

ICorr Aberdeen –TWI webinar
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# Introduction

## Maraging Steels

= martensitic + ageing

### Properties

- High strength
- Good ductility
- Reasonable corrosion resistance

### Applications

- Oil and Gas
- Aerospace

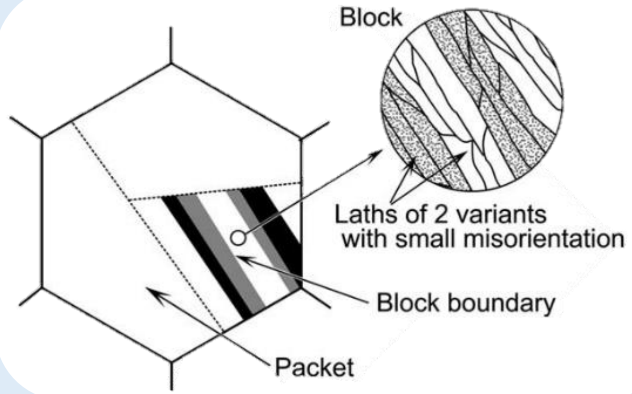
S. Morito, et al. *Acta Materialia*, vol. 51, 2003,

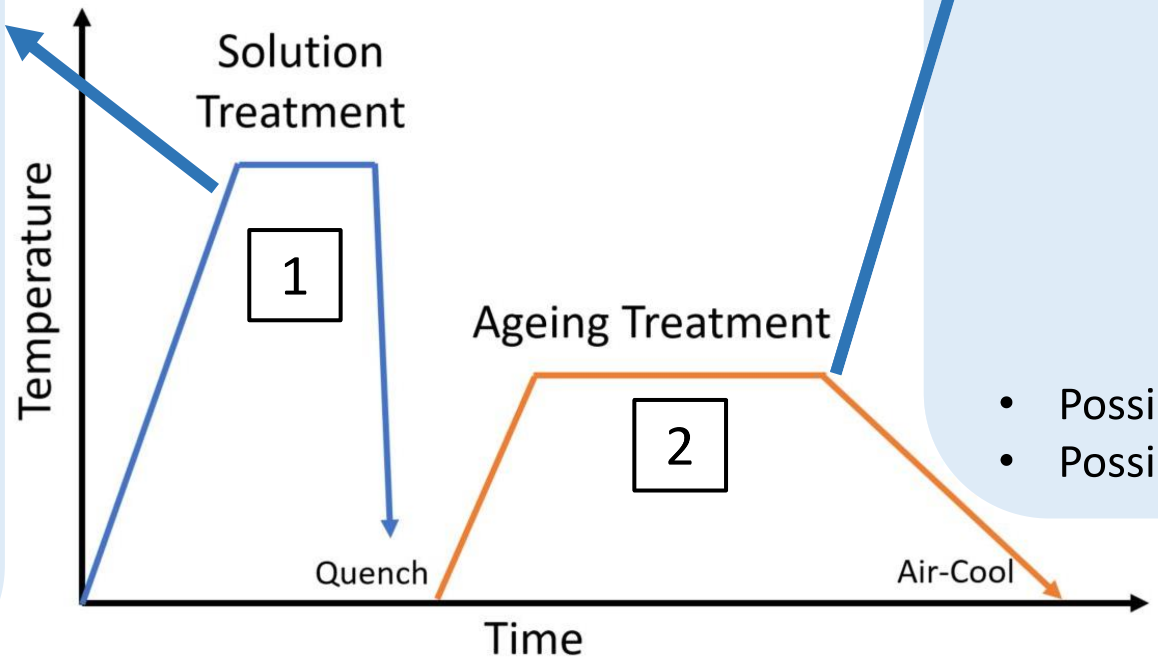
# Introduction

1

Solution treatment ~ 1038 ºC ~ 1 hr

Obtain fully martensitic microstructure (& small amounts of retained austenite)



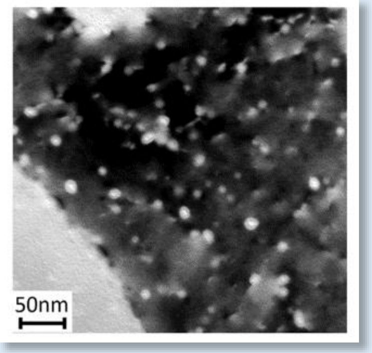




Schematic of typical heat treatment (not to scale)

2

Ageing treatment ~ Lower Temperature)

- Form fine intermetallic precipitates



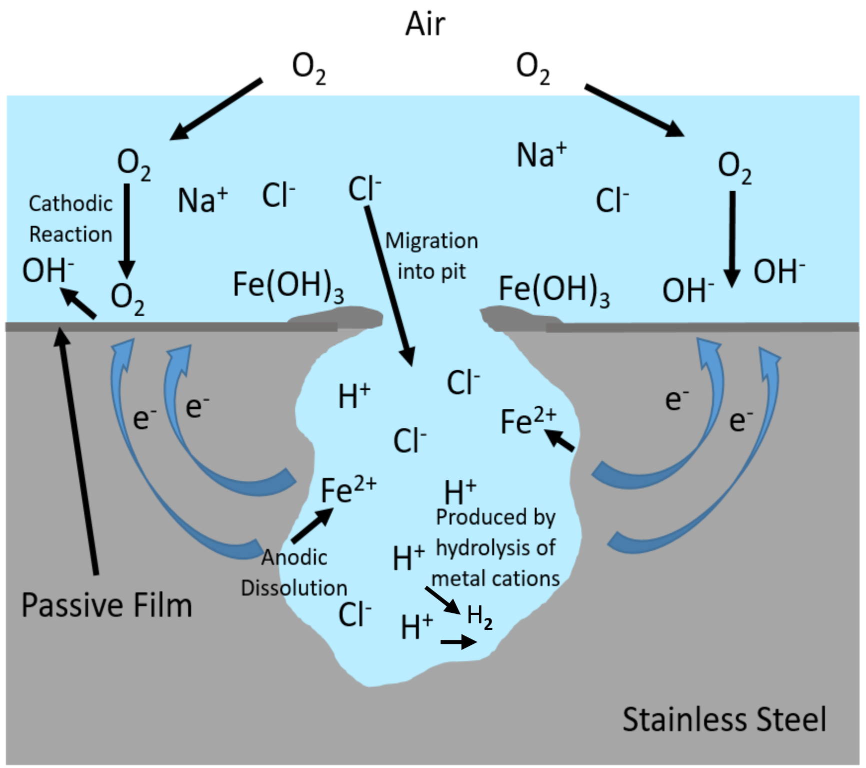

- Possible austenite reversion
- Possible carbide formation


L. Couturier, et al. *Materials and Design*, vol. 107, 2016,
S. Morito, et al. *Acta Materialia*, vol. 51, 2003,

# Introduction

**Problem:** Maraging steels can be susceptible to Localised Corrosion (pitting or crevice corrosion) under certain conditions, which can be a precursor to Environmentally Assisted Cracking (EAC); chloride–induced Stress Corrosion Cracking (SCC) and/or Hydrogen Embrittlement (HE)

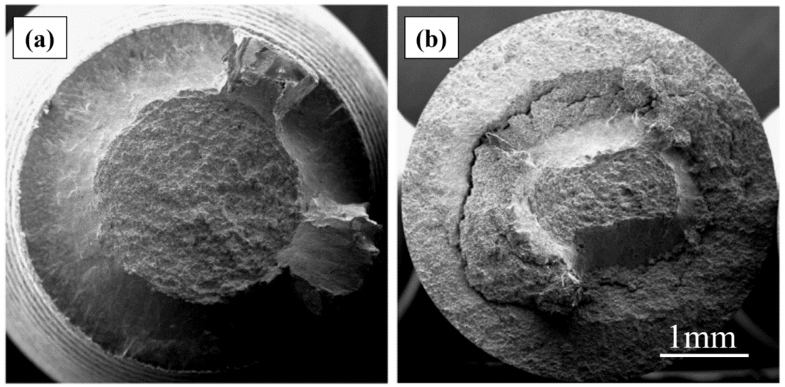
Pitting – accelerated corrosion within localised cavity resulting from increased acidity through hydrolysis of metal ions




Hydrogen Embrittlement causes…

- Loss of tensile ductility
- Reduction in fracture toughness
- Catastrophic failure

Without hydrogen After hydrogen charging



# Aims & Objectives

Understand the effect of microstructure on localised corrosion of 15-5PH to aid the design of future alloys

1. Characterise microstructure as a function of ageing treatment

2. Assess localised corrosion behavior of each microstructure

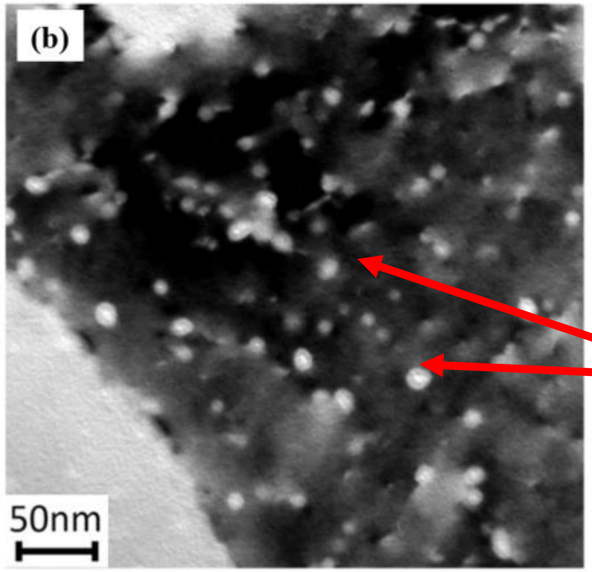
3. Link microstructural features to localized corrosion susceptibility

# Material Composition

15-5 PH

| Element | Fe | C | Cr | Ni | Cu | Mn | Si | Mo | Nb |
|---|---|---|---|---|---|---|---|---|---|
| Wt % | Bal | 0.018 | 14.7 | 4.88 | 3.09 | 0.745 | 0.398 | 0.259 | 0.195 |

- Forms Cu Strengthening precipitates during ageing
- Increased levels of reverted austenite also expected as ageing temperature increased




Cu precipitates

(1)

(1) L. Couturier, et al. *Materials and Design*, vol. 107, 2016

# Heat Treatment

1. Solution Treatment – 1 hr at 1038 °C
2. Ageing treatment – 4 hrs, varying temperature

**Under-Aged 450 °C**

**Peak-Aged 540 °C**

**Over-Aged 650 °C**

# Experimental Techniques

## Characterisation

- Mechanical Testing
  - Tensile properties
  - Hardness

- XRD
  - Austenite phase fraction
  Based on methodology used by Tanaka and Choi (2003)

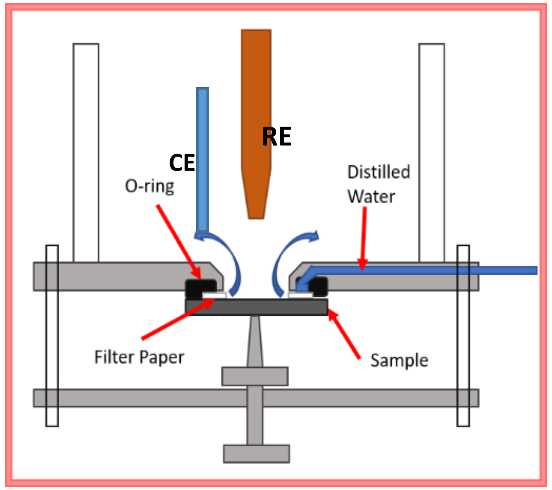
- Microscopy
  - SEM (Zeiss Sigma VP FEG)
  - TEM (ThermoFisher Talos F200X)

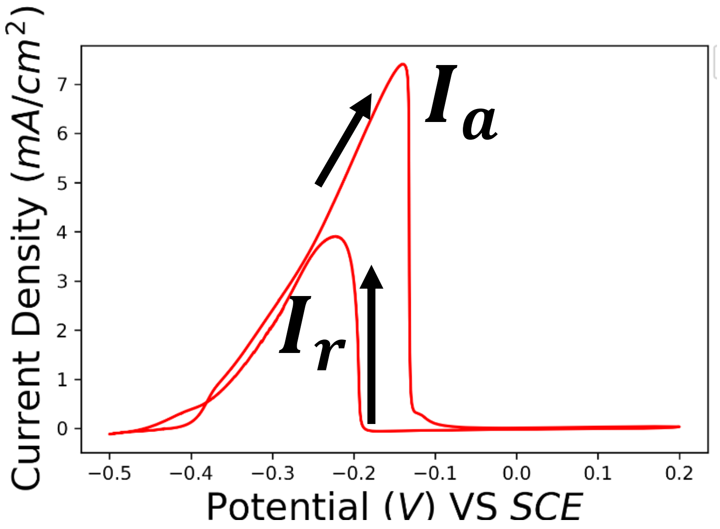

# Experimental Techniques

## Localised Corrosion

Electrochemical investigation of pitting susceptibility and reactivation behaviour

- Potentiodynamic Polarisation
  - Pitting susceptibility
- DL-EPR
  - Assessment of passive film integrity after heat treatment
- Electrochemical noise
  - Directly comparing microstructures



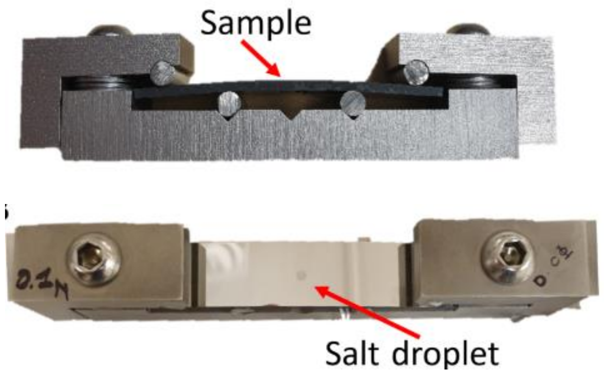



# Experimental Techniques

## Atmospheric Cracking

Study pit to crack transition and investigate cracking behaviour

- $MgCl_2$ salt deposits droplets
- Relative humidity (RH) of 30% or 90% in environmental chamber
- 50 °C
- Test performed over 5 or 10 days
- Surface features of crack and crack cross-section analysed by SEM post test



