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# A perspective on environmentally-induced cracking

R.M. Latanision  
*Exponent, Inc., USA, rlatanision@exponent.com*

A.K. Vasudevan  
*ONR Retired, USA*

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# **International Symposium on the Environmental Damage in Structural Materials under Static/Cyclic Loads at Ambient Temperature**

A Perspective on Environmentally-Induced Cracking

R.M. Latanision

Senior Fellow

Exponent – Failure Analysis Associates, and  
Director (Emeritus) The H.H. Uhlig Corrosion Laboratory  
Massachusetts Institute of Technology

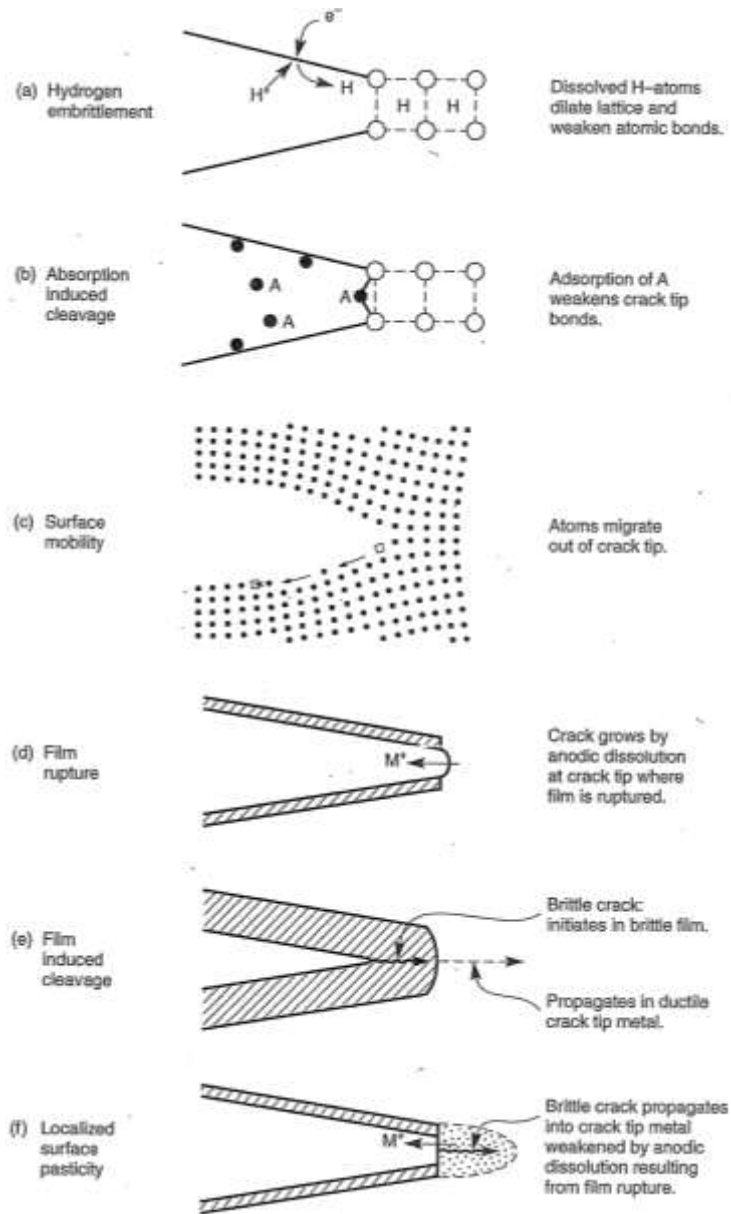
# Environmentally-Induced Cracking Phenomena

- Hydrogen Induced cracking
- Liquid Metal Embrittlement
- Static Fatigue of Silicate Glass
- Accelerated Crazeing of Polymers in Organics Media
- Corrosion Fatigue
- Stress Corrosion Cracking
  - Chloride Cracking
  - Caustic Cracking
  - Season Cracking
  - Sulfide Cracking
  - Others

The phenomenology is well understood, but the mechanisms remain unclear. Corrosion is not involved in many phenomena that are described as SCC.

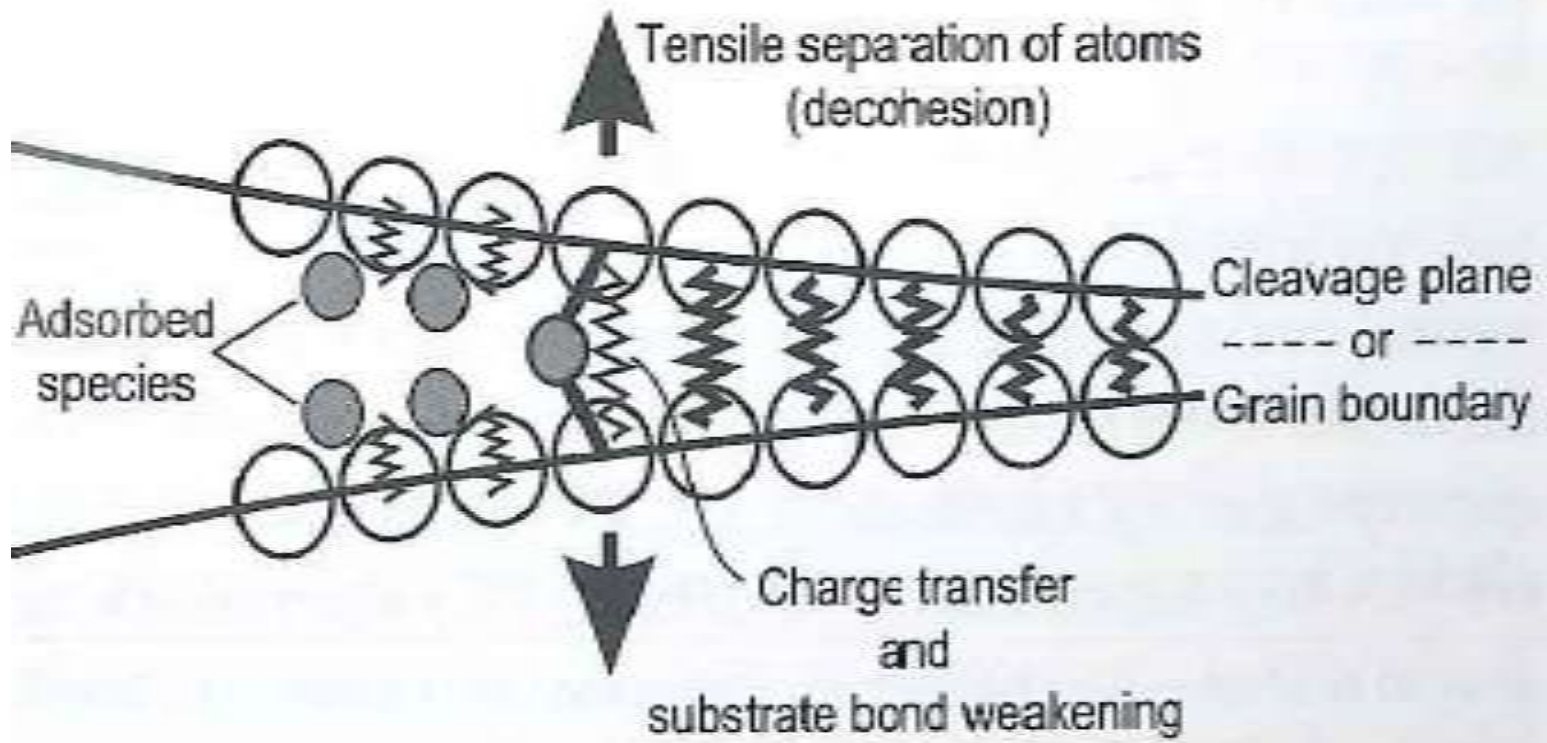
# Schematic Summary of Some Proposed Mechanisms

