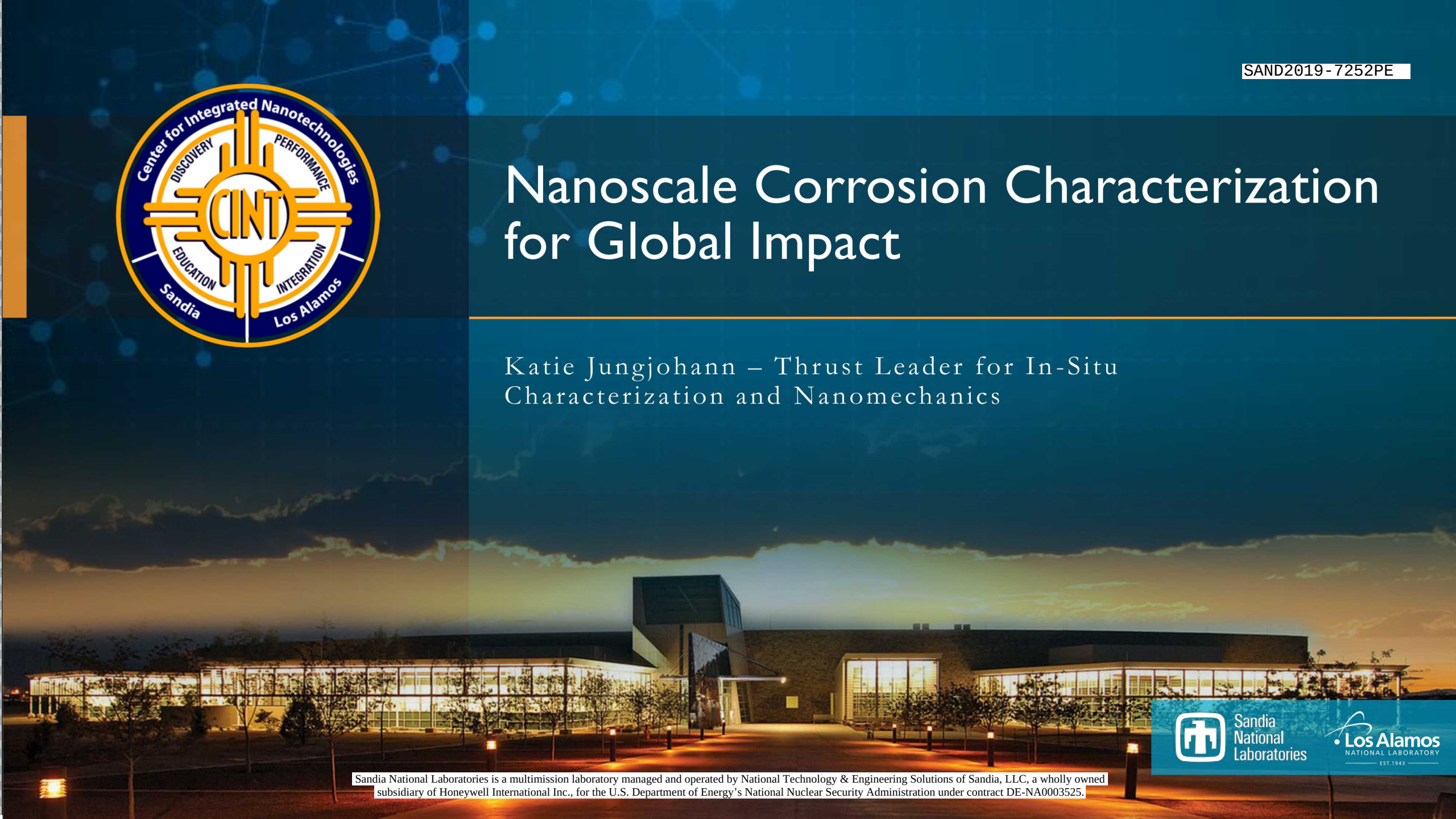
SAND2019-7252PE

Nanoscale Corrosion Characterization for Global Impact

Katie Jungjohann – Thrust Leader for In-Situ Characterization and Nanomechanics



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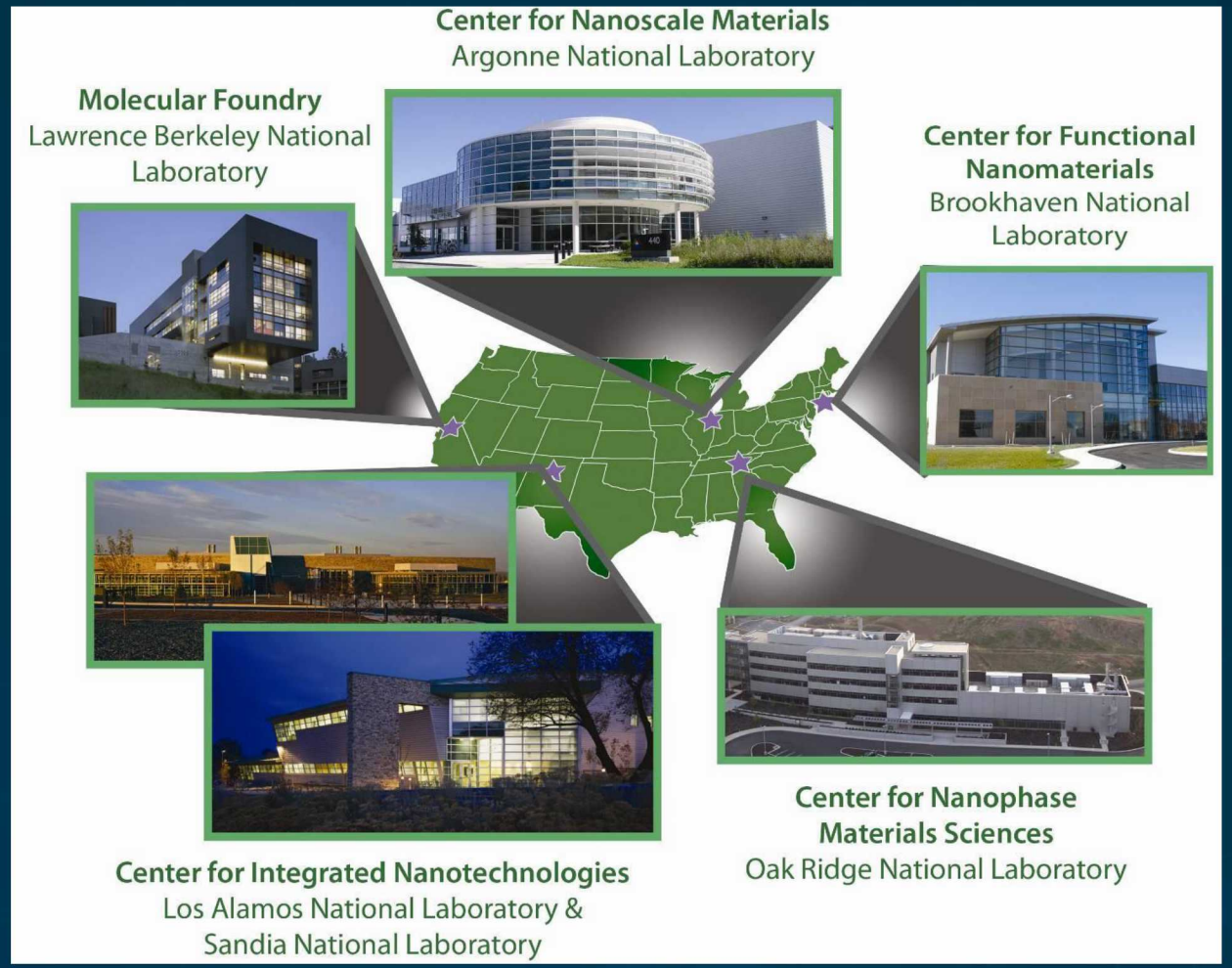
DOE Nanoscale Science Research Centers

"A DOE/SC user facility has unique world-class research capabilities and technologies which are available broadly to science community worldwide from universities, industry, private laboratories, and other Federal laboratories for work that will be published in the open literature."



CINT: Center for Integrated Nanotechnologies

About CINT:

- Free access to staff expertise and equipment for open science
- Two proposal calls per year; proposals for short-term projects are accepted continuously
- Simple 2-page proposal
- Proprietary research is possible with full-cost recovery

https://cint.lanl.gov
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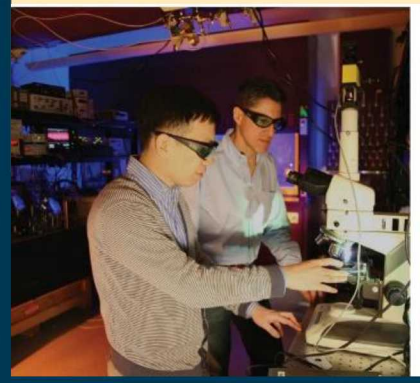
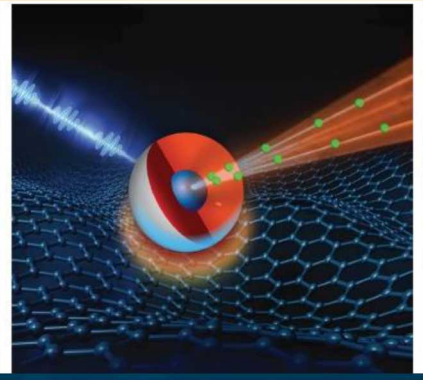
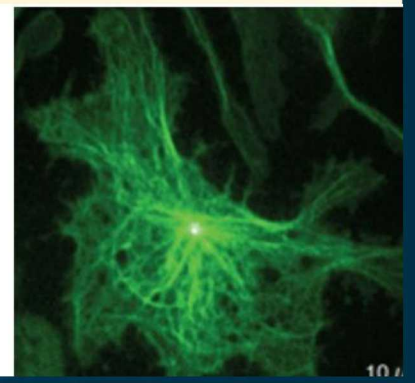
Research areas:

- **In-Situ Characterization & Nanomechanics –** Developing and implementing world-leading capabilities to study the dynamic response of materials and nanosystems to mechanical, electrical, or other stimuli.
- **Nanophotonics & Optical Nanomaterials –** Synthesis, excitation, and energy transformations of optically active nanomaterials and collective or emergent electromagnetic phenomena (plasmonics, metamaterials, photonic lattices).
- **Soft, Biological & Composite Nanomaterials –** Synthesis, assembly, and characterization of soft, biomolecular, and composite nanomaterials that display emergent functionality.
- **Quantum Materials Systems –** Understanding and controlling quantum effects of nanoscale materials and their integration into systems spanning multiple length scales.