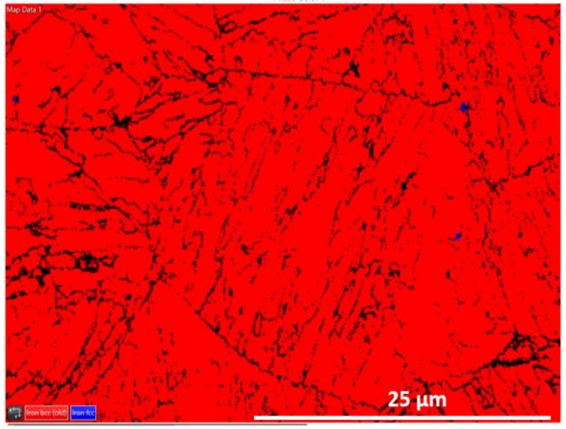
# Results

# Austenite Phase Fraction

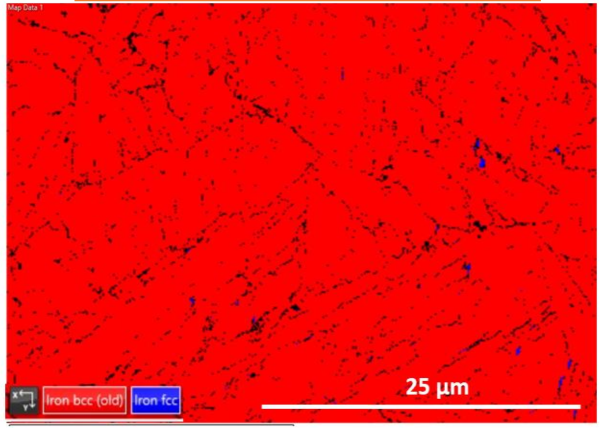
EBSD Phase maps

- α-martensite
- γ-austenite

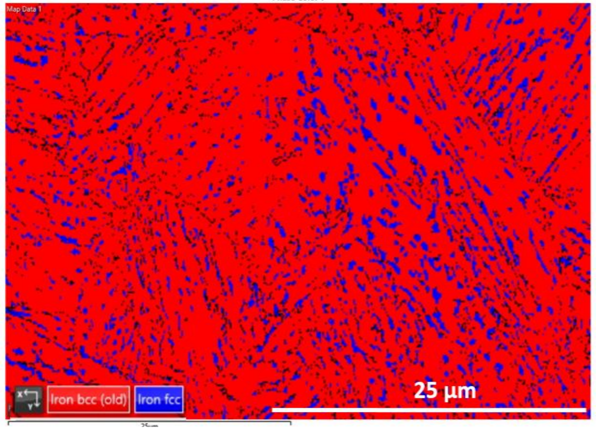
450 °C – Under-aged



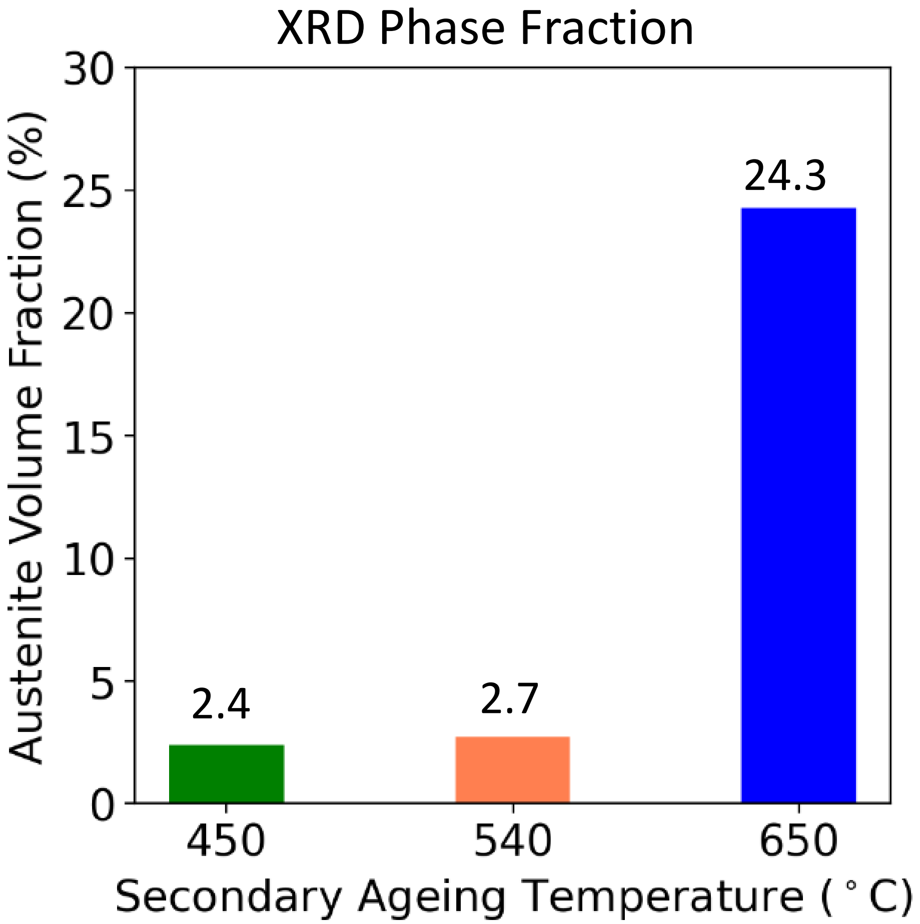

540 °C – Peak-aged




650 °C – Over-aged



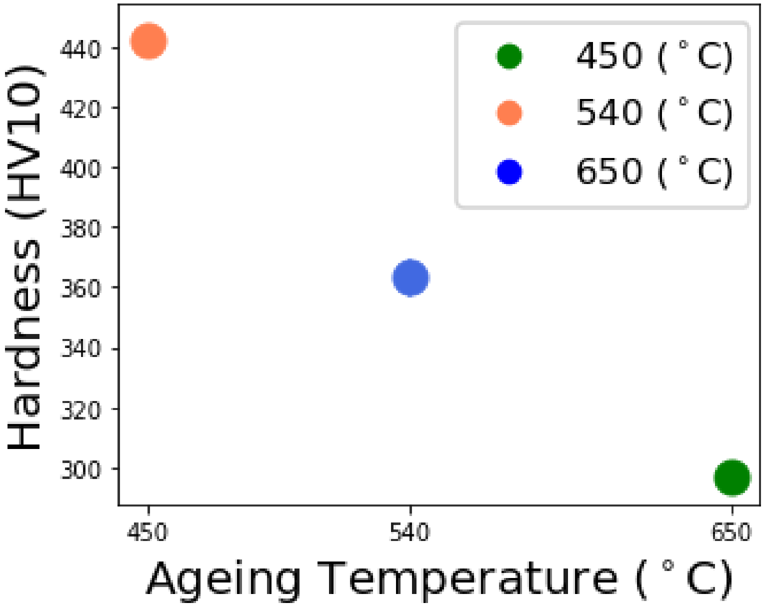

- Phase maps - qualitative measure of austenite content
- Austenite nucleates along lath boundaries and PAGBs
- Austenite reversion greatest with 650 °C ageing treatment



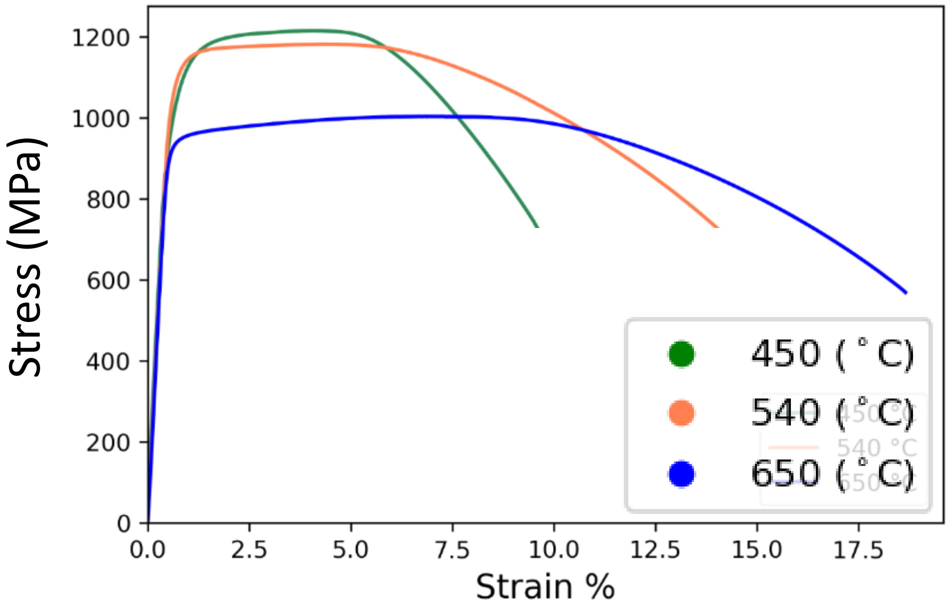

(1) M.Tanaka, C. Choi, et al. Trans ISIJ, 1974

# Mechanical Properties

Hardness




Tensile

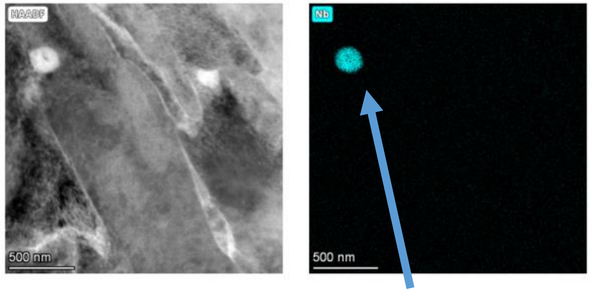



- Increase in ageing temperature results in:
  - Decrease in hardness
  - Decrease in UTS
  - Increase in tensile ductility

# Elemental Distribution as a Function of Aging Temperature

## STEM EDX - allows characterisation of different aspects of the microstructure

Nb



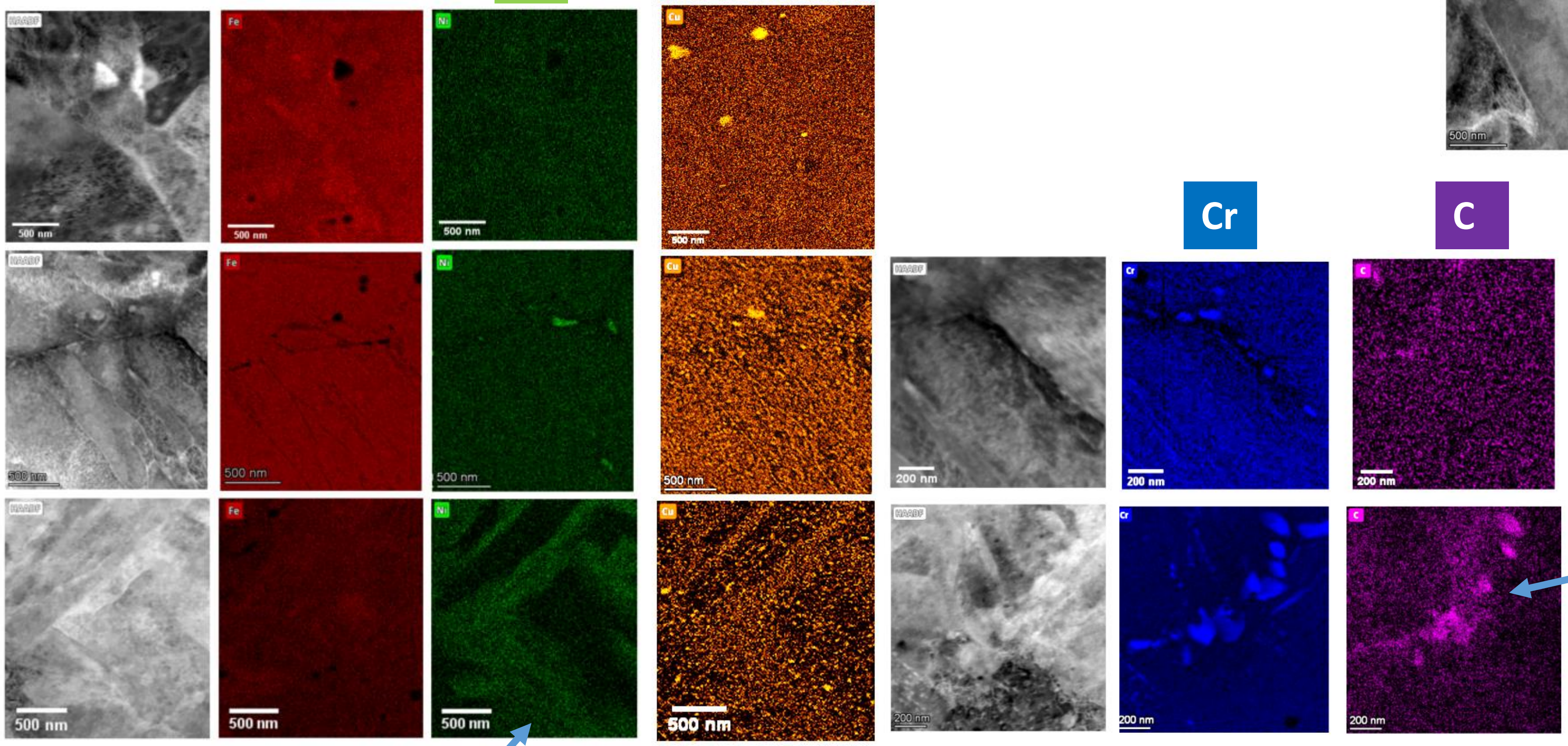

Nb carbides – found in all microstructures (formed during solution treatment)

Fe | Ni | Cu | Cr | C

450 °C

540 °C

650 °C

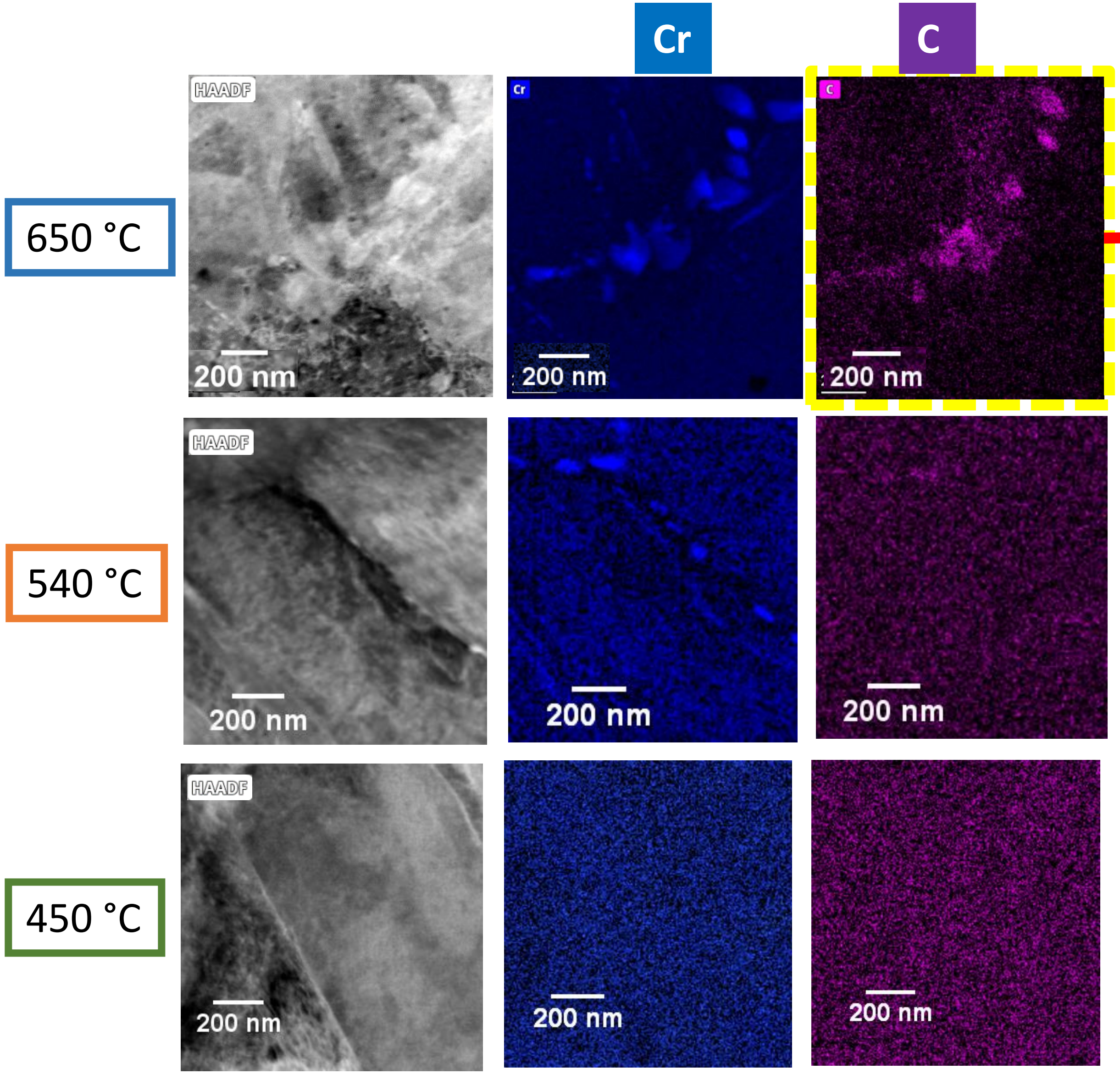


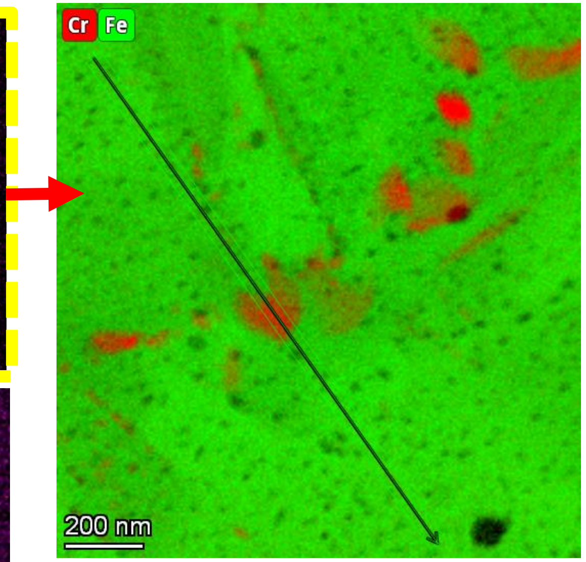

Cr Carbides
Possible Cr depletion (sensitization) at these sites as a result of Cr carbide formation

