A Scanning Probe Investigation of Inter-Granular Corrosion in Sensitised Stainless Steel Nuclear Fuel Cladding

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M2A EngD Seminar
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AGR Fuel Cladding

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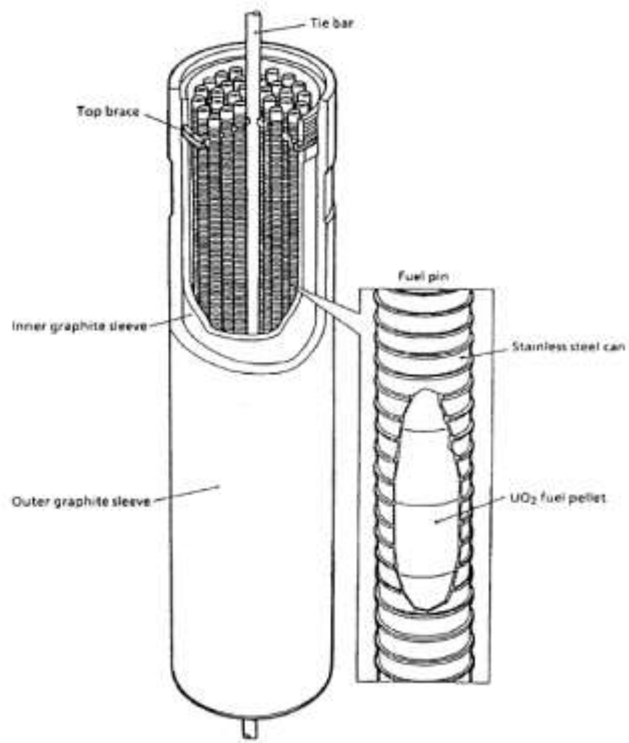
- Austenitic (γ-phase) stainless steel (SS) fuel cladding is used in British Advanced Gas-cooled Reactors (AGR)
- **High-nickel**, **high-chromium**, **niobium-stabilised** alloy specially designed for the AGR programme
- 'Typical' composition of AGR cladding shown below [1]



Cr	Ni	Mn	Si	Nb	C	N	Fe
19-21	24-26	0.55-0.85	0.46-0.75	<10 x wt%. C	0.025-0.065	0.004-0.010	Balance

[1] C. Taylor, The Formation of Sensitised Microstructures during the Irradiation of AGR Fuel Cladding, pp 60-73 Symposium on Radiation-Induced Sensitisation of Stainless Steels, 1986

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- Vast majority of fuel is unaffected by radiation during use
- Small proportion ~22 % are potentially affected by radiation, and may have become sensitised [2]
- We can induce sensitisation by heat treatments (**thermal sensitisation method**)

This represents a challenge, given the relative long storage life of cladding within cooling ponds, pending final geological disposal.

Some estimates envisage durations of 80 years in long-term storage.

[2] Martin Scott Adam. The Characteristics of Failed AGR Fuel. NNL Internal report, NNL (10) 1(8):1–39, 2012.

Thermal Treatment

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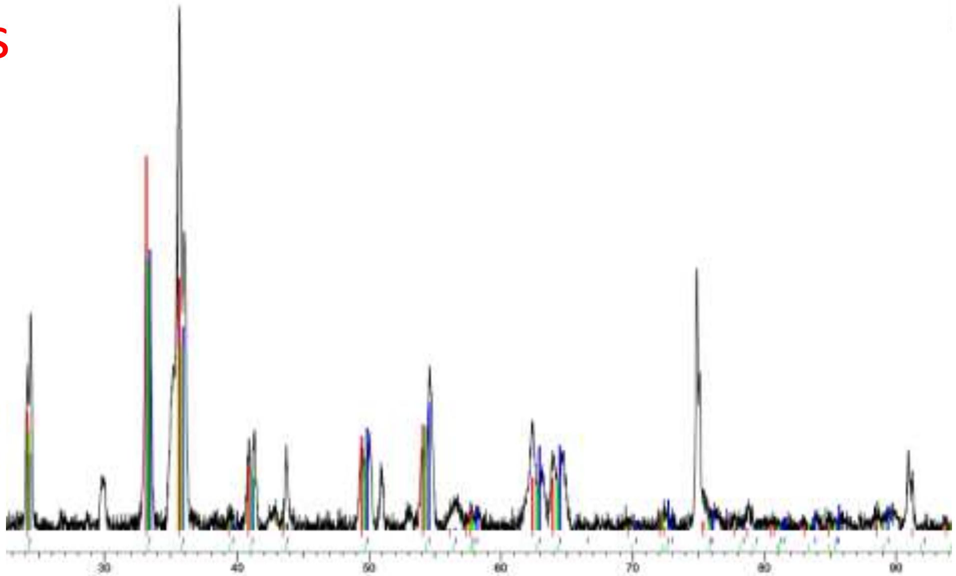
Heat treatment

- 1150 ^{o}C 30 minutes
- 600 ^{o}C 2 weeks
- SS is sensitised
- In aqueous environments may be susceptible to **Intergranular Corrosion (IGC)**