annual corrosion costs
240,000 broken US water mains

[1]National Association of Corrosion Engineers

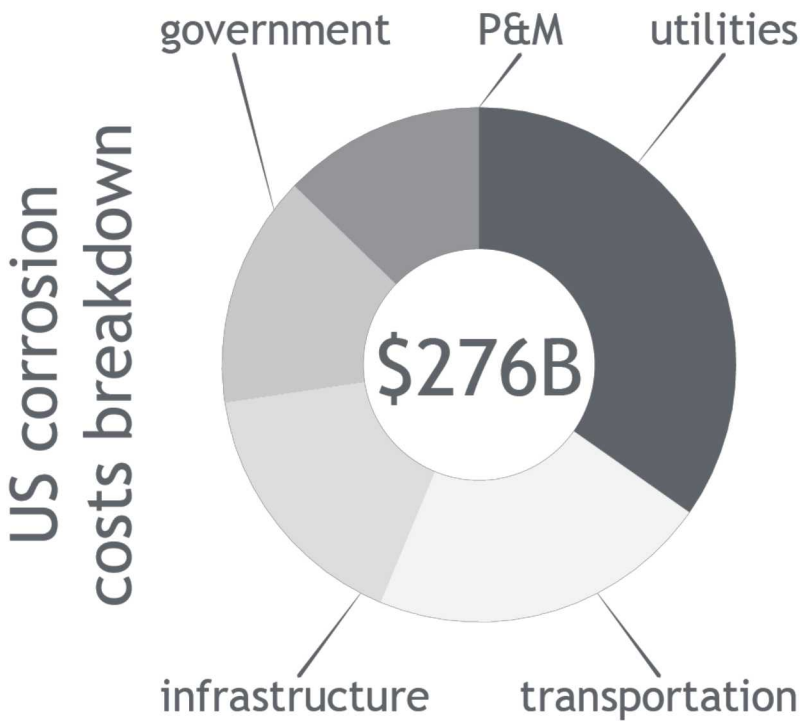
annual corrosion costs

1 in 3 US bridges rated

structurally deficient or functionally obsolete

[1] National Association of Corrosion Engineers

Corrosion: A Global Concern



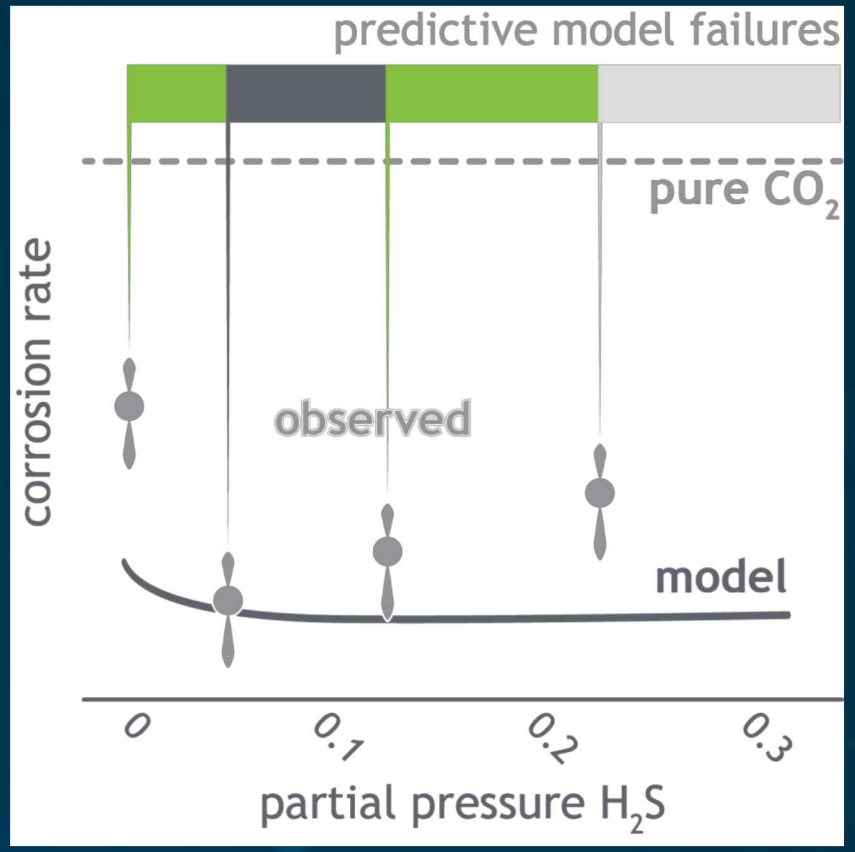
gross domestic product	$75,467,070,000,000	$ 75.4 T
annual corrosion costs	$2,505,400,000,000	$ 2.5 T

3.4% global GDP lost to corrosion

investing in controls | dealing with failures

Pipeline Corrosion: Oil and Natural Gas Transportation

- Strategic replacement programs
- Mechanisms for initiation are unclear



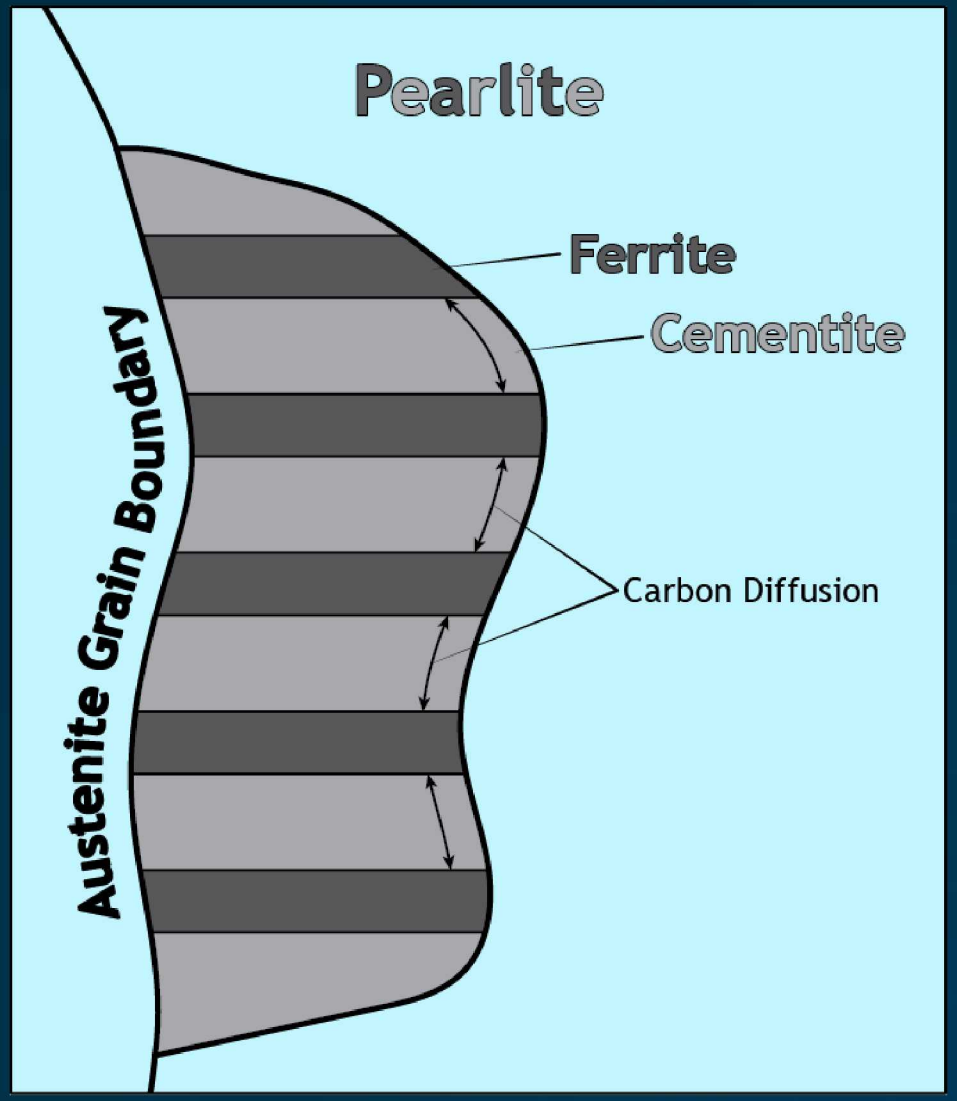
Carbon Steel

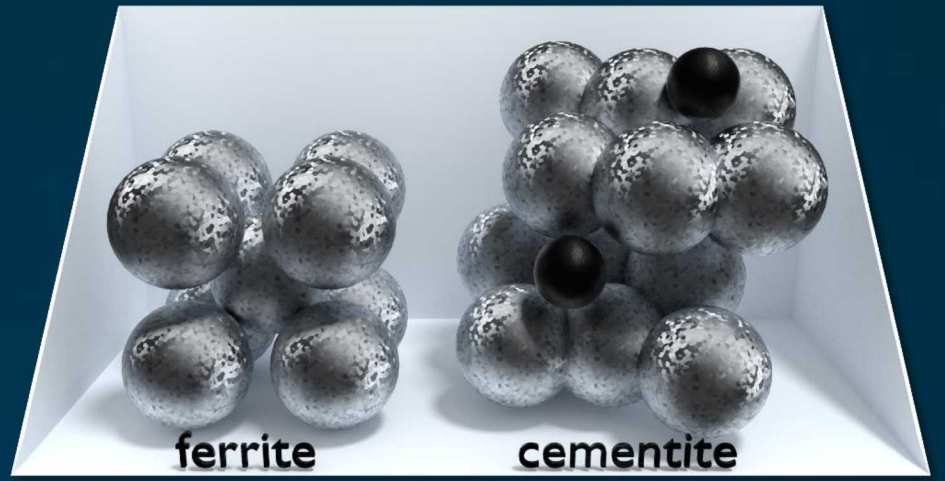
High yield strength &
maintains fracture toughness

