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Direct Observations of Corrosion Cracking in a TEM

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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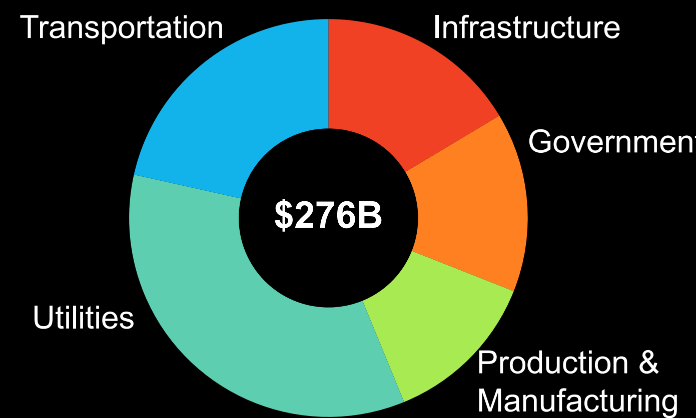
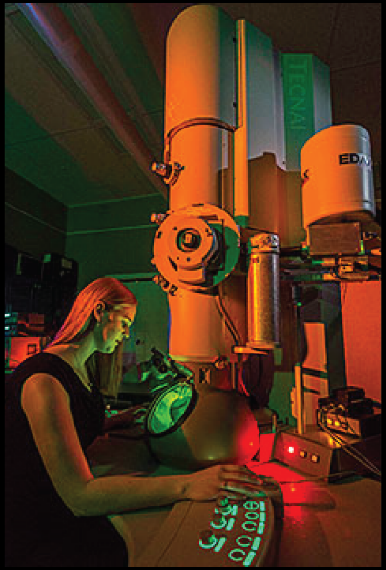
Motivation

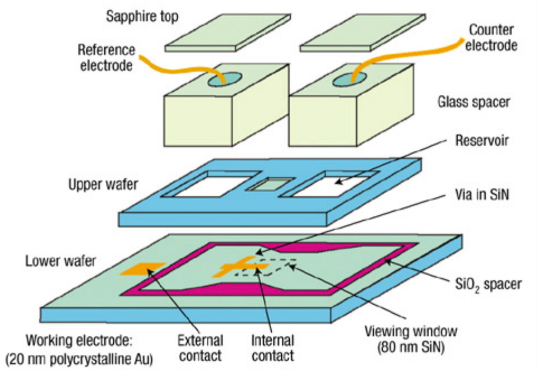
- Costly
  - R&D
  - Managing failures
- Complex
  - Environmental: solution composition, pH, temperature, pressure, flow rate, microbes
  - Material: composition, microstructure, surface treatments
- Experimental limitations
  - Macro-scale
  - Ex-situ
- TEM
  - Sub-Å spatial resolution
  - Sub-ms temporal resolution
- In-Situ TEM Experiments
  - Chip-based systems
  - Commercial holders
  - Very few metals corrosion experiments