(from D.A. Jones, *Principles and Prevention of Corrosion*, 1996)



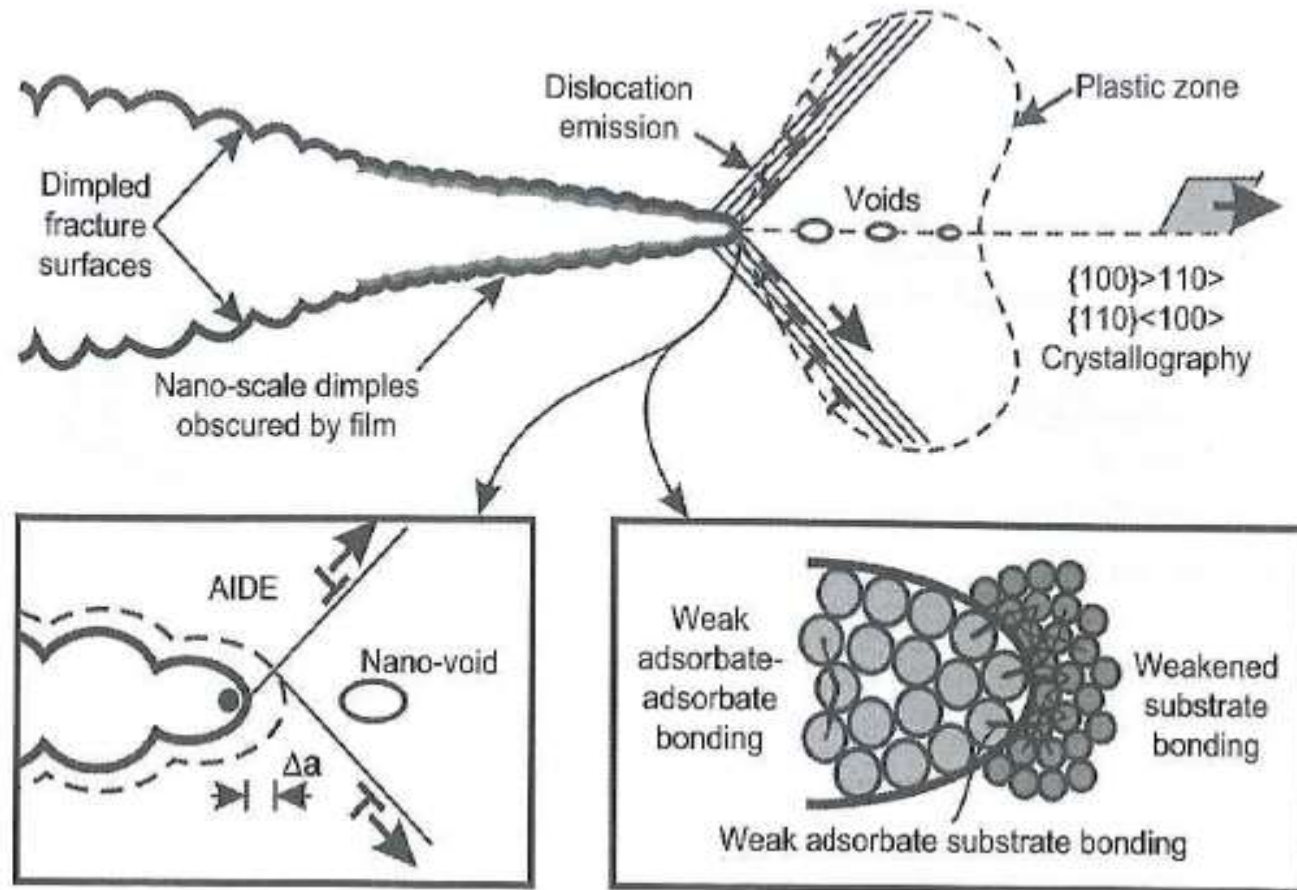
# Schematic of Adsorption-Induced Cracking

(from S. Lynch, *Corr. Rev.* , 30, 63 (2012))