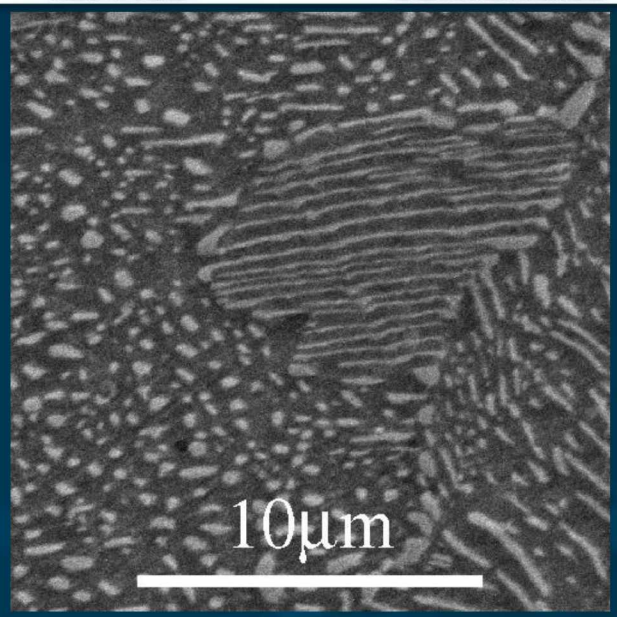
Low Carbon Steel

U.S. is top 4 steel producer,
85% is low-carbon

CINT: Transmission Electron Microscopy



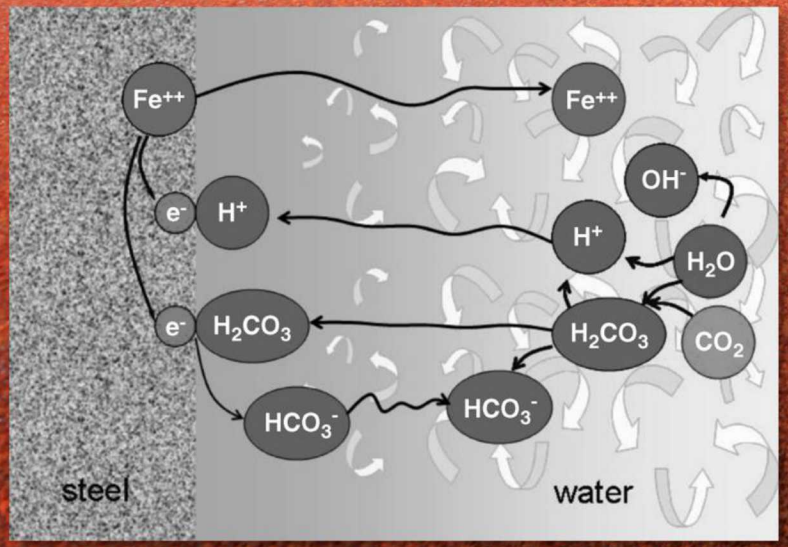




aqueous CO_2 corrosion: uniform

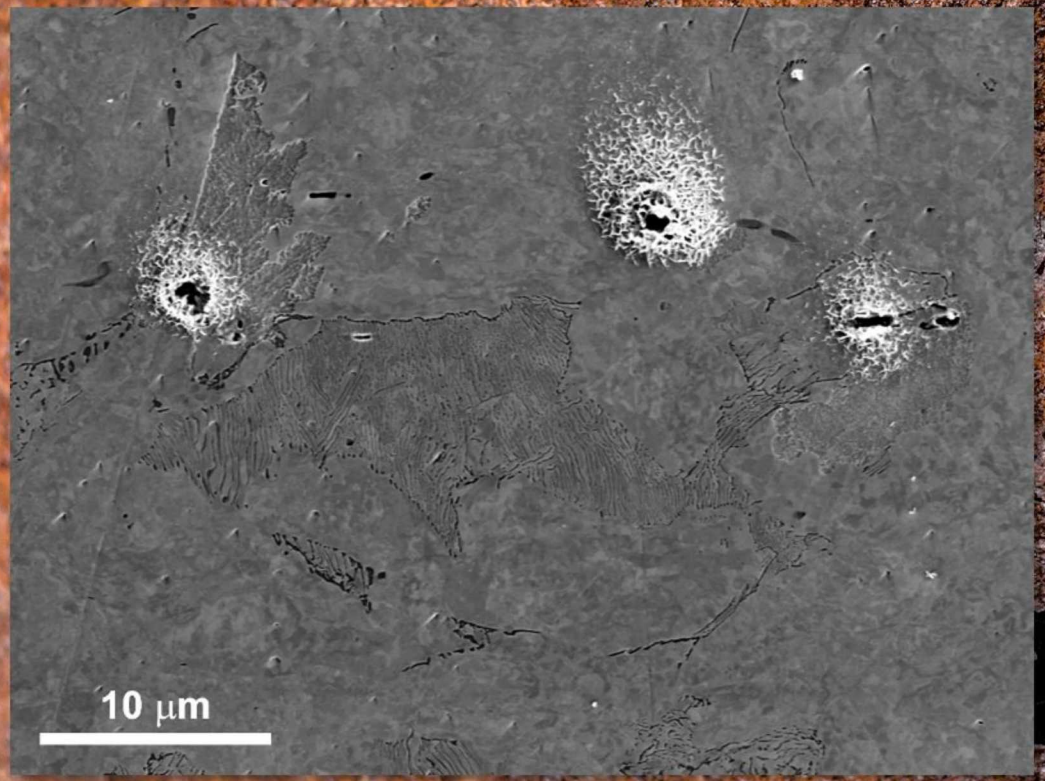
CO_2

H_2CO_3



- non-specific
- solvation of oxidized iron
- *M*/*aq* contact surface
- affected by flow

aqueous CO_2 corrosion: localized



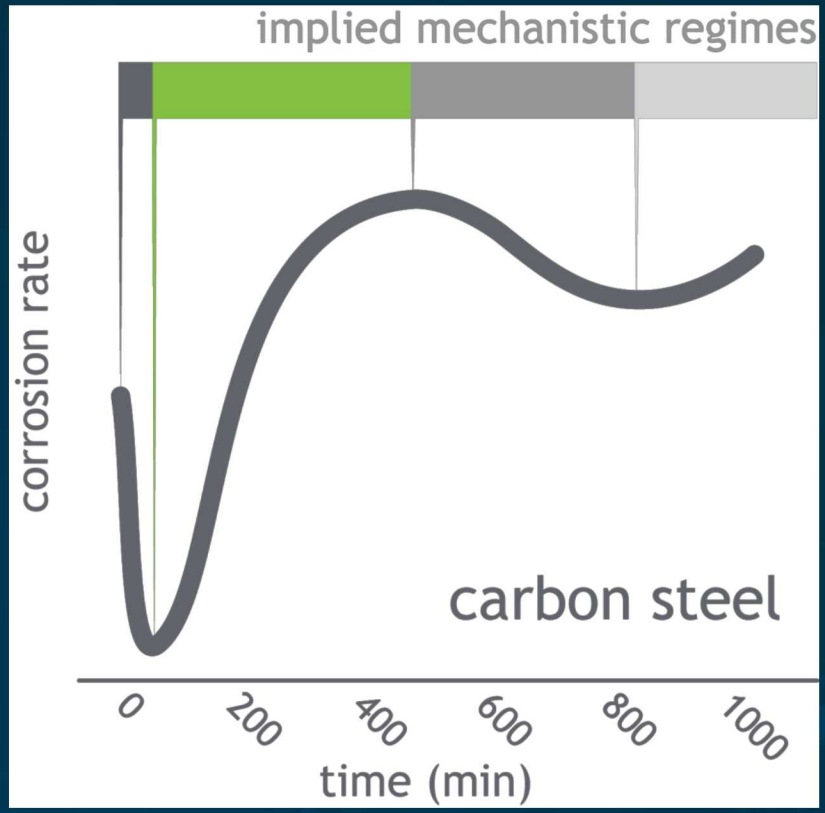
- selective attack – discrete regions
- localized corrosion hotspots
- material defects
- not affected by flow

Steel Corrosion Rates Over Time

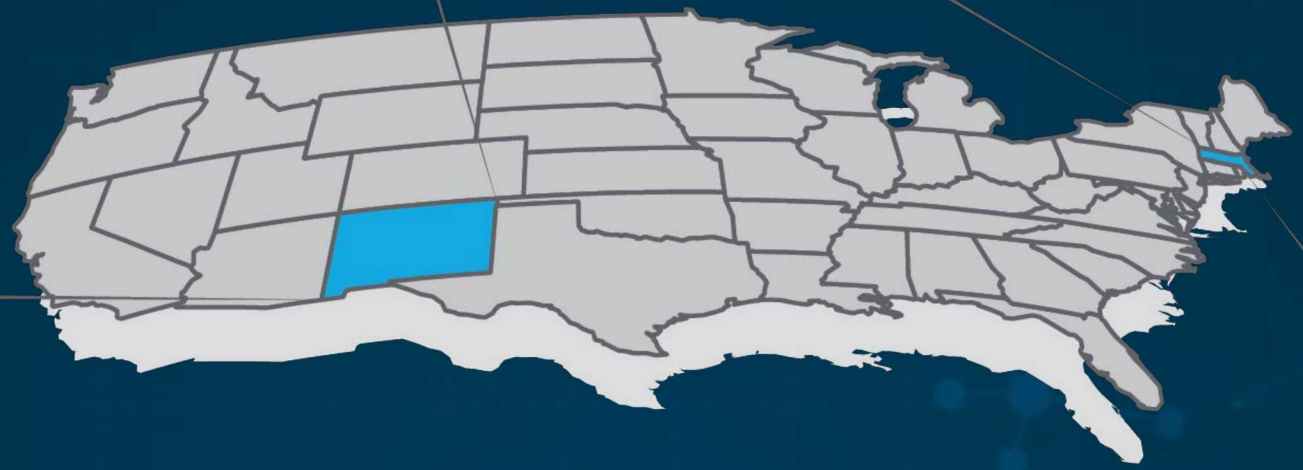
Corrosion rate over time

- Example curve, many inflections
- Prevalence of mechanism changes

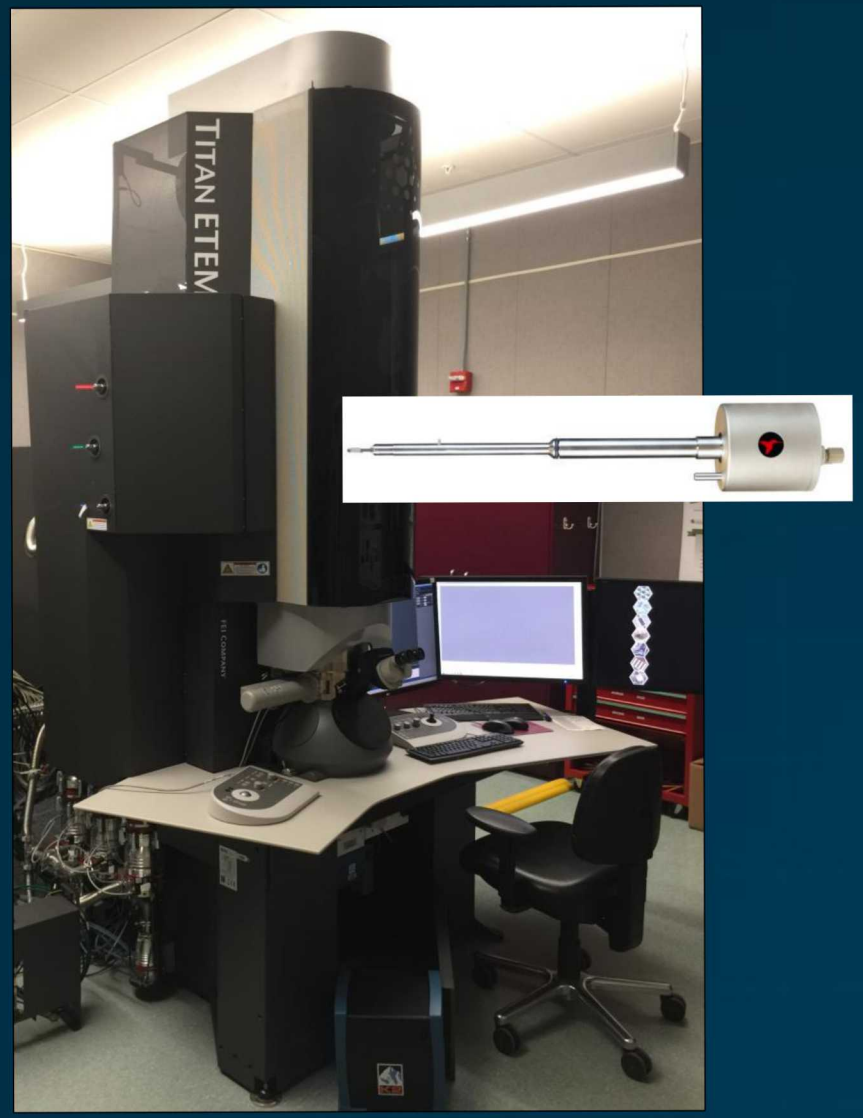
- Can we start at the initiation site, understand that mechanism?