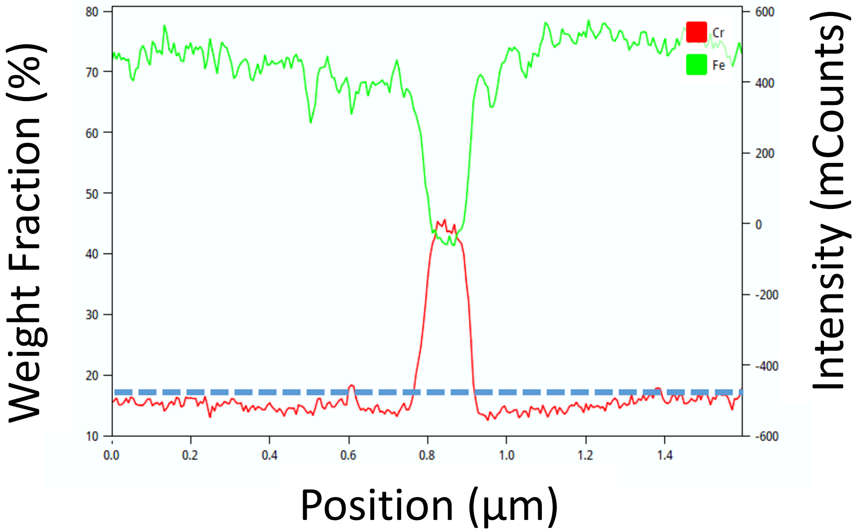
Increased Austenite content in 650 °C indicated by presence of Ni

Coarsening of Cu Precipitates with increased aging temperature

# Chromium Carbide Precipitation as a Function of Ageing Temperature



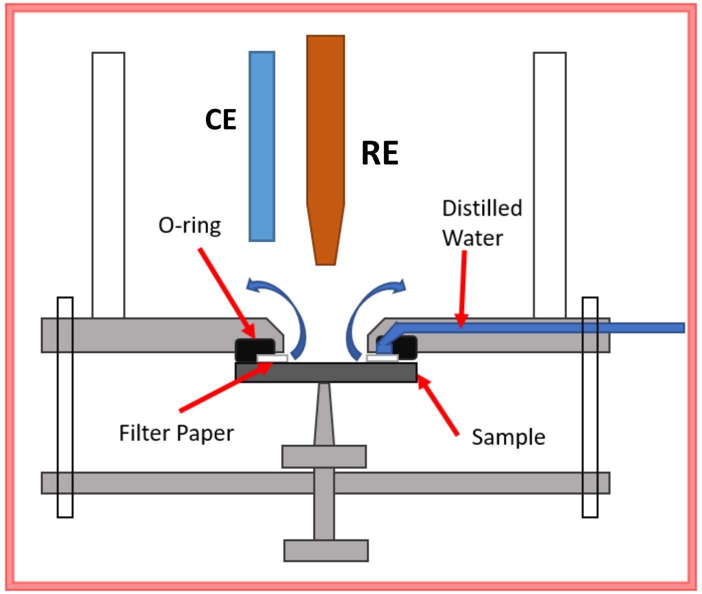



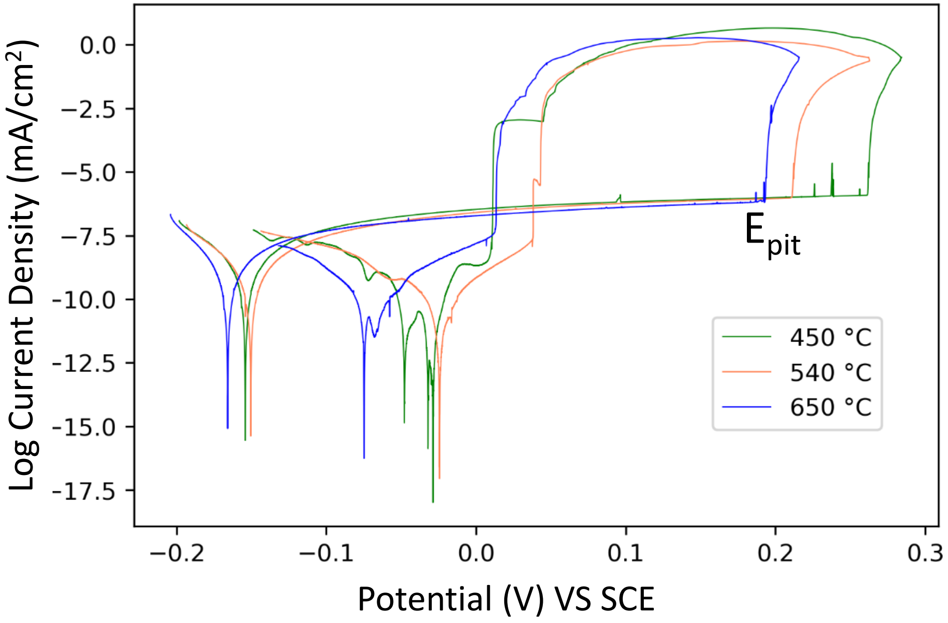



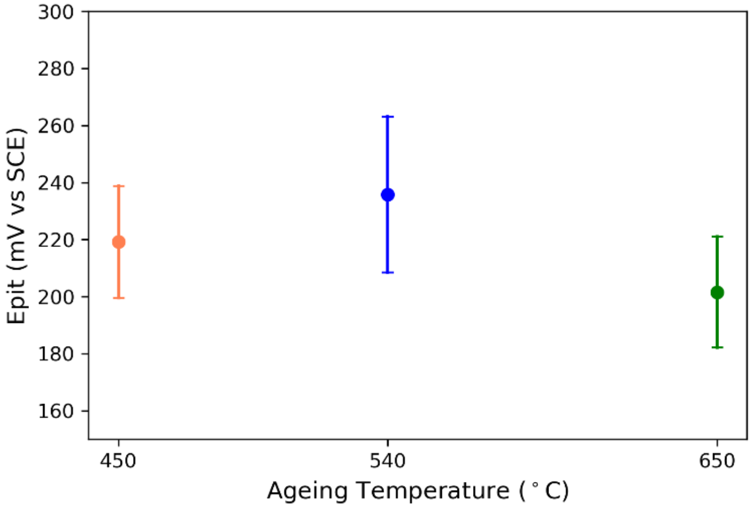

- Cr carbides found in 540 °C and 650 °C microstructures
- Line scan reveals slight Cr depletion around carbide in sample aged at 650 °C
  - Possible initiation site for localised corrosion

# Microstructural Effects on Pitting Susceptibility

Tests conducted in an Avesta Cell
– Inhibits crevice corrosion




- 0.6 M NaCl
- 0.5 mV/s
- 1 µm diamond polish
- OCP measured for one hour

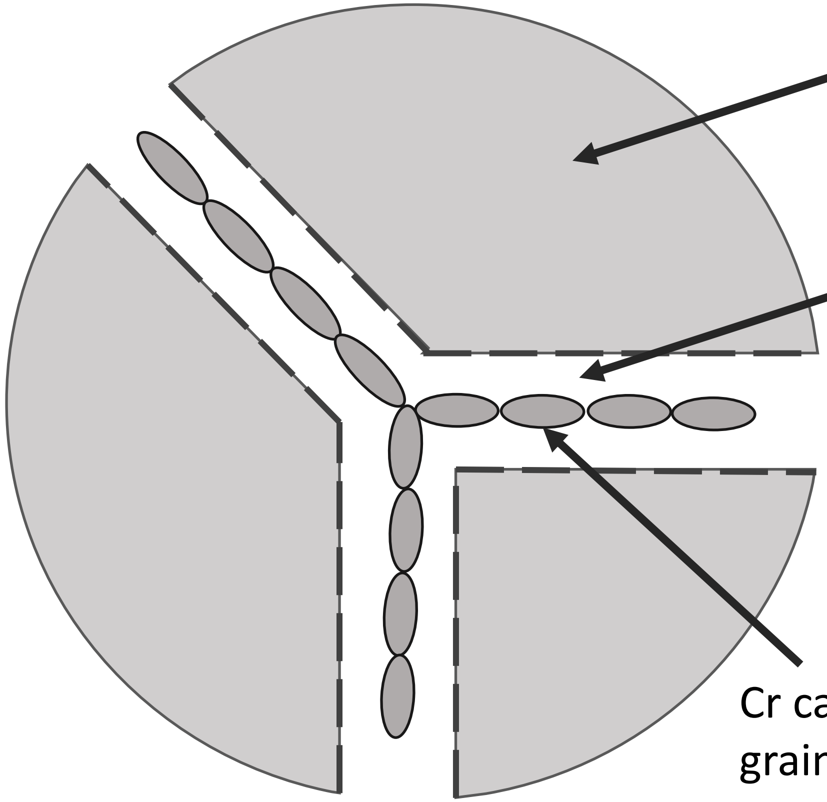
- On average 650 °C has the lowest $E_{pit}$
- However scatter is too large for $E_{pit}$ to be considered statistically different
- Pitting is a stochastic process and PDP may not account for slight differences in microstructure

# Effect of Aging Temperature on Passive Layer Integrity

## DL-EPR (Double Loop Electrochemical Potentiokinetic Reactivation)

Technique detects degree of reactivation (DOR) in steels:

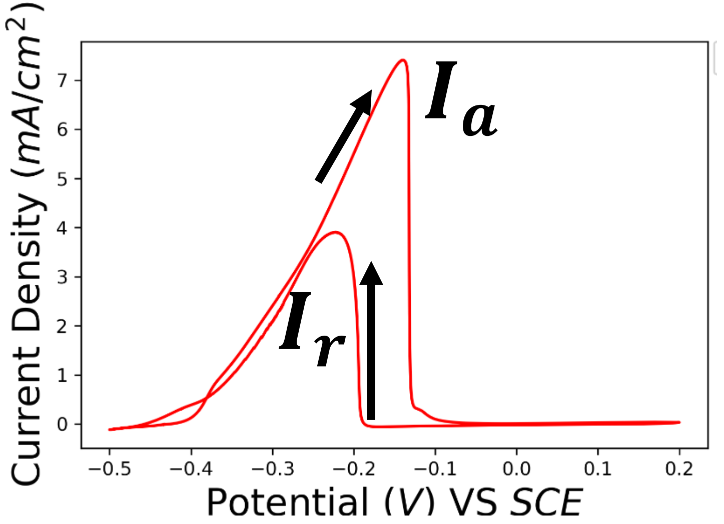
- Reactivation loop usually related to loss of passive film on grain boundaries where Cr depletion has lead to sensitization




$$DOR = \frac{I_r}{I_a}$$

Experimental Conditions:

- 0.25 M $H_2SO_4$ 0.01 M KSCN
- Scan rate: 0.5 mV/s
- 1200 grit surface finish

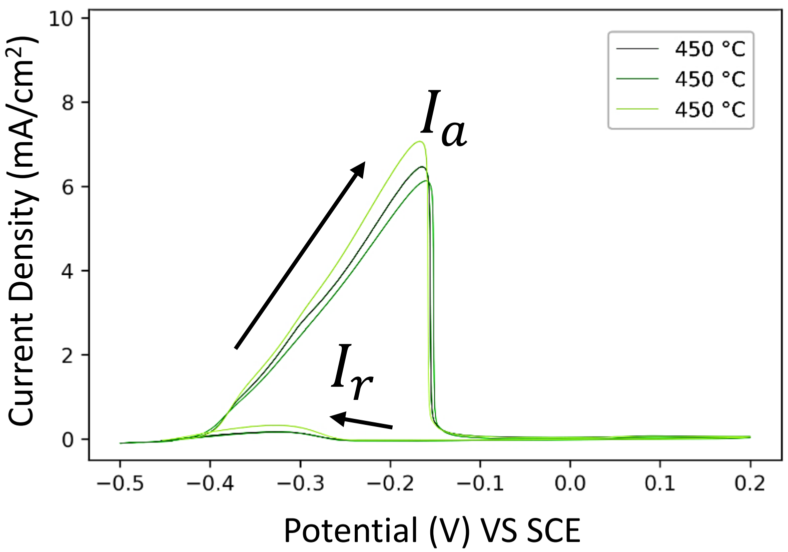


# Effect of Aging Temperature on Passive Layer Integrity

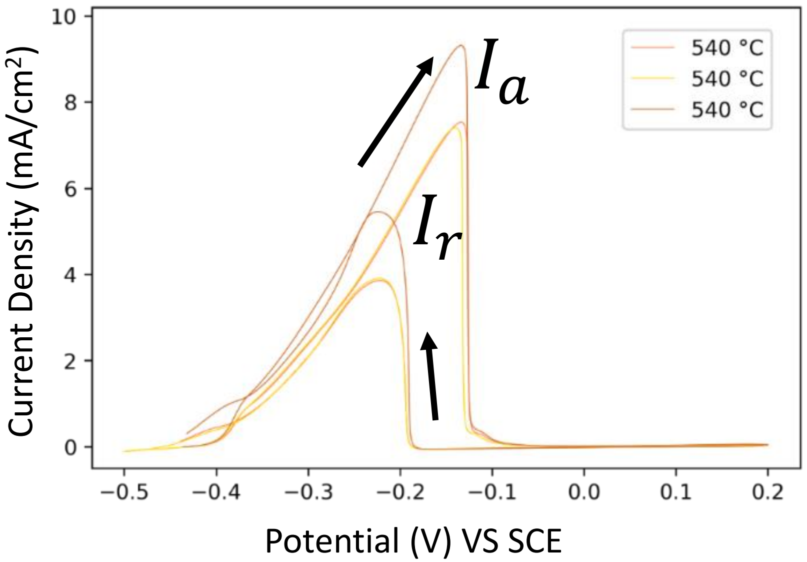
DL-EPR

Experimental Conditions:
- 0.25 M $H_2SO_4$ 0.01 M KSCN
- Scan rate: 0.5 mV/s
- 1200 grit surface finish

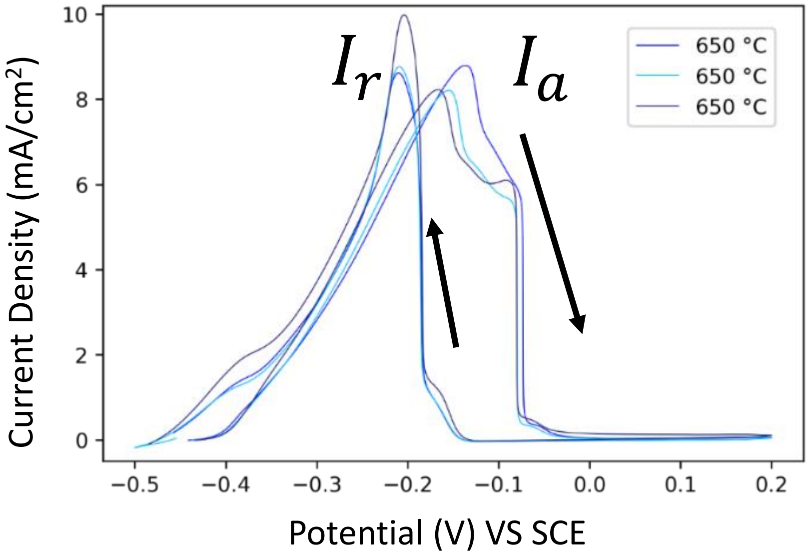
450 °C




540 °C




650 °C



# Effect of Aging Temperature on Passive Layer Integrity

DL-EPR

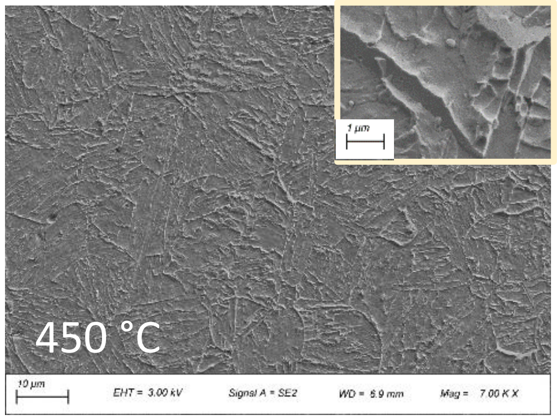
Experimental Conditions:
- 0.25 M $H_2SO_4$ 0.01 M KSCN
- Scan rate: 0.5 mV/s
- 1200 grit surface finish