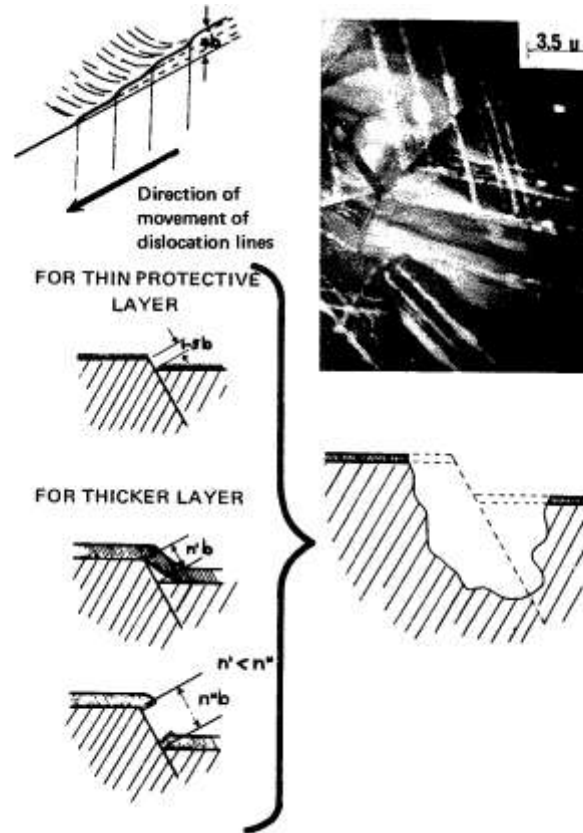
# Schematic of Adsorption-Induced Dislocation Emission

( from Lynch, *Corr. Rev.* , 30, 63 (2012))



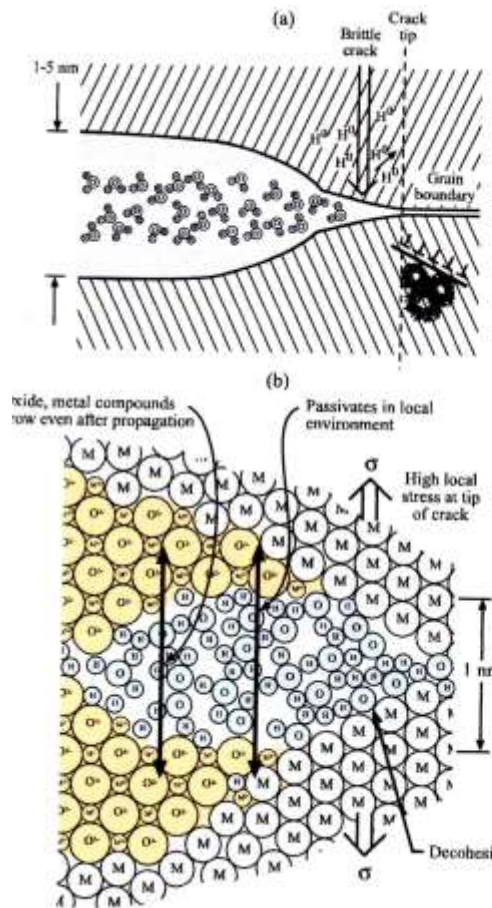
# Schematic of Slip Step Dissolution

(Latanision and Staehle, *SCC of Fe-Cr-Ni Alloys*, 1969)



# Schematic of (a) a “tight crack”, (b) an atomistic description of a brittle crack event at the crack tip, (c) options for producing brittle events at the crack tip

(from Staehle, *Corr. Rev.*, 28, 1 (2010)).



(c)

## Apparent Options for Crack Advance

- Surface energy lowering embrittles
- Brittle films due to dealloying
- Oxygen diffusion in grain boundary
- Hydrogen facilitates movement of dislocations which causes barriers to fail
- Cold-work embrittled layer at edge of plastic zone—further embrittled by hydrogen
- Vacancy from dissolution produce crack nucleus
- Brittleness due to surface-film formation
- Film break and repassivation
- Film thinning and increased reactivity



# Environments Which Lead to Cracking of Certain Alloys

Aluminum Alloys

Seawater (chloride and other halides)

Copper Alloys

Ammoniated aqueous solutions

Nickel Alloys

Caustics, high purity water, H<sub>2</sub>S

Mild Steels

Caustics, nitrates, anhydrous ammonia,  
carbonate/bicarbonate mixtures

High Strength Steels

Water, moist air, H<sub>2</sub>S

Stainless Steels (austenitic)

Caustics, halides

Titanium Alloys

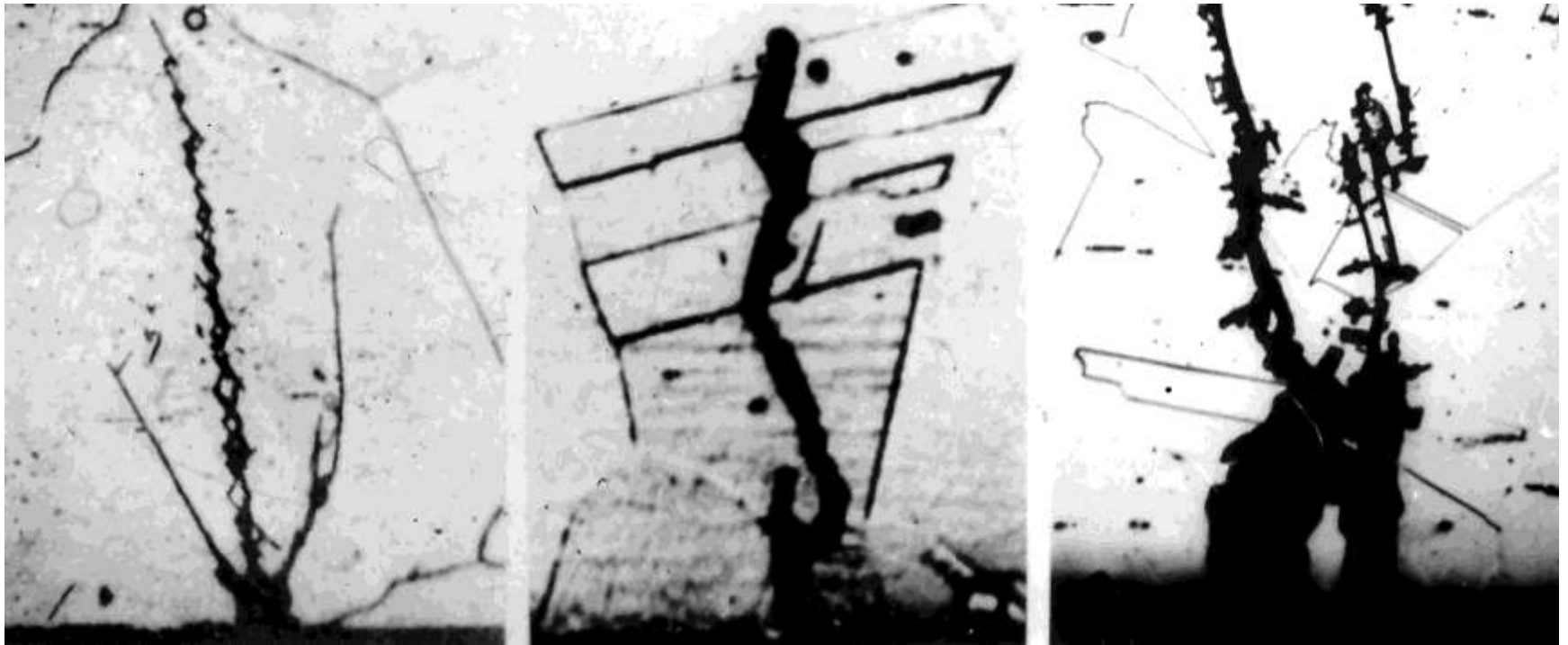
Seawater, halides, CCl<sub>4</sub>, N<sub>2</sub>O<sub>4</sub>,  
methanol