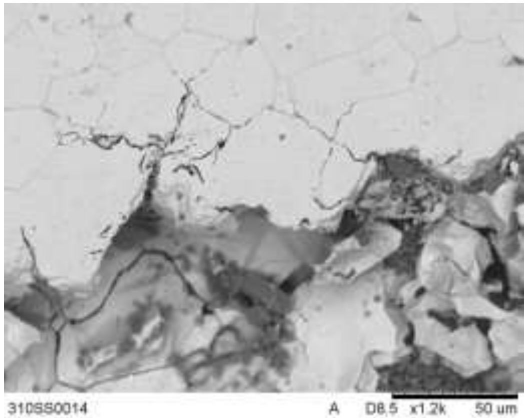
XRD Characterisation

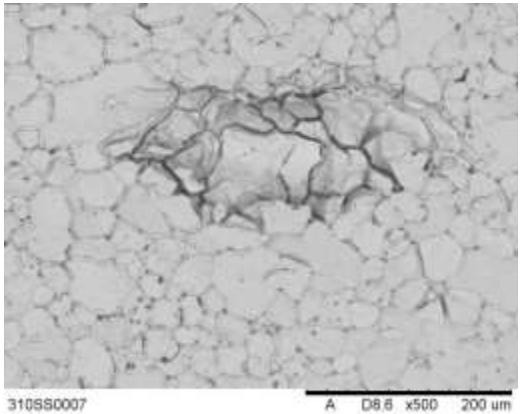
- Hematite iron oxide present

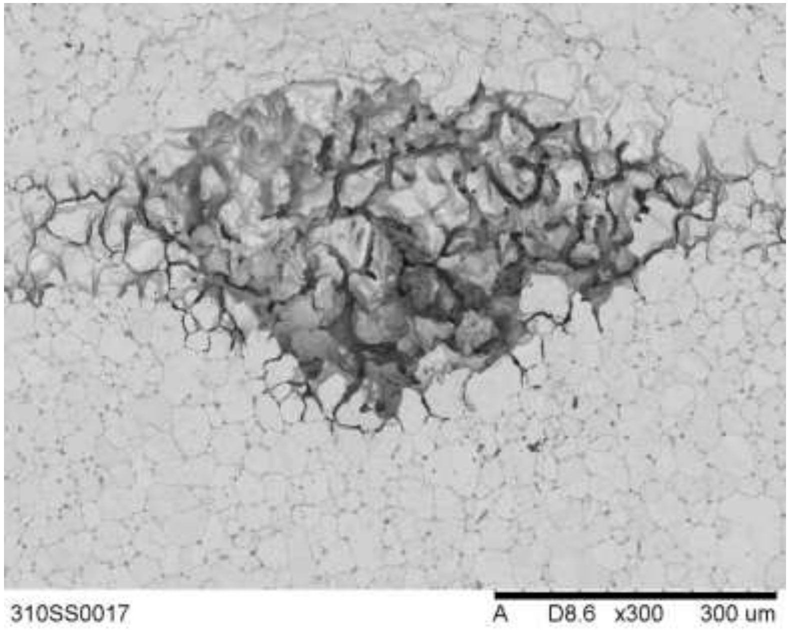


Intergranular Corrosion

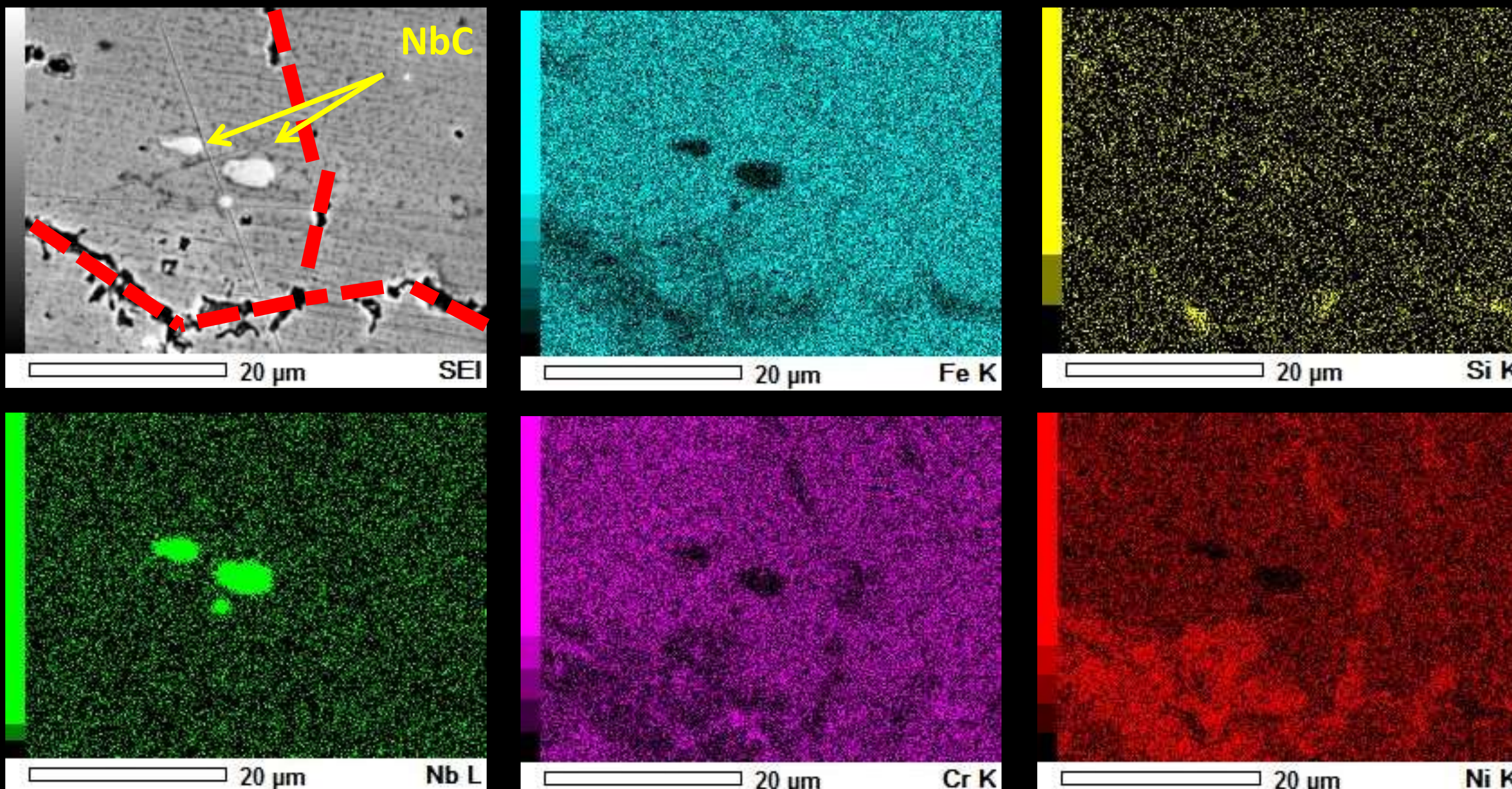
- IGC is a type of corrosion affecting grain boundaries
- Attack is focussed on Cr-depleted zones
- Example given: Sensitised 310SS exposed to 10 wt% $FeCl_3$, Crevice sites, 24 Hr





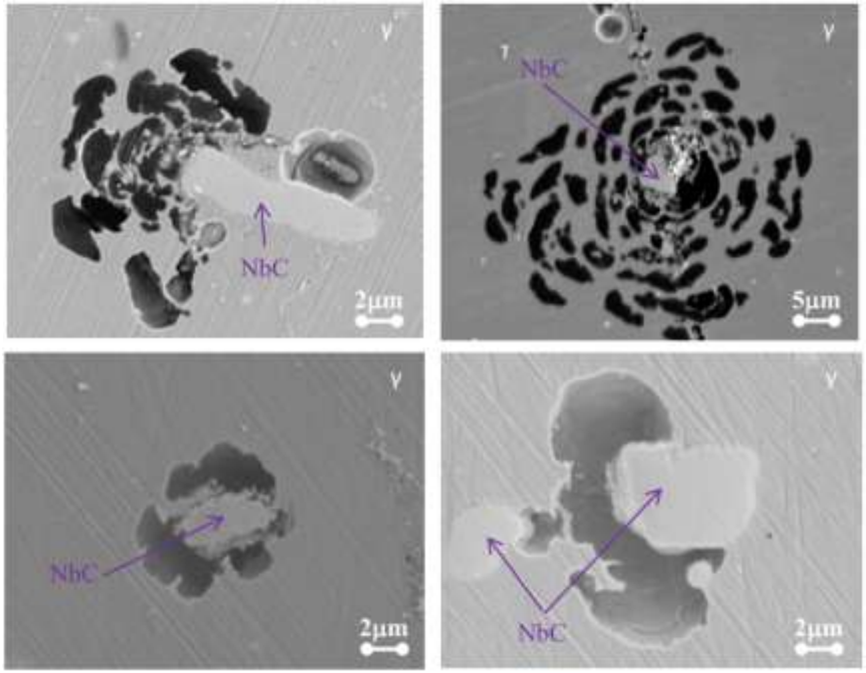


SEM/EDS



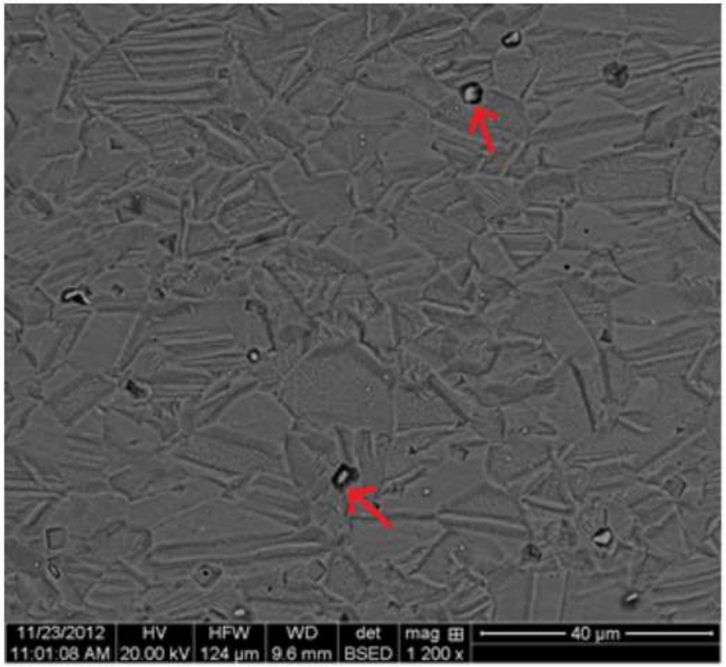
Fe and Cr depletion Ni and Si enrichment

Niobium Carbide



Post corrosion (polarised) SEM analysis of sensitised 800^{o}C, 192 Hr 20-25-Nb tube where pits initiate at NbC inclusions.

C. H. Phuah, "Corrosion of Thermally-Aged Advanced Gas Reactor Fuel Cladding," Imperial College London, 2012.

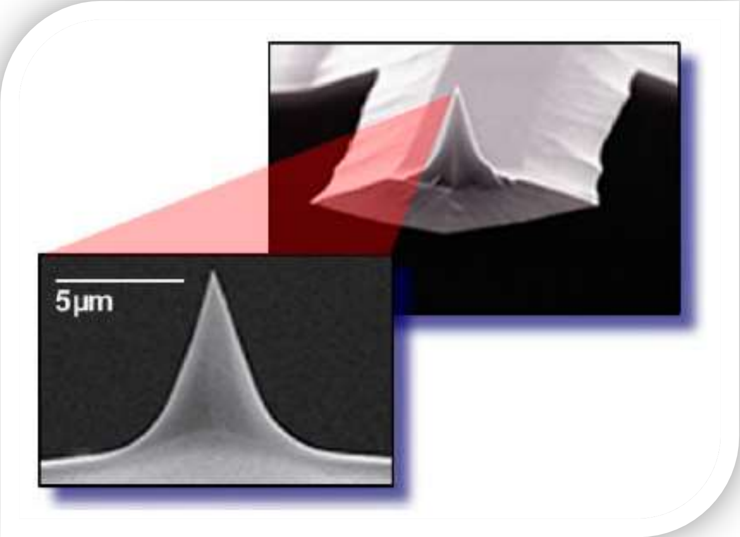


"Localised corrosion seems to nucleate on NbC interfaces"

C. M. Chan, "Localised Corrosion of AGR Fuel Cladding, 2nd NDA seminar, Manchester, 2013."

AFM / SKPFM

- Atomic Force Microscopy (AFM) is a type of scanning probe microscopy
- Probe is in the form of a small cantilever which rasters across the surface under interaction of localised forces
- Using feedback from the topography, the probe hovers at a user defined height (50 nm) to conduct Scanning Kelvin Probe-Force Microscopy (SKP-FM) mapping
- Analysis of **Volta potential differences** on the microscale allows for evaluation on the **relative nobility** of phases within the SS