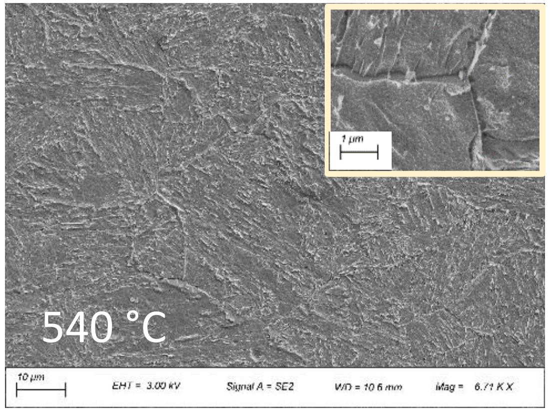
450 °C

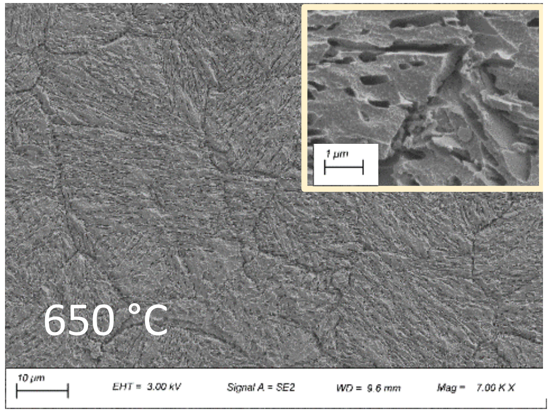
540 °C

650 °C

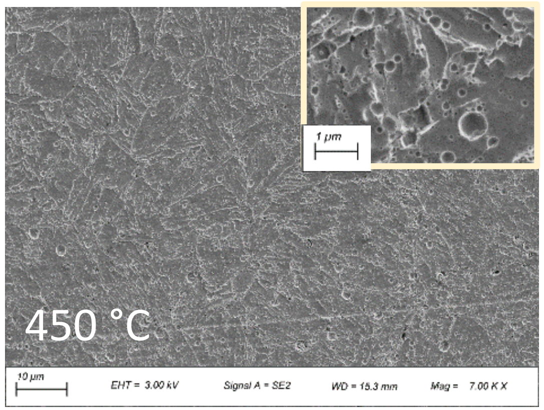
## After Anodic Scan

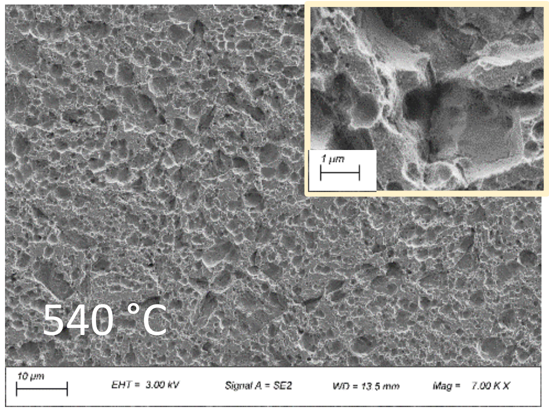


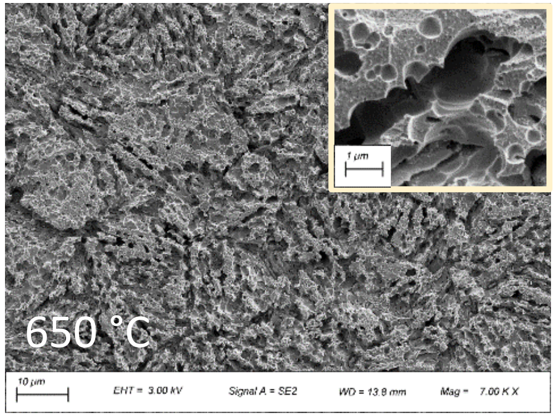



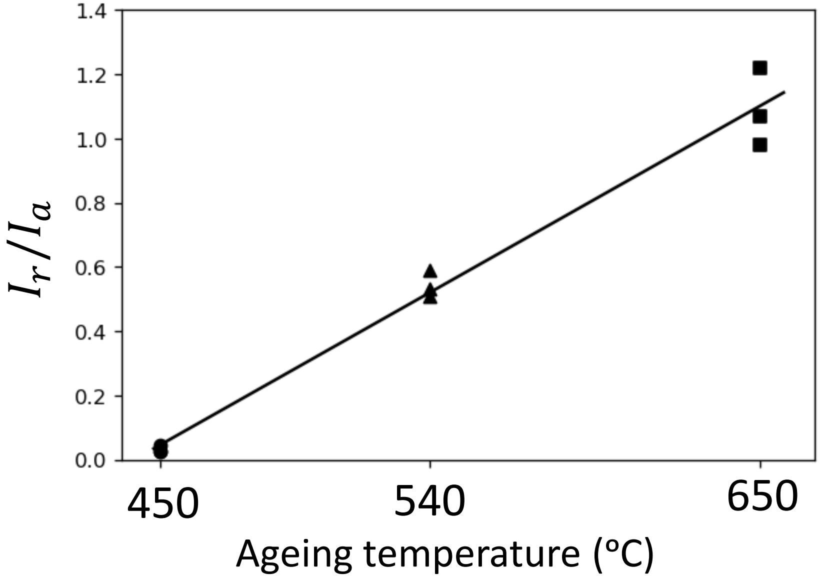

## After Reverse Scan




Calculated DOR



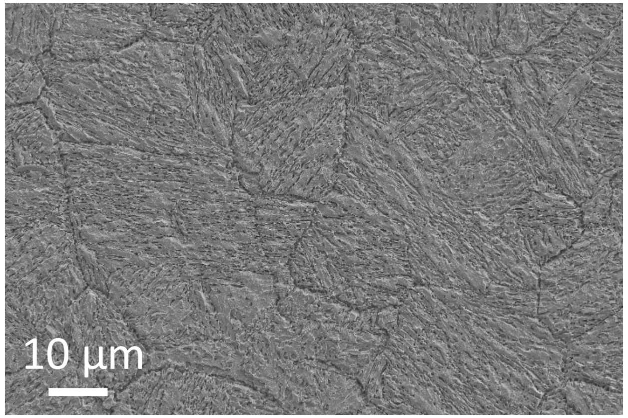

- Results are reproducible
- DOR increases with ageing temperature
- May be related to presence of Cr carbides in the microstructure

# Effect of Aging Temperature on Passive Layer Integrity

650 °C

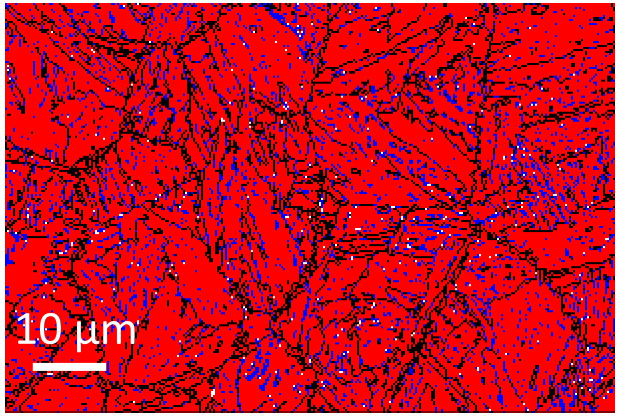
EBSD data

After anodic scan (DL-EPR)

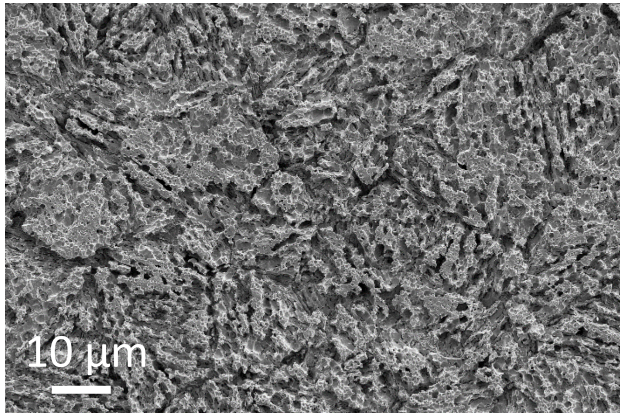



Phase fraction

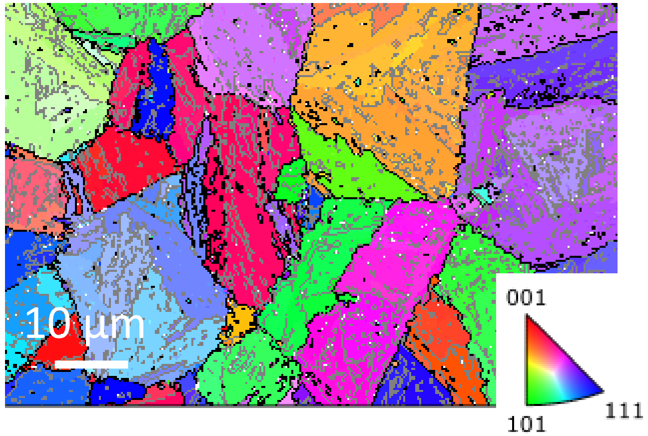
- α-martensite
- γ-austenite

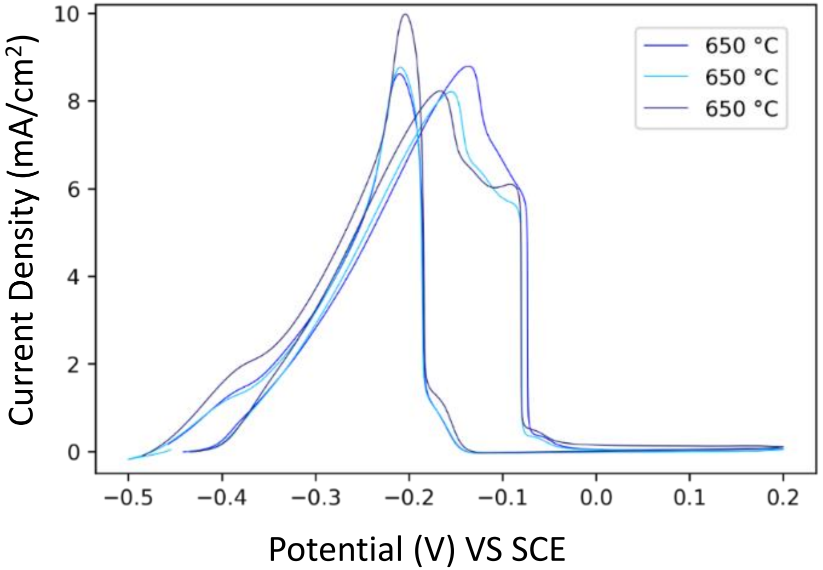



After reverse scan (DL-EPR)




Reconstructed austenite grains



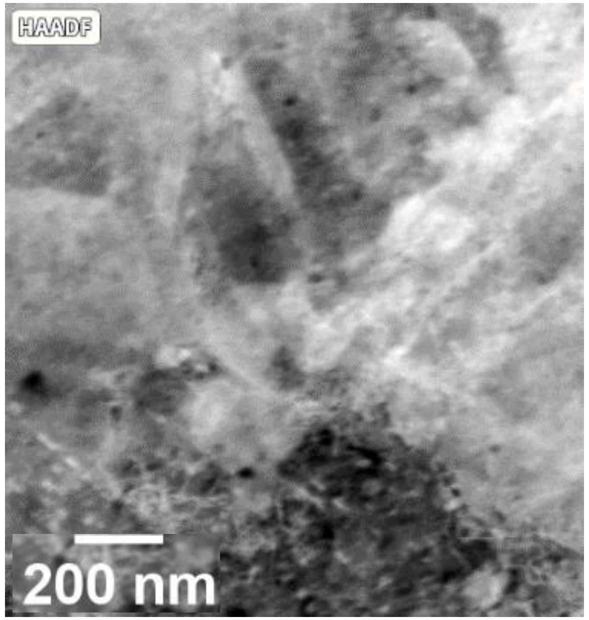



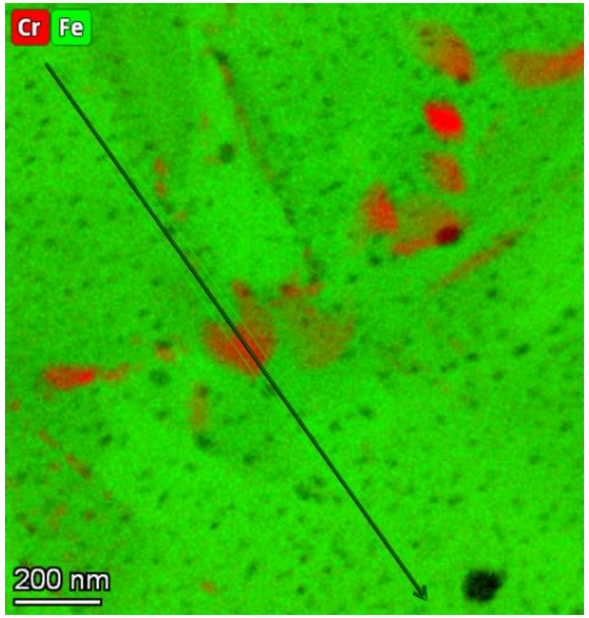

- Deeper etching along PAGBs
- High DOR measured through DL-EPR
  - Possible that reverted austenite has lower Cr content than matrix (1)

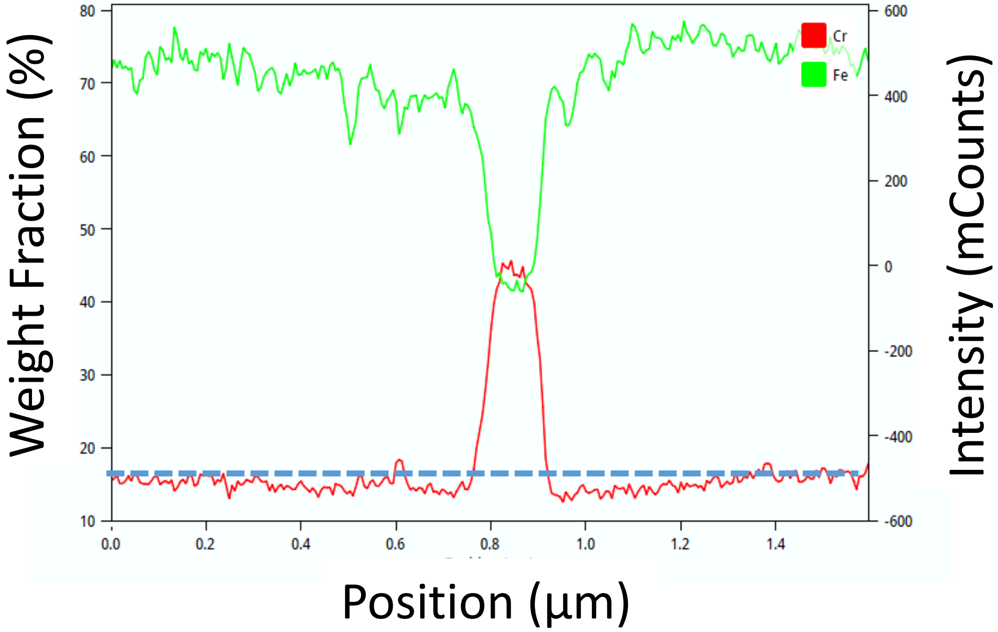
(1) L. Couturier, et al. *Materials and Design*, vol. 107, 2016

# Effect of Aging Temperature on Passive Layer Integrity

650 °C




- Evidence of Cr depletion around Cr carbides
- High DOR in samples aged at 650 °C may be due to an increase in the heterogeneity of Cr in the microstructure, disrupting the passive film creating more initiation sites for localised corrosion

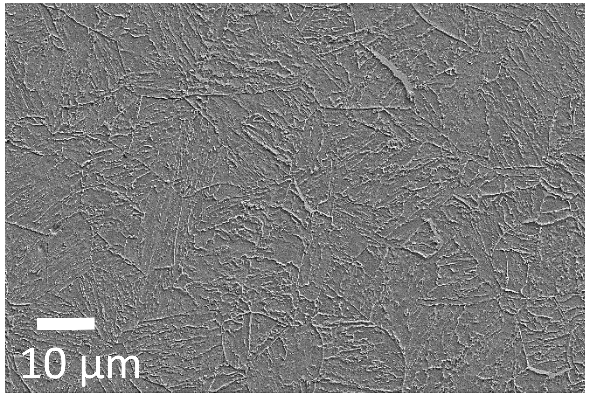
# Effect of Aging Temperature on Passive Layer Integrity

## 450 °C

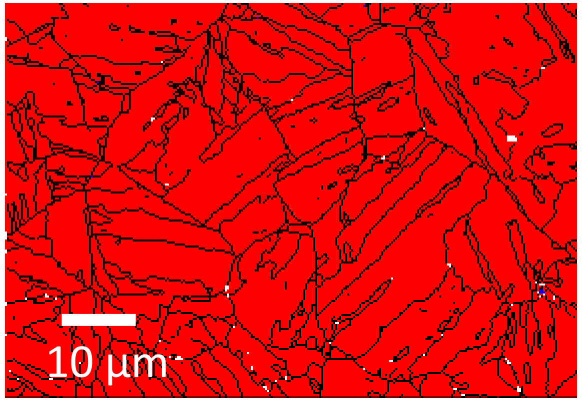
EBSD data

- α-martensite
- γ-austenite

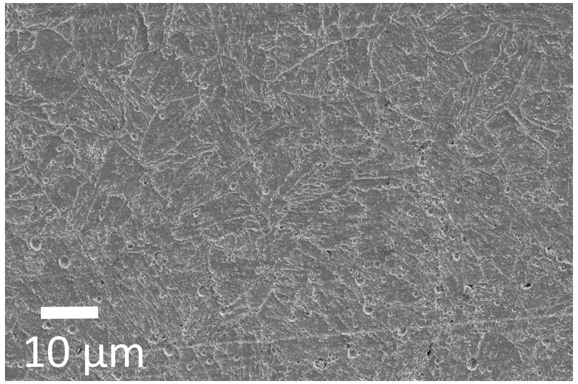
After anodic scan (DL-EPR)