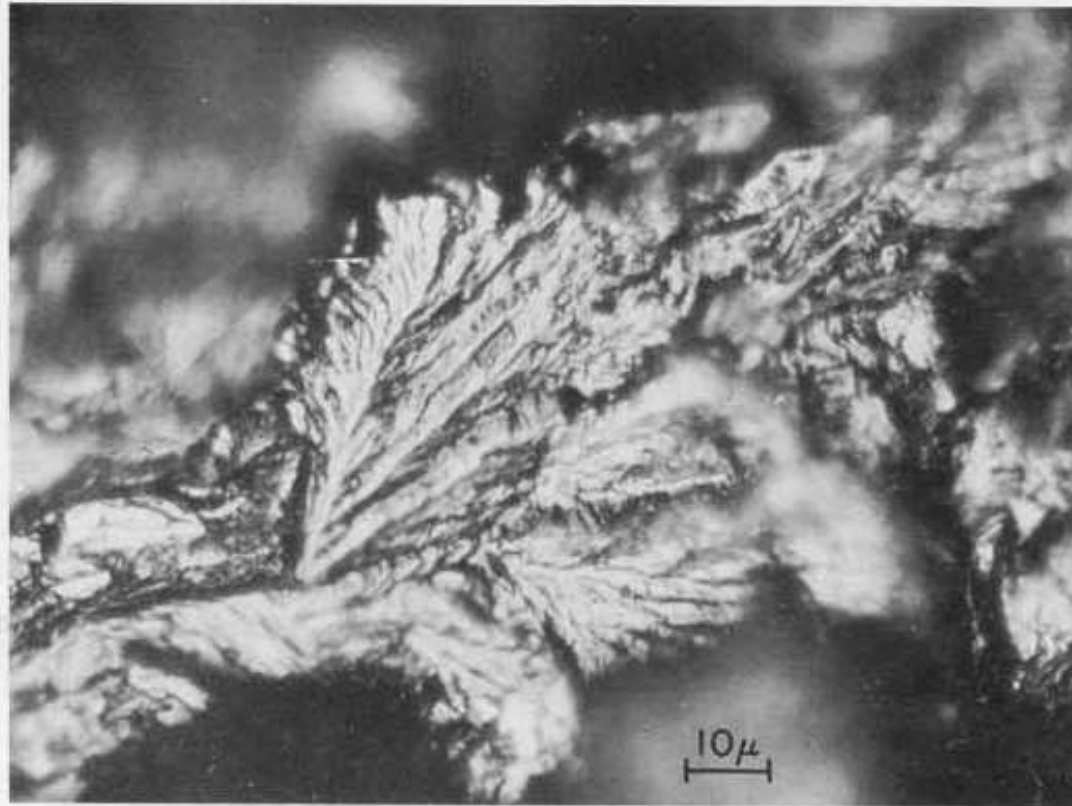
# The Following Observations Must be Explained by Any Acceptable Working Theory:

- The pronounced specificity of the damaging environment
- The brittle fracture of ordinarily ductile metallic materials in the presence of specific environmental species
- The general observation that metallic materials that are among the most resistant to uniform corrosion are particularly susceptible
- The crack inhibiting effect of anions added to the damaging environment
- The observation that cracking occurs in zones of natural potential corresponding to active/passive transitions, i.e. critical potentials for cracking.

# Chloride Induced Transgranular SCC of Type 304 Stainless Steel

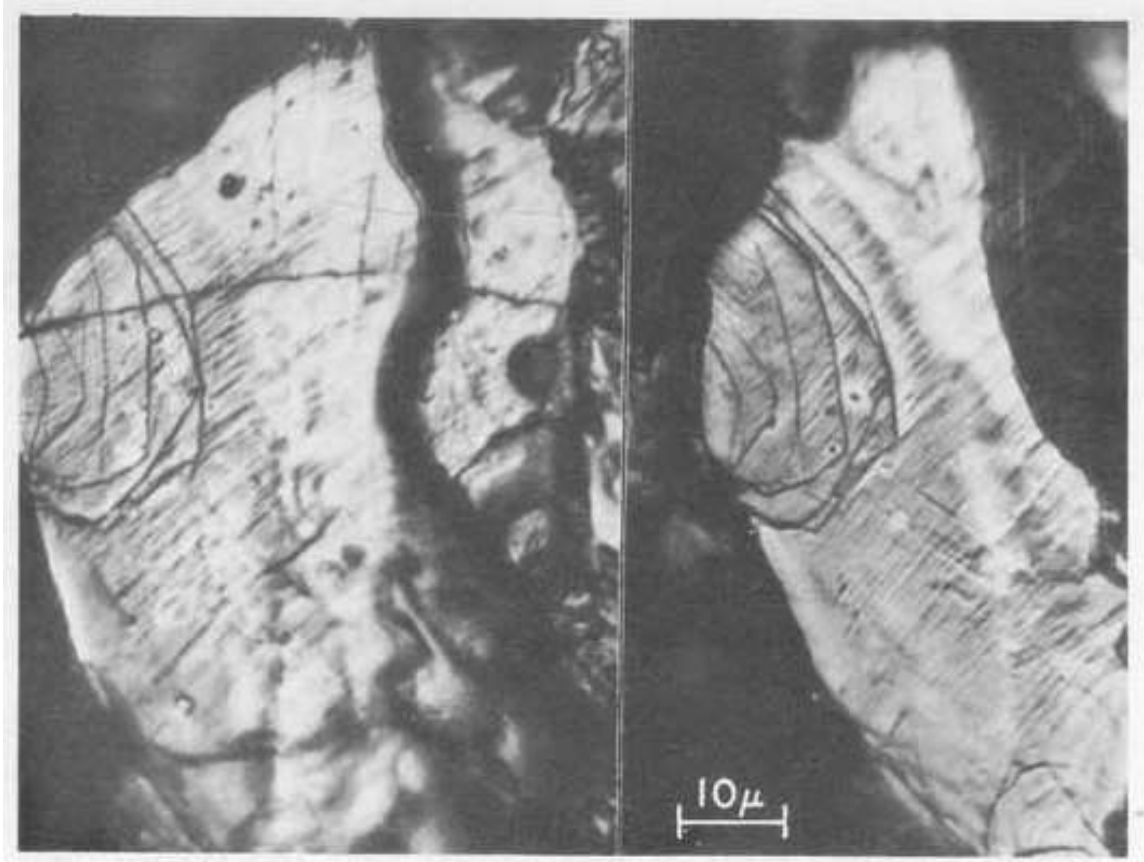
(Latanision and Staehle, *SCC of Fe-Cr-Ni Alloys*, 1969)