US Corrosion Costs



nace.org



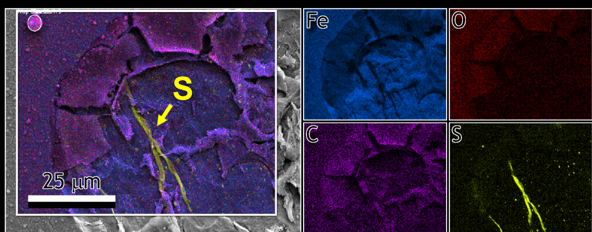


MJ Williamson, et. al., Nature Mat. 2, 2003

Background

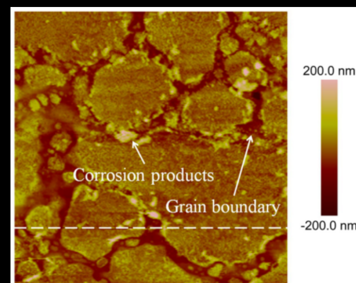
- Macro-Scale/Ex-Situ Corrosion

Pitting linked to impurities



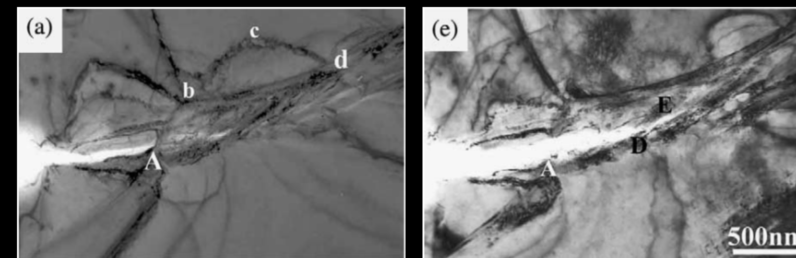
Aramco Services Company

GB preferential etching



P Bei, et.al., Corr Sci 93, 2015

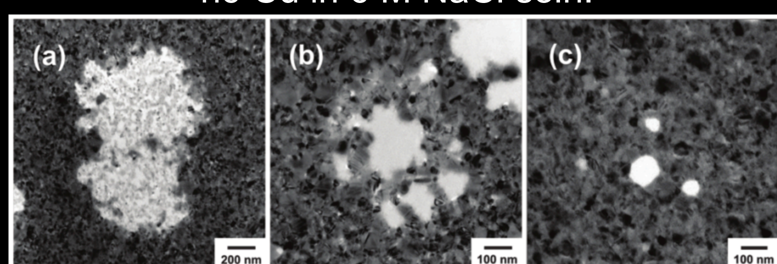
Corrosion-enhanced plasticity



JX Li, etl.al., Corr Sci 45, 2003

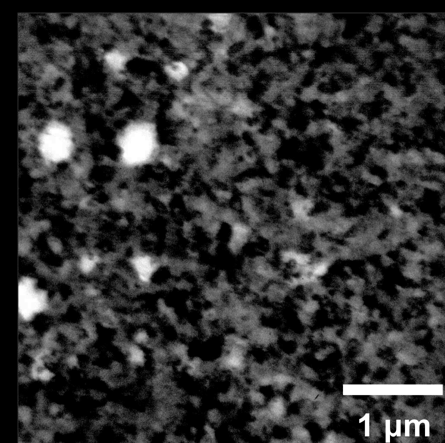
- In-Situ TEM Corrosion
  - Highly localized events
  - Model materials: Al, Cu, Fe

nc-Cu in 6 M NaCl soln.