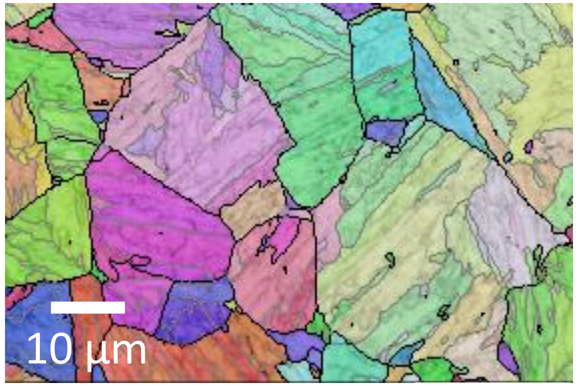

Phase fraction

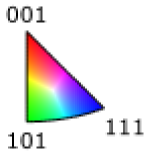



After reverse scan (DL-EPR)




Reconstructed austenite grains



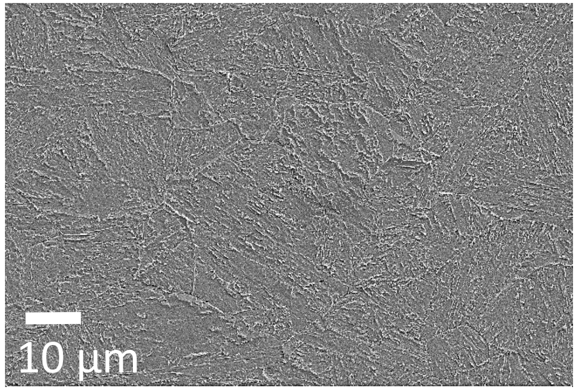




## 540 °C

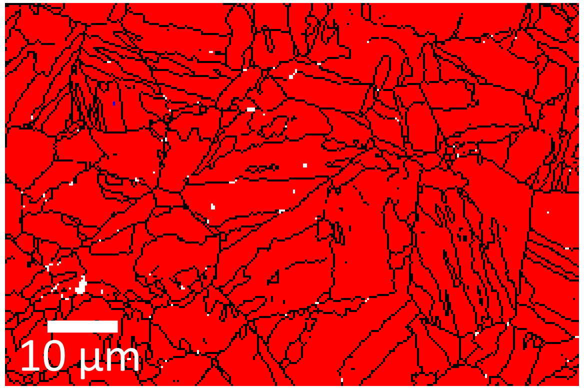
EBSD data

- α-martensite
- γ-austenite

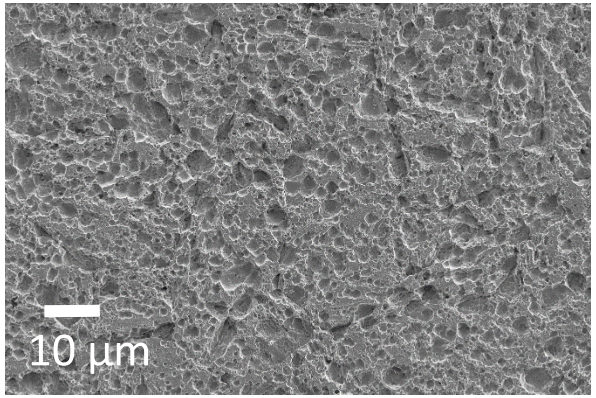
After anodic scan (DL-EPR)




Phase fraction




After reverse scan (DL-EPR)

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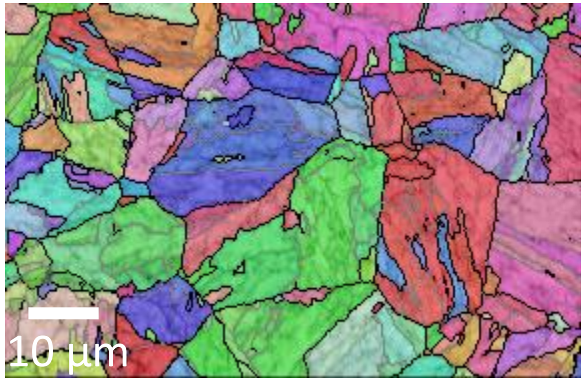
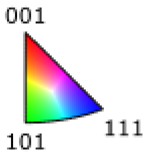
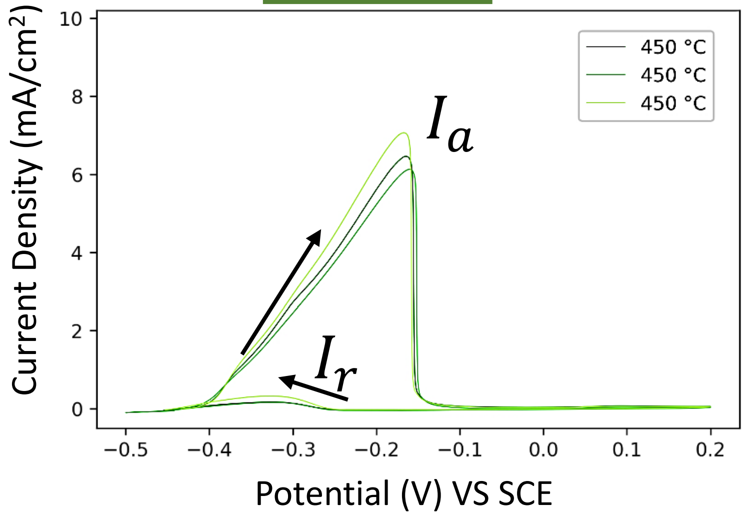
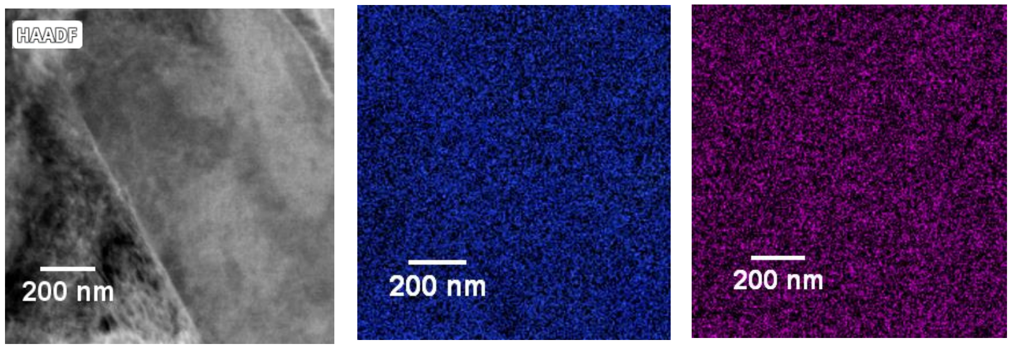


# Effect of Aging Temperature on Passive Layer Integrity

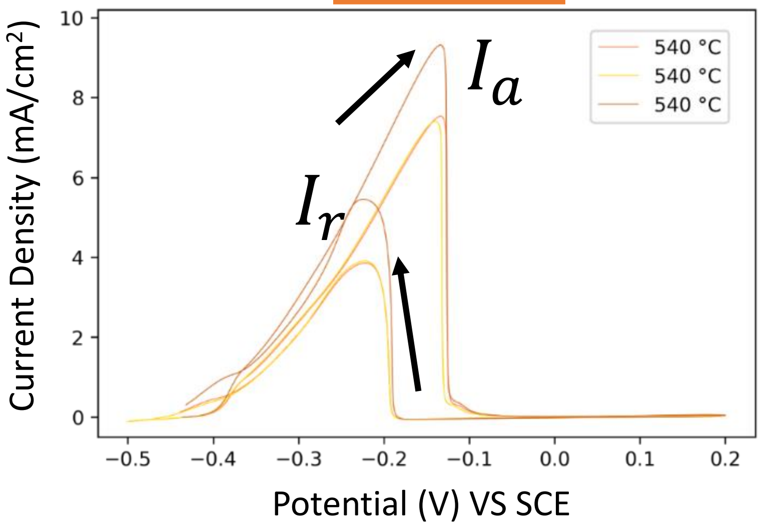
450 °C

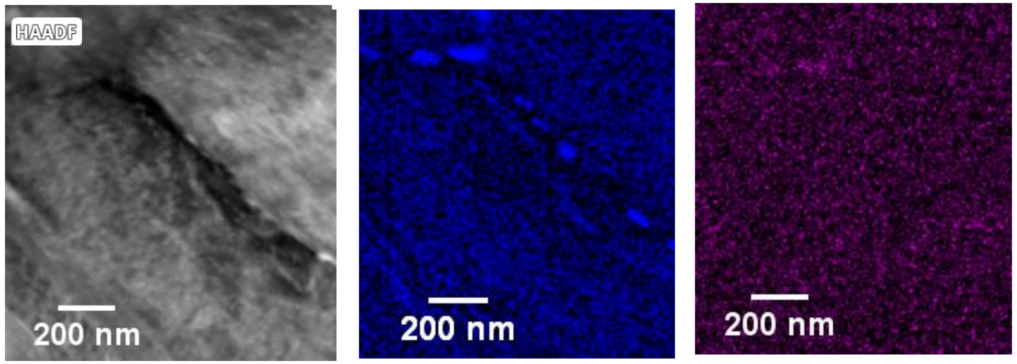



- Low DOR – indicates more even distribution of Cr in the microstructure

540 °C



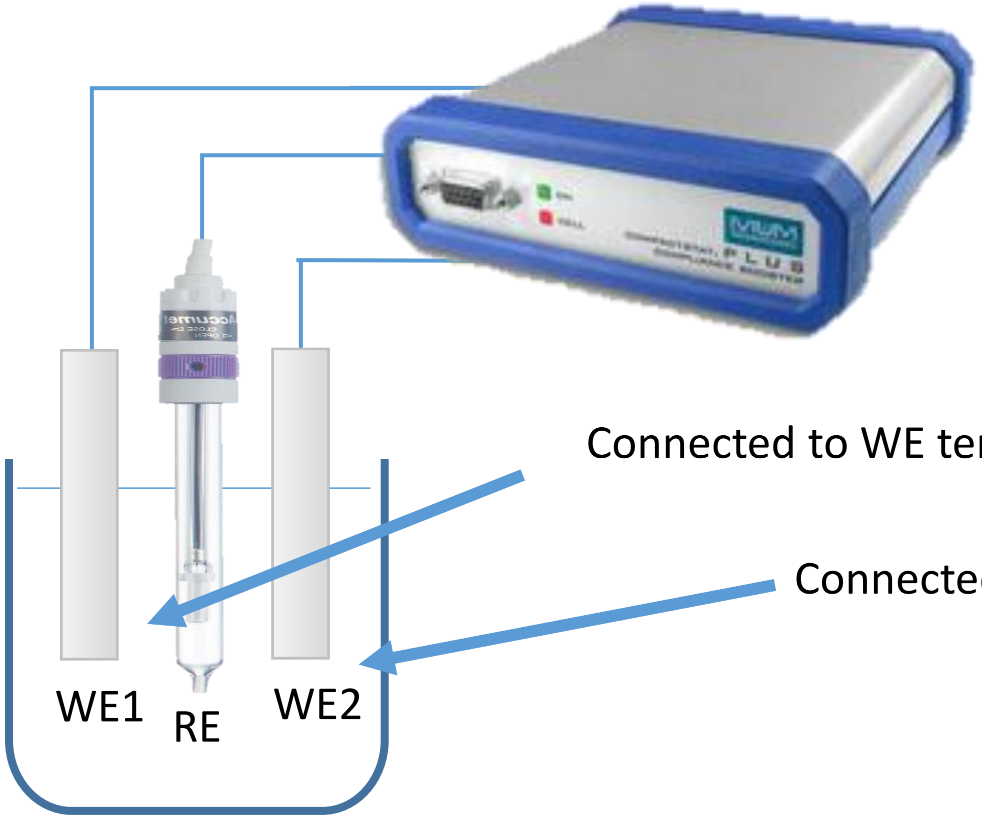




- Increase in DOR – Cr carbides found along GBs

# Comparison of Pitting Susceptibility via Electrochemical Noise

ECN - Direct comparison of pitting susceptibility in 2 different microstructures

Electrodes coupled via Compact Stat in ZRA configuration




Connected to WE terminal

Connected to ground

Experimental Conditions

- 0.15% $FeCl_3$ + NaCl (total $Cl^-$ 0.6 M)
- Surface finish – 400 grit SiC

**Resultant current transients resulting from metastable pitting measured**

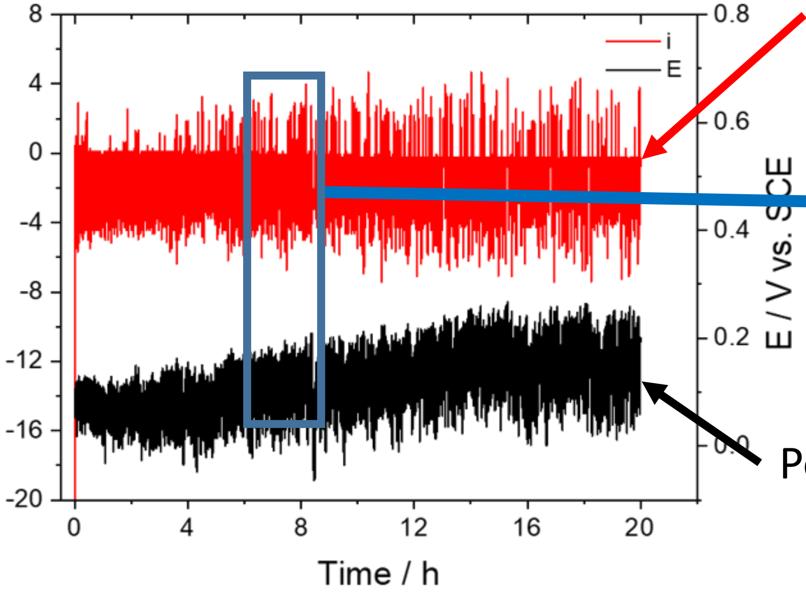
- +ve transients indicate pitting on WE1
- -ve transients indicate pitting on WE2

# Comparison of Pitting Susceptibility via Electrochemical Noise

Typical Time Record

WE 1 = 450 °C

WE2 = 650 °C




Current

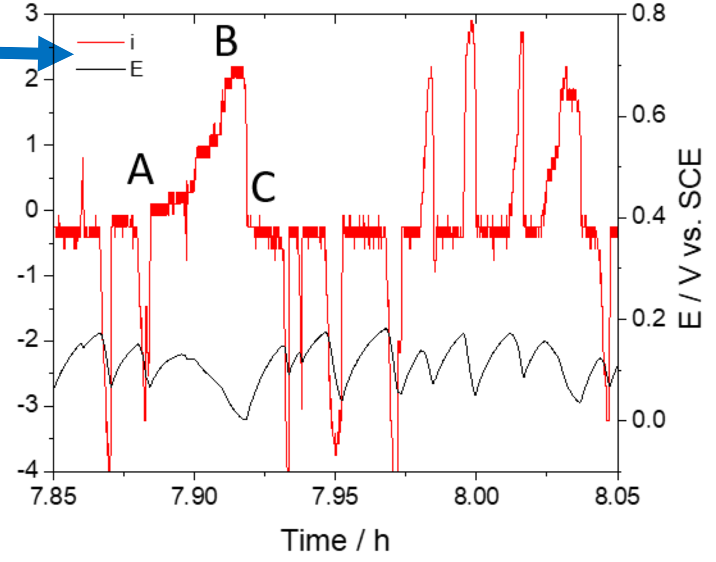
Potential

Note :
- +ve current indicates WE1 is pitting (450 °C sample)
- -ve current indicates WE2 is pitting (650 °C sample)

Experimental Conditions
- 0.15% $FeCl_3$ + NaCl (total $Cl^-$ 0.6 M)
- Surface finish – 400 grit SiC

450 °C

650 °C




A - pit initiation on WE1 (450 °C)