AFM - Carbide Site

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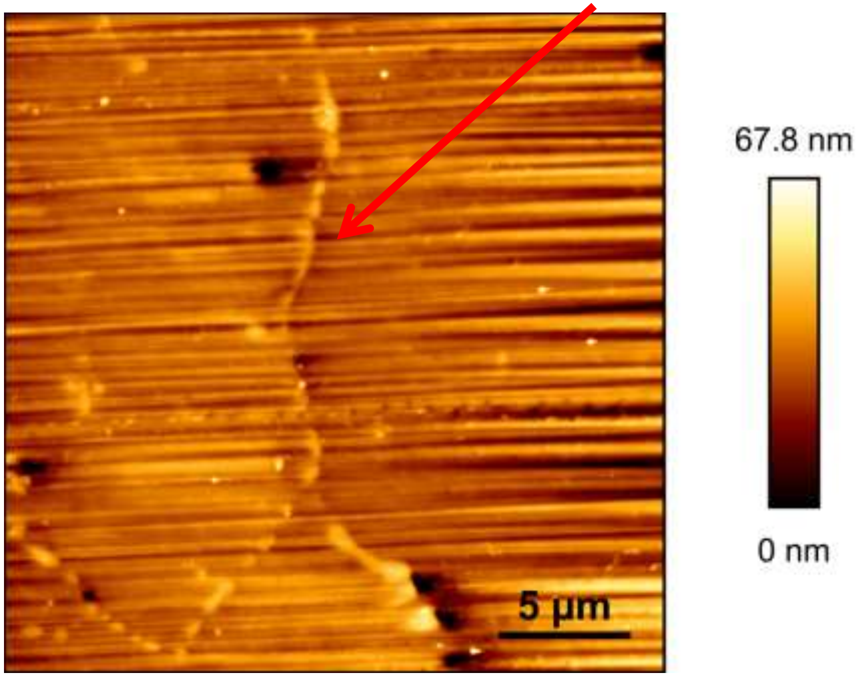
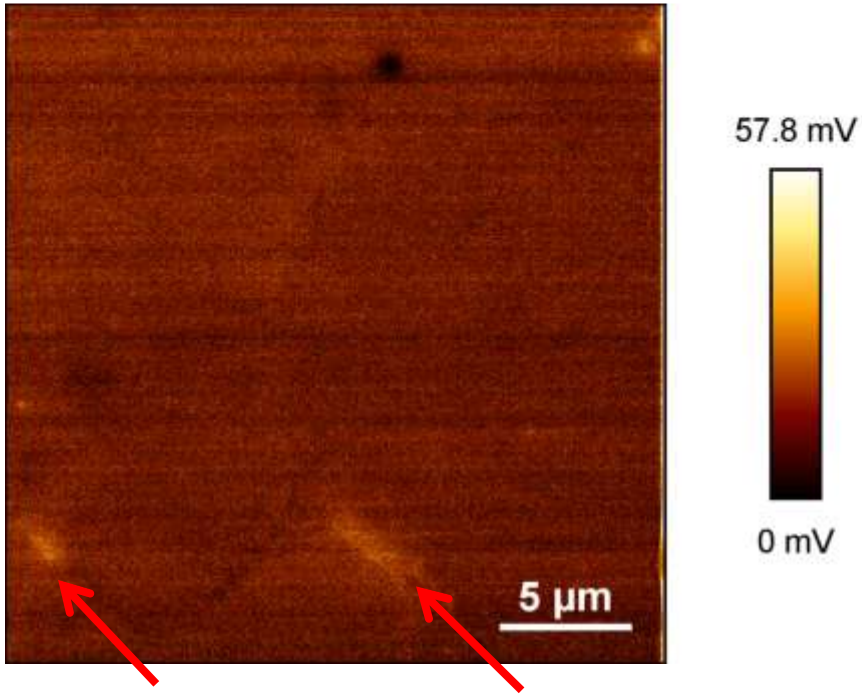
AFM