SW Chee, et.al., Chem Comm 51, 2015

nc-Fe in acetic acid



D Gross, et.al., Ceramic Trans, MS&T'16

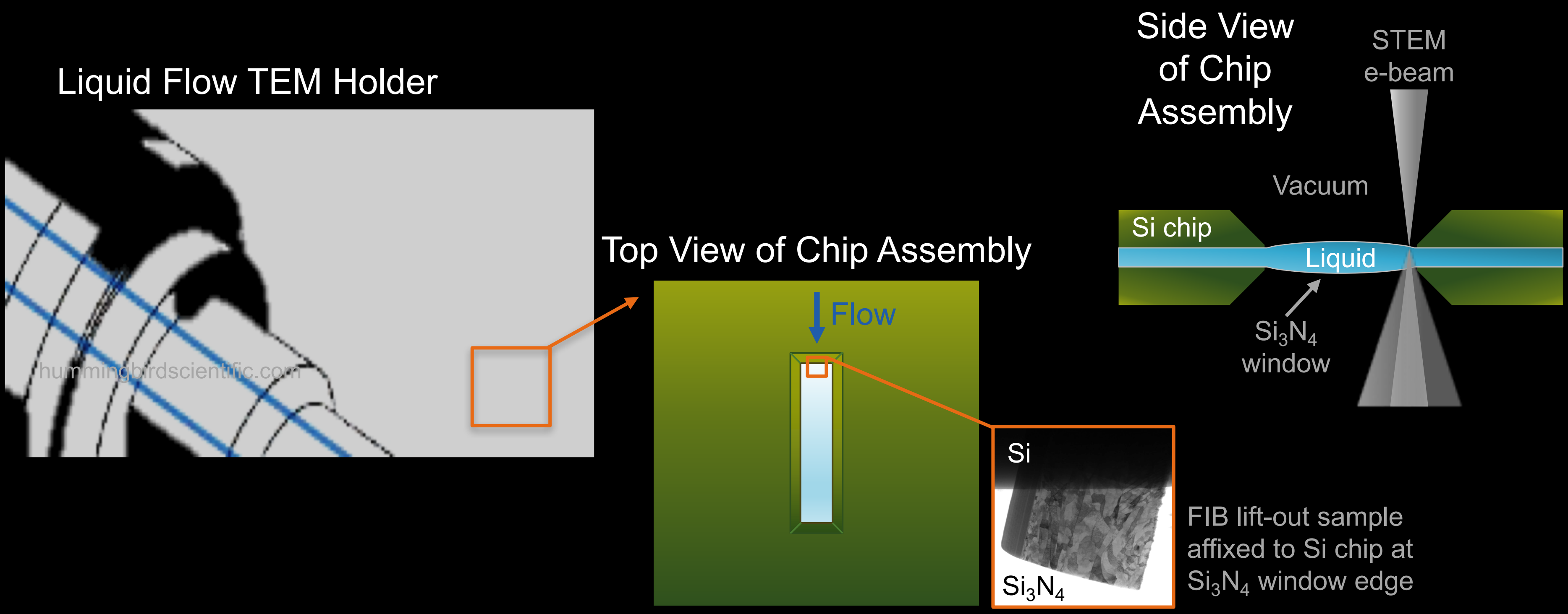
In-Situ TEM Corrosion

- Here we present a methodology to directly investigate the onset of corrosion at the nanoscale using in-situ TEM corrosion techniques
- Results from used pipeline steel in a sweet, aqueous environment

Chemical Composition of Pipe Steel (wt%, balance Fe)		
C 0.160	Ni 0.107	N 0.009
Mn 0.710	S 0.021	Al 0.003
Cu 0.345	Mo 0.017	Pb 0.002
Si 0.167	Sn 0.017	V 0.002
Cr 0.116	P 0.016	Ti 0.001

Experimental Setup

- 1018 steel from used Aramco pipeline
- Deionized H_2O with 1390 μM Na_2SO_4 and 6 μM CO_2
- 2 μL/min flowrate
- Low-dose STEM at 300 keV



