The Story of Microstructure-Sensitive Corrosion Pit Growth and Mechanical Performance

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COMSOL CONFERENCE
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The Navy and Marine Corps Corporate Laboratory

US Naval Research Laboratory

THOMAS A. EDISON

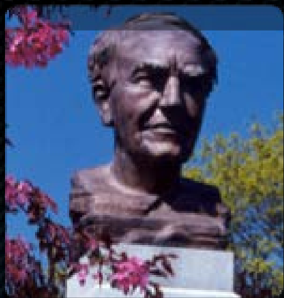
"GOVERNMENT SHOULD MAINTAIN A GREAT RESEARCH LABORATORY TO DEVELOP GUNS, NEW EXPLOSIVES AND ALL THE TECHNIQUE OF MILITARY AND NAVAL PROGRESSION WITHOUT ANY VAST EXPENSE."

THE NEW YORK TIMES MAGAZINE
SUNDAY, MAY 30, 1915

- Idea followed the sinking of the Lusitania in 1915.
- Secretary Josephus Daniels Established Naval Consulting Board with Thomas Edison as Chair: October 7, 1915.
- August 29, 1916 Congress appropriates funds.
- Delayed by WW-I, Assistant Secretary of the Navy, Theodore Roosevelt, Jr. commissions the lab on July 2, 1923.

The MULTIPHYSICS Laboratory

NRL Commissioned
1923



First radar installed on USS New York
1939

Principles of modern fracture mechanics
1947

Vanguard I launched
1958

First U.S. intelligence satellite
1960

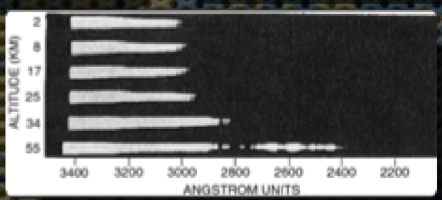
- Sound Navigation and Ranging (SONAR)
- Plan-Position Indicator
- Liquid Thermal Diffusion Process
- Synthetic lubricants
- Improved Aircraft Canopy
- Deep Ocean Search

1920 — 1930 — 1940 — 1950 — 1960

- Gamma-Ray Radiography
- First U.S. radar patents
- Submarine, airborne & OTH radars & IFF
- First Detection of X-Rays from the Sun
- Submarine life support
- Over the Horizon Radar

Skip distance effect
1925-1926

First concept & proposal for nuclear sub
1939



First experiment in space
1946

Purple K Powder
1959

Aqueous Film Forming Foam
1966

First fiber-optic acoustic biosensor
1977

Permanent Magnets
1980

Nobel Prize in Chemistry to Jerome Karle
1985

Decadal Impact of El Nino discovered
1994

SHARP Reconnaissance
2001

Dragon Eye UAV
2002

Lunar camera

Excimer laser

Advanced Narrowband Secure Voice Terminal

Extreme Ultraviolet Imagine Telescope

CBR sensors for Fleet & Homeland Security

ANDE-2 Spacecraft

1970 | 1980 | 1990 | 2000 | 2010

GPS prototype in orbit

(GaAs) production techniques

Blood Surrogate

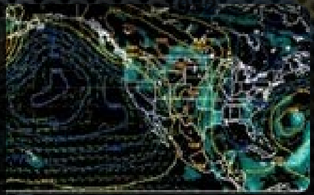
IPsec, IPv6, NKDS

Specific Emitter ID

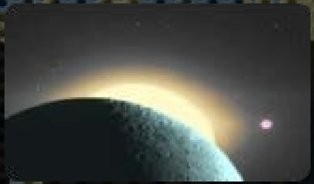
Intrinsic Magnetism at Silicon Surfaces

Timation - GPS
1964-1977

Navy Operational Global Atmospheric Model
1982



NQR detection for explosives & narcotics
1992



Clementine Spacecraft
1991-1994

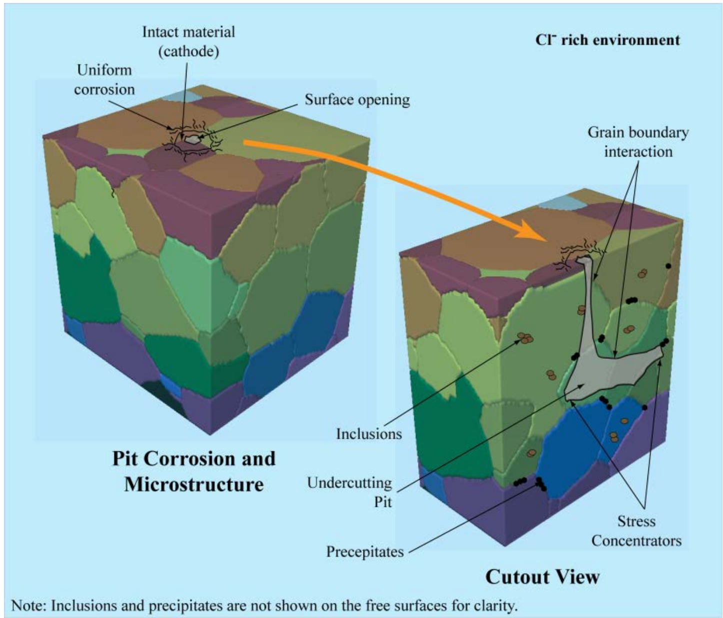
WindSat Spacecraft
2003

QuadGard
2005

The MULTIPHYSICS Laboratory

Objective & Context

Pitting in Saline environment



Objective: Determine the effect of microstructure, specifically crystallographic orientation, on stable pit growth by incorporating actual 3D microstructure in computational models.

Use the Force with Wisdom

- Comsol is a high-level problem solving tool: not your traditional finite element kernel (so 90's)
- With its easy modularity and universal options, its optimal use requires that one:
  - Knows both one's math and physics → Be the master of most multiphysics problems (PDE's, ODE's)
- To be one with the Force, always perform:
  - Benchmarking/Verification
  - Validation
- **Advice:** Go from simple to complex!

Corrosion is Everyone's Problem

National Research Council, National Academy of Sciences Report
Research Opportunities in Corrosion Science and Engineering (2010)

"Lack of a **fundamental knowledge** about corrosion and its application to practice is directly reflected in the **high societal cost** of corrosion (2-4 percent of the U.S. gross national product)."

Corrosion Fatigue

Incident: Aloha Airlines 243 (1988)
Credit: Associated Press library photo.