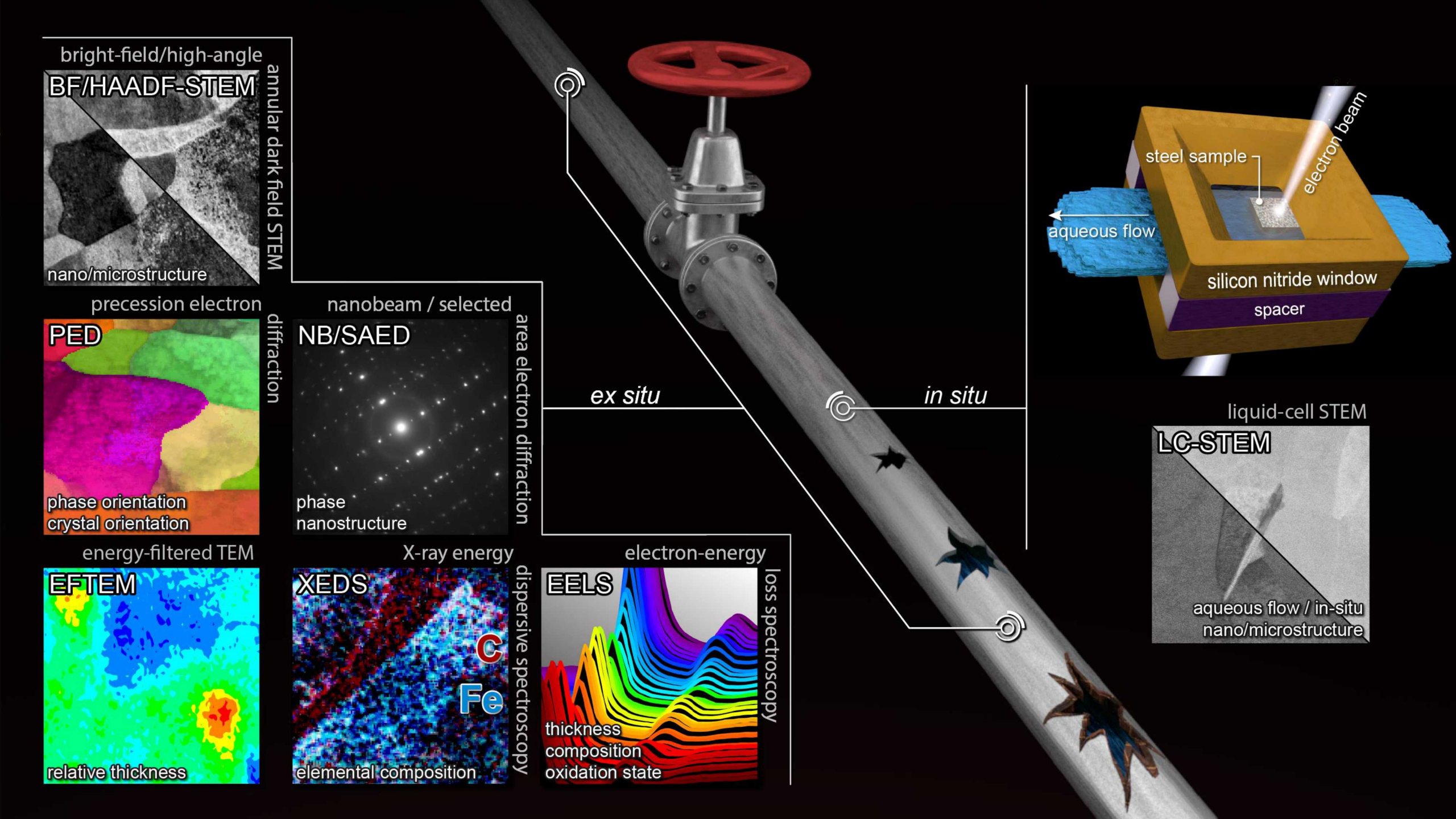


CINT User Project: Nanoscale Corrosion

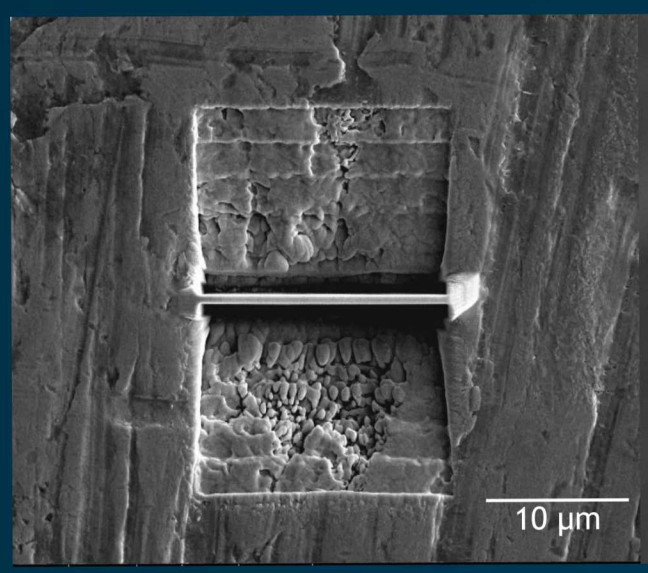


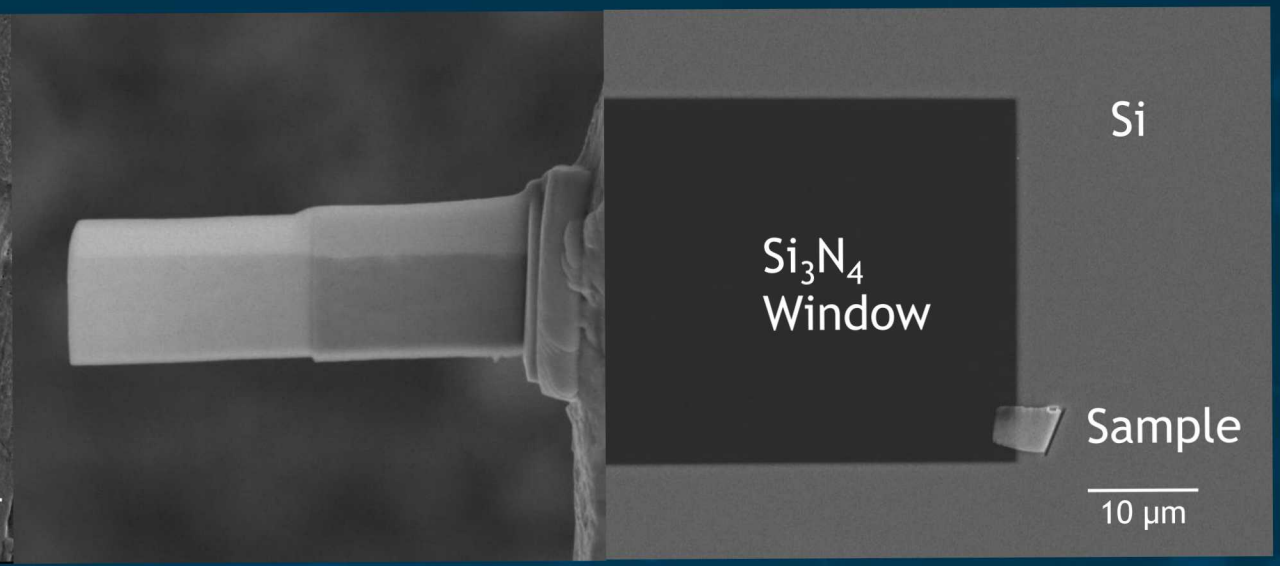
CINT: Transmission Electron Microscopy



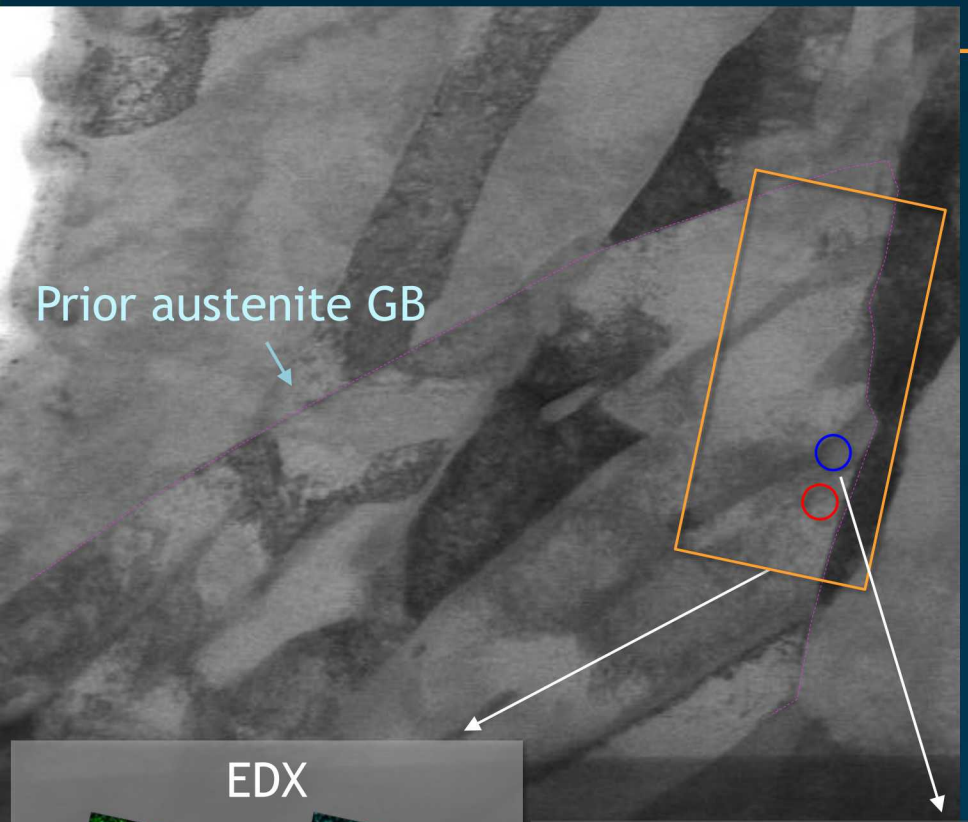

bright-field/high-angle
annular dark field STEM
BF/HAADF-STEM
nano/microstructure
precession electron
diffraction
PED
phase orientation
crystal orientation
nanobeam / selected
area electron diffraction
NB/SAED
phase
nanostructure
energy-filtered TEM
EFTEM
relative thickness
X-ray energy
dispersive spectroscopy
XEDS
C
Fe
elemental composition
electron-energy
loss spectroscopy
EELS
thickness
composition
oxidation state
ex situ
in situ
steel sample
electron beam
aqueous flow
silicon nitride window
spacer
liquid-cell STEM
LC-STEM
aqueous flow / in-situ
nano/microstructure