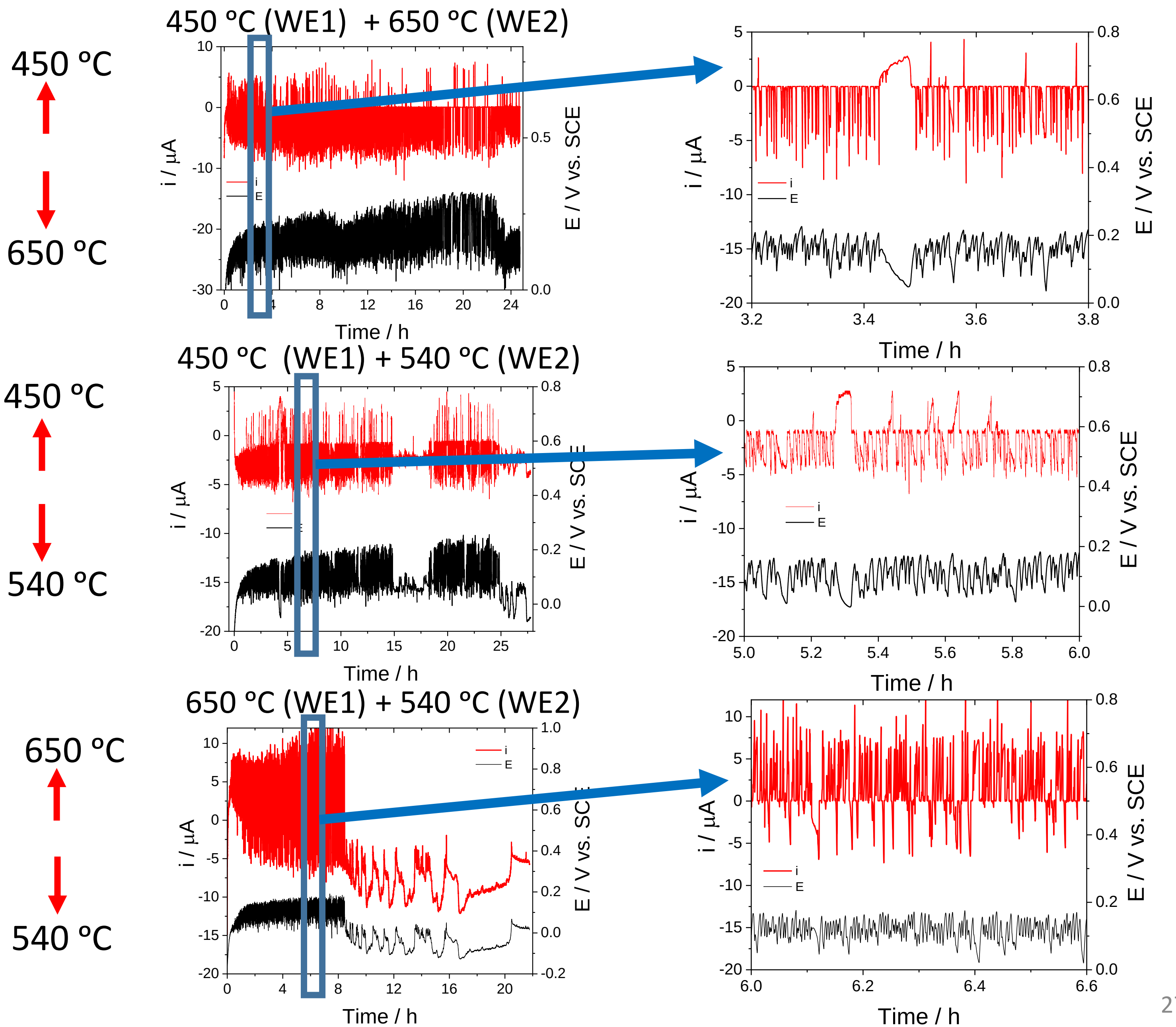
A → B pit growth

B → C pit repassivation

Potential drops when pit initiates and rises when pit repassivates

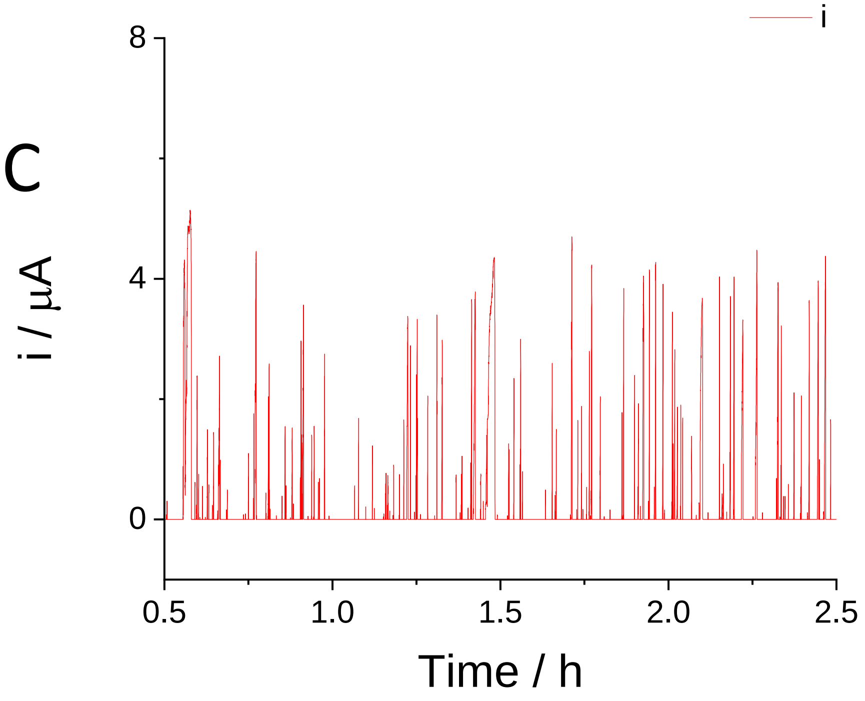
# Comparison of Pitting Susceptibility via Electrochemical Noise

- More frequent metastable events on 650 °C compared to 450 °C
- More frequent metastable events on 540 °C compared to 450 °C
- More frequent metastable events on 650 °C compared to 540 °C

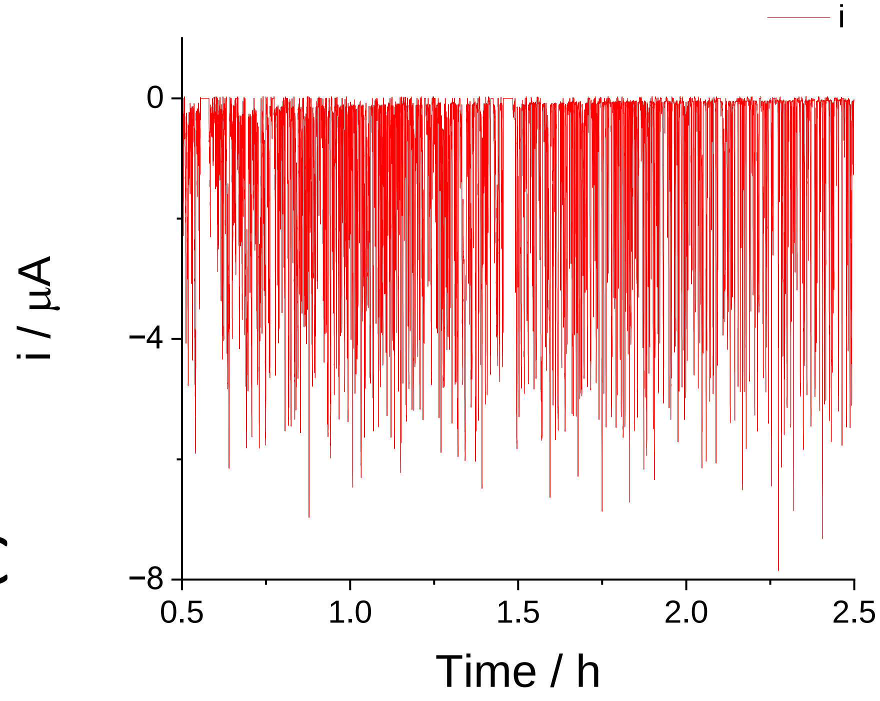


# Comparison of Pitting Susceptibility via Electrochemical Noise

450 ºC




650 ºC




- Transients were split into positive and negative
- Frequency analysis was conducted on the transients

# Comparison of Pitting Susceptibility via Electrochemical Noise

- Metastable events more frequent on microstructure with higher ageing temperature (650°C)
- Results indicate pit initiation easier on 650°C microstructure – would also suggest this microstructure is more likely to develop stable pits

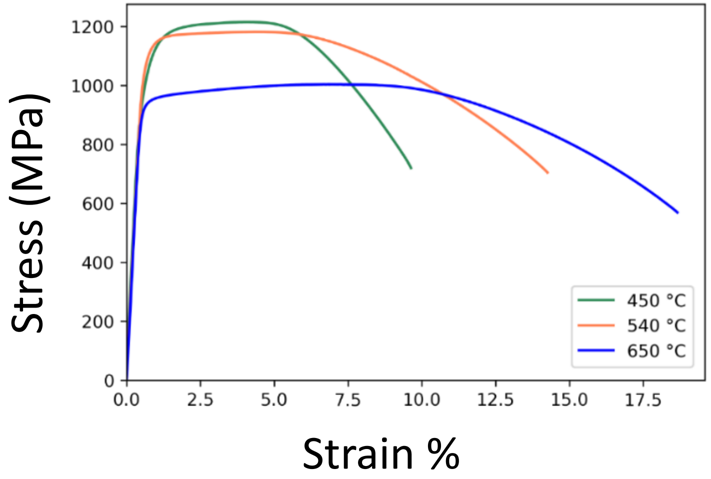
Likely pitting susceptibility:
650 °C > 540 °C > 450 °C

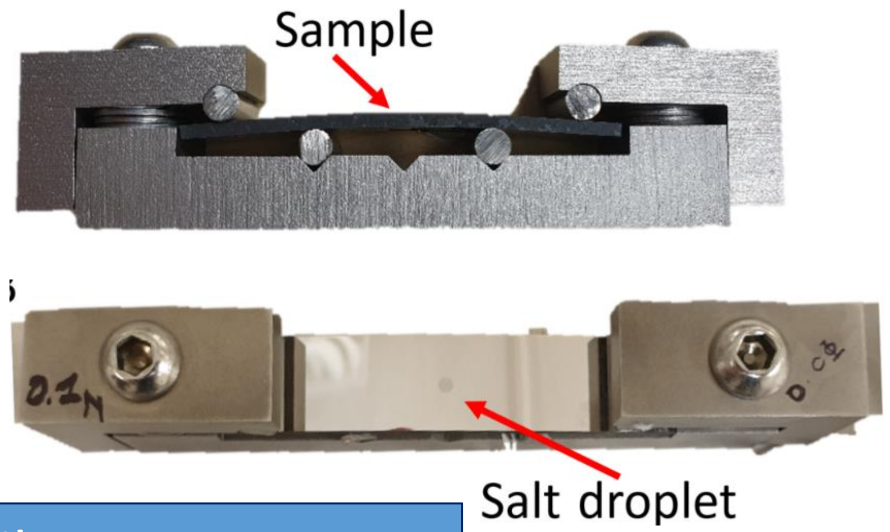
| | Frequency of events / Hz | | |
|---|---|---|---|
| Galvanic Couple | 450 °C | 540 °C | 650 °C |
| 450_650 (650GRD) | $4 \times 10^{-3}$ | | $3 \times 10^{-2}$ |
| 450_540 (540GRD) | $3 \times 10^{-3}$ | $2 \times 10^{-2}$ | |
| 540_650 (540GRD) | | $1.5 \times 10^{-2}$ | $5 \times 10^{-2}$ |

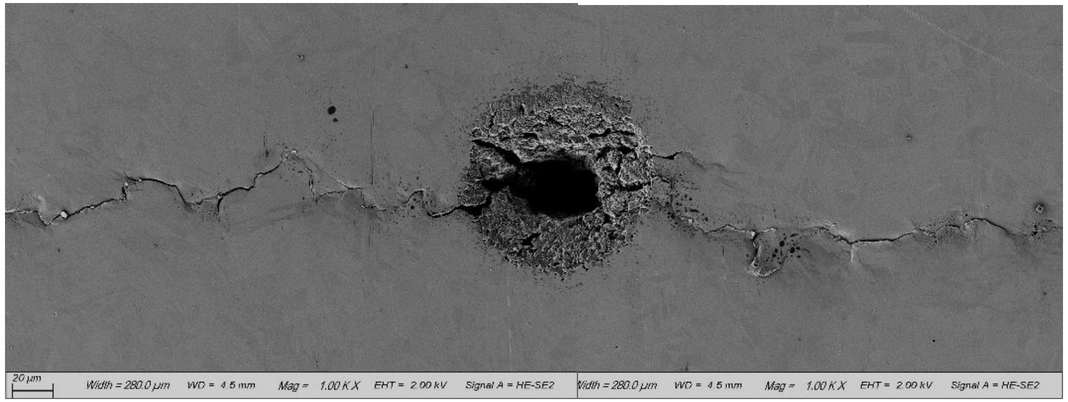
# Susceptibility to Environmentally Assisted Cracking

## Testing method allows:

- Investigation of microstructure effect on SCC
- Study of pit to crack transition
- Investigation of cracking behaviour



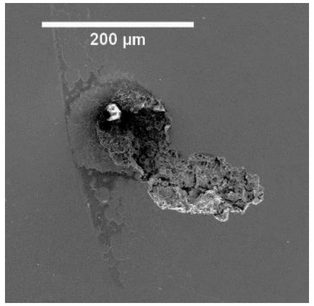
## Test details:

- Stress applied via 4-point bend to 80% YS of 540 °C sample
- 1 µl $MgCl_2$ salt deposits with concentrations 1M, 0.1 M or 0.01 M
- Temp = 50 °C, Time = 5 and 10 day
- Pit diameter and crack length measured post test
- Stress-free specimens tested under identical conditions

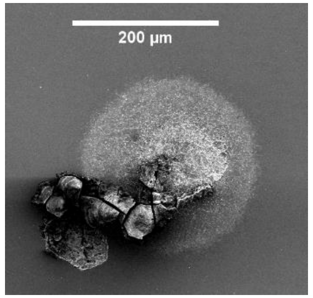
# Corrosion Morphology (Non-Stressed Specimens)

10 Days

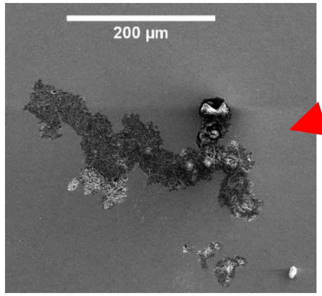
450 °C




540 °C



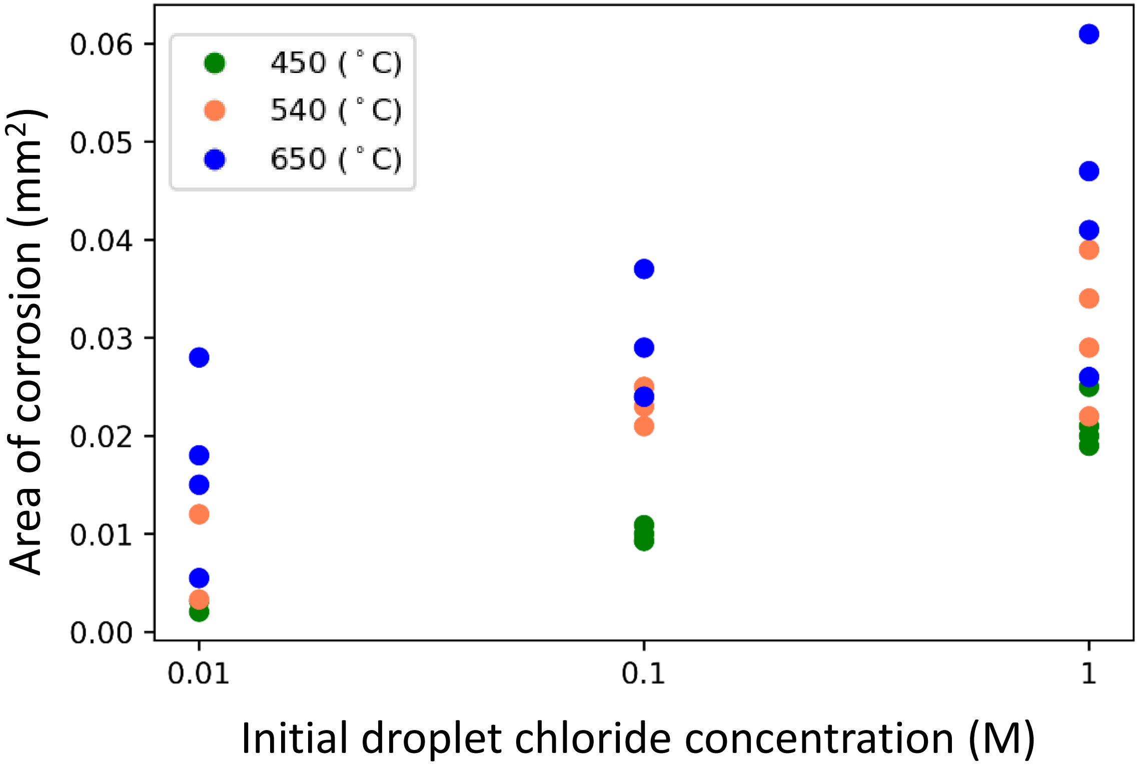

650 °C




Area of corrosion pits measured and plotted for each ageing temperature

Experimental Conditions
- 1 µl droplet from 1M $MgCl_2$
- Temperature – 50 °C
- RH – Saturated $MgCl_2$ ca. 30%
- Stress – 0 MPa