Incident: Prestige Tanker Oil Spill (2002)
Credit: dpa-info.com

Pitting Corrosion

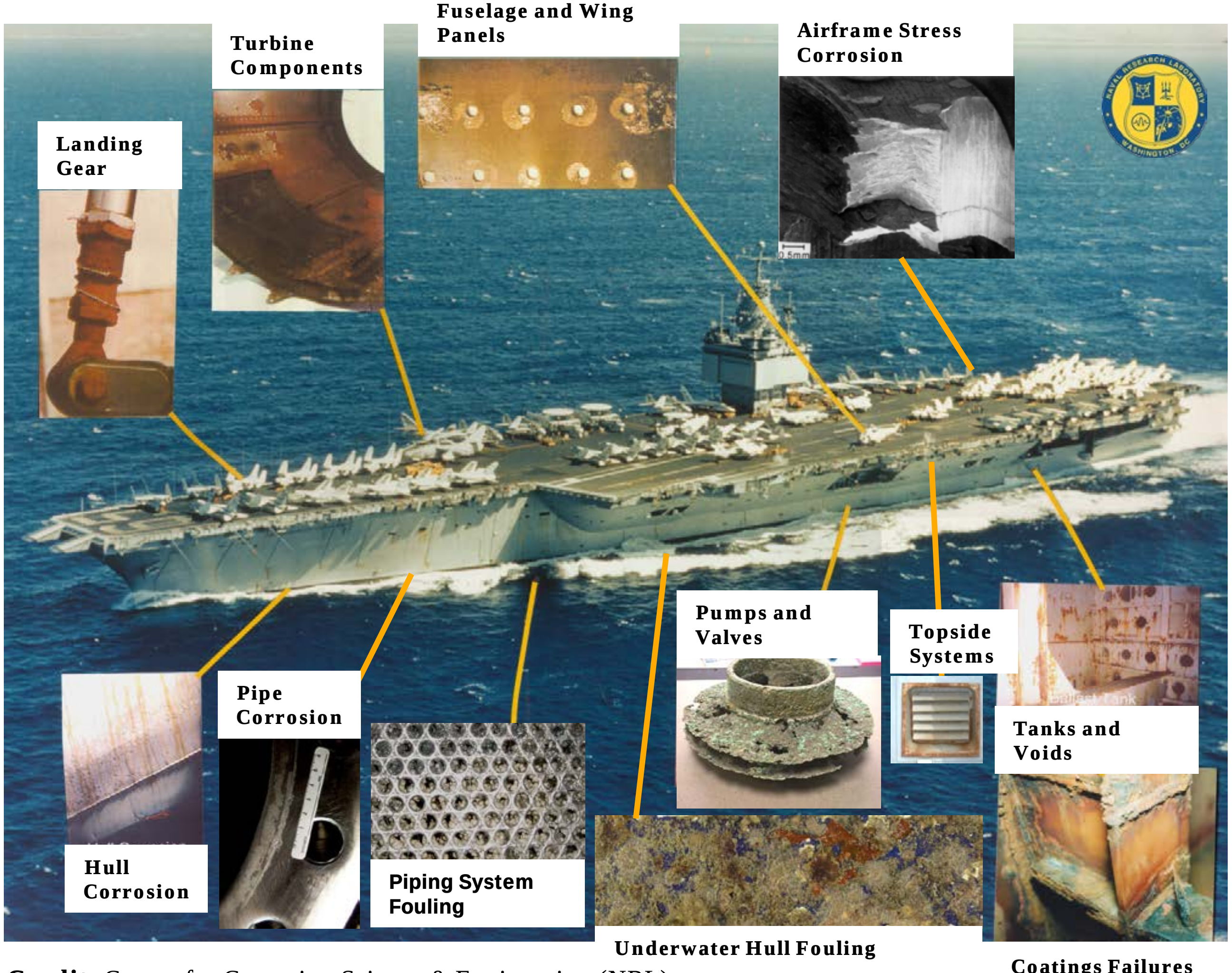
Incident: Guadalajara Sewer Explosion (1992)
Credit: José M. Malo, Electrical Research Institute, Mexico

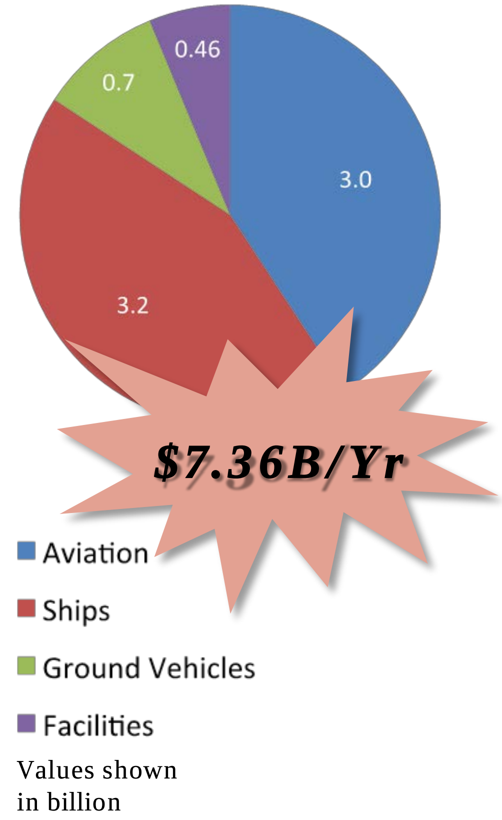
Corrosion Research Grand Challenges (CRGC):

- CRGC I: Corrosion-resistant materials and coatings
  - Understanding the nature of protective films/scales, including structure.
  - Complete and comprehensive understanding of electrochemistry - from the electronic to microscale-level.
- **CRGC II: High-fidelity modeling for prediction**
  - **Development of a better understanding of corrosion mechanisms.**

Credit: Paul Natishan, Center for Corrosion Science & Engineering (NRL)

Corrosion: NAVY's #1 Maintenance Problem



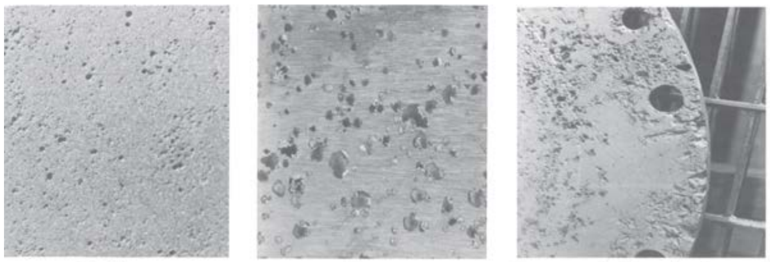


Ships and corrosion are life-long friends!

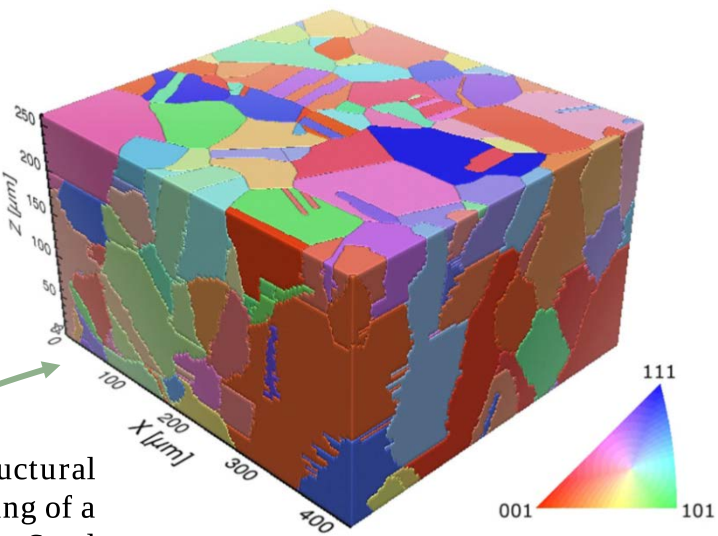
Credit: Center for Corrosion Science & Engineering (NRL)

Pitting: What Does It Look Like?

Examples of Pitting in Stainless Steel*

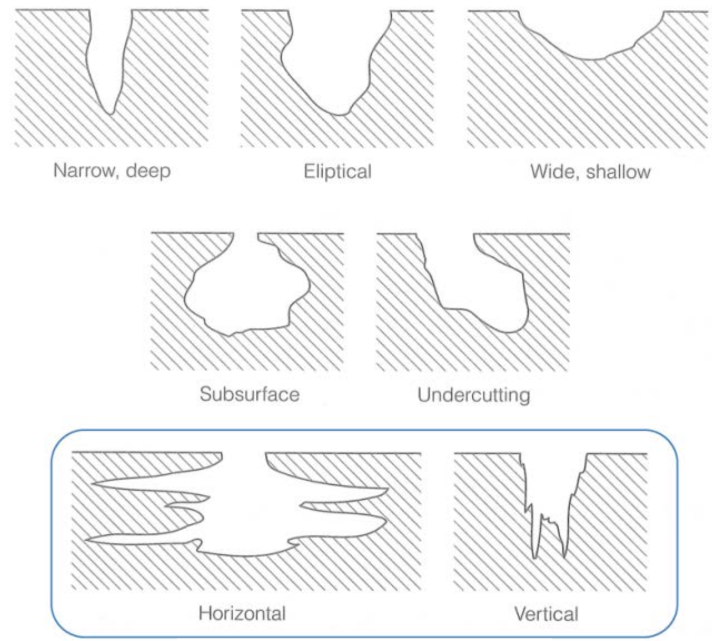


Shallow Deep Deep and Closely Spaced



3D Microstructural Rendering of a Stainless Steel

Variations in Pit Shapes Due to Metallurgical and Environmental Conditions*



Intergranular Growth

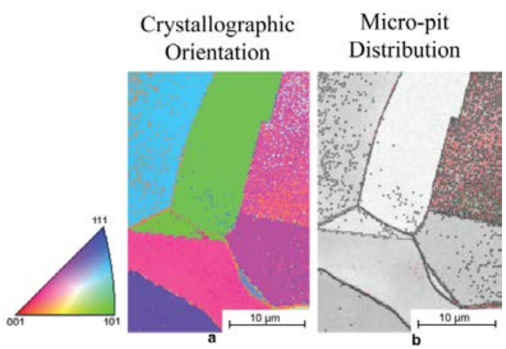
***Source:** D. A. Jones, *Principles and Prevention of Corrosion*, Macmillan Publishing Company, New York, NY, 1992.