Cr-carbides



KPM



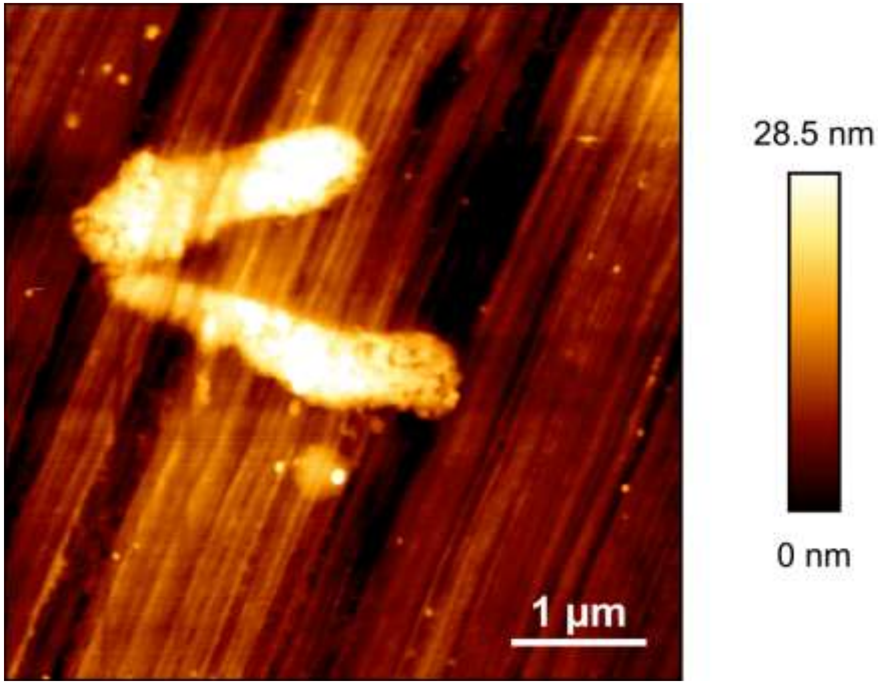
AFM: Lighter areas proud of matrix

KPM: Darker areas represent nobility

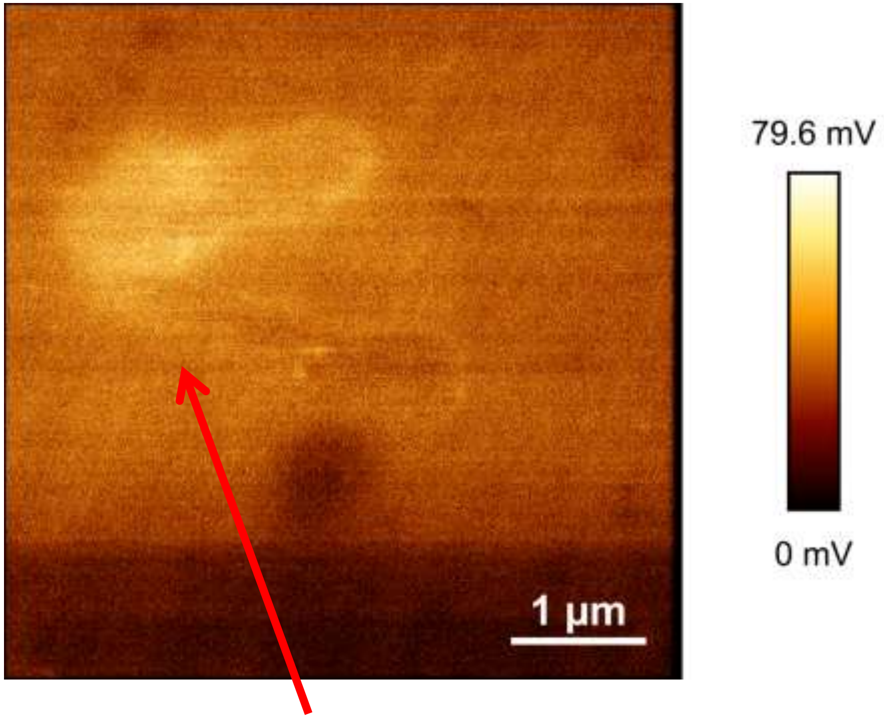
Not all GBs show high Volta potentials

AFM - Carbide Site

AFM



KPM



Cr carbide appears to show a higher potential wrt matrix

AFM - Carbide Site

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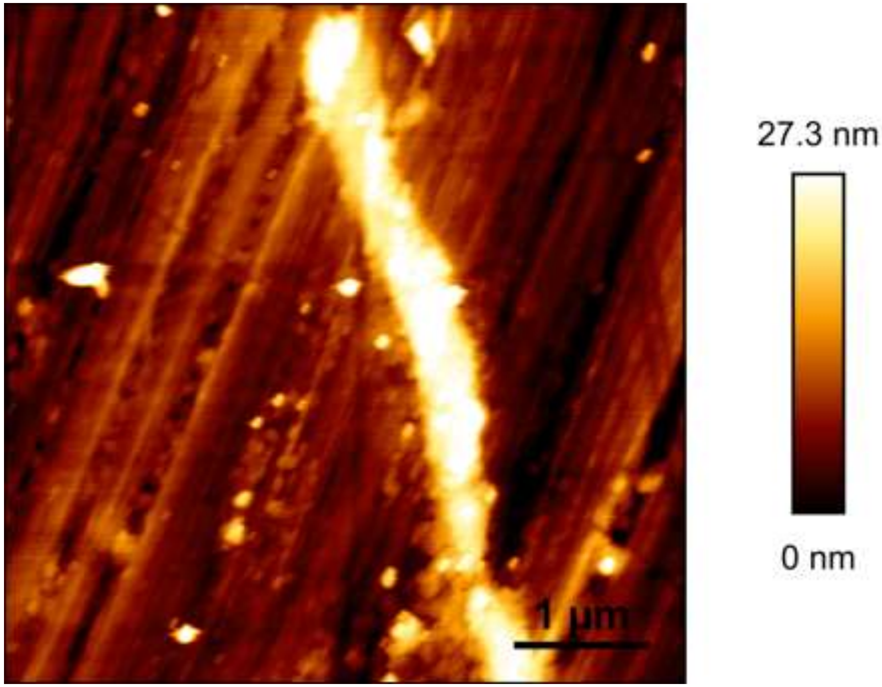
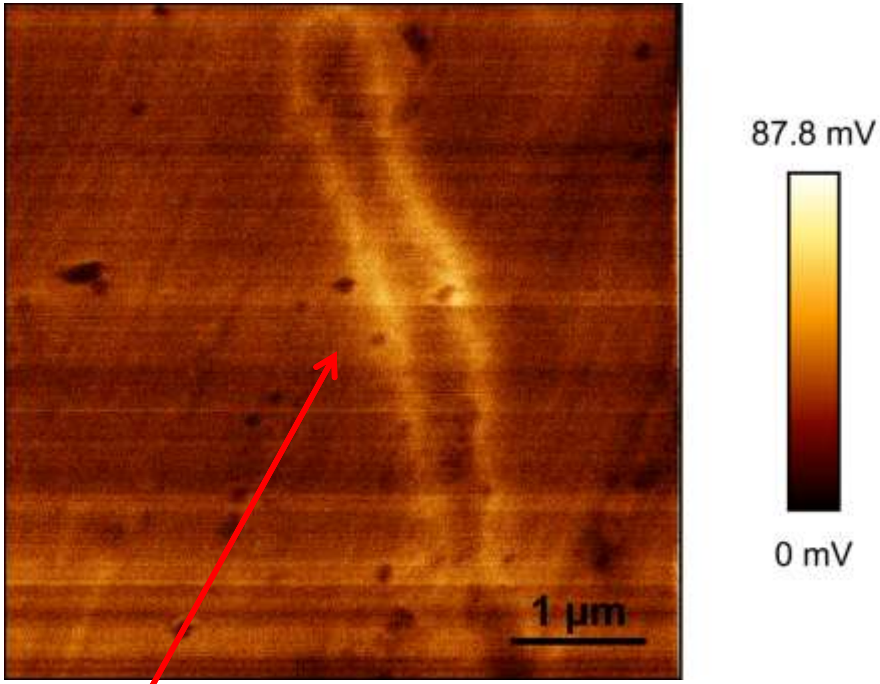
AFM



KPM



Heavily Cr-depleted area, discrete areas sensitive to IGC

AFM - NbC Site

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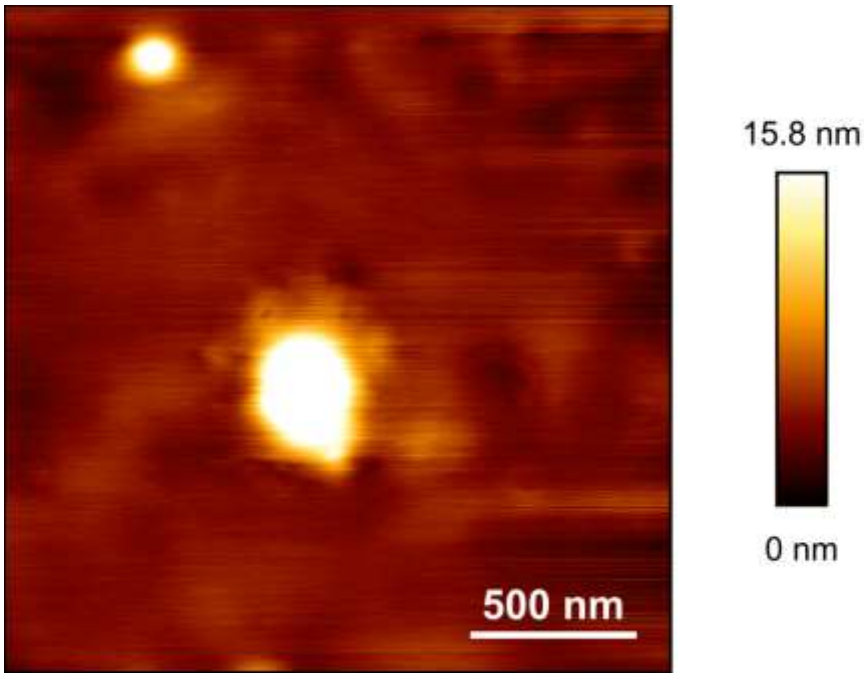
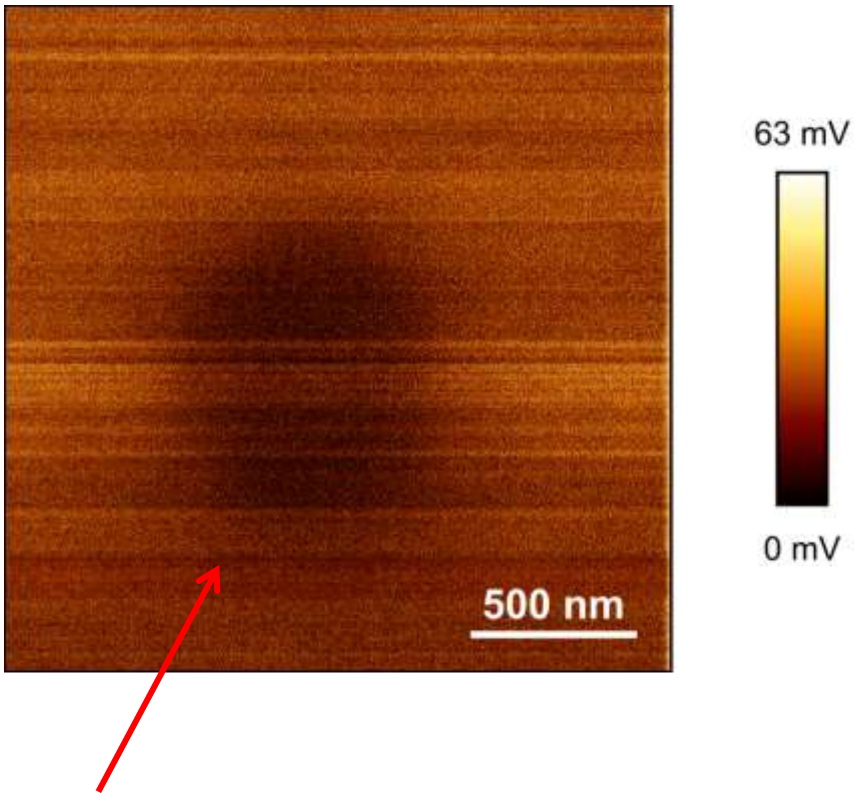
AFM



KPM



NbC acts cathodic with respect to the matrix

DL-EPR Test

- Test for sensitisation
- 0.5 Mol dm^{-3} sulphuric acid + 0.01 Mol dm^{-3} potassium thiocyanate
- Ratio of charge and current are a function of the degree of sensitisation (DOS)
- Both current and charge decrease with polish depth

- → **Less sensitised away from surface**

	Anodic charge, C	Repassivation charge, C	Anodic max current, mA	Repassivation max current, mA	Ratio (Charge)	Ratio (Current)
Scale	179.2	66.3	117	56	**0.37**	**0.48**
22 µm Polish	247.5	50.2	141.1	55.2	**0.2**	**0.39**
70 µm Polish	298.4	54.48	149	57	**0.18**	**0.38**

Specimen Preparation Technique

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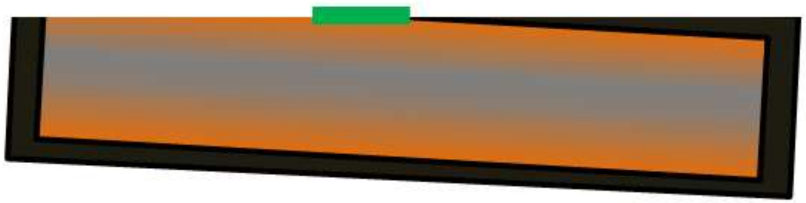
Swansea University Prifysgol Abertawe

- Mount specimen in resin at an oblique angle
- Grind hematite scale away
- This leaves highly sensitised areas to be investigated
- Green area represents area to be imaged
- The dark outer box represents the Hematite oxide which forms after conducting the heat treatment
- Orange sections represent areas in which there is a greater degree of sensitisation, compared to the grey area in the centre