Morphology of Fracture in 316 Stainless Steel  
Exposed to Boiling MgCl<sub>2</sub>

(from Nielsen, *SCC of Fe-Cr-Ni Alloys*, 1969)

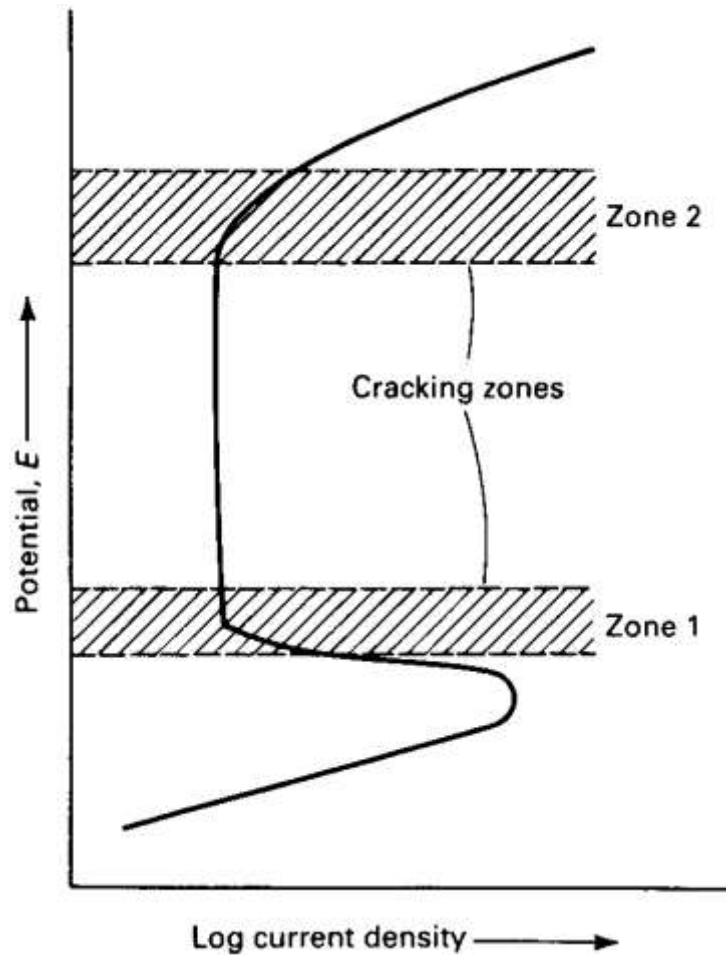


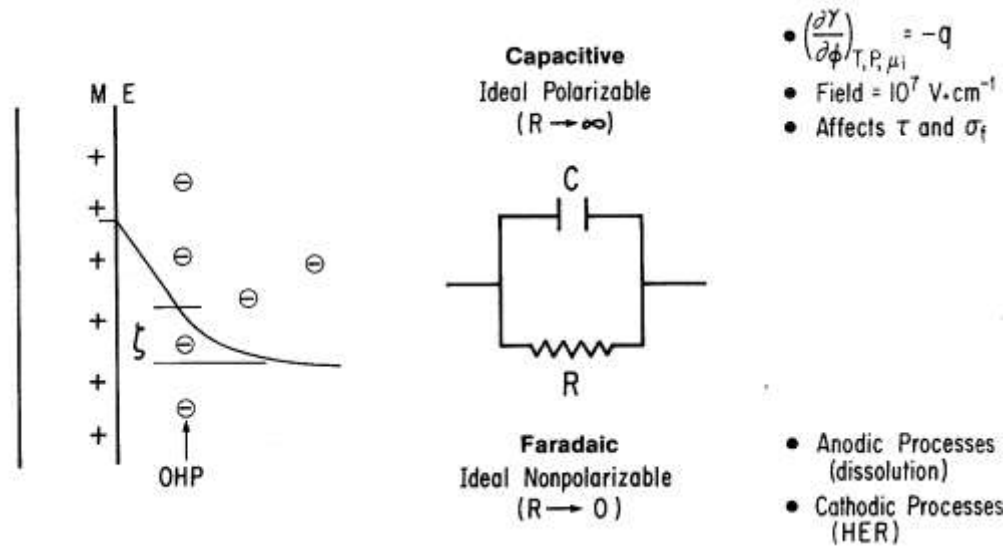
Matching detail in fracture surfaces of 304  
Stainless Steel Exposed to Boiling MgCl<sub>2</sub>

(from Nielsen, *SCC of Fe-Cr-Ni Alloys*, 1969)