Pit growth and shape are related to microstructure.

Microstructural Influences

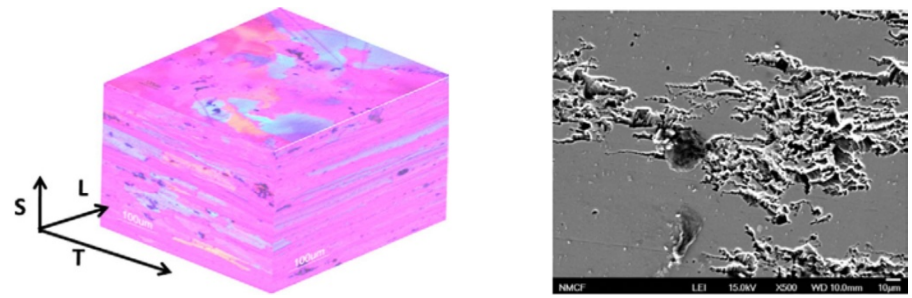
In-situ Experimental Evaluation is not Easy

Micro-Pit Density Variation with Crystal Orientation in 316LVM Steel



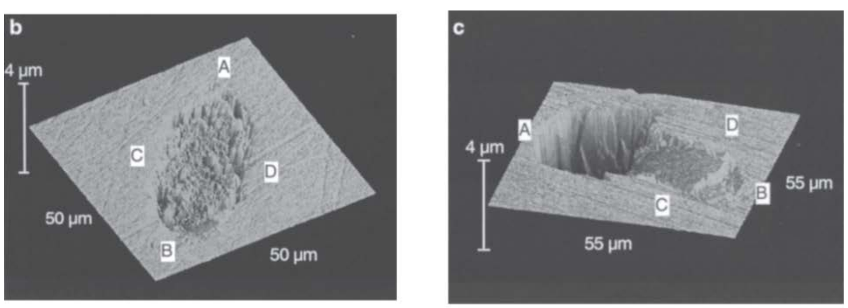
Source: A. Shahryari, et al., *Corrosion Science*, 51, 677-682, 2009.

Intergranular and Pitting Corrosion in AA5083 due to b-Phase at Grain Boundaries and Grain Aspect Ratio



Source: S. Jain et al., *Corrosion Science*, 59, 136-147, 2012.

Metastable and Stable Pitting at MnS Inclusion in 304 SS



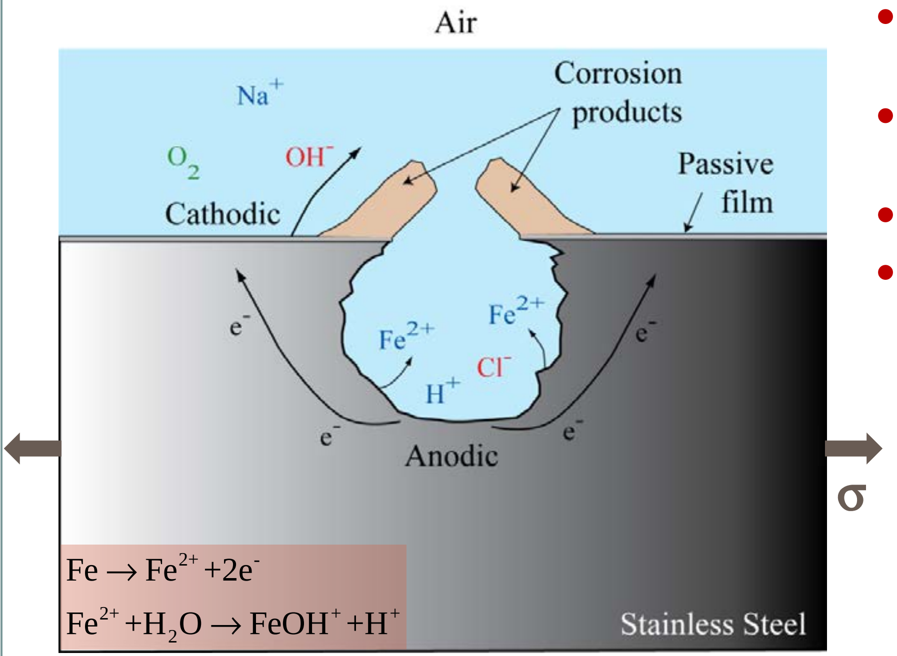
Source: T. Suter, et al., *Journal of the Electrochemical Society*, 148(5), B174-B185, 2001.

Features of Interest

- **Crystallographic orientation**
- Grain shape (aspect ratio)
- Molar concentration variations:
  - Constituent migrations (precipitates)
  - Secondary particles or phases
- Grain boundaries

The Physics and Math of Pitting Corrosion

Dissolution and Diffusion in the Stable Pit: The Fully Coupled Phenomenon



Species, c_i: Fe^{2+}, $FeOH^{+}$, Cr^{3+}, $CrOH^{2+}$, OH^{-}, H^{+}, Cl^{-}, Na^{+}, …
Potential: φ

NOTE: There is no diffusion in the solid!

- Electrochemical reactions at the corrosion front and chemical reactions throughout the pit.
- Species available for reactions are being transported throughout the pit.
- Corrosion front moving outward due to dissolution of metal.
- Mechanical loading takes place concurrently to pitting.

Balance of Species: $$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{J}_i + R_i$$

Ionic Flux: $$\mathbf{J}_i = D_i \nabla c_i + z_i \frac{D_i}{RT} F \left(c_i \nabla \phi \right) + c_i \mathbf{v}$$

Transport: diffusion, electro-migration, convection

Species Generation: $$R_i := -k_i^f c_{\text{reactants}} + k_i^b c_{\text{products}}$$

Charge Neutrality: $$c_i z_i = 0$$

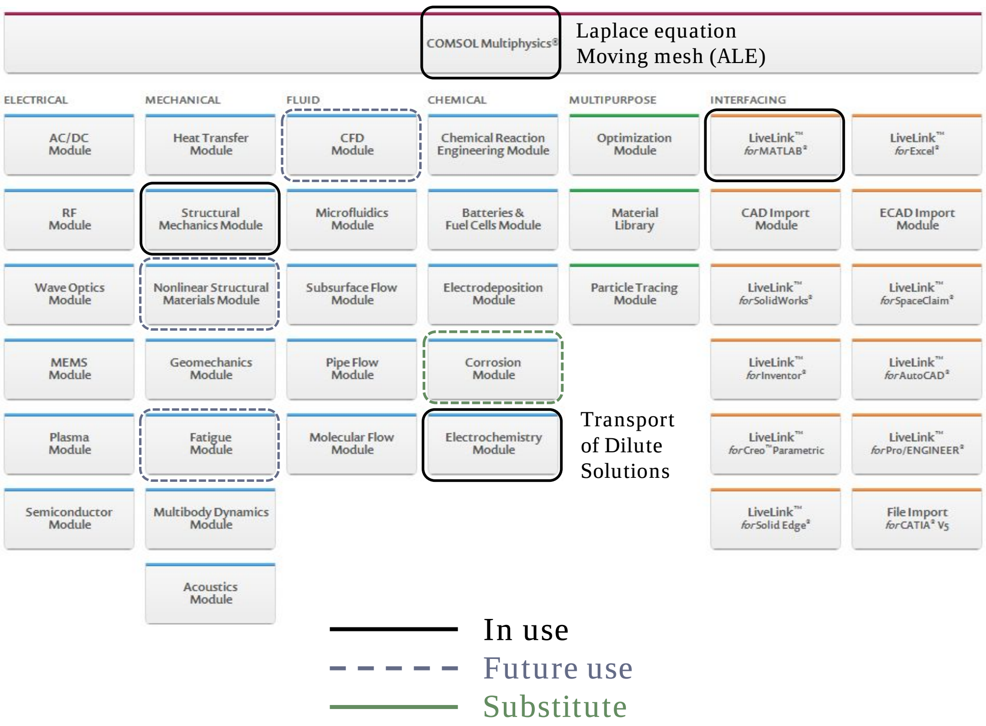
Interface Condition: $$\{ \| \mathbf{J}_i^I \| - \| c_i \| \mathbf{V}^I \} \cdot \mathbf{N} = 0$$

Research Approach
Take Baby Steps!