Focused Ion Beam Extraction



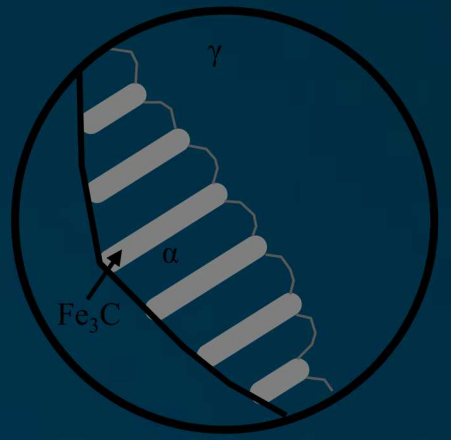


Crystalline/Chemical Mapping of Initial Steel Sample

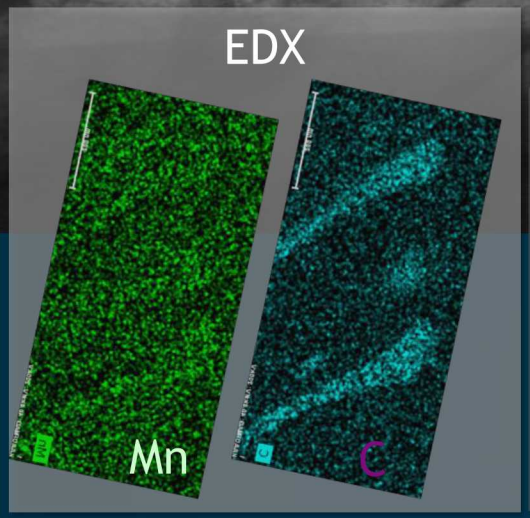


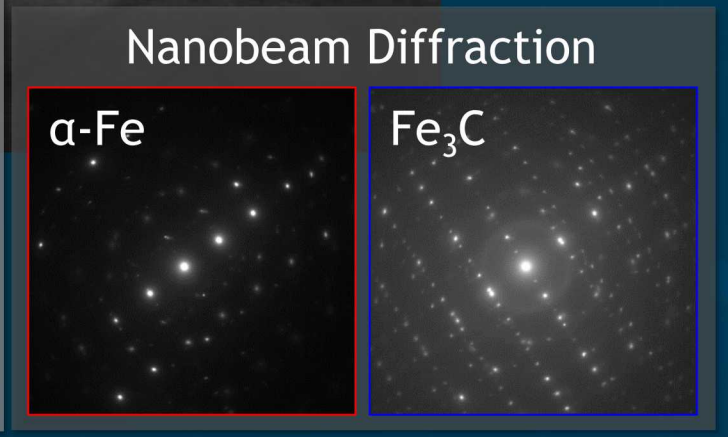
Primarily BCC α-Fe

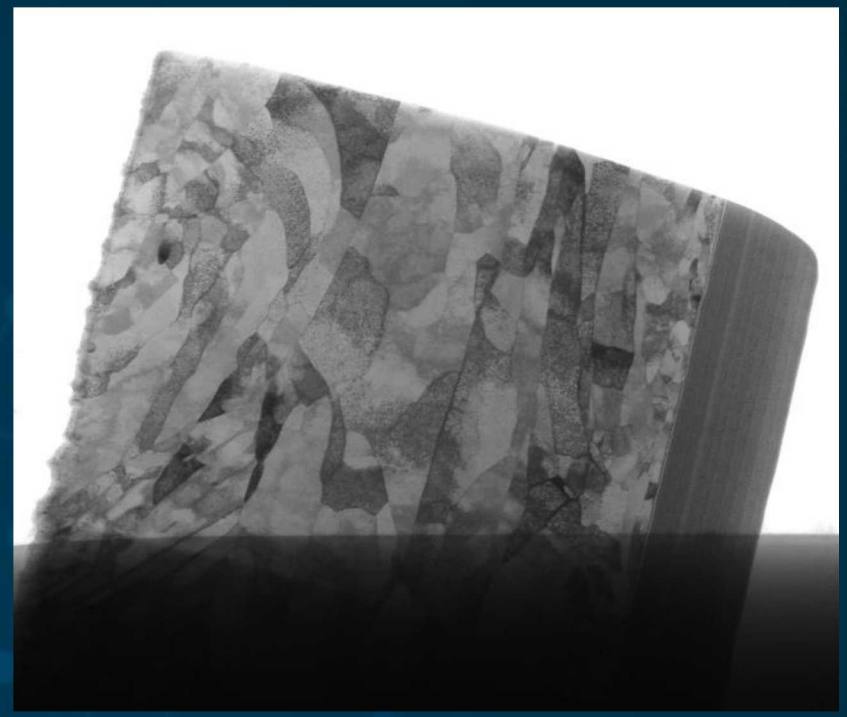
EDX and nanobeam diffraction show presence of Mn-rich Fe_3C lamellae



As steel cools past the eutectic temperature from the FCC γ-Fe (austenite) phase, orthorhombic Fe_3C (cementite) and BCC α-Fe (ferrite) grow, starting at a prior austenite grain boundary

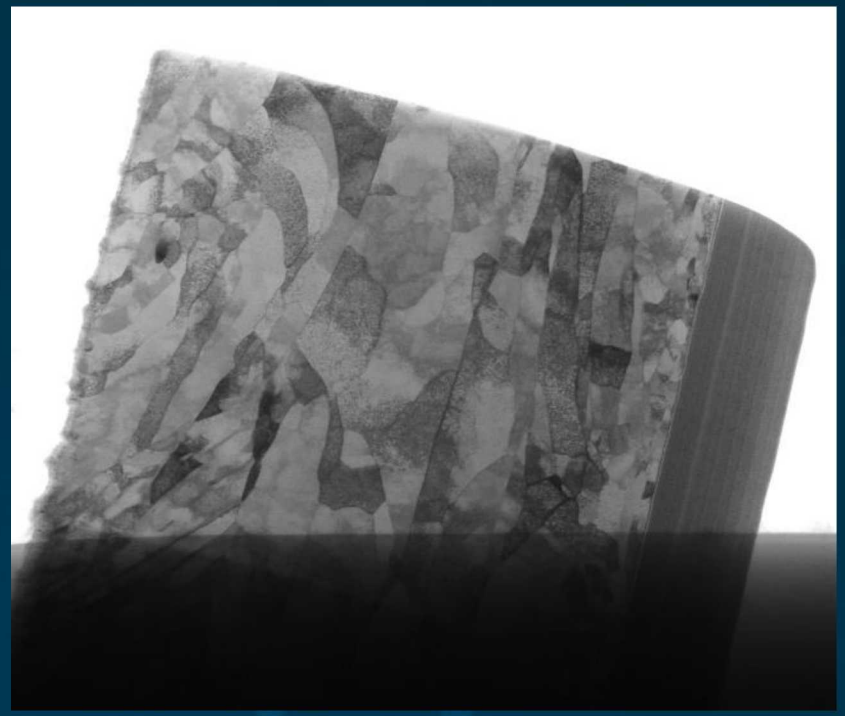






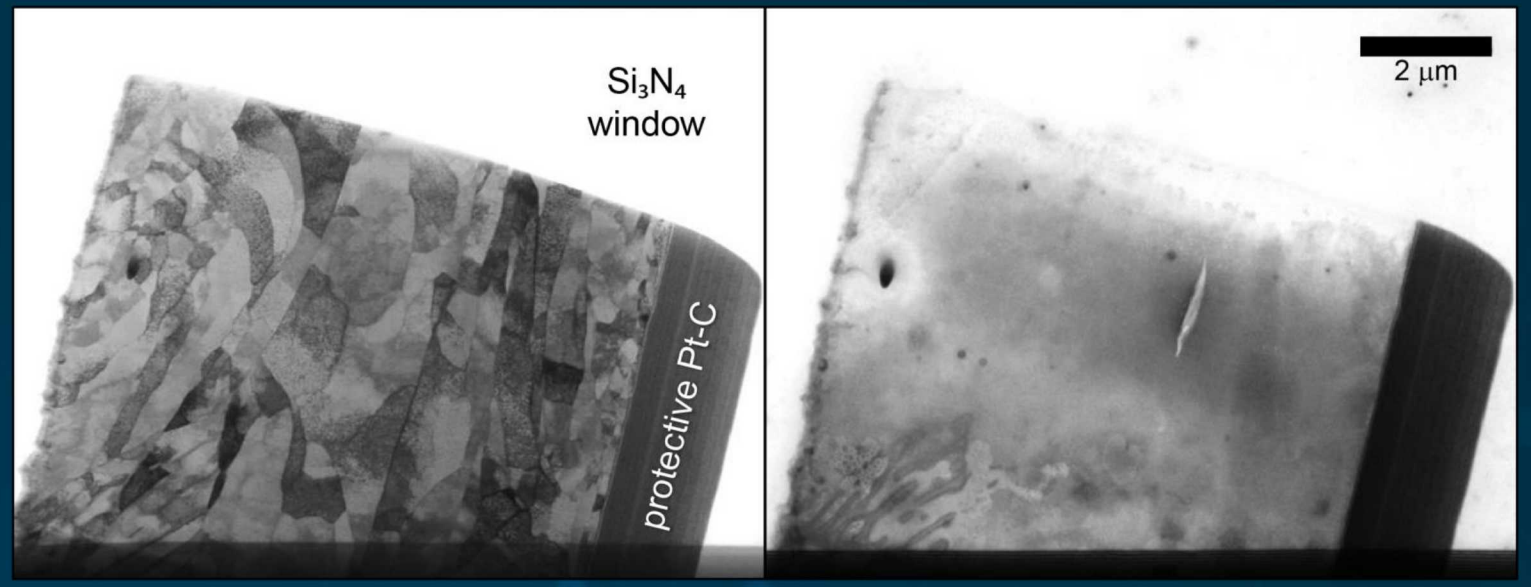
TEM Sample for In-Situ Observation

- 1018 carbon steel
  - extracted / mounted
  - LC-TEM cell
  - TEM
  - microfluidic pumping