Time Lapse Microscopy

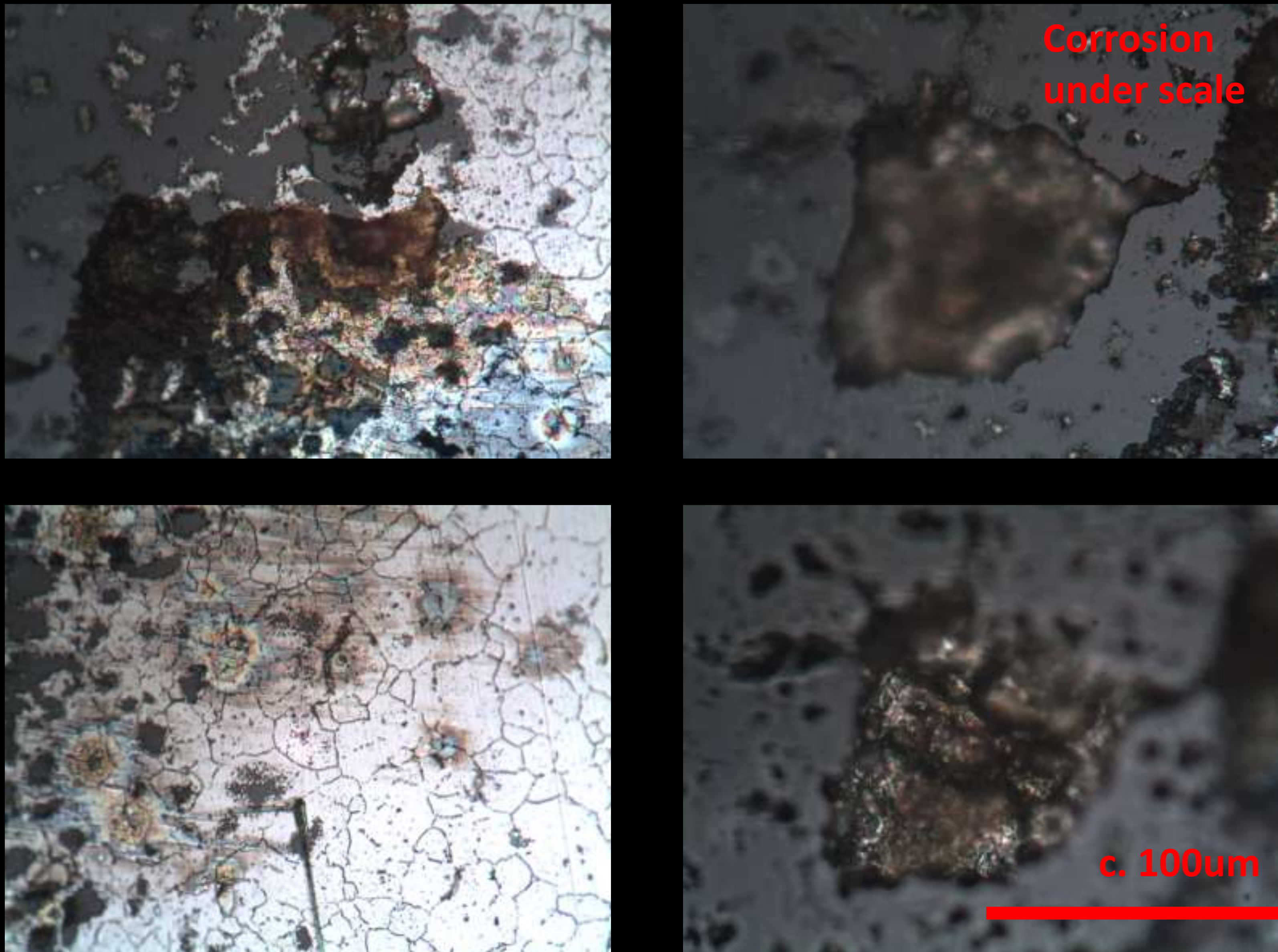
c. 175um

3 Mol dm^{-3} NaCl, OCP, 48hr

c. 400um

Pre/Post Experiment

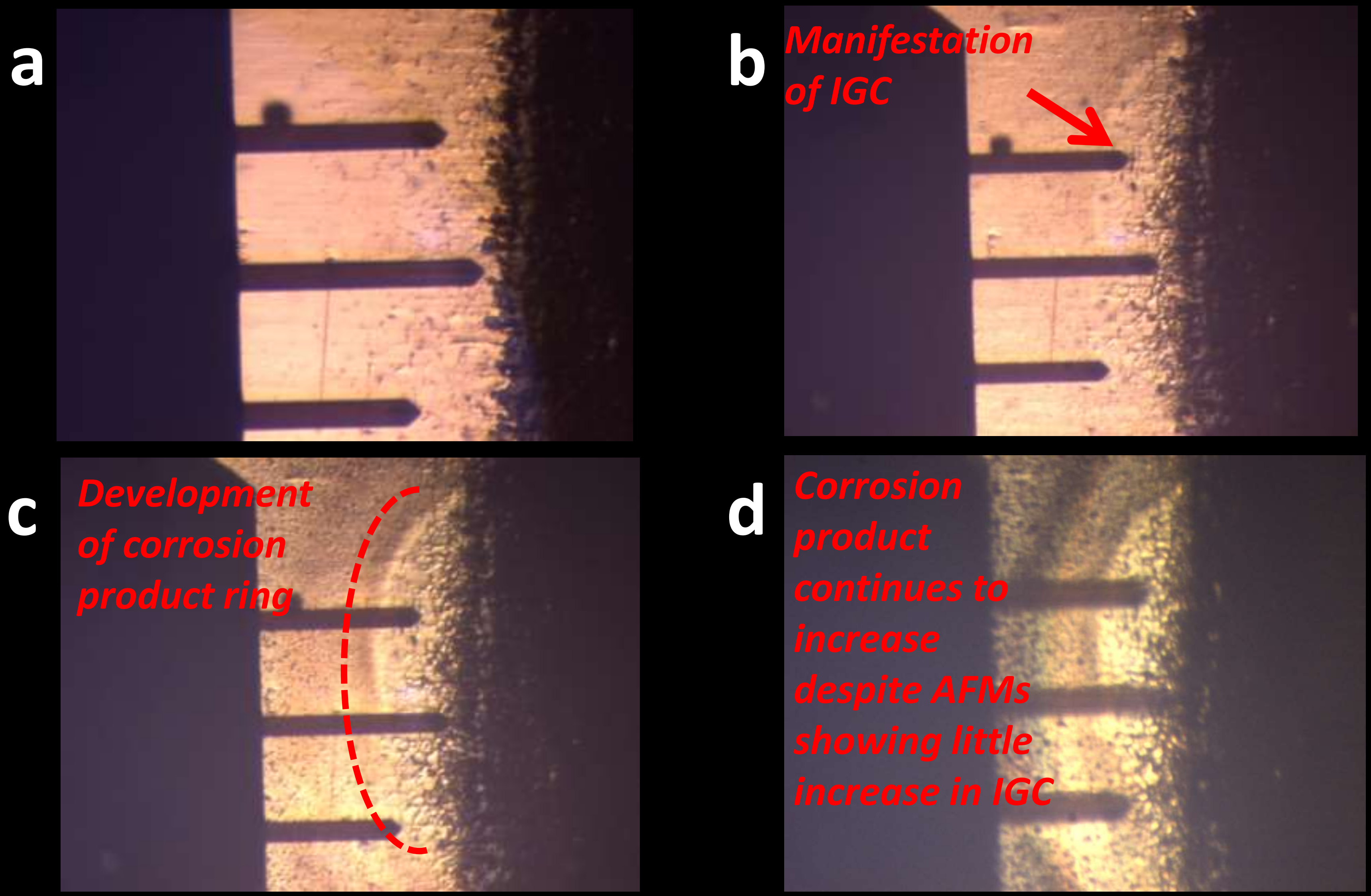
c. 400um


Corrosion
under scale
c. 100um

TL-AFM

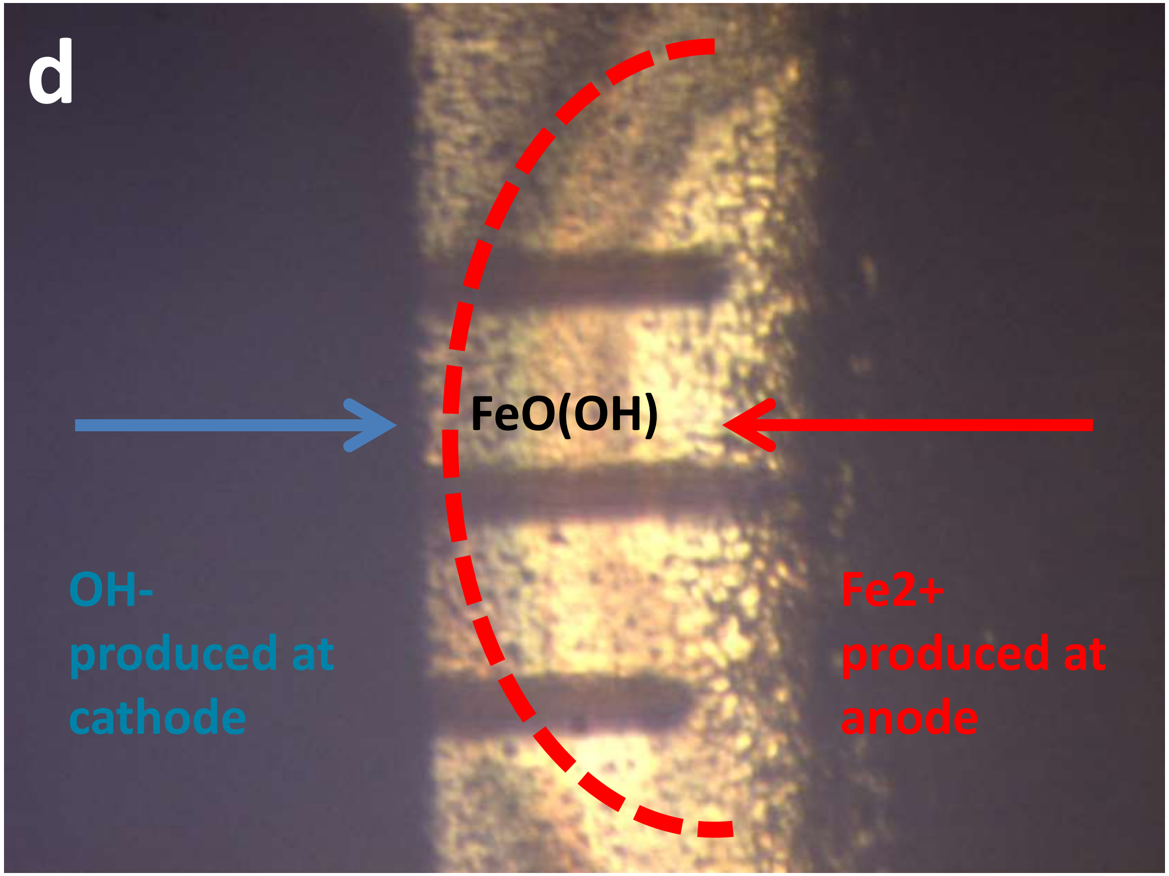
- Electrochemical cell glass block used with o-ring
- Contact mode imaging used with low (relative) setpoint; 0.36 V - 0.51 V
- Tip velocity 30 μs^{-1} (0.3 Hz line rate)
- 50 μm^2 scans = ~30 mins
- 1 Mol dm^{-3} NaCl