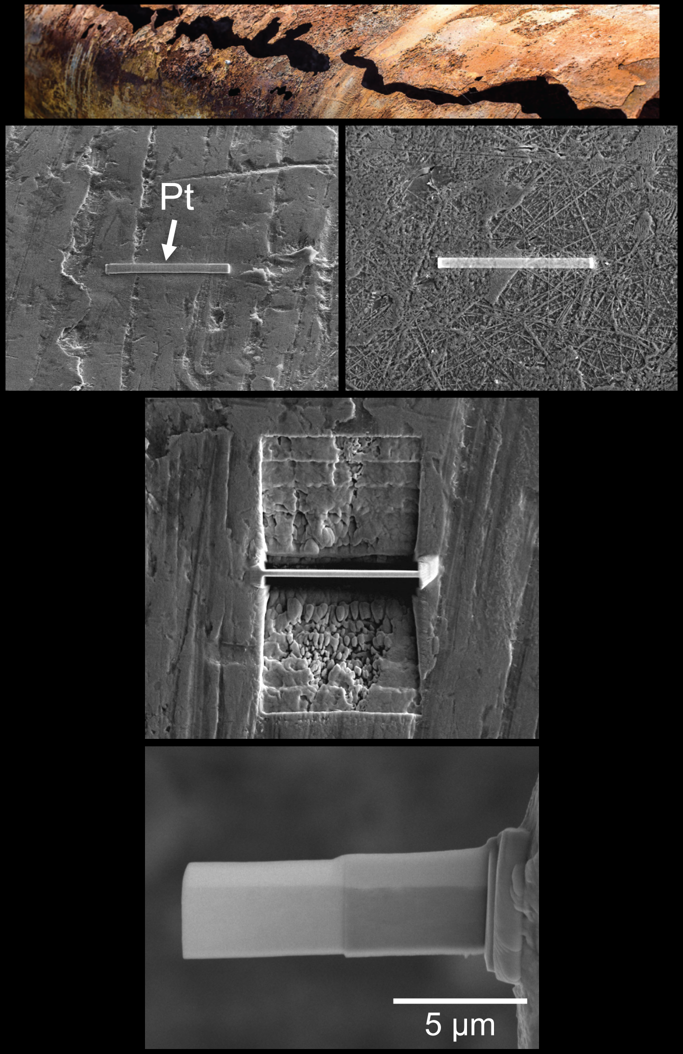
Electron Beam Effects

- Radiolysis of water[1]
  - Products include: e^{-}_{aq}, $H^{\bullet}$, $HO^{\bullet}$, $HO_2^{\bullet}$, OH^-, H_3O^+, H_2, H_2O_2
  - Dose-dependent yield
- Heating[2]
  - Only a few degrees can increase reaction kinetics
- Charge accumulation[3]

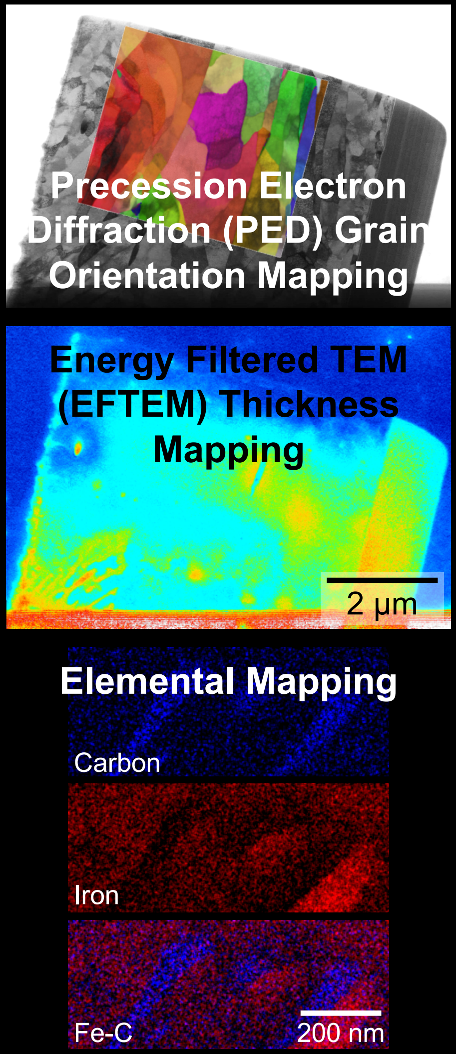
[1] S Le Caer, Water 3, 2011
[2] N de Jonge & FM Ross, Nature Nanotech 6, 2001
[3] TJ Woehl, et.al., Ultramicroscopy 127, 2013