# Schematic Anodic Polarization Curve Showing Zones of Susceptibility to Cracking

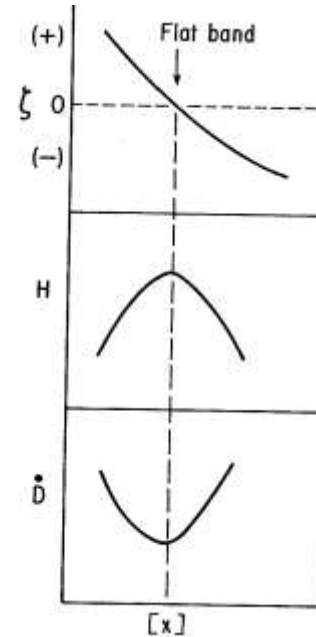
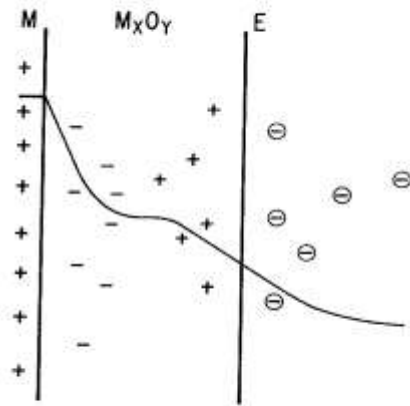
( From R.A. Jones, *ASM Handbook*, Volume 13A: Corrosion)





## The Charge and Potential Distribution at a Metal-Electrolyte Interface

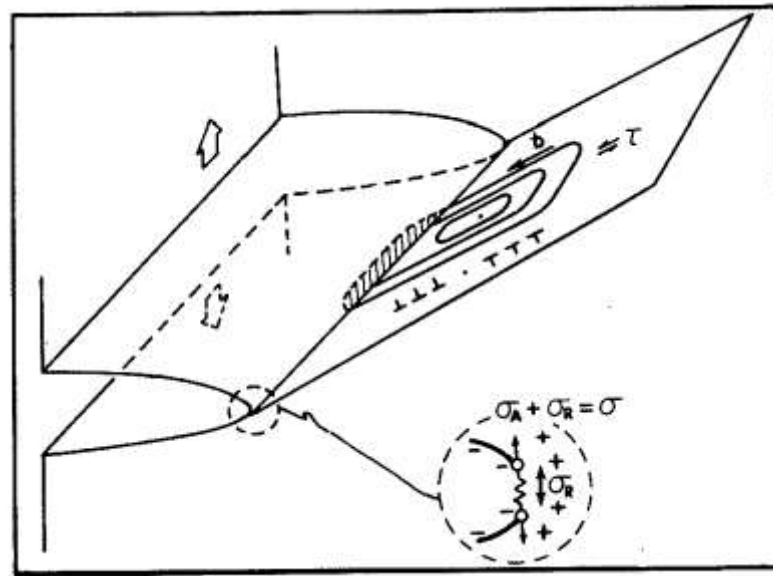
(From Latanision, *Atomistics of Fracture*, 1983.)



Charge and Potential Distribution at a Metal/Oxide Interface  
and Corresponding Mechanical Behavior Effects

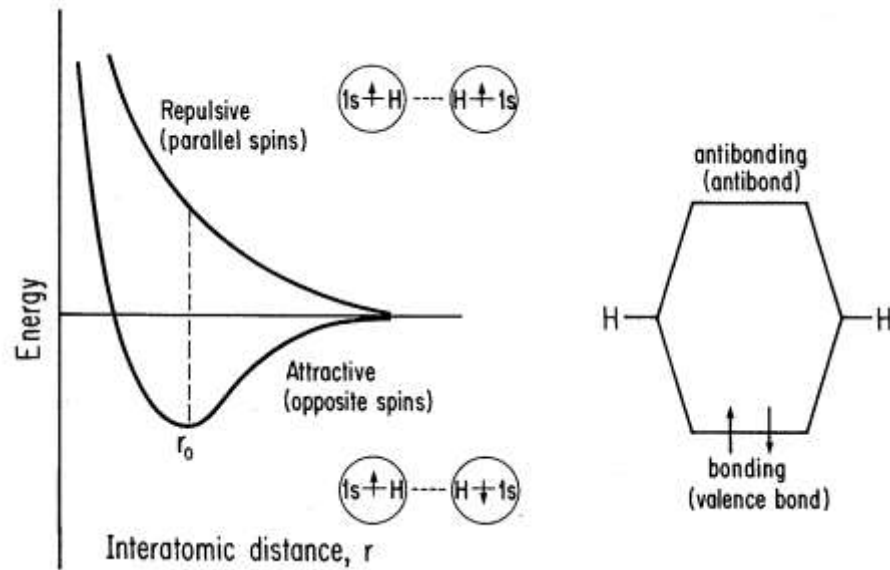
(From Latanision, Atomistics of Fracture, 1983.)



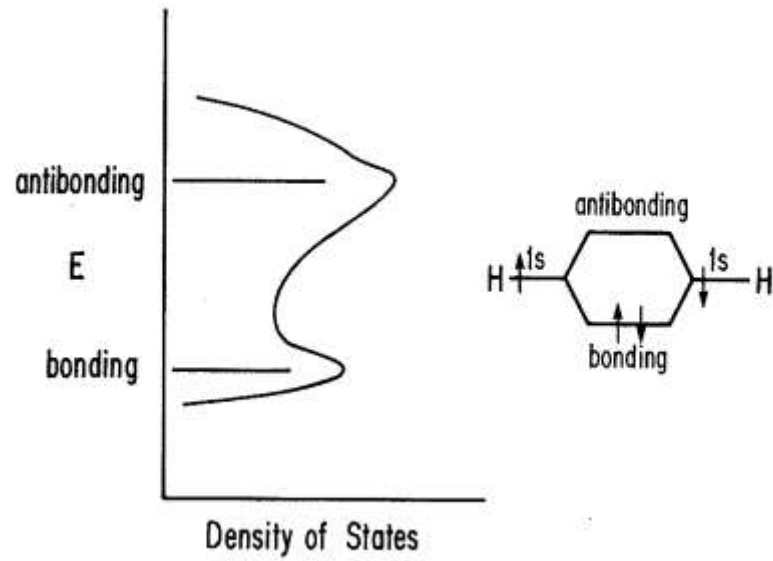


Crack Tip Showing the Possible Influence of the Double Layer on Shear and Fracture Processes.

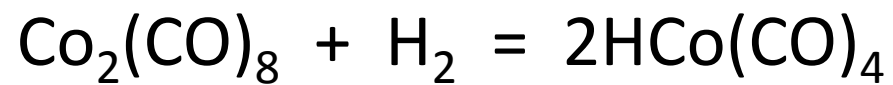
(From Latanision, *Atomistics of Fracture*, 1983.)