TL-AFM Optical



TL-AFMs at (a) 30, (b) 60, (c) 120, (d) 240 minutes Immersion at open circuit potential in 1 Mol dm-3

Corrosion Product



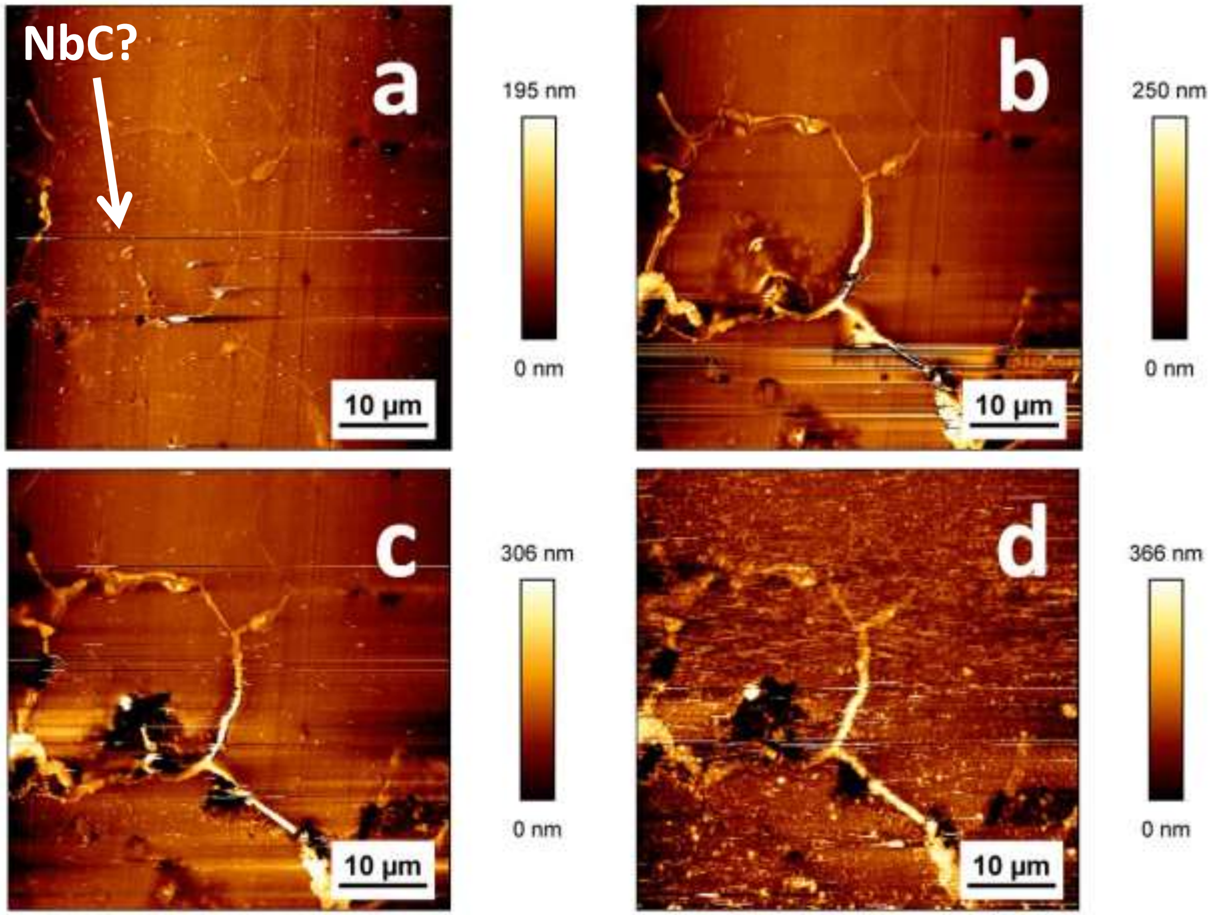
$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

$$Fe^{2+} + 8FeO(OH) + 2e^{-} \rightleftarrows 3Fe_3O_4 + 4H_2O$$

$$3Fe_3O_4 + 0.75O_2 + 4.5H_2O \rightleftarrows 9FeO(OH)$$

S. B. Lyon, "Corrosion of Carbon and Low Alloy Steels," *Shreir's Corros.*, 2009.

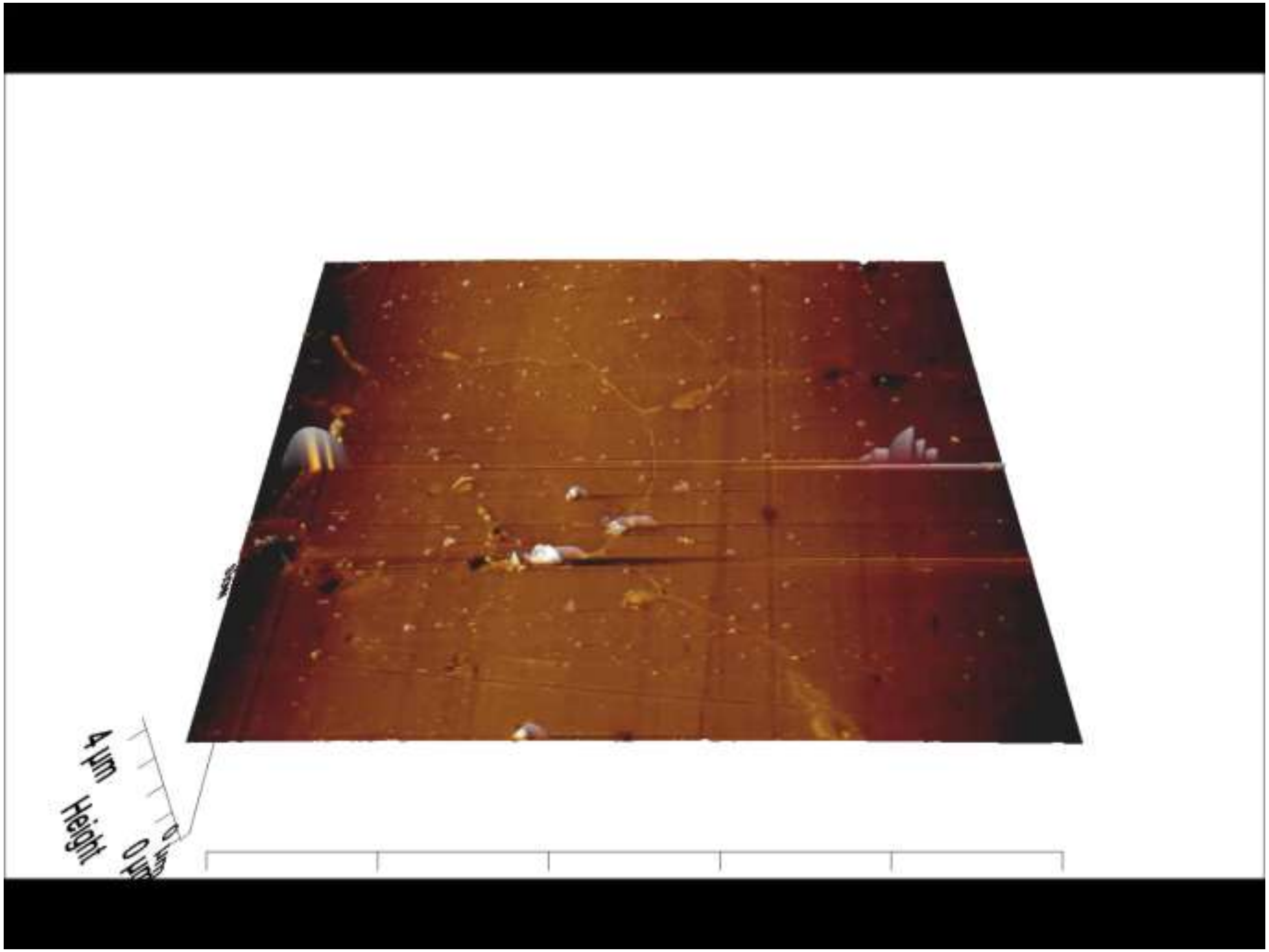
TL-AFM



- **Anodes appear as intergranular pits**
- **Pit covers evident**
- **Grain boundary swelling**
- **Corrosion around what appears to be NbC inclusion**