- Area of corrosion increases with initial droplet concentration – likely due to higher surface area remaining for higher concentrations
- 650 °C has largest area of corrosion – suggests pit initiation time is smaller compared to 450 °C and 540 °C



# Atmospheric Corrosion - 1M $MgCl_2$

- Time – 10 days

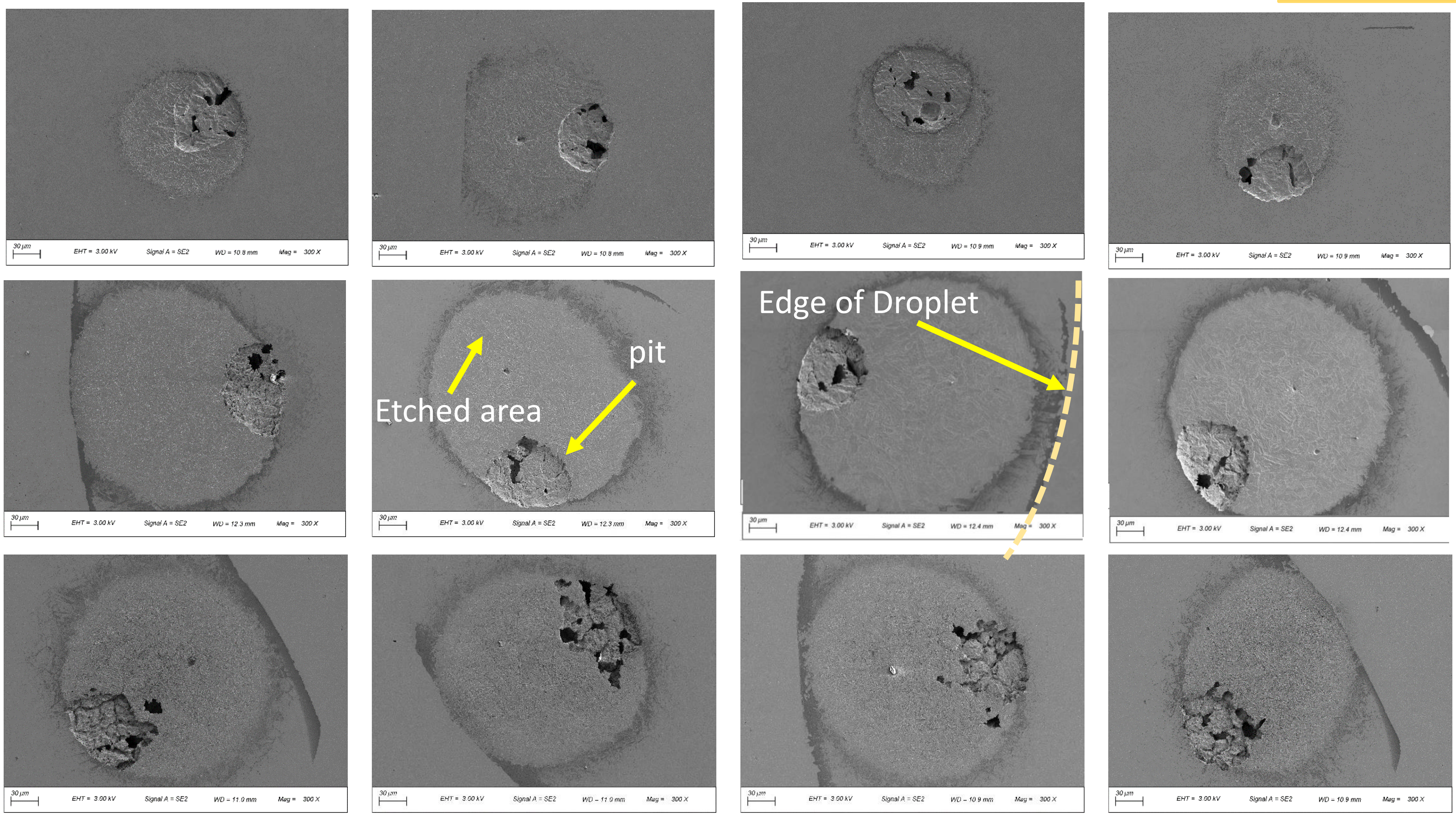
Samples tested without stress

- RH ~ 90% - 1M $MgCl_2$
- 50 °C

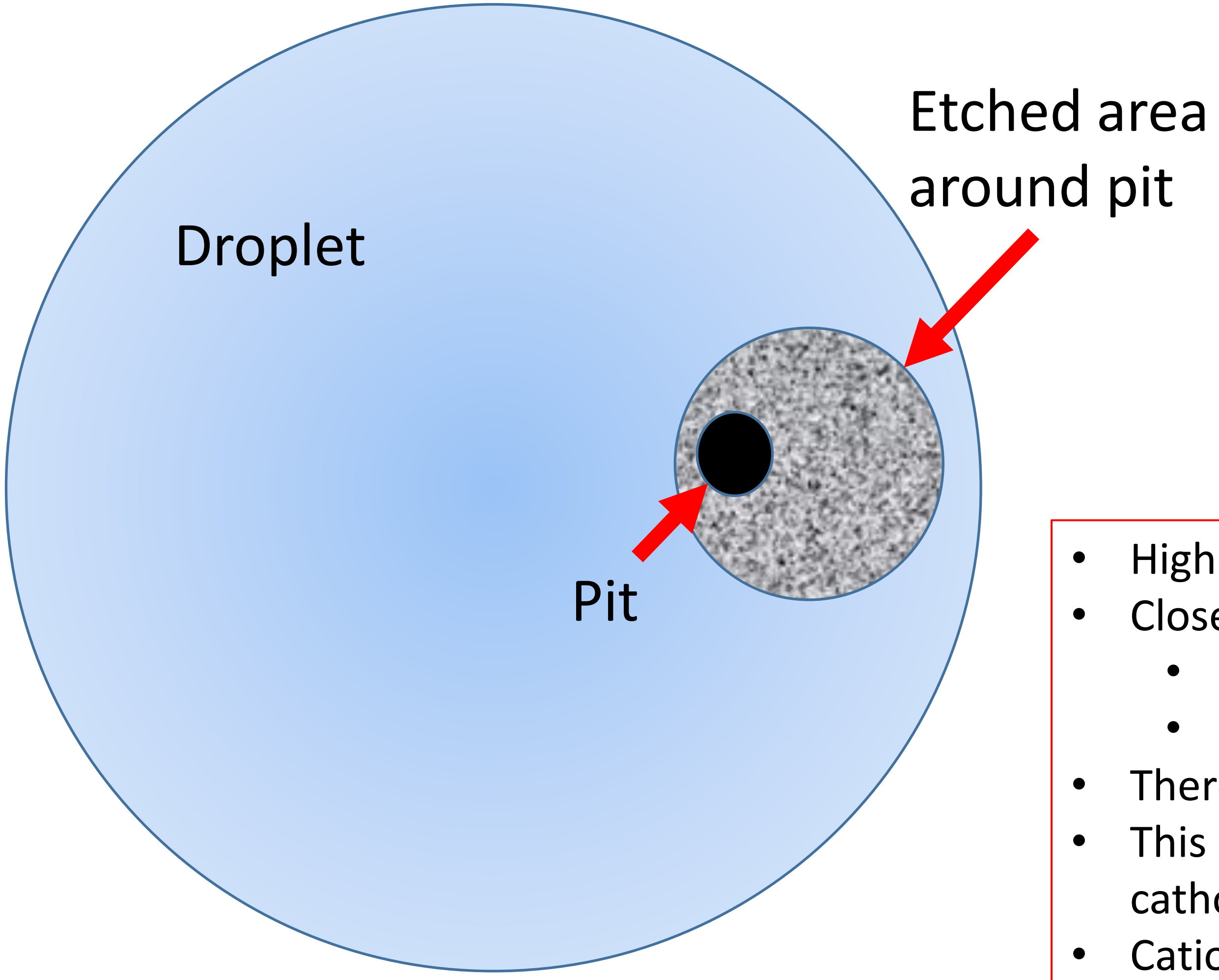
450 °C

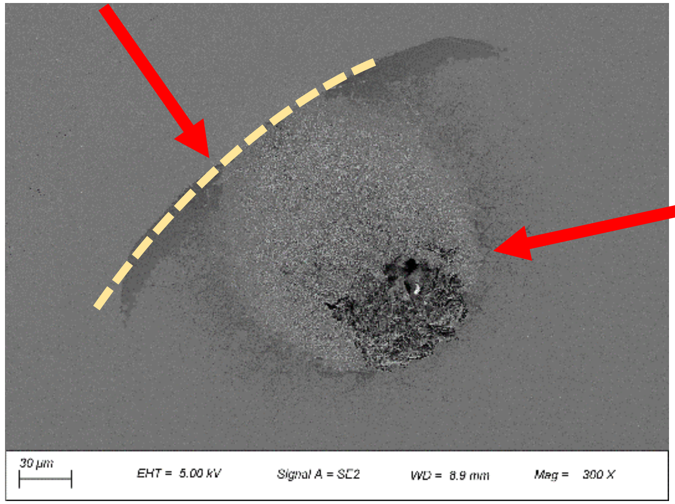
540 °C

650 °C



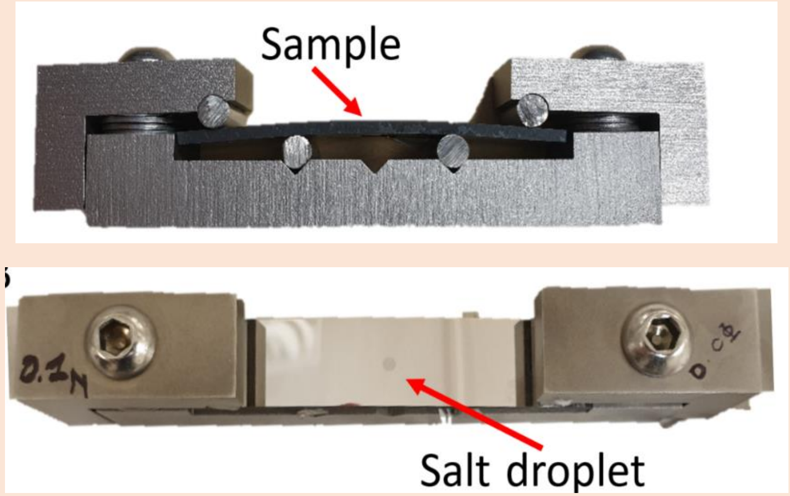
# Droplet  Etching in Pit Viscinity




- Higher pH near edge of droplet
- Close to the middle there is:
  - Low oxygen
  - Low Cathodic activity
- Therefore potential is higher near the edge
- This causes the pit to nucleate near edge as it needs cathodic activity to support
- Cations are created within pit and migrate to cathode (near edge) which causes local acidification and therefore etching of area shown

# EAC in Four-Point Bend Specimens




Stressed samples with MgCl2 salt droplet

Experimental Conditions

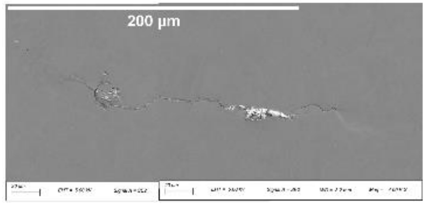
- 1 µl droplet from 1M $MgCl_2$
- Temperature – 50 °C
- RH – Saturated $MgCl_2$ - 30%

Cleaning

Samples analysed post test with SEM to understand extent of SCC

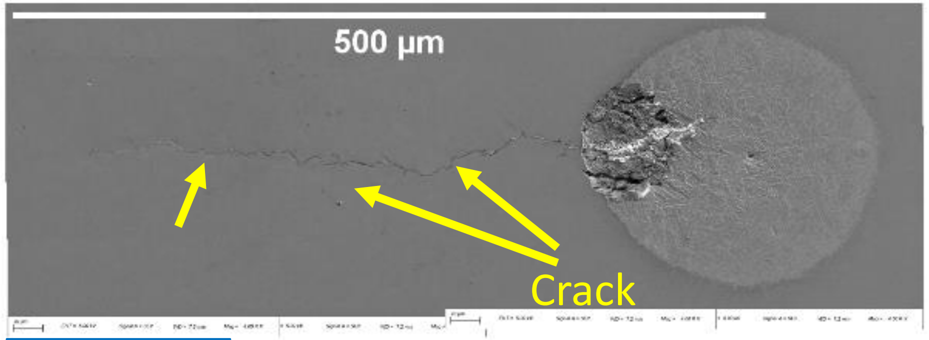
# EAC in Four-Point Bend Specimens

450 °C

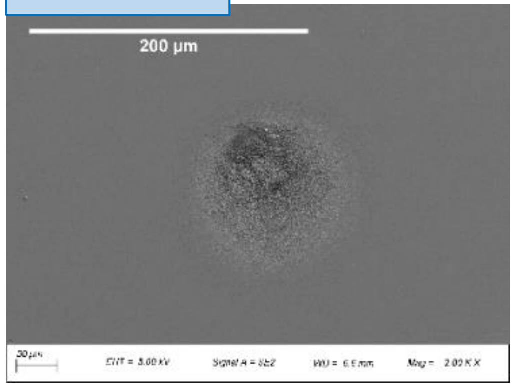



σ

540 °C




650 °C




σ

Time = 5 days

Experimental Conditions

- 1 µl droplet from 1M $MgCl_2$
- Temperature – 50 °C
- RH – Saturated $MgCl_2$ - 30%

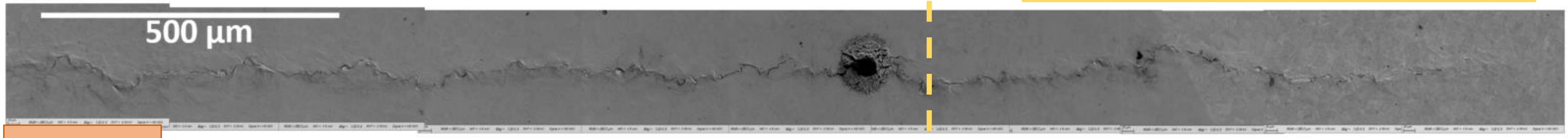
- All samples susceptible to localised corrosion under conditions tested
- Cracks observed on material aged at 450 °C and 540 °C
- Extent of corrosion on 540 °C is greater than that on 450 °C
- No cracks in material aged at 650 °C

# EAC in Four-Point Bend Specimens

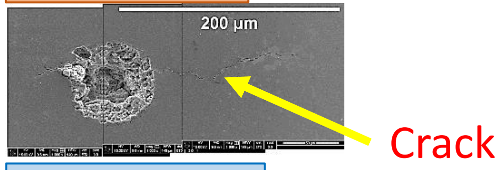
450 °C

10 days

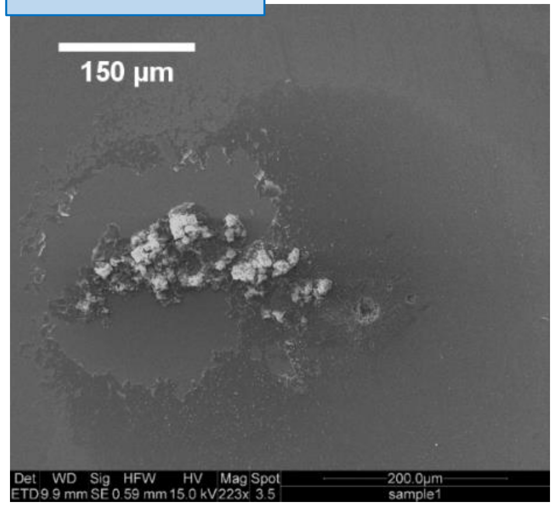
Experimental Conditions
- 1 µl droplet from 1M $MgCl_2$
- Temperature – 50 °C
- RH – Saturated $MgCl_2$ ca. 30%