- Material: 316 Stainless steel.
- Incorporate actual microstructure from Orientation Image Microscopy data.
- Use Comsol to simulate and analyze stable pitting at the microstructural scale: Multiphysics capability.
- Track corrosion front movement through advanced ALE meshing technique.

(Good Practice) Strategy

- **# 1: Benchmark** implementation against existing, simpler numerical studies!
- **# 2:** Perform modeling from **simpler to complex** coupling with front movement:
  - Laplace equation (maximum corrosion rate),
  - Mass transport (activation/diffusion-controlled),
  - Decoupled mechanical analysis,
  - Electrochemical-mass transport,
  - Electrochemical-mass-transport-mechanical
  - 3D?!



Galvanic Corrosion (Laplace Eq.):
Benchmarking ALE Meshing

- Reduced physics → Solve for potential distribution in the electrolyte:

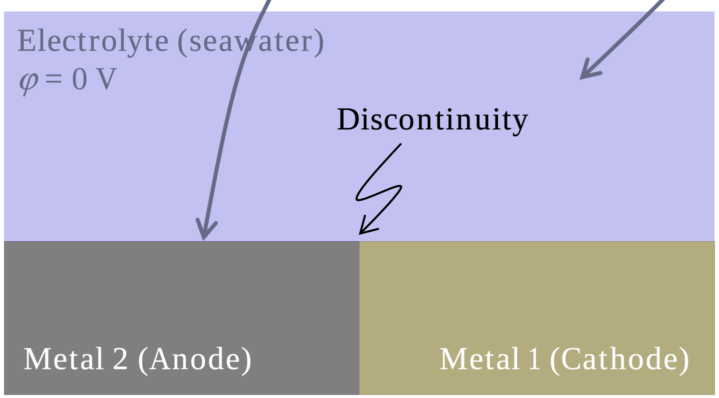
$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \left(D_i \nabla c_i + z_i \frac{D_i}{RT} F \left(c_i \nabla \varphi \right) + c_i \mathbf{v} \right) + R_i \longrightarrow \nabla^2 \varphi = 0$$

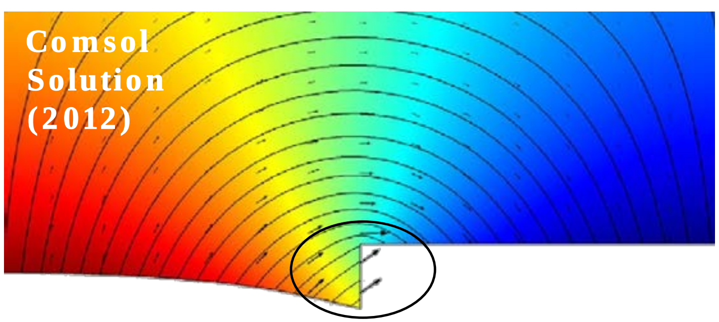
- Corrosion front velocity (~dissolution rate) is obtained through Faraday's Law: $V_n = \frac{M}{zF\rho} \nabla \varphi \cdot \mathbf{n}$

Simpler problem from the literature (based on COMSOL) to gain confidence and verify the implementation of ALE meshing technique.

Source: Deshpande KB. Corrosion Science 2010;52:3514.

Electric Potential Distribution with Deformed Mesh



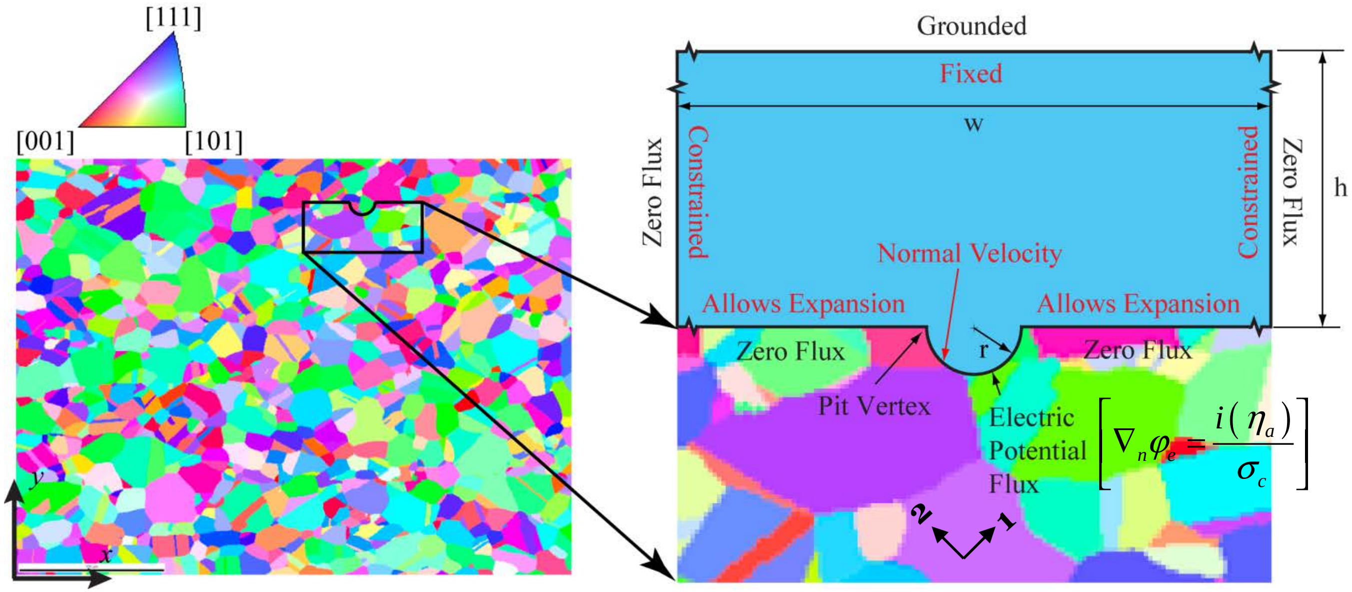


What Did We Learn?

- Scary flexibility of Comsol!
- Nuances of ALE meshing "art": mesh relaxation, remeshing, coarse vs. fine mesh, solver settings.
- ALE meshing strategy GOT us the solution we wanted, but was it the right one?
- **Experimental validation is the key!**

Pit Growth in the Microstructure:
Boundary Conditions and Constraints

OIM Reconstructed Microstructure | **Computational Model**



- Pit initialized with a semi circular geometry.
- Only anode required.
- Unrealistic pit growth due to relatively high potential at the corners!
- Buffer zone--vertical segment near vertex.
- Mesh relaxation conditions horizontally.
- **There is no active physics in the solid!**

$$\nabla^2 \varphi = 0$$

$$V_n = \frac{i(\eta_a)}{z_{\text{metal}} F c_{\text{metal}}}$$

$$\eta_a = V_{\text{app}} - V_{\text{corr}} - \varphi$$

$$i(\eta_a) := \overline{z} F A_{diss} \exp\left[\frac{zF(V_{\text{corr}} + \alpha\eta_a)}{R_g T}\right]$$

- Pit front velocity is a function of corrosion potential.
- Corrosion potential is a function of crystal orientation.

What is Needed at the Moving Pit Front

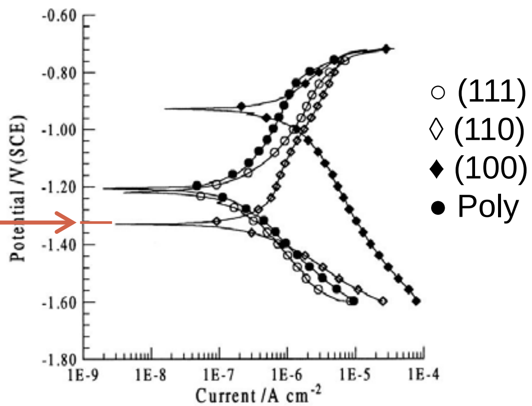
- Corrosion potential value at each nodal point.
- Crystal orientation at each nodal point.