TL-AFMs at (a) 30, (b) 60, (c) 120, (d) 240 minutes Immersion at open circuit potential in 1 Mol dm-3

TL-AFM 3D



- Each frame = 30 mins
- Corrosion pits but **passivate** rapidly as **pit covers disturbed**
- Large amount of corrosion product visible

Conclusions

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- RIS simulated by a heat treatment
- NbC still present after solution anneal (SEM/EDS)
- NbC appear **noble** wrt matrix (SKPFM)

- *In-situ* IGC successfully imaged (Optical, AFM)
- IGC does not appear to affect NbC (TL-AFM)
- NbC appears to be acting as a **cathodic activator** (TL-AFM)

- Corrosion initiates at inclusion, and highly sensitised grain boundaries through an <u>intergranular pitting mechanism</u>

Acknowledgements

- Geraint Williams
- Steve Walters
- Justin Searle
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- May Chan
- MACH1, Swansea University

- Nuclear Decommissioning Authority
- National Nuclear Laboratory
- Westinghouse fuels Ltd.

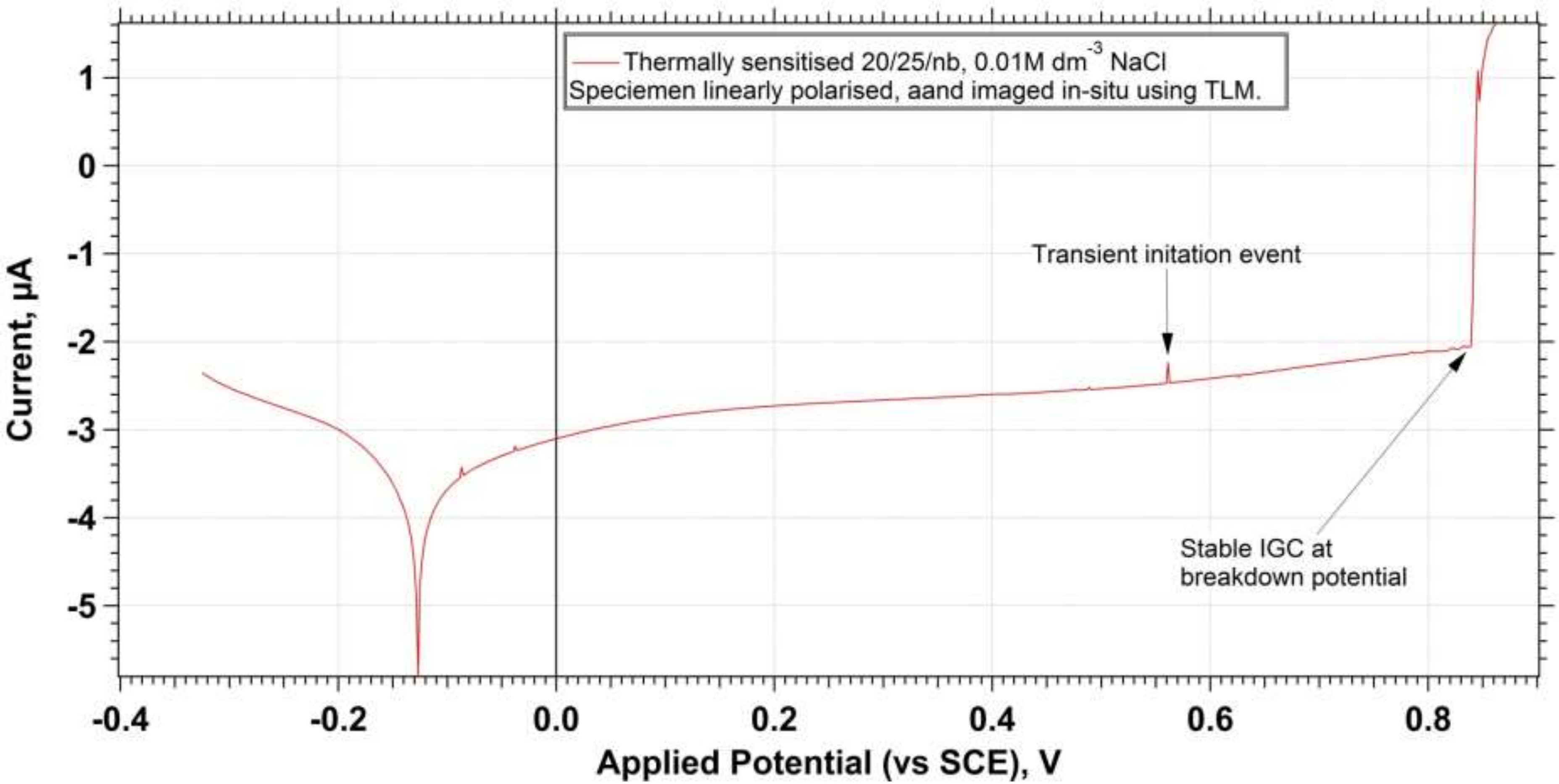
Thank you!!