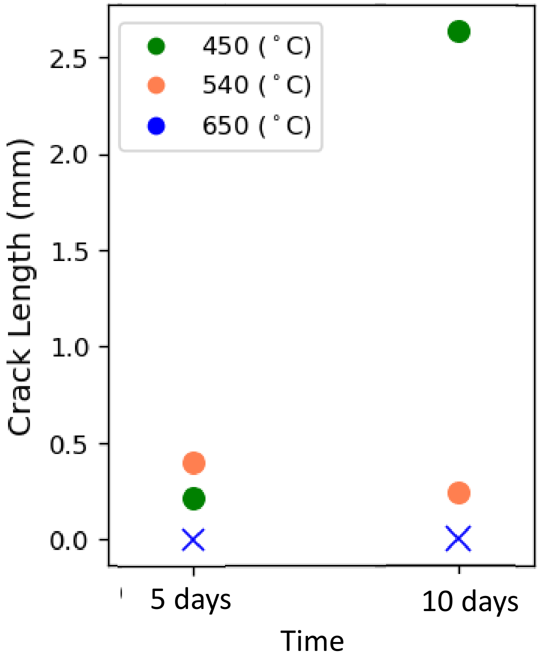

540 °C




650 °C

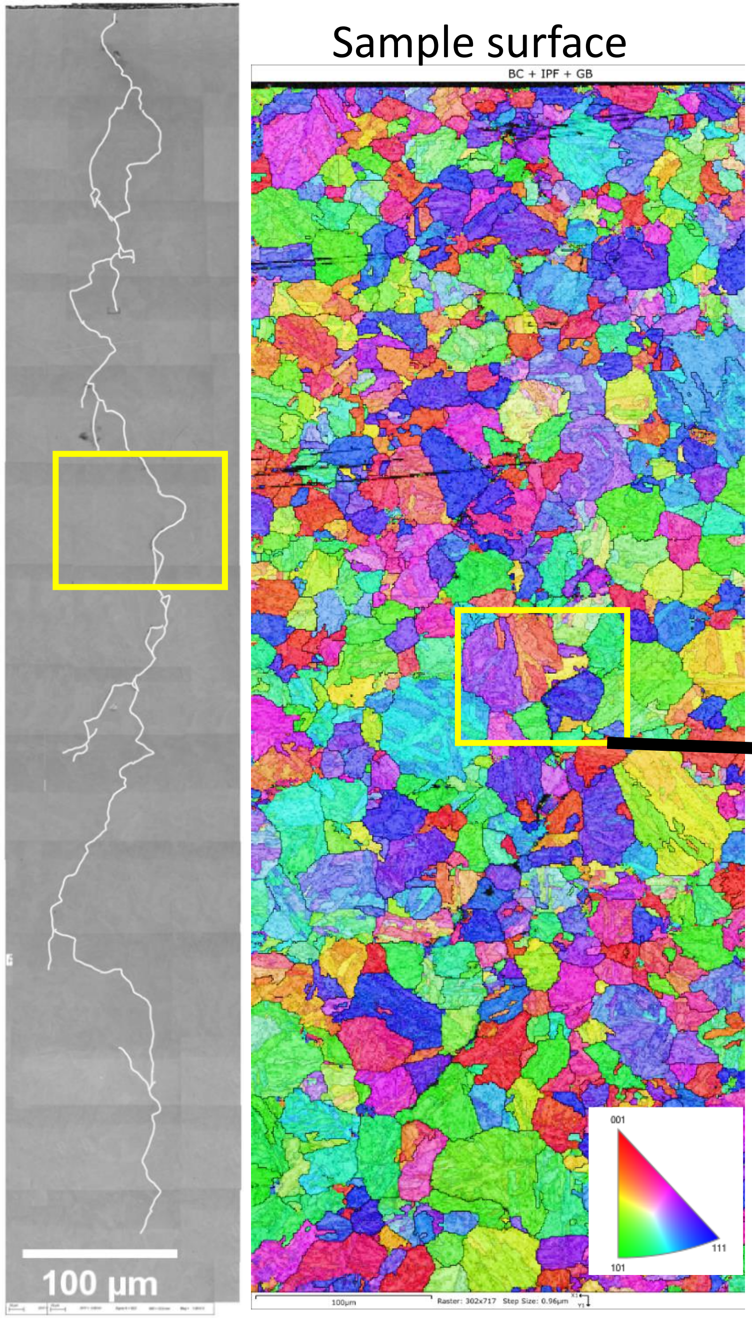



- Long cracks seen material aged at 450 °C
- Shorter cracks seen in 540 °C
- No cracks in material aged at 650 °C under the conditions tested



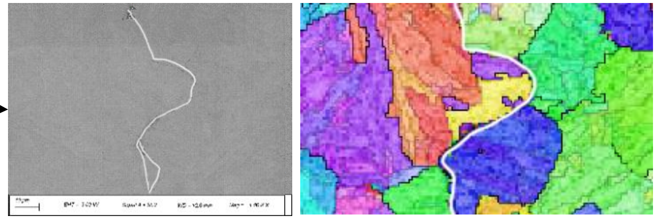
# Crack Pathway as a Function of Ageing Temperature

Sample surface



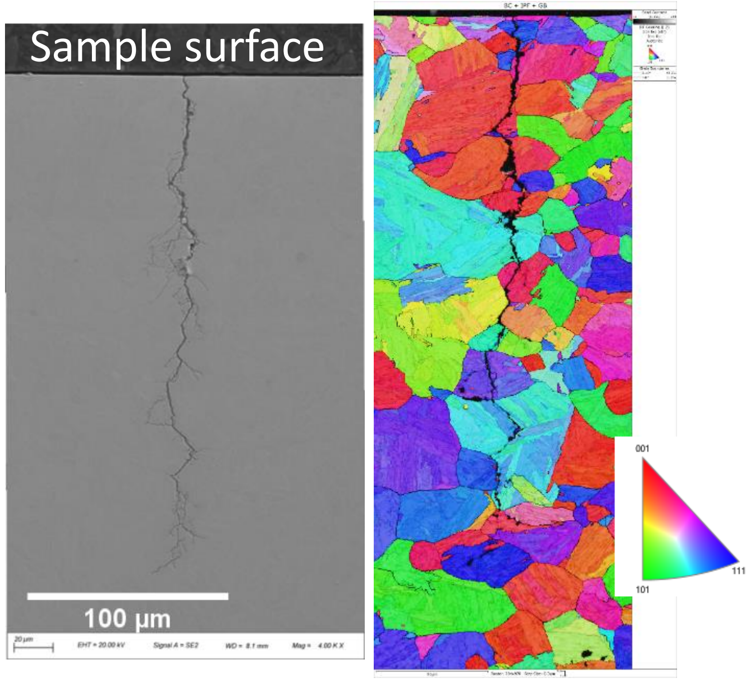

450 °C

- 450 °C – thin crack travels along PAGB (Pathway entirely IG)
- Suggests decohesion and susceptibility to HE



PAGBs reconstructed using AztecCrystal parent grain analysis

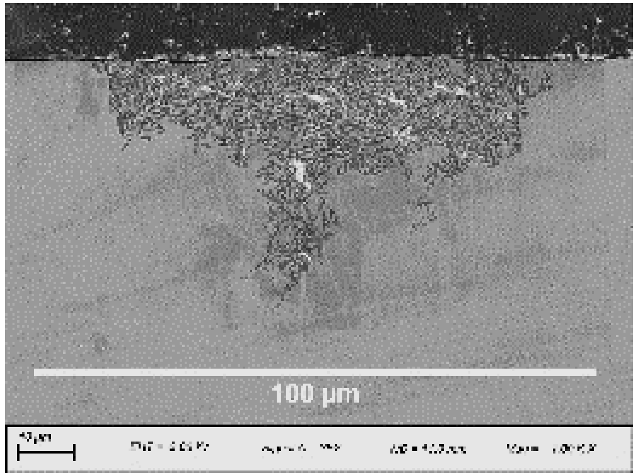
540 °C



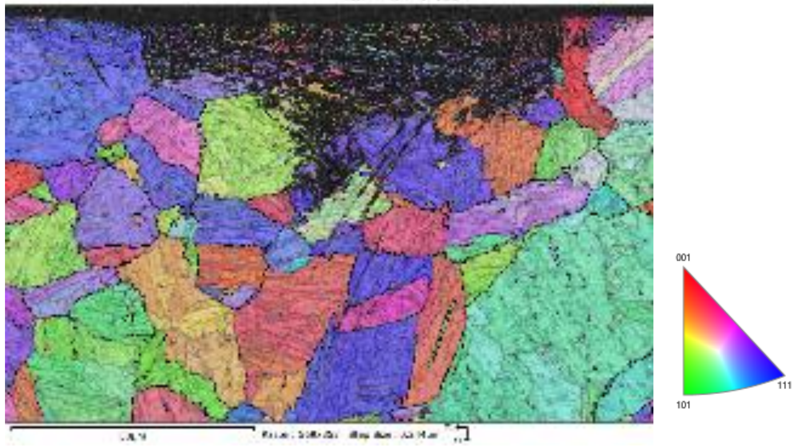

- Crack travels through some grains for 540 °C – mixture of TG and IG cracking
- Possible Cl induced SCC

# Crack Pathway as a Function of Ageing Temperature

650 °C




Sample surface

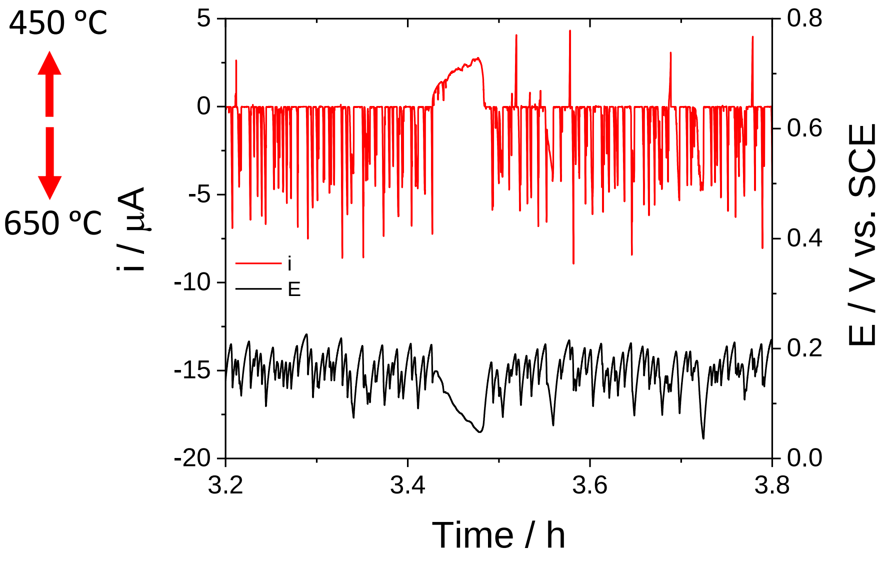


PAGBs reconstructed using AztecCrystal parent grain analysis

- Dish shaped pit - large area of corrosion near surface. No cracking
  - Possibility that pit is fast growing
  - Initiation time required for pit to crack transition not reached

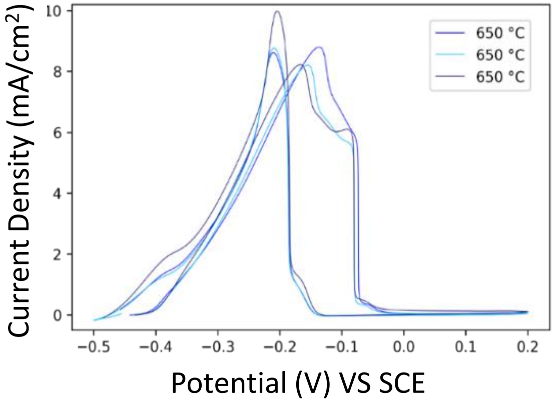
# Summary and Conclusions

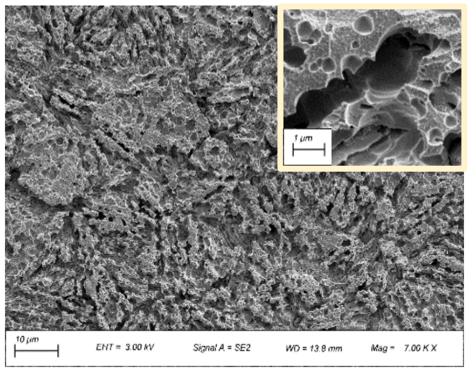
- Electrochemical investigations indicate 650 °C microstructure is most susceptible to pit initiation & most resistant to environmentally assisted cracking



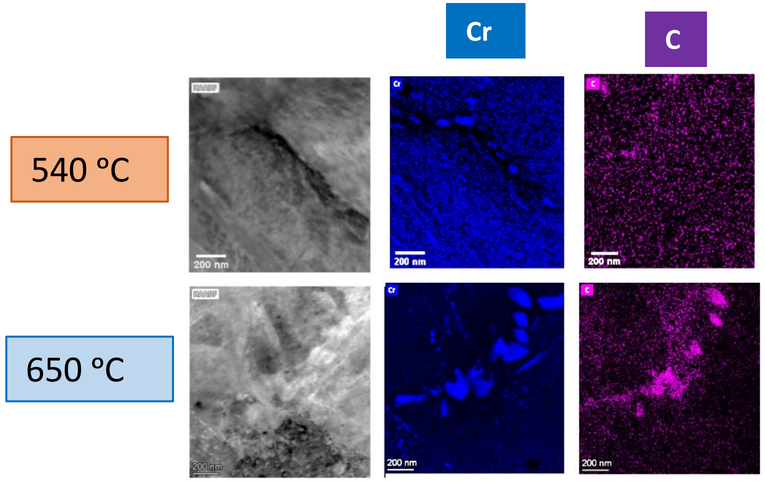

- Greater frequency of metastable events indicates more susceptible pitting sites on 650 °C

- High DOR for 650 °C found through DL-EPR – may explain high frequency of pit initiation



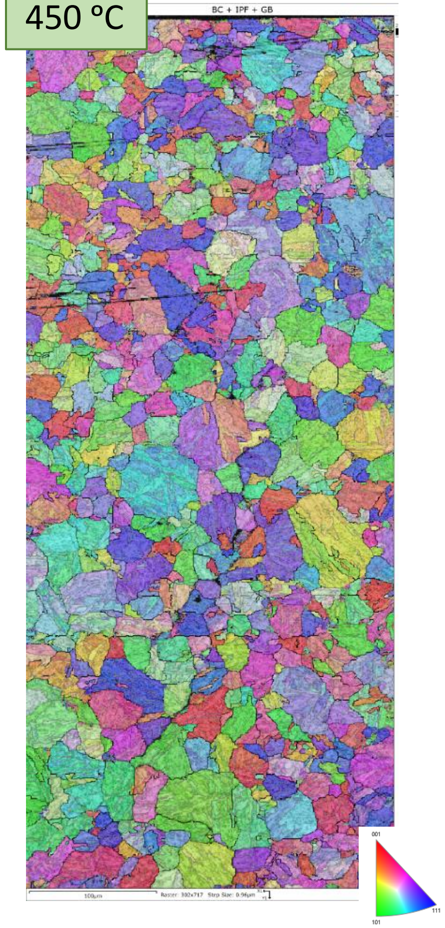
- Susceptible sites likely related to Cr depleted zones associated with Cr Carbide formation or lower Cr content in reverted austenite



# Summary and Conclusions

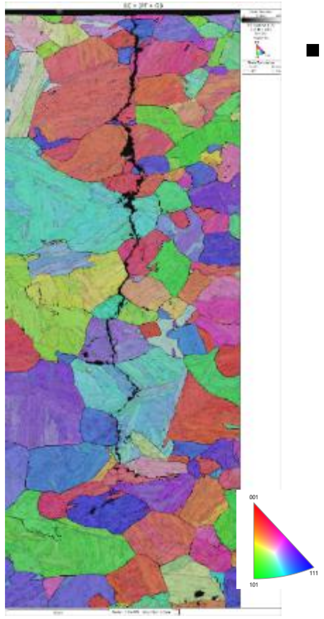
Susceptibility to EAC decreases with increasing ageing temperature – opposite to pit susceptibility

450 °C



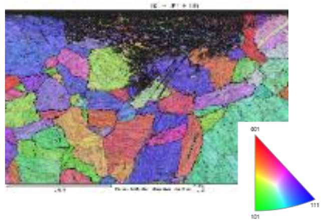

- Pit initiation time is longest (metastable pit frequency low with long lived events) for 450 °C microstructure
- Microstructure very susceptible to cracking – IG pathway suggests a mechanism involving decohesion via HE

540 °C



- 540 °C susceptible to cracking but mechanism may be $Cl^-$ induced SCC indicated by TG crack pathway

650 °C



- 650 °C develops large dish-shaped pits transition to cracking does not occur
- Initiation time associated with pit-to-crack transition may not have been reached
- Presence of austenite may inhibit cracking – due to lower mechanical driving force

# Thank you for Attending our Joint Meeting.

# Any Questions?

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LinkedIn

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