Sample Preparation

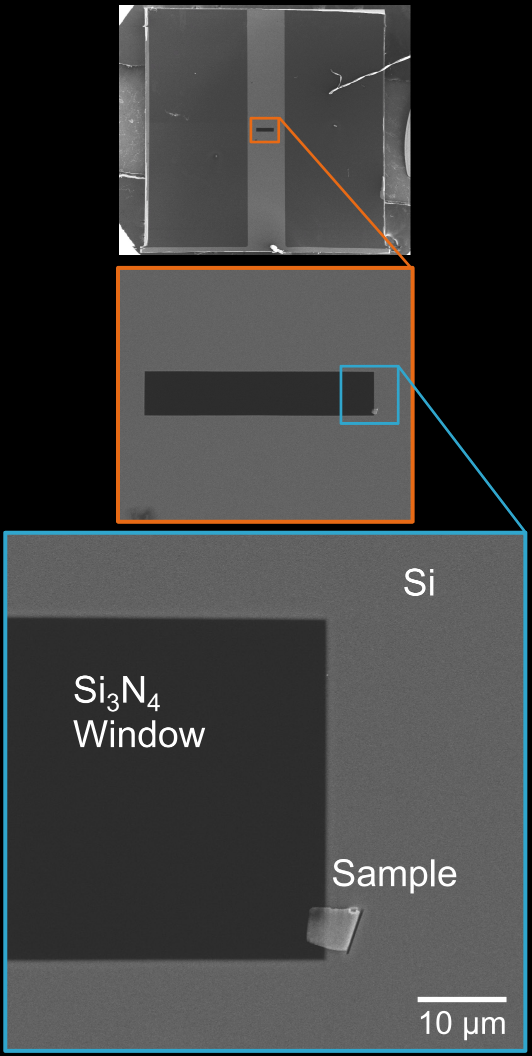
FIB Lift-Out



Characterization

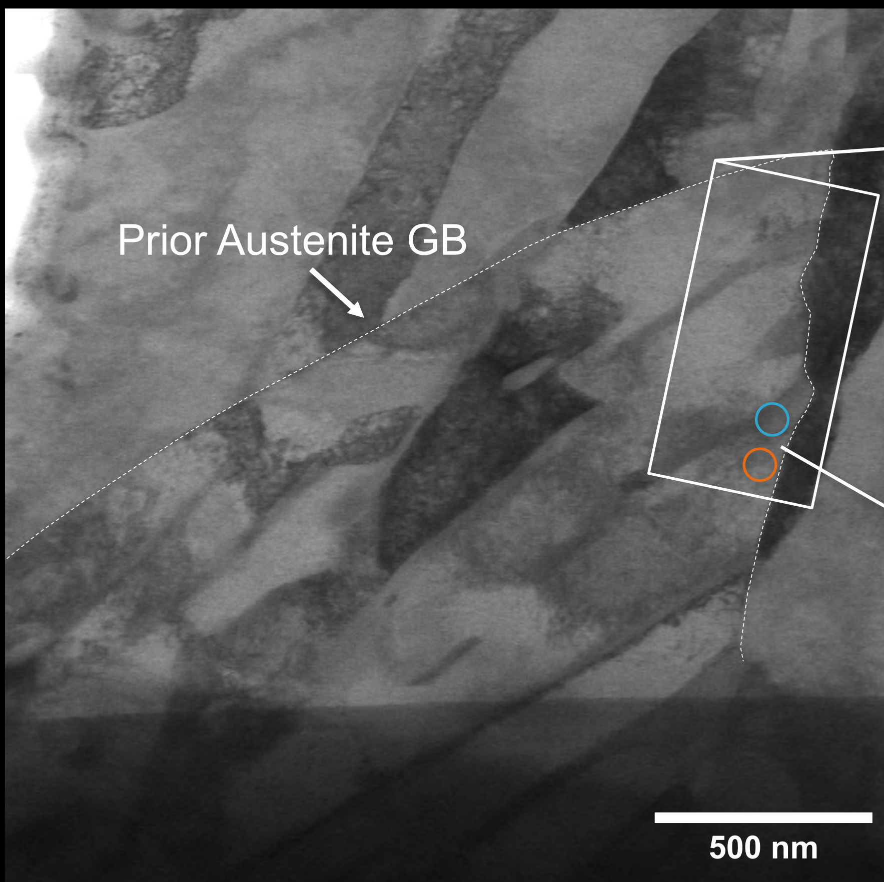


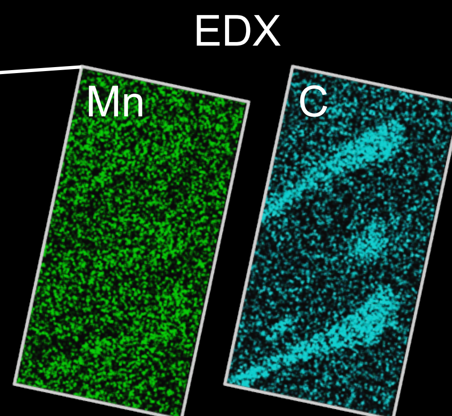
Transfer to LC Chip