EXTRA SLIDES

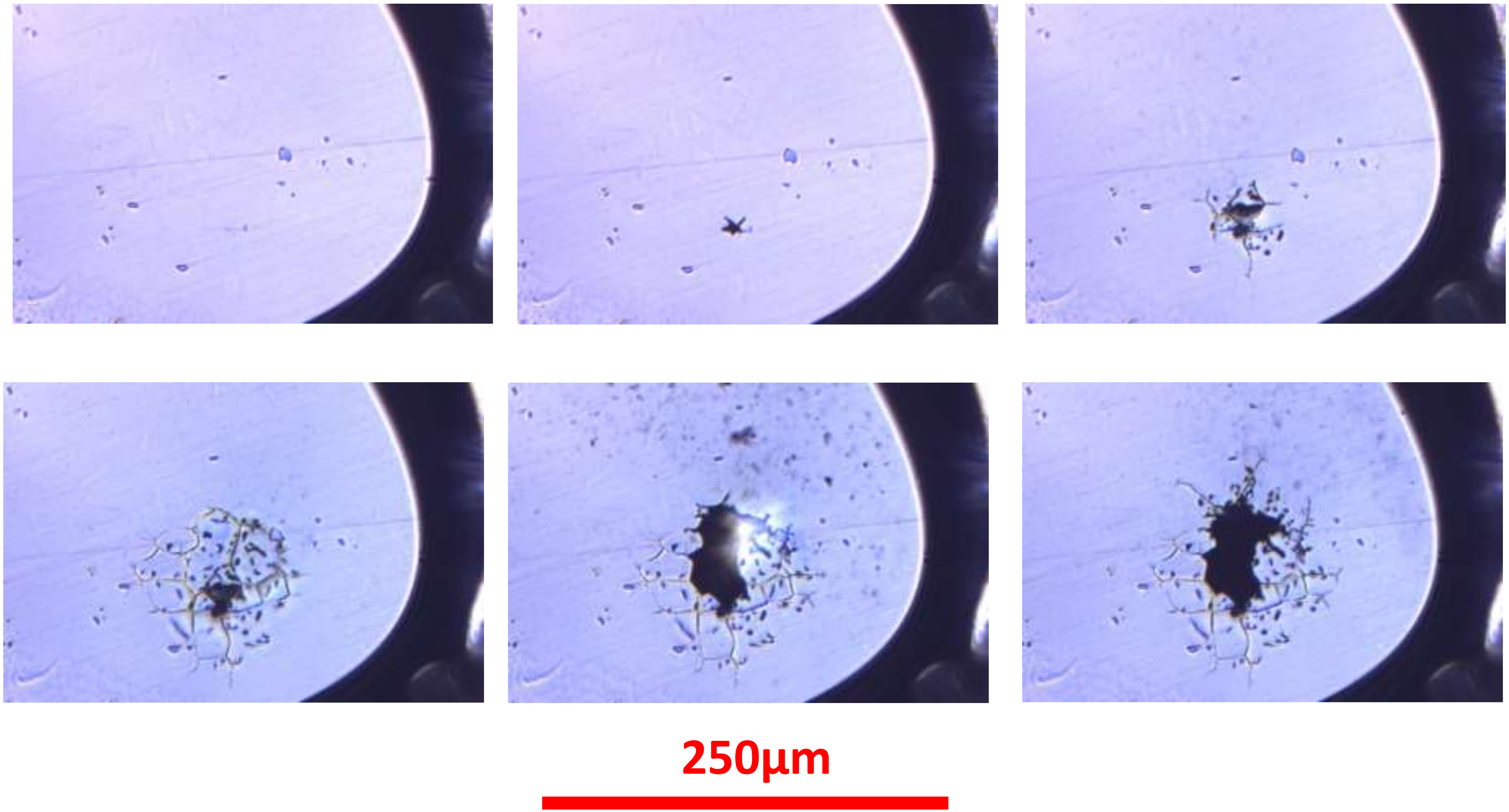
Polarised Time-lapse Microscopy

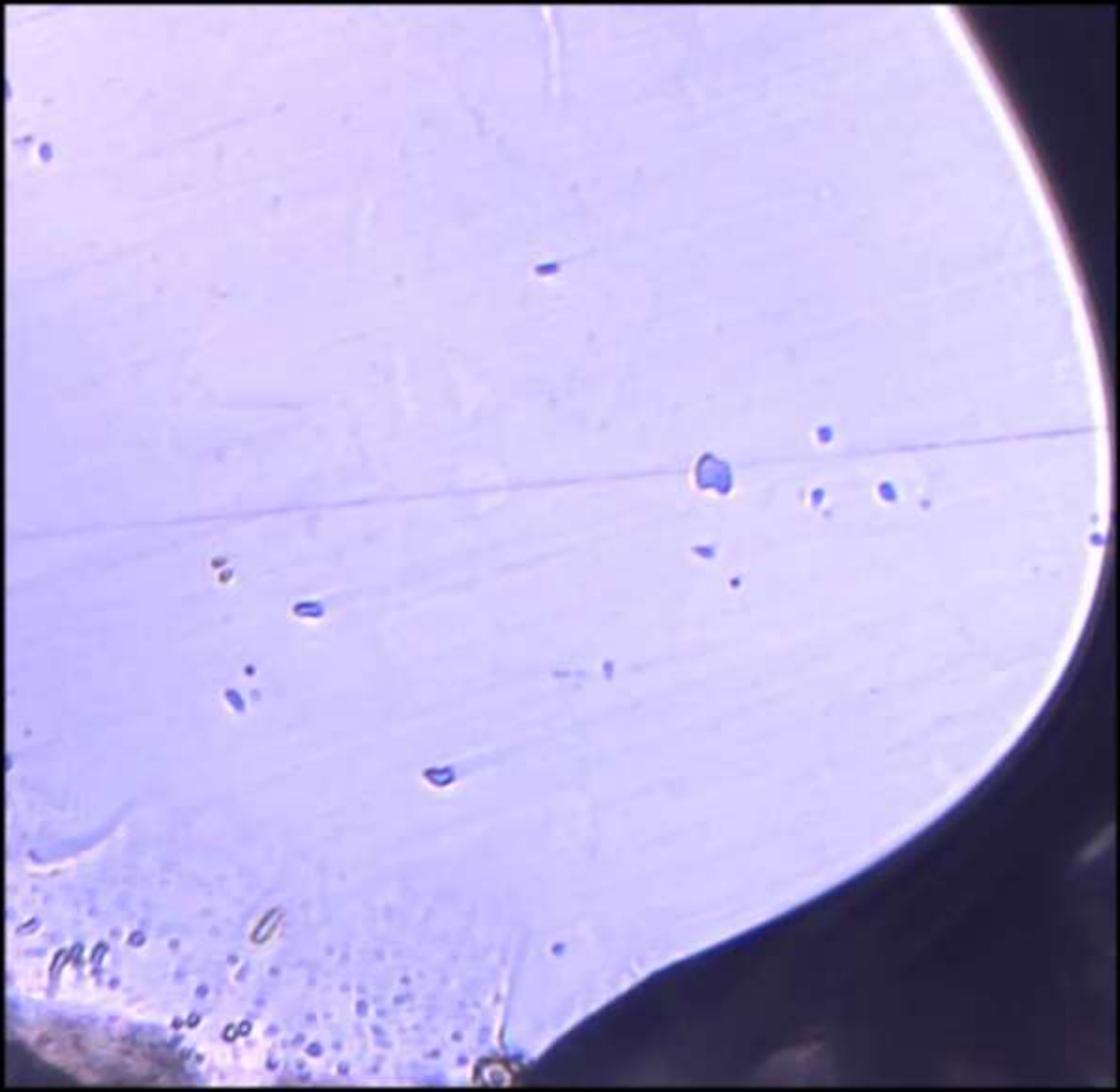
- 0.01 Mol dm^{-3} NaCl
- SCE reference, Pt gauze counter electrode
- Corrosion follows grain boundaries
- **Intergranular-pitting** mechanism present
- IGC initiates at surface scratch which is also the location of **triple point grain boundary**
- **NbC** inclusions appear to be **unaffected** (perturbed system)

Potentiodynamic Trace



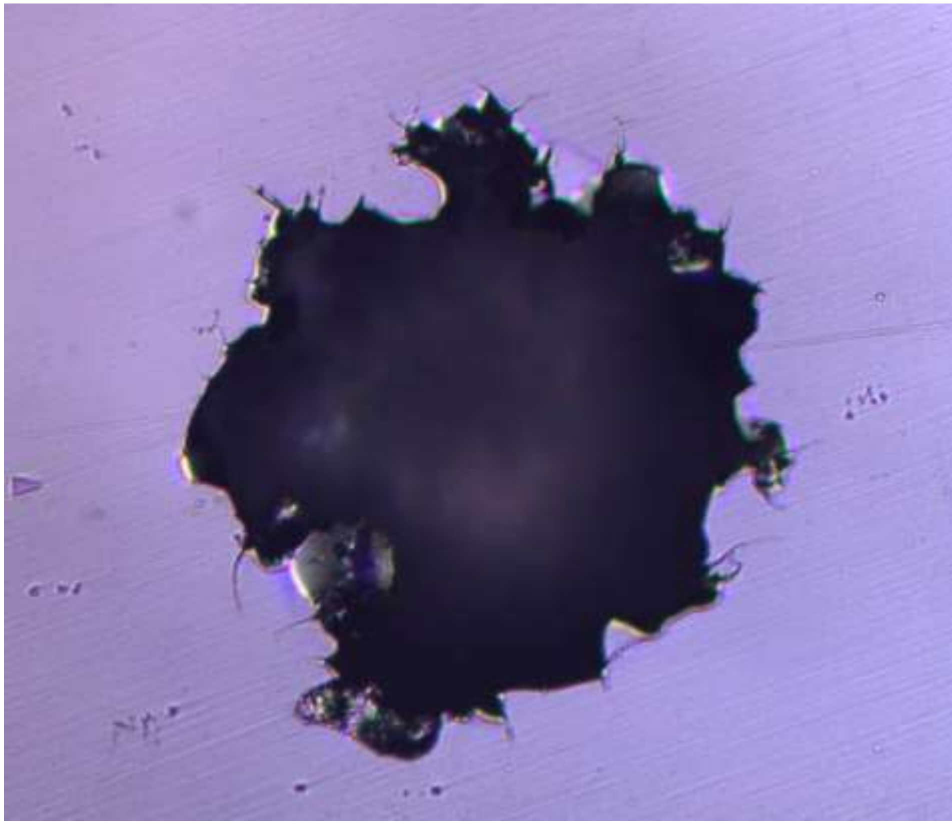
TLM

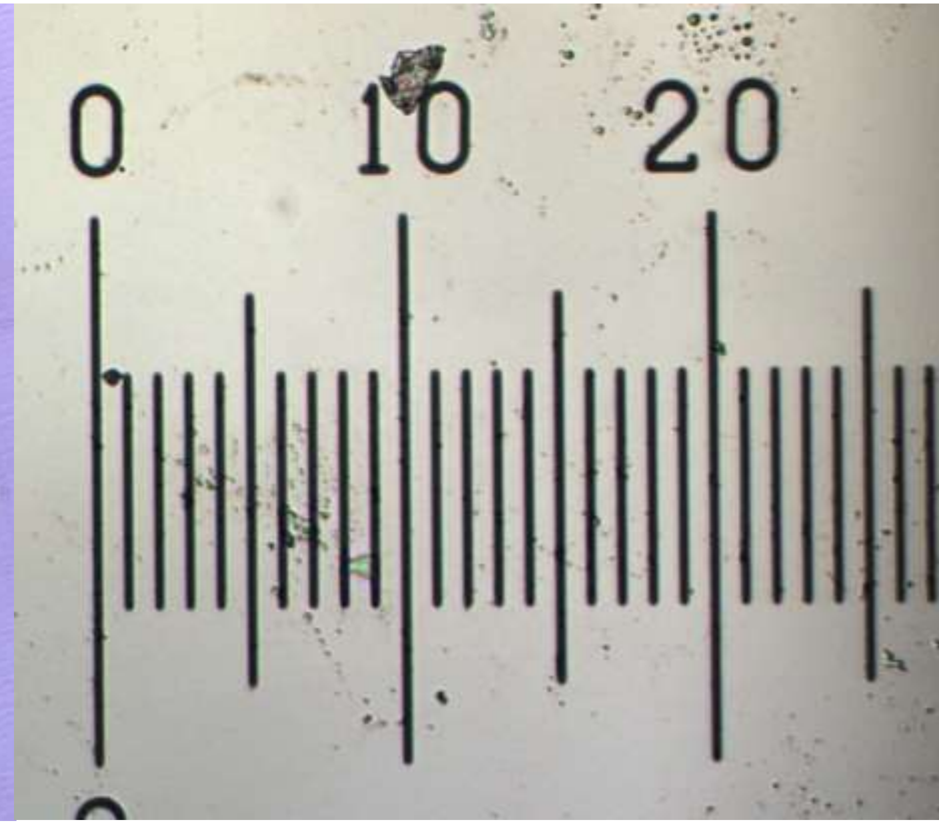




200μm

Post TLM - Optical





IG Pitting