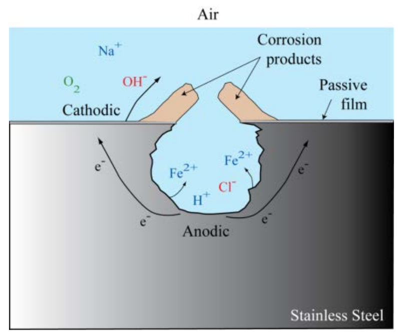
Microstructure-Sensitive Corrosion Potential

Polarization Behavior of Al Single Crystal Oriented in Principal Directions

$$i(V_{\text{corr}},\varphi) = A\sigma_c \exp\left[-b\left(V_{\text{app}} - V_{\text{corr}} - \varphi\right)\right]$$

Corrosion Potential



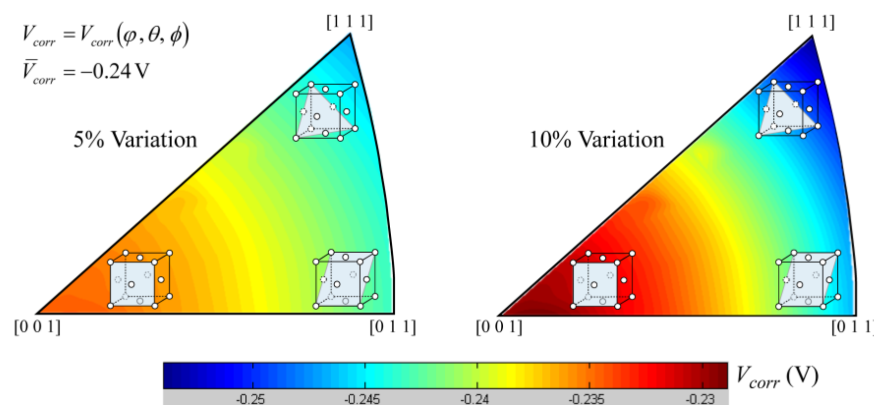


Assumption 1: The corrosion behavior of 316 SS is similar to that of 304 SS in 1M NaCl solution.

Assumption 2: Corrosion potential of FCC 316 SS varies the same way as that of FCC Aluminum.

Source: G. Treacy & C. Breslin, *Electrochimica*, 43(12-13), 1715-1720, 1998.

Corrosion Potential Variation w.r.t Orientations



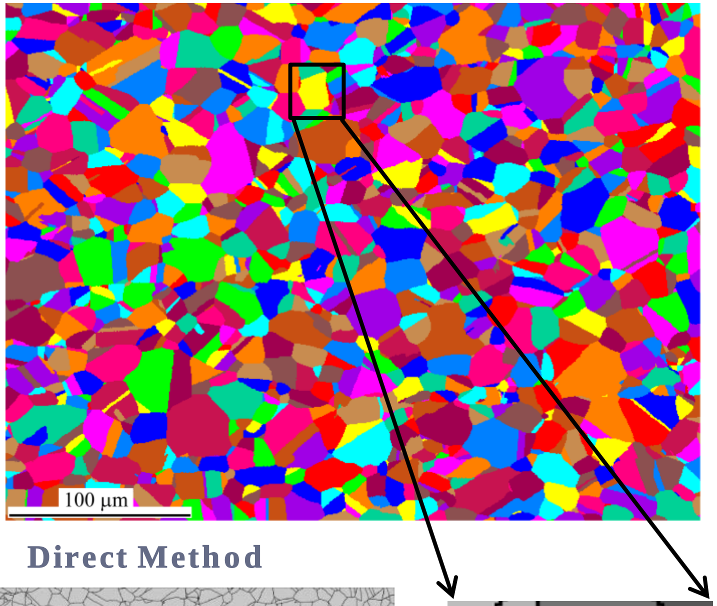
Variation of Pitting Corrosion for Aluminum

Material	Orientation	pH	E_{pit} mV$_{SCE}$	E_{pit} σ, mV
Al	{001}	6.5	−700	16
Al	{011}	6.5	−724	6
Al	{111}	6.5	−739	15

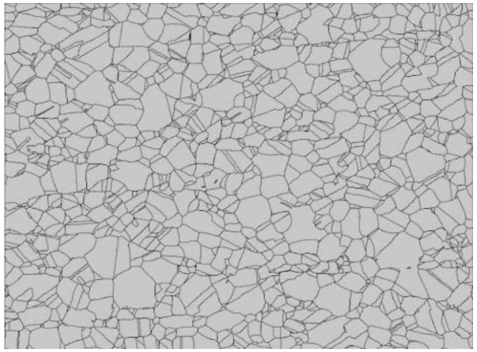
Source: M. Yasuda et al., J. Electrochem. Soc., 137(12), 3708-3715, 1990.

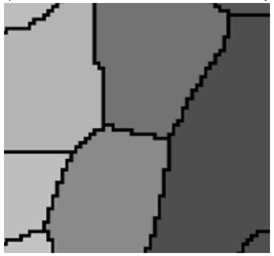
Incorporation of Microstructure
Not as Straightforward

2D OIM-Based Reconstruction of 316 Stainless Steel (383 μm x 286 μm)



Direct Method





Indirect Method

- Direct Method (Solid Mesh):
  - TIFF (raster format) → DXF (vector format)
  - Import DXF into COMSOL
  - **Domain identification for properties?**
- Indirect Method I (Functional Form):
  - Image → Grain identifier data on grid (Matlab)
  - COMSOL interpolates on the grid
  - **Subsequent operations for corrosion potential determination made it costly**
- Indirect Method II (Matlab):
  - COMSOL-Matlab integration
  - Single Matlab function to determine corrosion potential at pit location
  - **Successful and fast!**

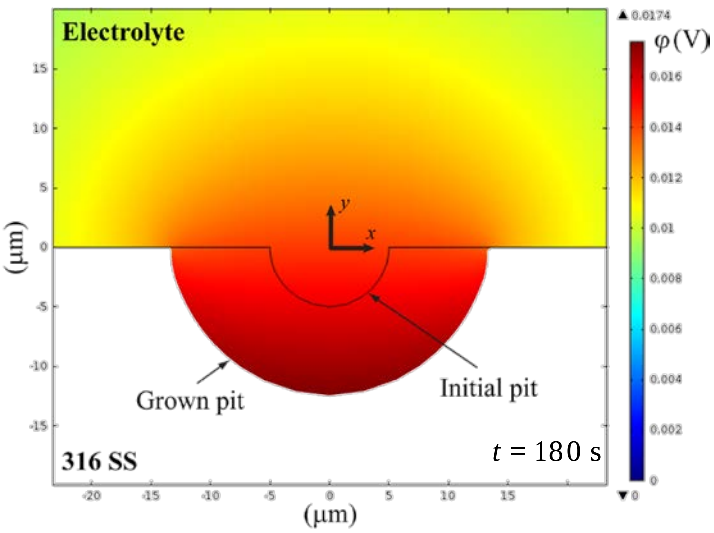
What Did We Learn?

- Neither imported mesh nor internal grain boundaries amenable to ALE meshing!
- Lots of effort spent … but
- We do not need a mesh in the solid!

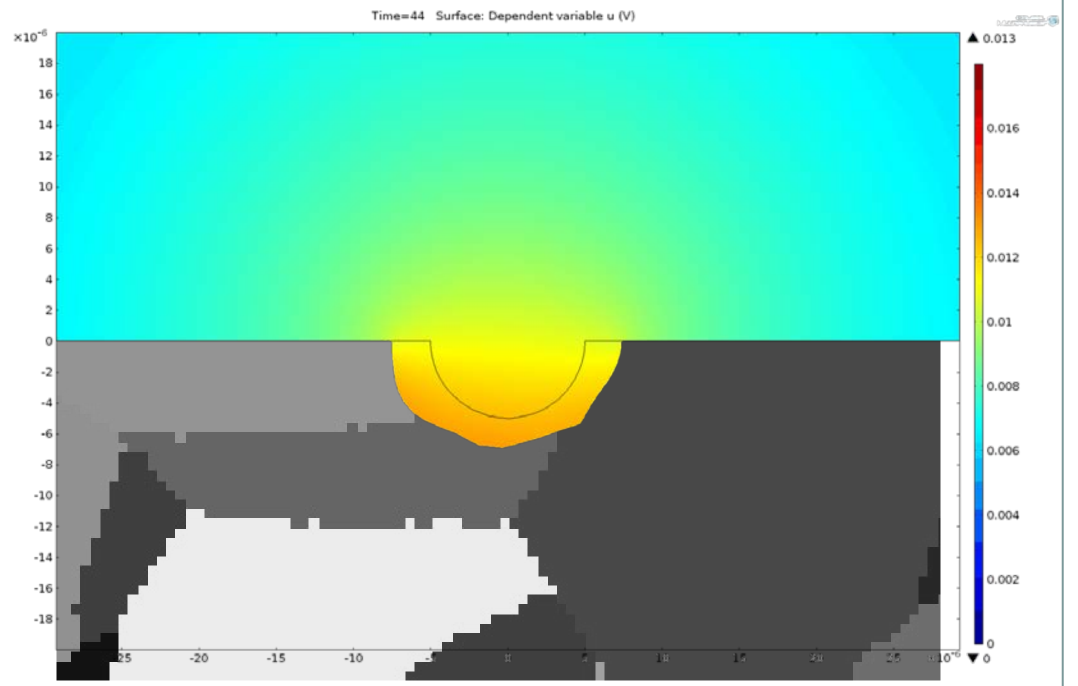
Effect of Microstructure on Evolution of Pit