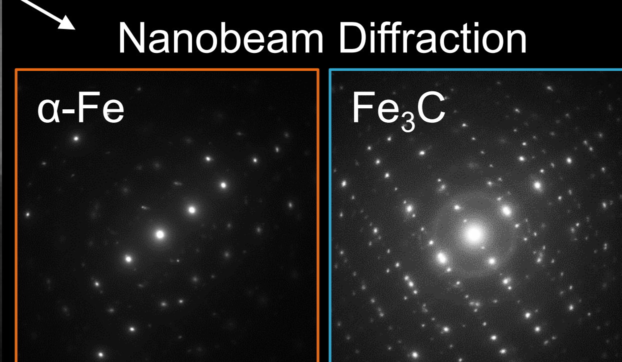


Initial Microstructure

- α-Fe and Mn-rich Fe_3C
- Pitsch-Petch OR







With Paul Kotula, SNL

Chemical Composition of Pipe Steel (wt%, balance Fe)		
C 0.160	Ni 0.107	N 0.009
Mn 0.710	S 0.021	Al 0.003
Cu 0.345	Mo 0.017	Pb 0.002
Si 0.167	Sn 0.017	V 0.002
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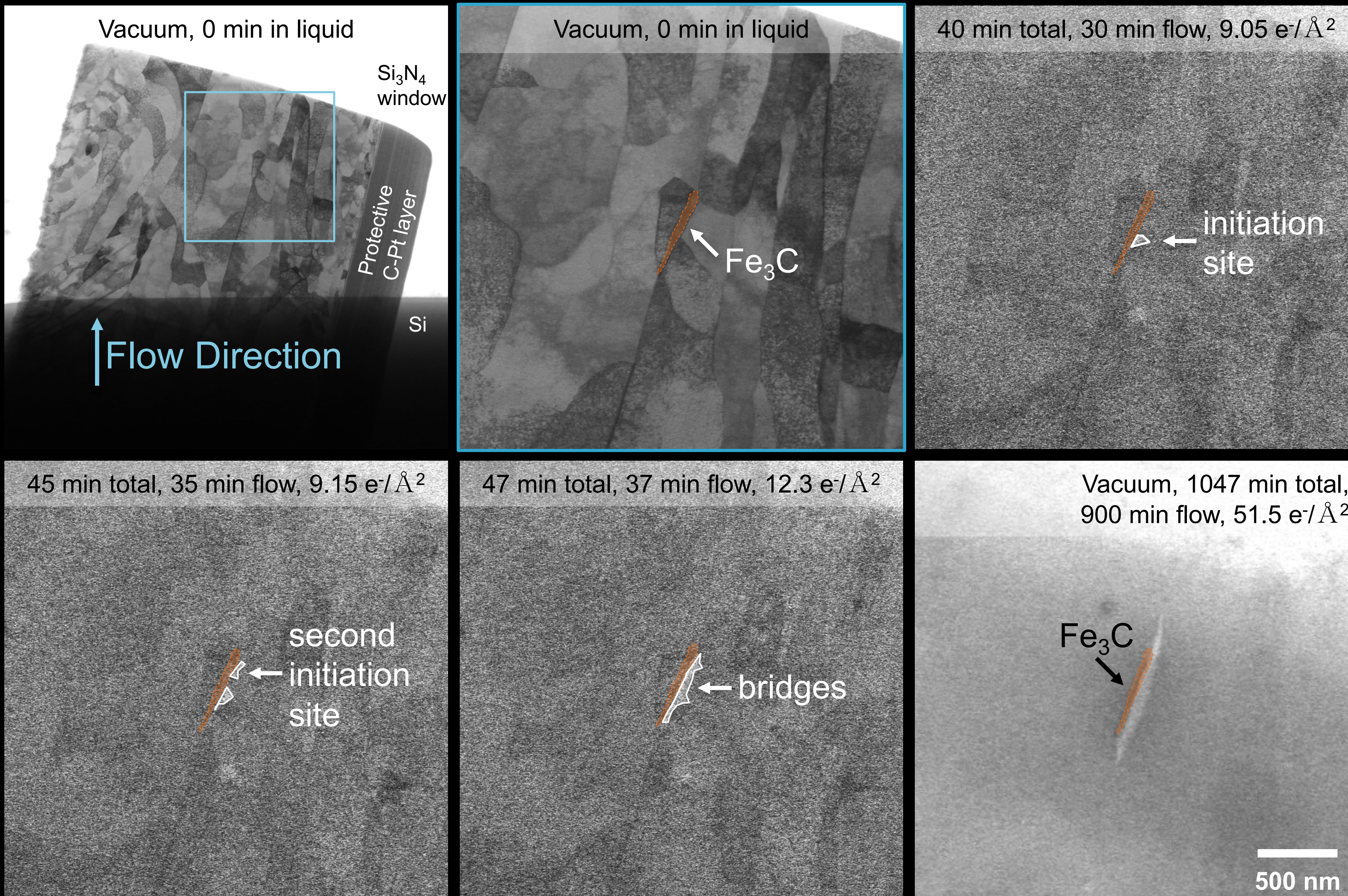
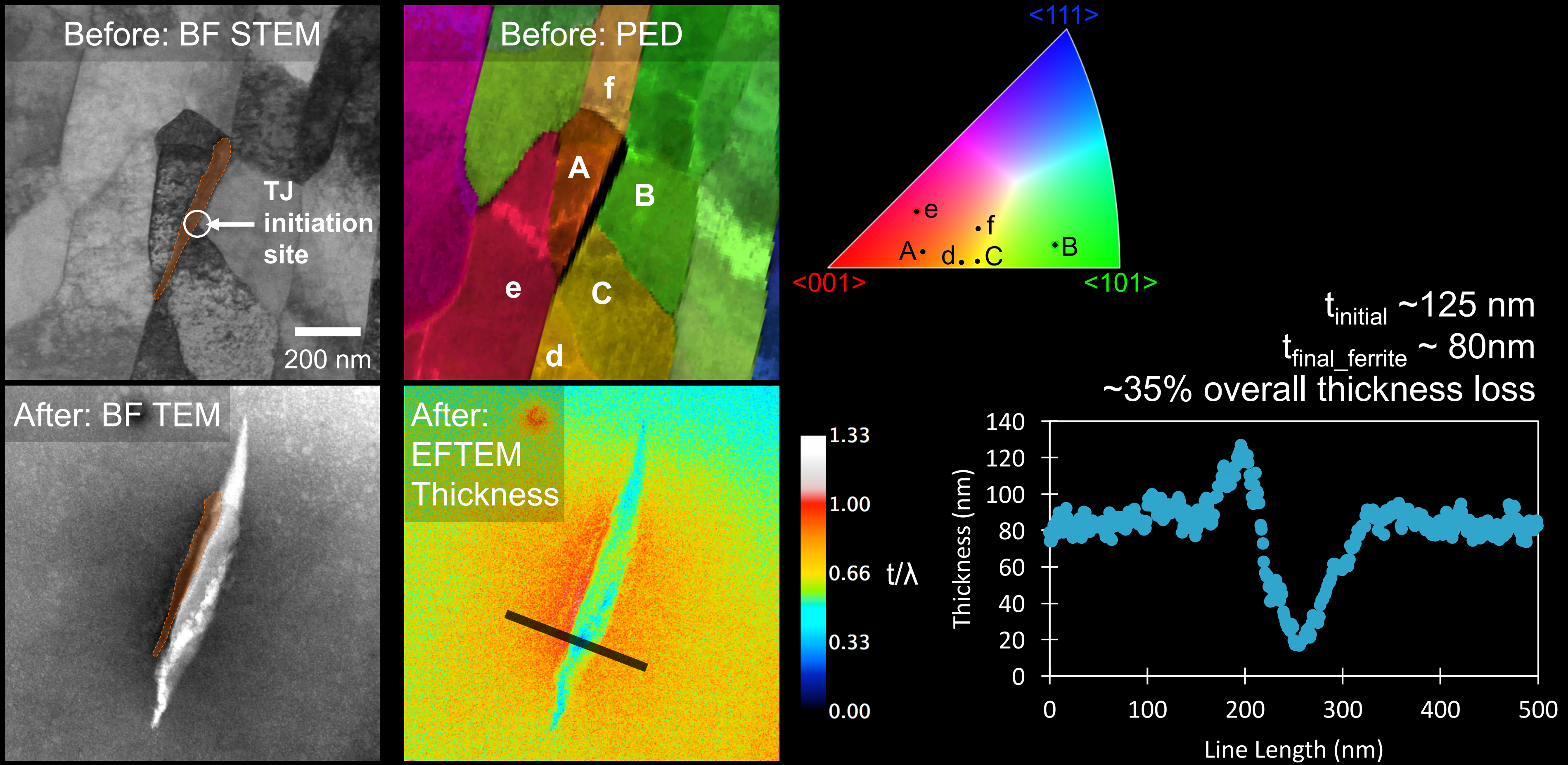
Corrosion Crack Initiation