Initial and Post-Corrosion Sample

- 1018 carbon steel
  - extracted / mounted
  - LC-TEM cell
  - TEM
  - microfluidic pumping
- Direct observation
  - STEM (BF/HAADF)
  - 102 mins
- *Ex situ* examination
- Corrosion observed
  - uniform
  - localized



Localized Corrosion in Low Carbon Steel

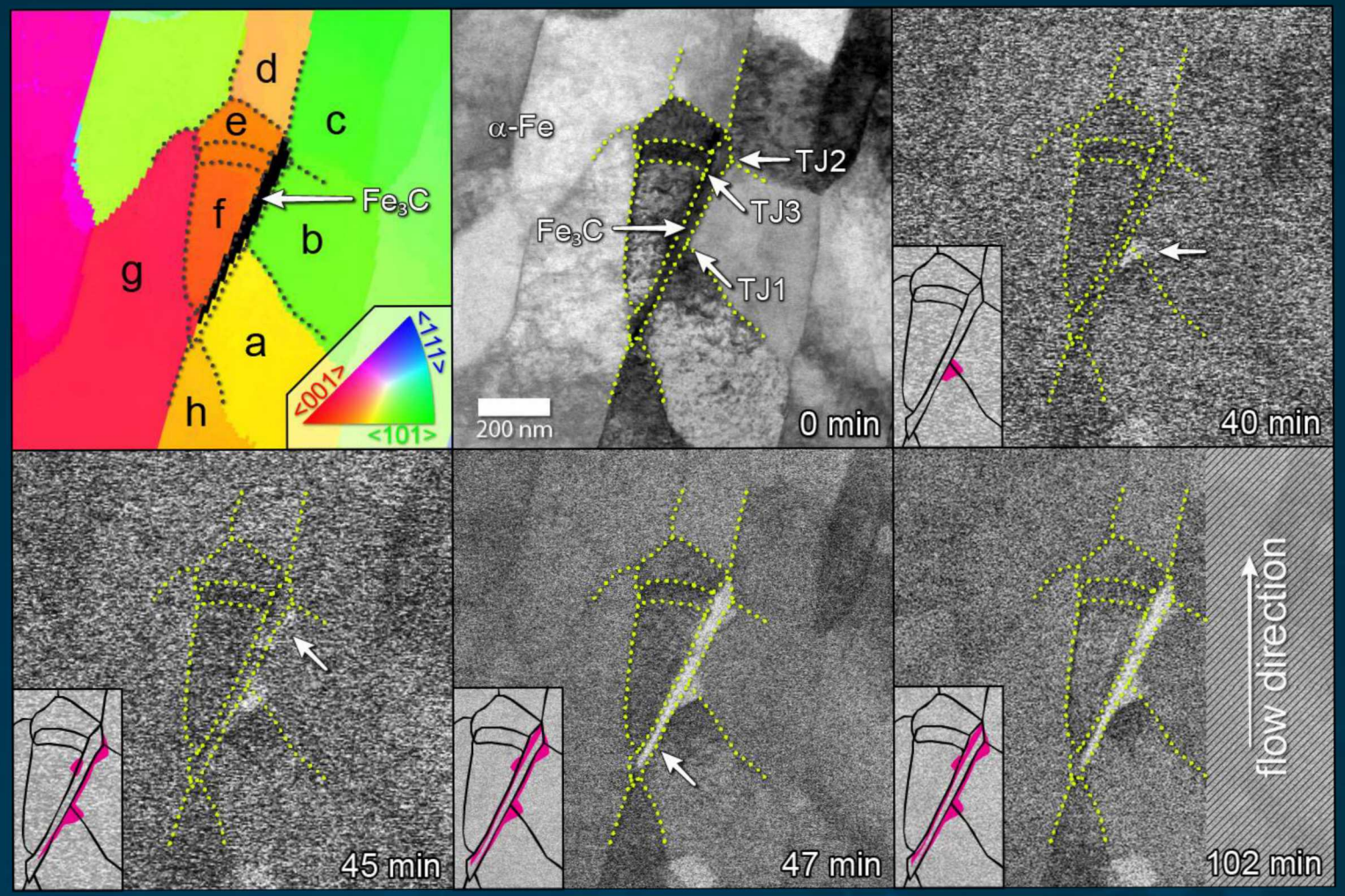
isolated cementite in ferrite matrix

40 min
- TJ initiation
- 11° disorientation

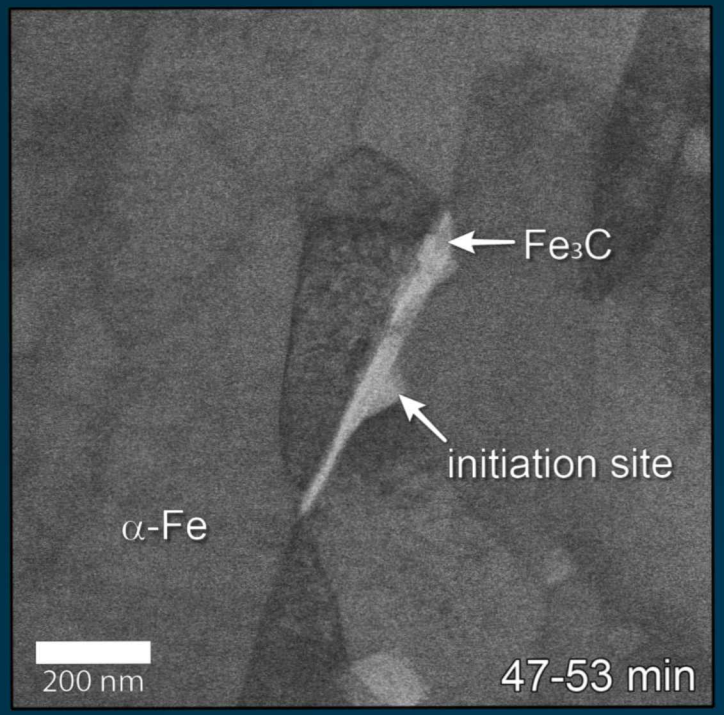
45 min
- interfacial activity
- TJ etching (2/3)
- b/c=5° | e/f=4°

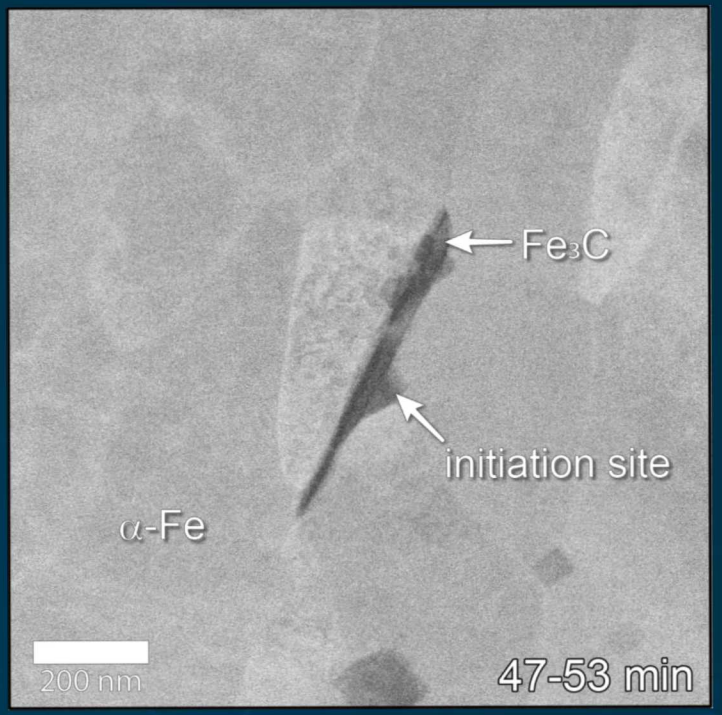
47 min
- lateral progression (ferrite)
- <111> direction ([110] face)

final
- loss of contact = arrest

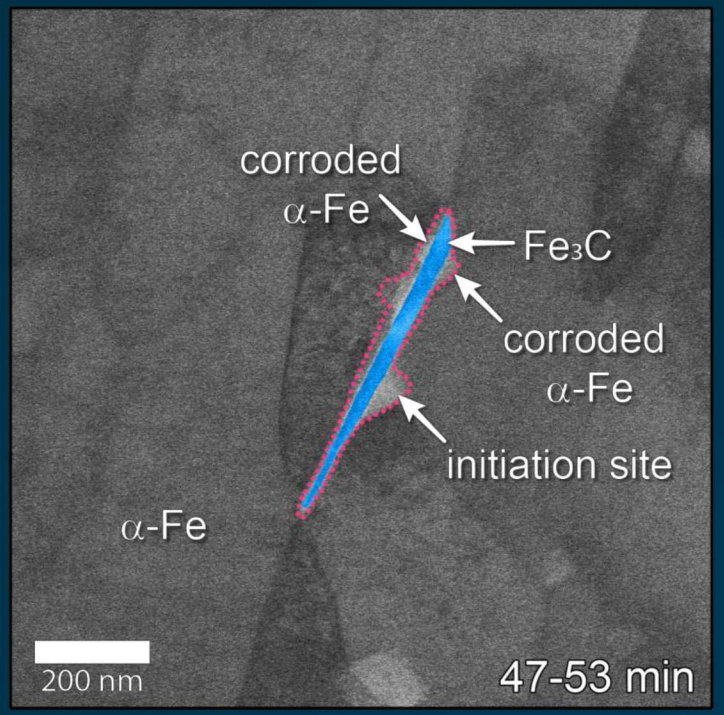


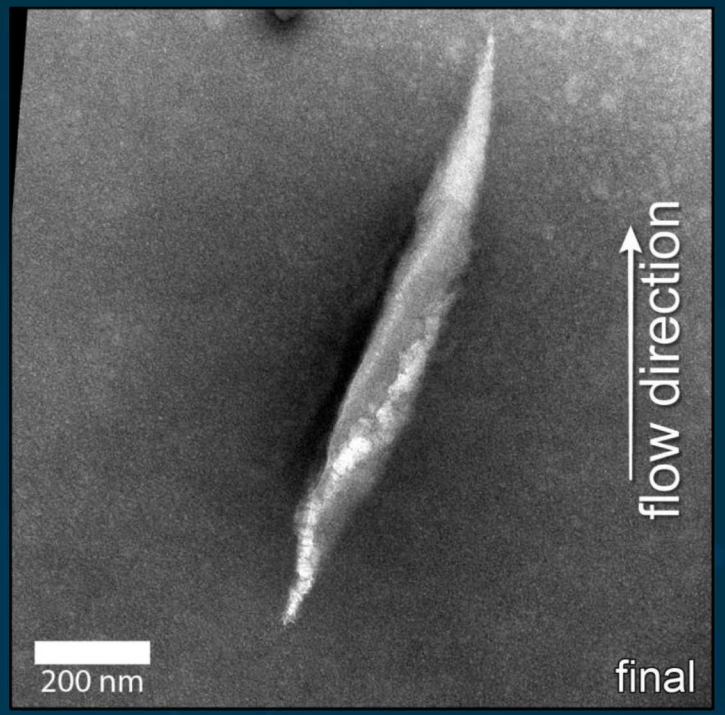
In-Situ Localized Corrosion Site Identification