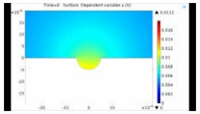
Potential Distribution and Shape of the Pit

Growth in Homogeneous Medium

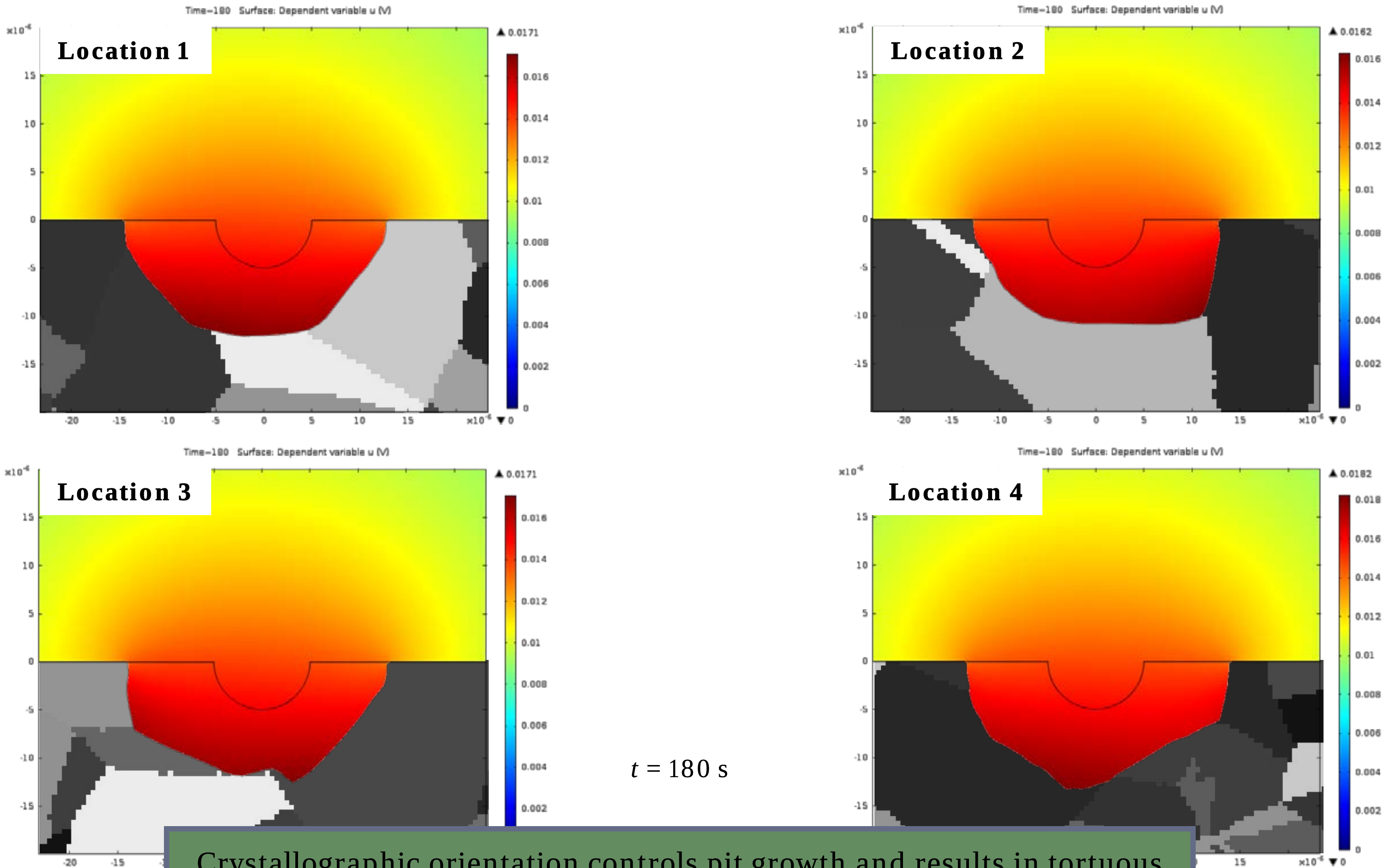


Growth in Microstructure





Pit Shapes



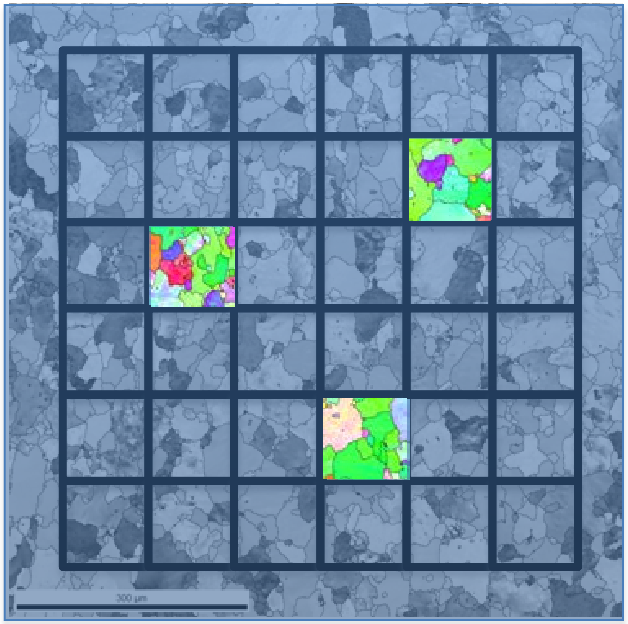
Crystallographic orientation controls pit growth and results in tortuous shapes commonly observed in experimental studies.

Progress Toward Validation
Modeling Driving Experiments

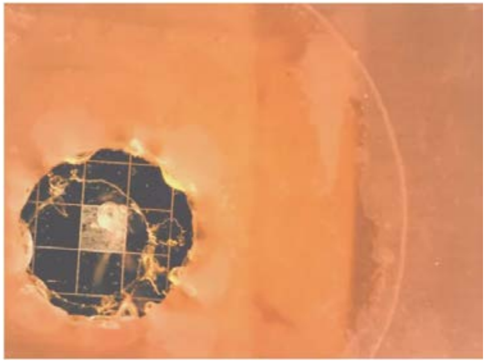
Even though the (new-found) modeling capability is driving the experimental effort, it is quite incomplete (to say the least) without experimental validation.