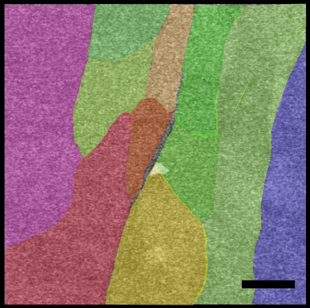


Corrosion Crack Initiation

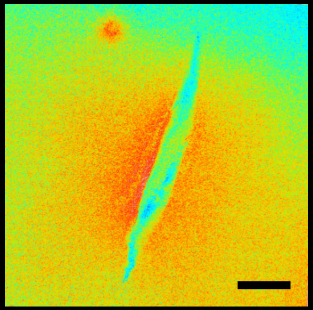
- Initiates at Fe_3C/α-Fe/α-Fe TJ
- Intergranular crack progression
- Results in very sharp intergranular crack, r ~ 5 nm
- Crack growth ~ 30 nm/h



Conclusions

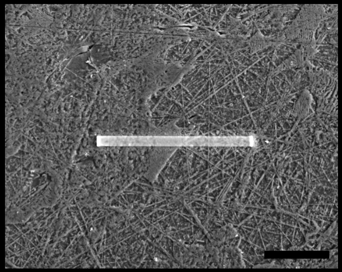


- Directly observed the nucleation of a corrosion crack at Fe_3C/α-Fe/α-Fe triple junction



- Intergranular crack grew at 30 nm/h
  - same order as field observations of near-neutral pH SCC crack growth rate, $10^{-11}\ m \cdot s^{-1}$

- Can begin to explore microstructural effects such as cementite size and spacing on corrosion rate



- Can begin to explore environmental effects, such as sweet vs. sour environments or temperature

Acknowledgements





Steven Tanya Tim Rachael Michele

cint.lanl.gov

In-situ TEM techniques available at CINT include:

- Heating
- Cooling
- Mechanical: compression, tension, bending, etc.
- Electrical
- Chemical: liquid, gas
- Electrochemical
- Laser
- Ion irradiation/implantation
- More to come!

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