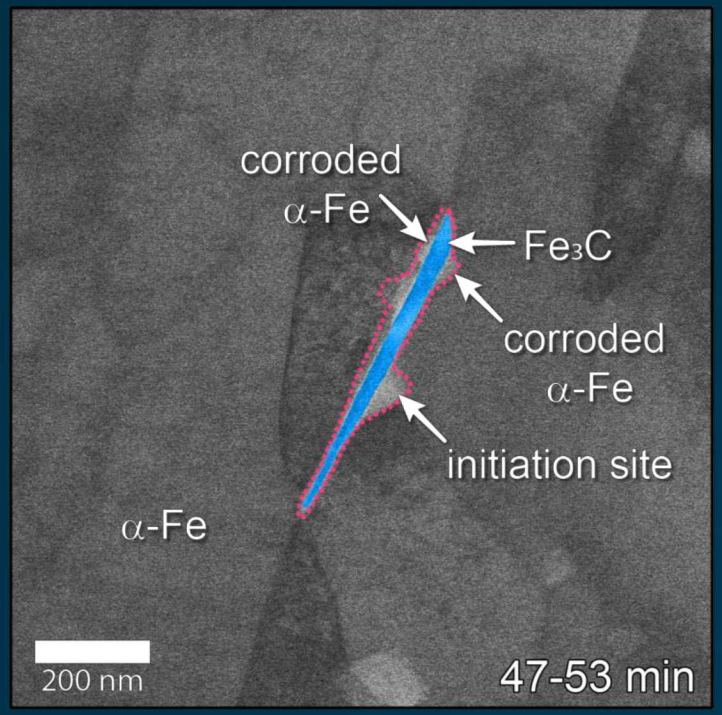


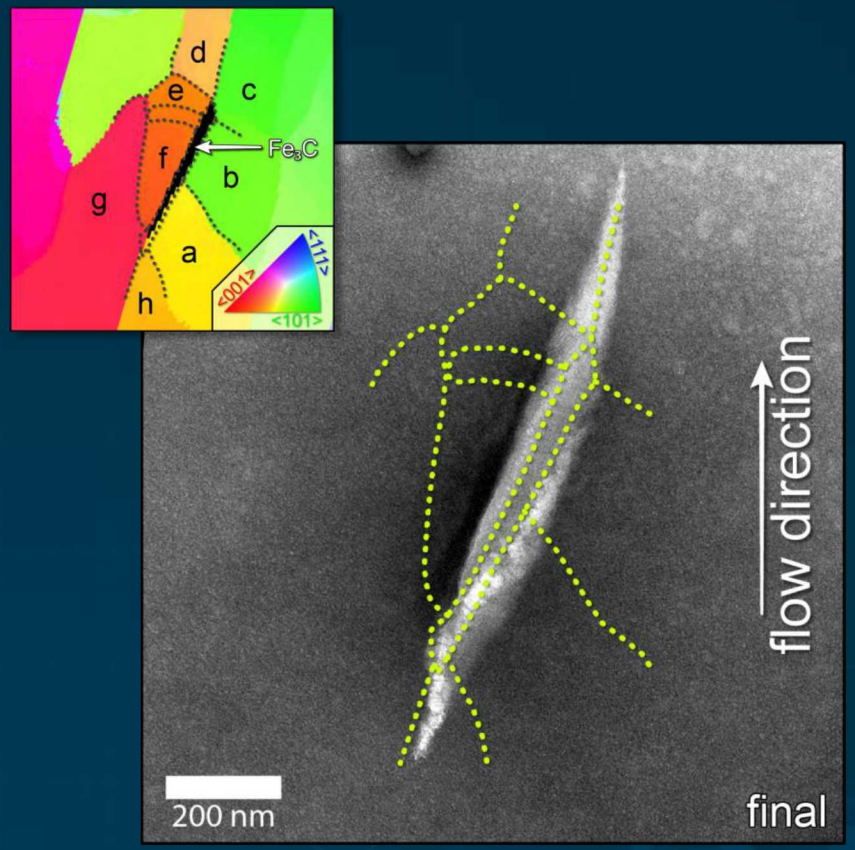
In-Situ and Ex-Situ Post Localized Corrosion



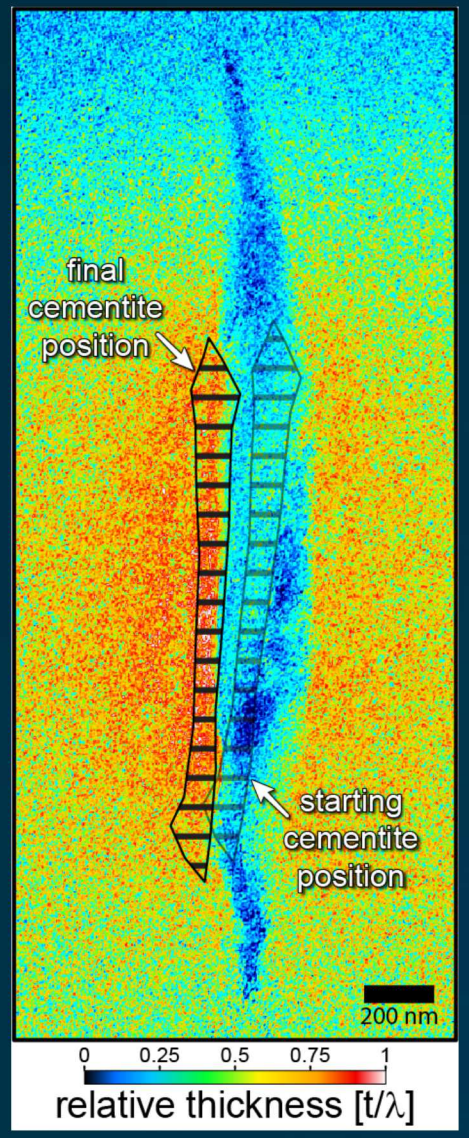


Cementite Grain Corroded Away?