Selective Masking by Photolithography (SMP)

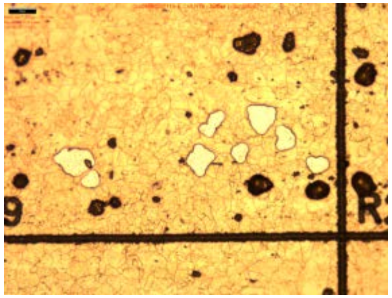
- Polish Specimen down to 0.05 colloidal silica for EBSD characterization
- Laser-machine grid on specimen surface
- Characterize surface microstructure of individual cells using EBSD
- Use Photo-Resist coating to cover specimen
- Use laser lithography techniques to expose specific cells
- Cure photo-resist to isolate individual cells during electro-chemical testing



In-situ Material Dissolution Video

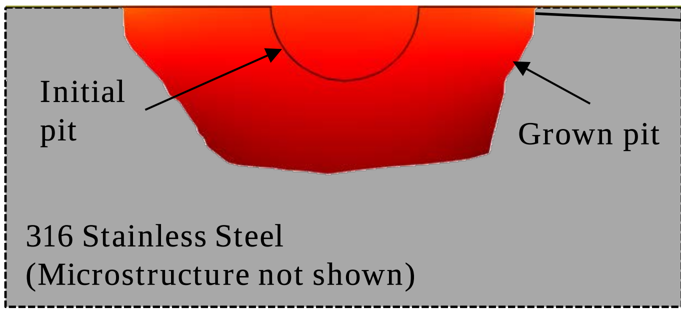


Grain Interiors

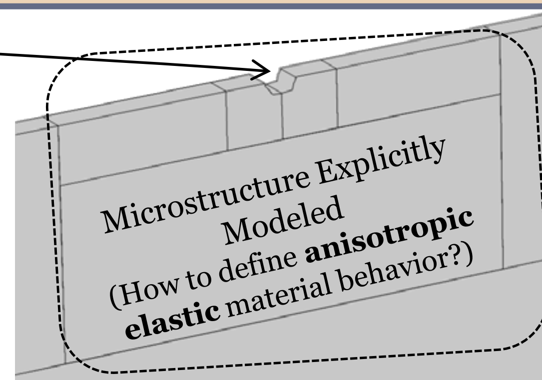


Decoupled Stress-Corrosion Analysis

Goal: Link pitting to mechanical performance based on bounds on maximum stress around the pit and identify the characteristics length scale for nonlocal effects.

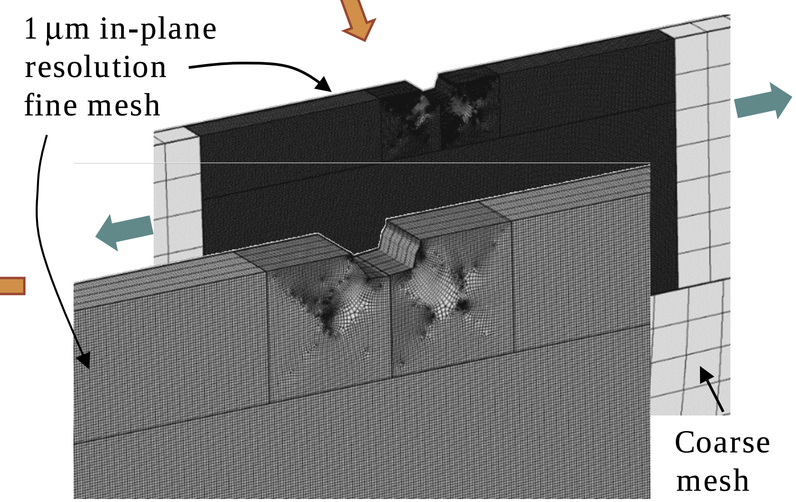


Separate
Extend
Extrude



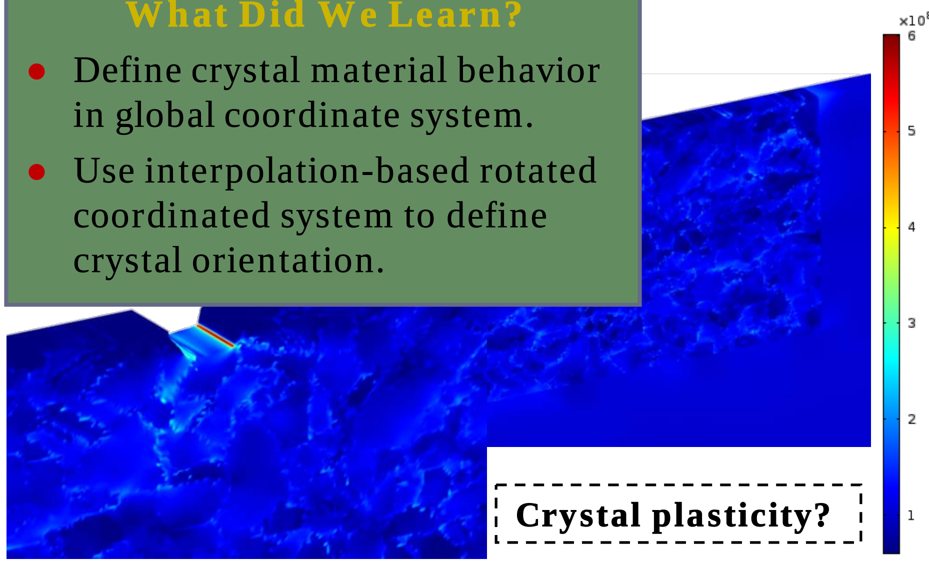
Maximum stress depends upon :

- shape of the pit
- Grain network (nonlocal effect).



What Did We Learn?

- Define crystal material behavior in global coordinate system.
- Use interpolation-based rotated coordinated system to define crystal orientation.



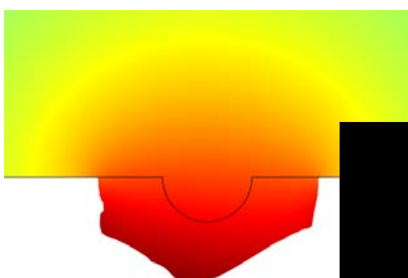
Pit Tortuosity and Stress Concentration

- Use tortuosity measures to quantify the irregularity of pit shapes.
- Investigate the correlation between tortuosity measures and bounds of maximum stress.

$$\tau_{\kappa} := \int_{s_i}^{s_f} \left|\kappa(s)\right| ds,$$

$$\tau_{\kappa}^{norm} := \frac{\tau_{\kappa}}{p}; \qquad p = \int_{s_o}^{s_f} s\, ds,$$