The Energetics of the Hydrogen Molecule



Adsorption of Hydrogen on Metal Surfaces

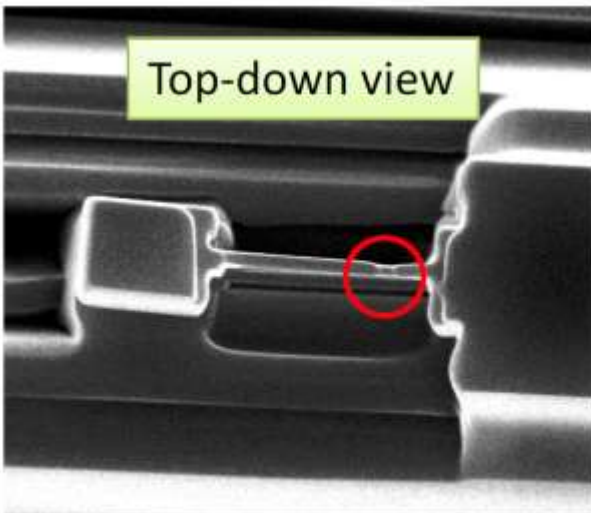


The Dissociation of Cobalt Carbonyl in the Presence of  
Molecular Hydrogen

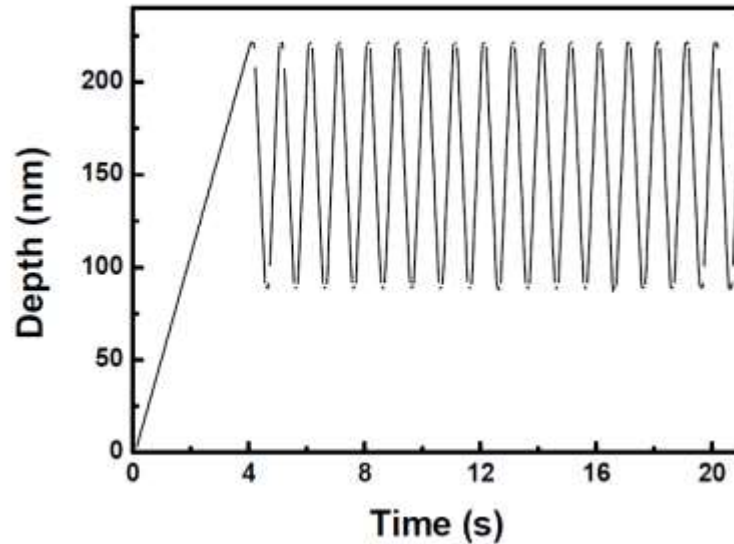
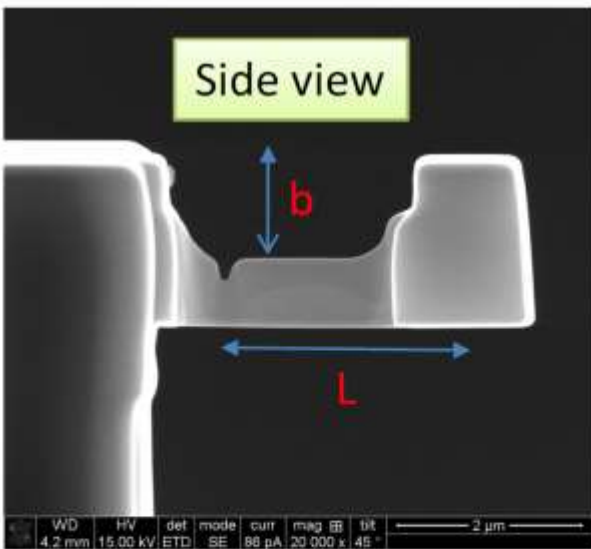
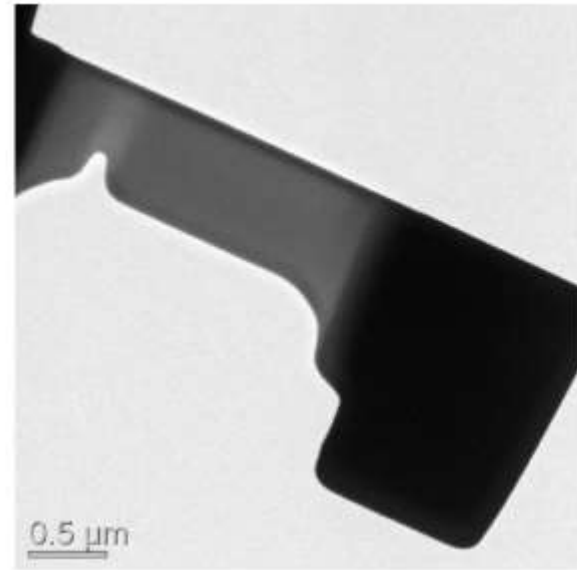
# Experimental Resolution vs. Computational Fidelity

- Experimental Resolution is on the Order of Atomic Dimensions
  - ATEM, Atom Probe (3D), AES
  - FIB Techniques for Sample Preparation
- Modeling & Simulation Can Now Handle Atomic Scale Dimensions-Volumes of Near Engineering Significance