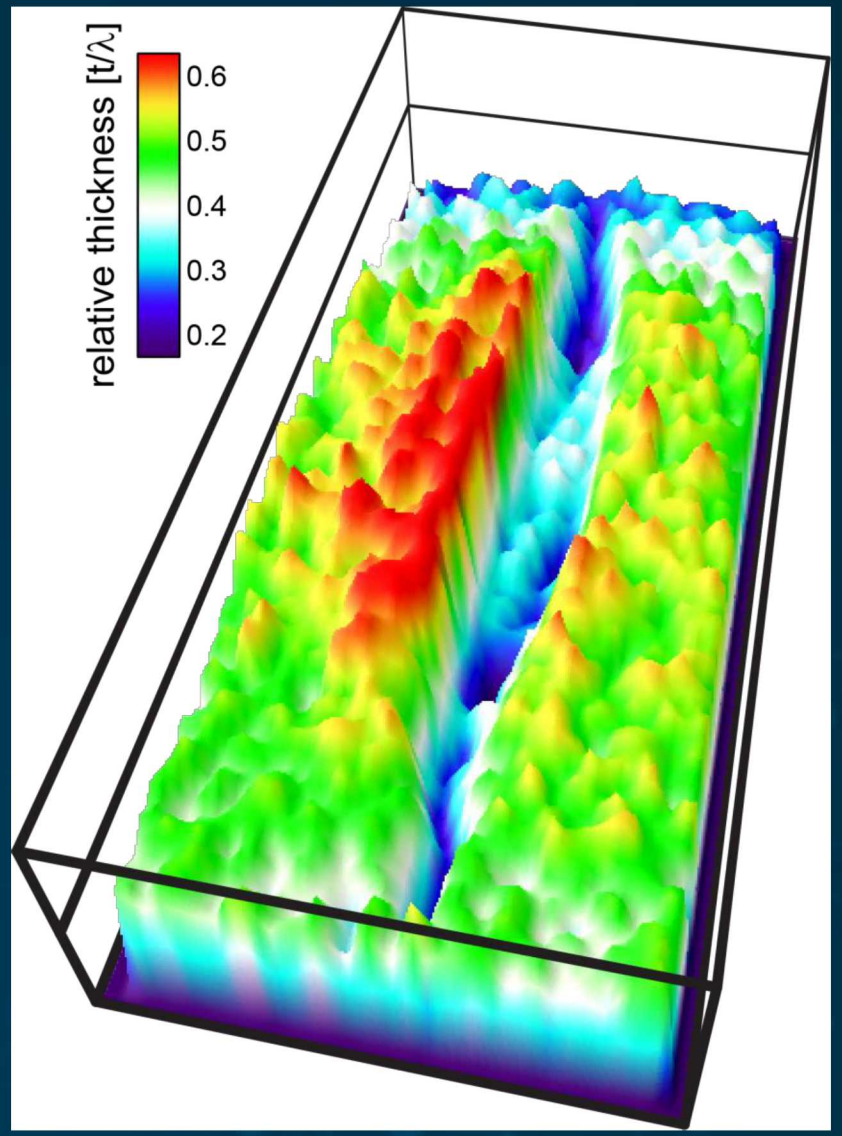




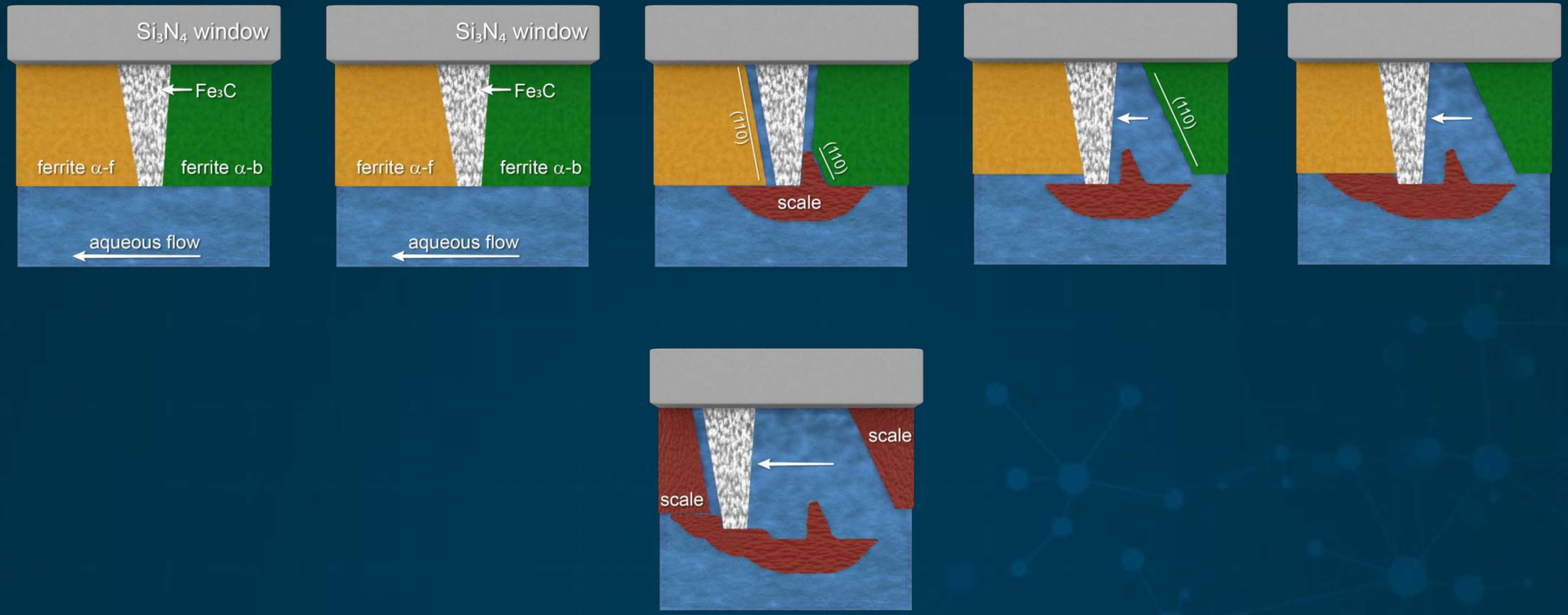
Cementite Grain Remained in Sample

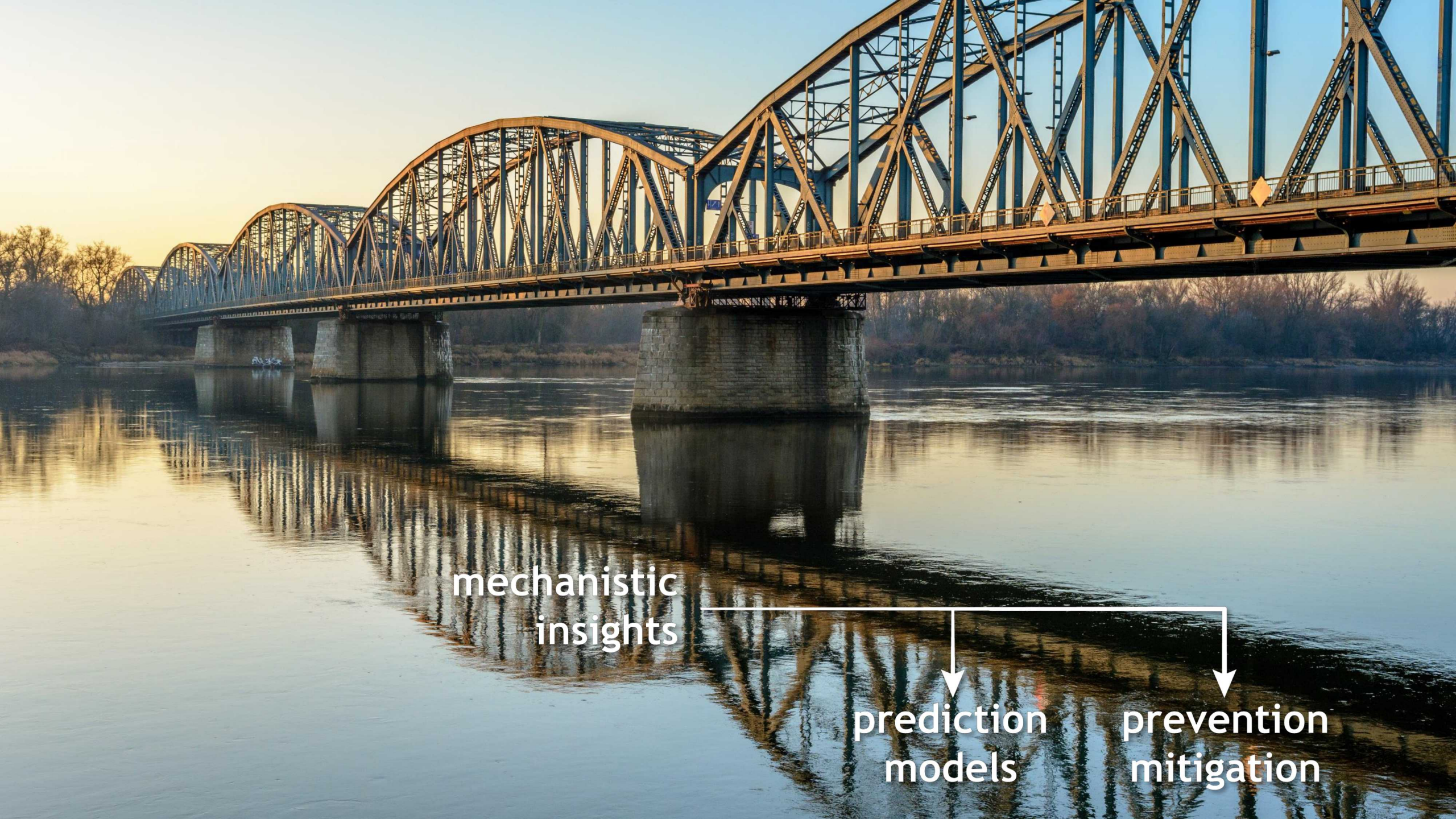


- cementite grain
  - shifted
  - 5° rotation
  - overlapping with scale

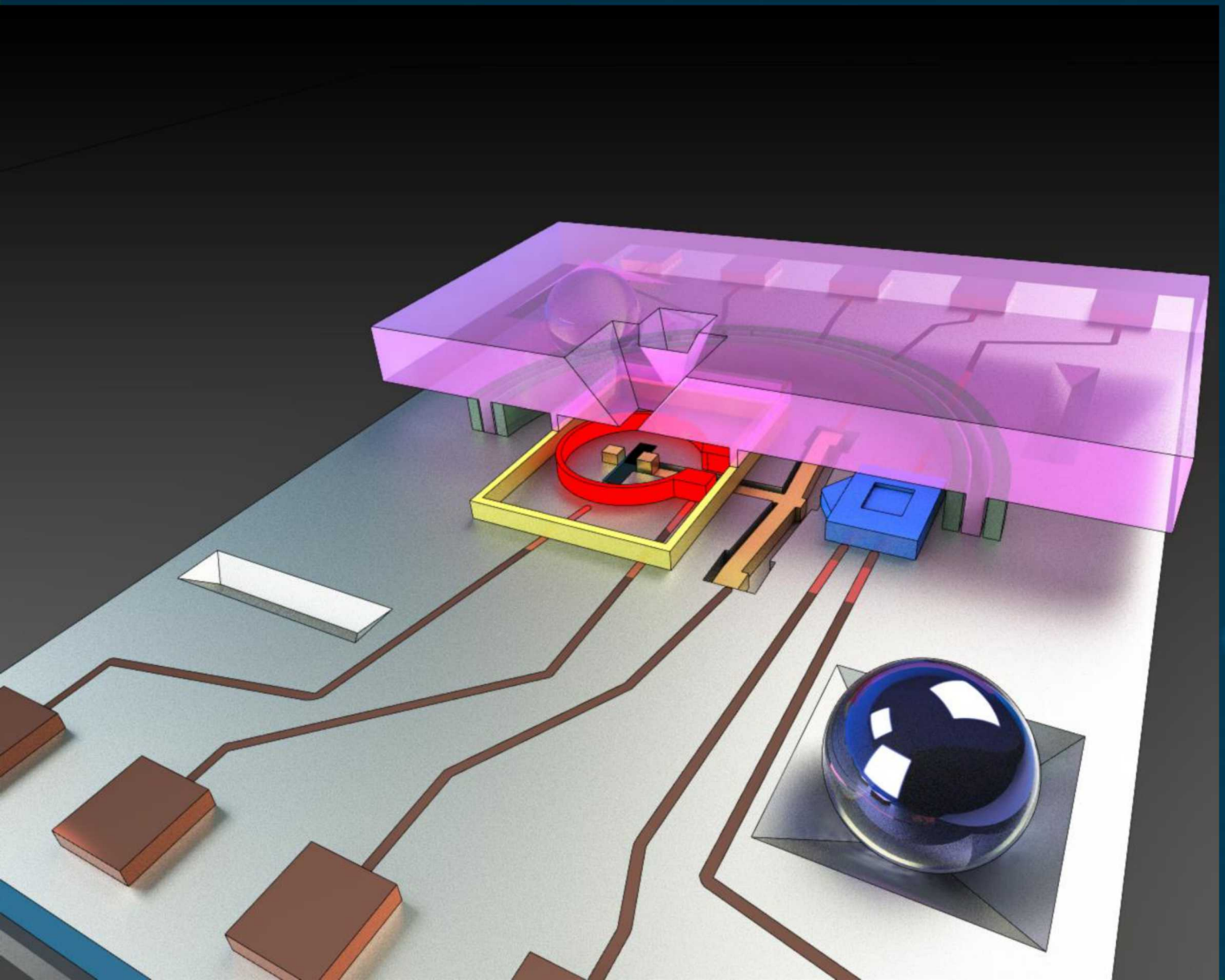


Proposed Mechanism for Localized Corrosion




mechanistic
insights
prediction
models
prevention
mitigation

Future Platform for Stress-Corrosion-Cracking TEM Studies



Acknowledgements

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Rachael Grudt | Tatiana Pilyugina | Timothy Kucharski | Michele Ostraat | Steven Hayden