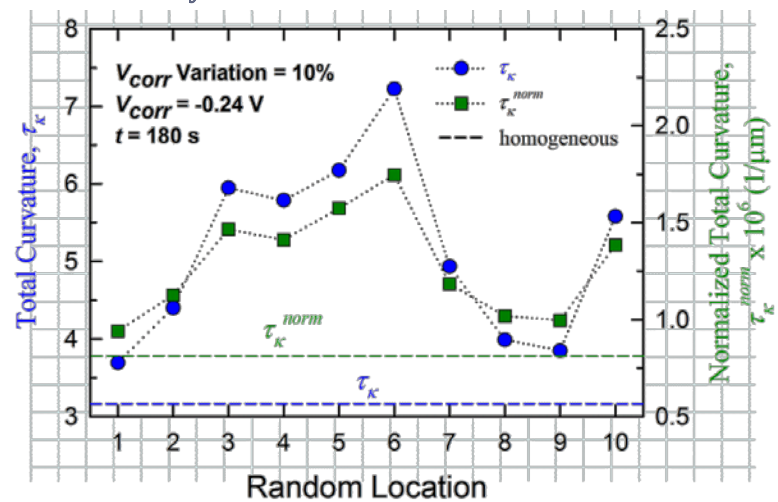
Simulation

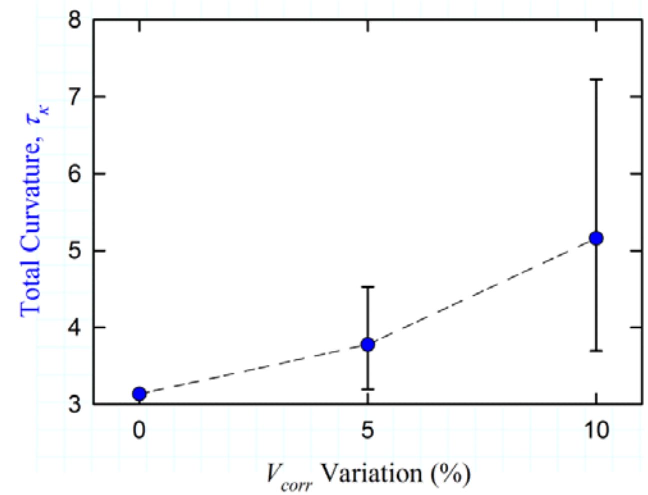


Edge Detection and Perimeter

Domain Assignment and Area

Tortuosity Values at Random Locations

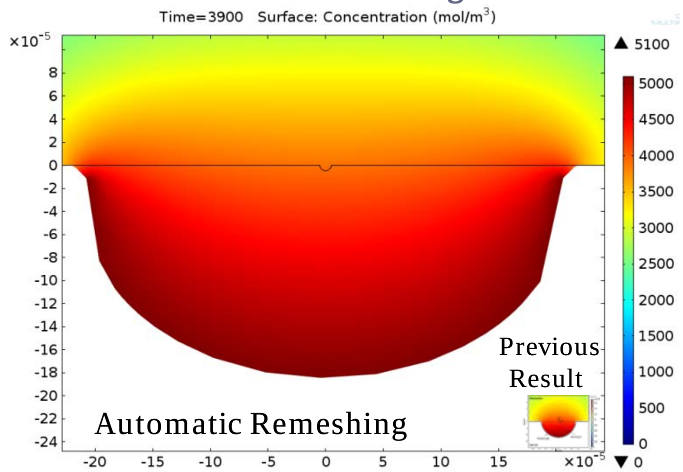




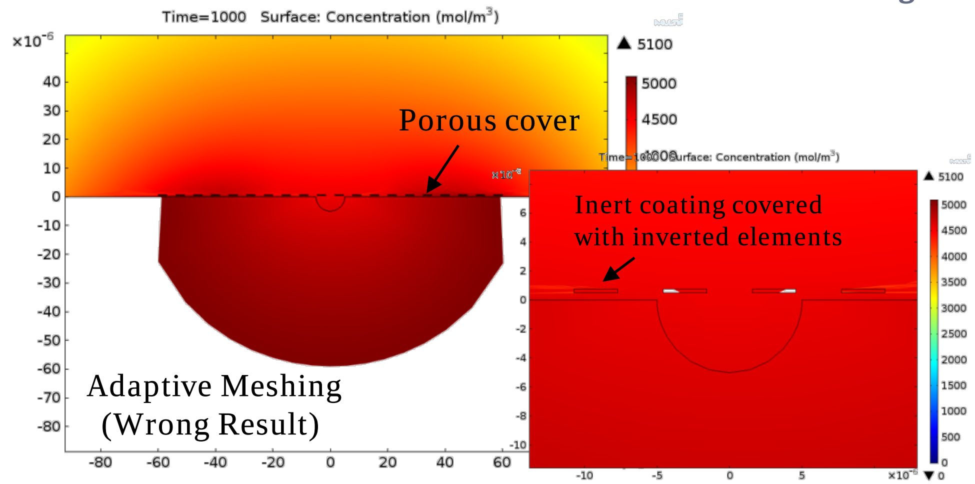
Numerical Improvements

Mind them!

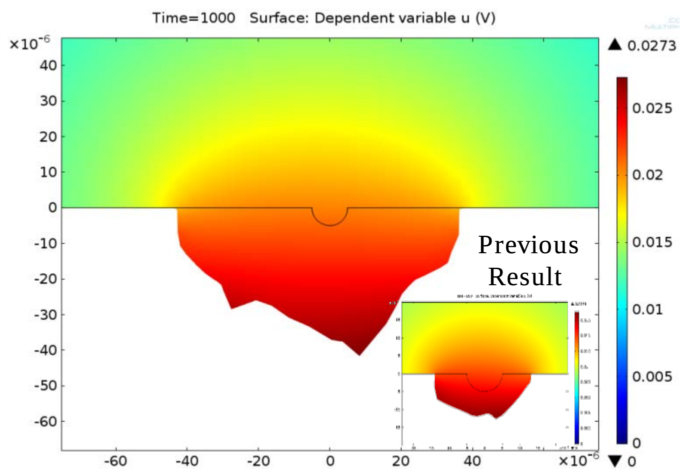
Diffusion-Controlled Homogeneous Growth



Diffusion-Controlled Growth with Porous Coating

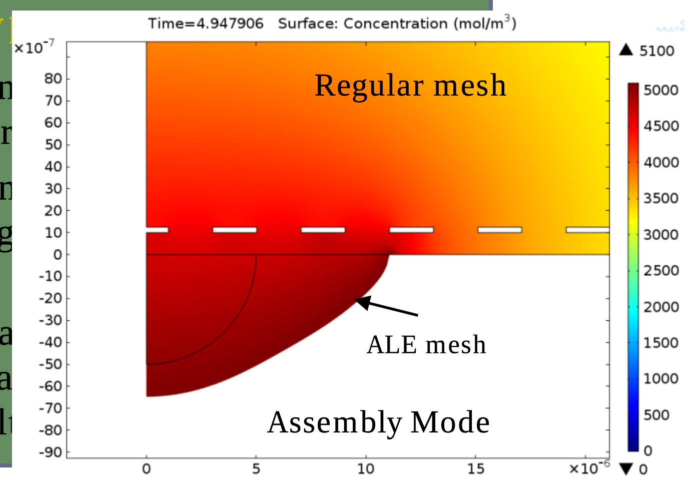


Growth in Microstructure



Diffusion-Controlled Growth with Porous Cover II

- With n… numer…
- The on… throug… you!
- Keep a… you ha… default…



Capabilities, Accomplishments and Directions

- Microstructure-sensitive corrosion growth modeling capability
  - Actual or synthetic microstructure can be incorporated,
  - Corrosion front movement is explicitly tracked with ALE meshing,
  - **No limit** on type of corrosion phenomena or multiphysics coupling.

- Demonstrated strong effect of the crystallographic orientation on pit shapes and growth.
  - Small variation in corrosion potential → complex shape evolution,
  - Tortuous shapes → stress concentrations.
- Simulated diffusion- and activation-controlled mechanisms.
- Performed decoupled stress-corrosion simulations.

- A work in progress … with evolving objectives.
- Microscale experimental data and verification is needed.
- Coupled electrochemical-mass transport formulation is under way.
- 3D **fully-coupled** predictive capability is the ultimate goal!

About the Force

- COMSOL is a very powerful, *evolving* tool:
  - Modelers should gradually move from simpler to complex problems leading to the target problem,
  - They should benchmark their results with existing (analogous) examples from the literature along the way,
  - Should they learn both their Math and Physics then *voila*!
  - Use COMSOL support resources: community portal, Q&A, case studies, and technical staff,
  - **With power comes responsibility (of V&V), use the tool wisely!**

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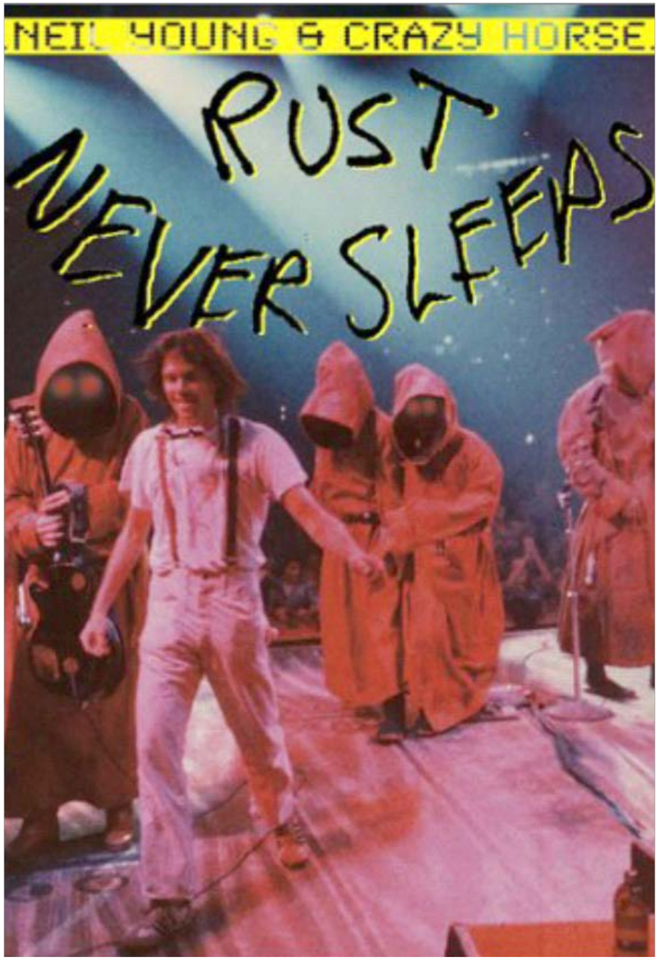
  - Dr. Alexis Lewis: Microstructural characterization
  - Dr. Andrew Geltmacher and Dr. Steve Policastro: Experimental characterization
- **Corrosion goals and Naval cost:** Dr. Paul Natishan, Center for Corrosion Science and Engineering, NRL.
- **NRL history:** Dr. Peter Matic, Superintendent, Materials Science & Technology Division, NRL.



Credit: Rust Never Sleeps, album by Neil Young and Crazy Horse, 1979.