# $Al_{88}Fe_7Gd_5$ MG



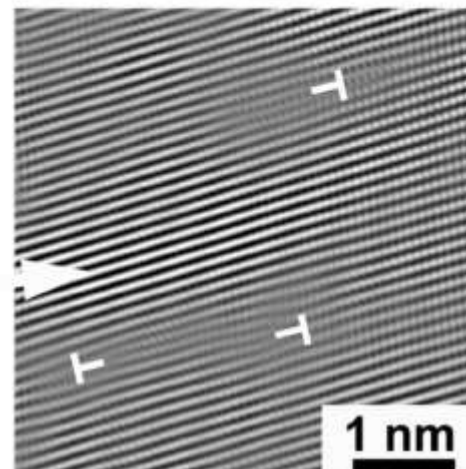
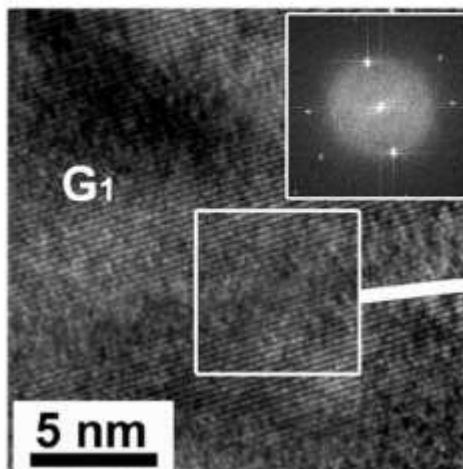
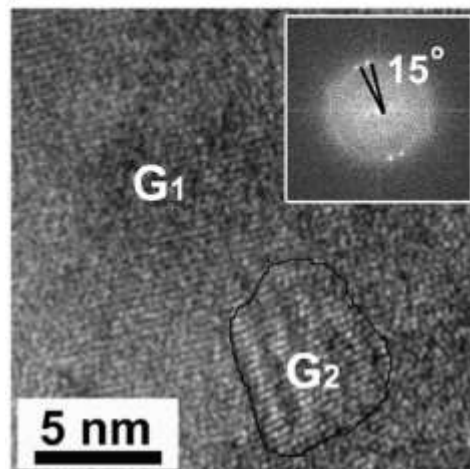
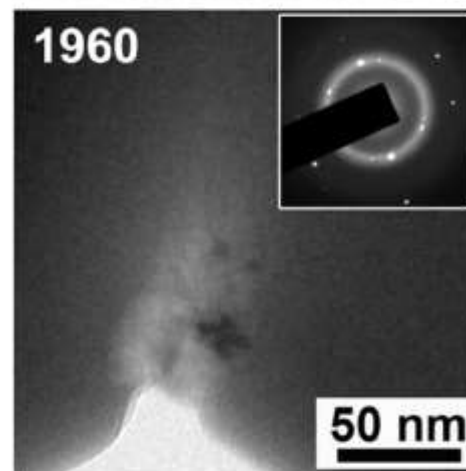
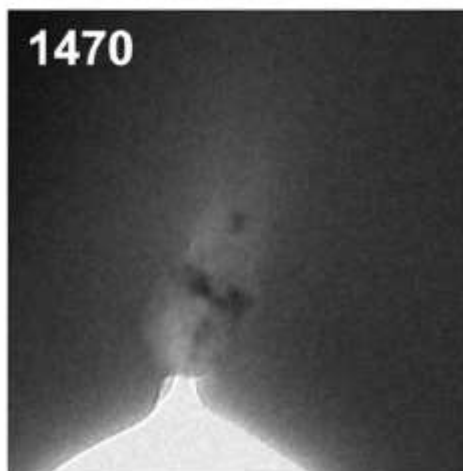
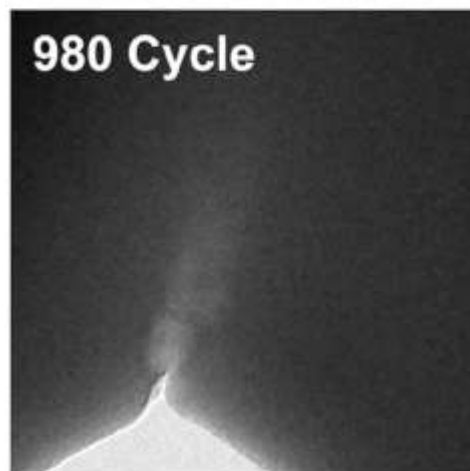
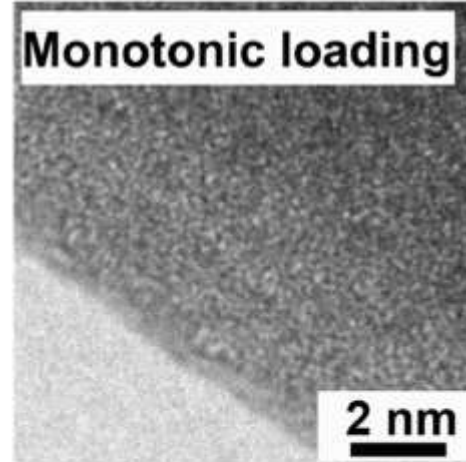
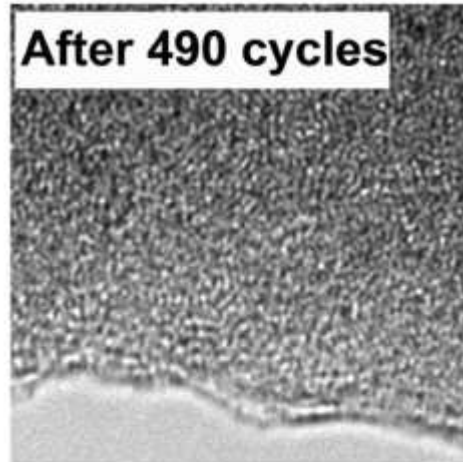
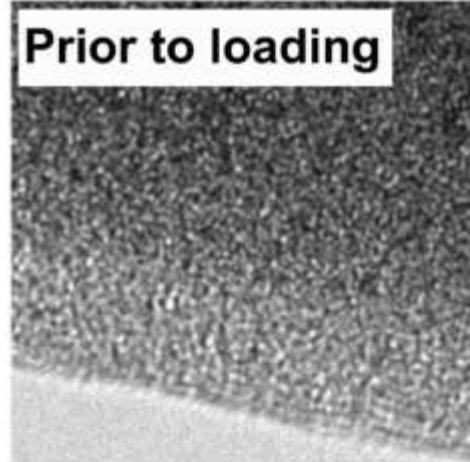
Thickness (t)=120 nm  
Width (W)=741 nm  
Length (L)=2540 nm  
a: notch length  
W-a=498 nm  
b=1115 nm



Depth: 88~220 nm;  
Frequency: 1 Hz;  
Largest cycle No. is less than 500 in one running test;

SEM

Real-time, high-resolution study of nanocrystallization and fatigue cracking in a cyclically strained metallic glass, *PNAS* **110** (2013) 19725



*PNAS* **110** (2013)  
19725

[Li.mit.edu/video](http://Li.mit.edu/video)

# A New Era: Atomistic Analysis of The Material-Environment Interface

The convergence of increased experimental resolution and increased sophistication in modeling and simulation provides extraordinary tools to experimentalists and to modelers. This has the potential to lead to a new era in developing an understanding the atomistics of environmentally-induced fracture.