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Center for Electrochemical Science and Engineering

University of Virginia

Quantitative Analyses of the Severity of Attack on Crevice Corrosion Surfaces

Presented to:
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Corrosion '06

Presented by:
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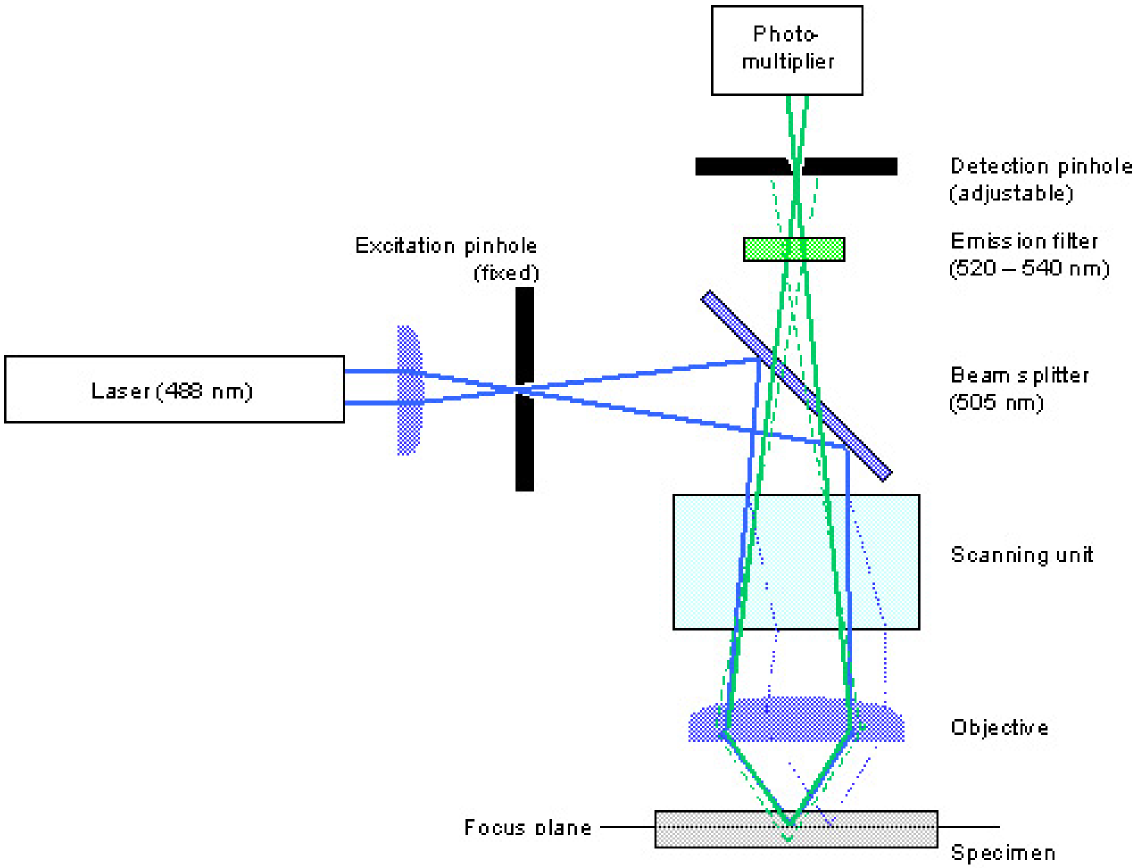
- **The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OST&I.**

The Need for Quantification of Localized Corrosion Damage

- Damage from general corrosion is easily quantified
  - Mass loss allows calculation of average penetration rate
- Quantification of localized corrosion has been limited, especially for crevice corrosion
  - Pitting metrics: #/cm^2, average of "deepest" pits
  - Crevice corrosion metric: # sites attacked in Multiple Crevice Assembly
- Depth of damage can be more important than number of damage sites
- Quantifying the morphology would allow direct comparisons to model predictions

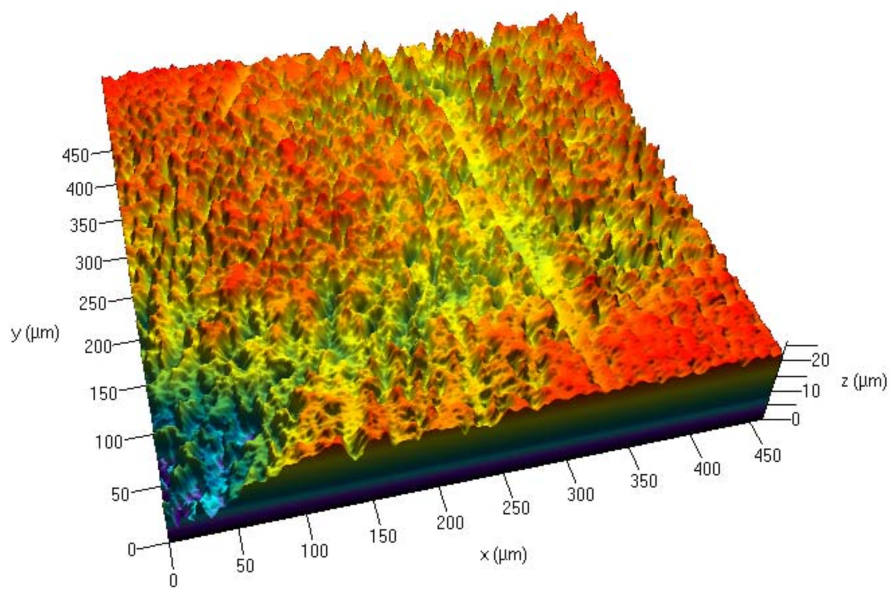
Confocal Laser Scanning Microscopy Allows Quantified Topography

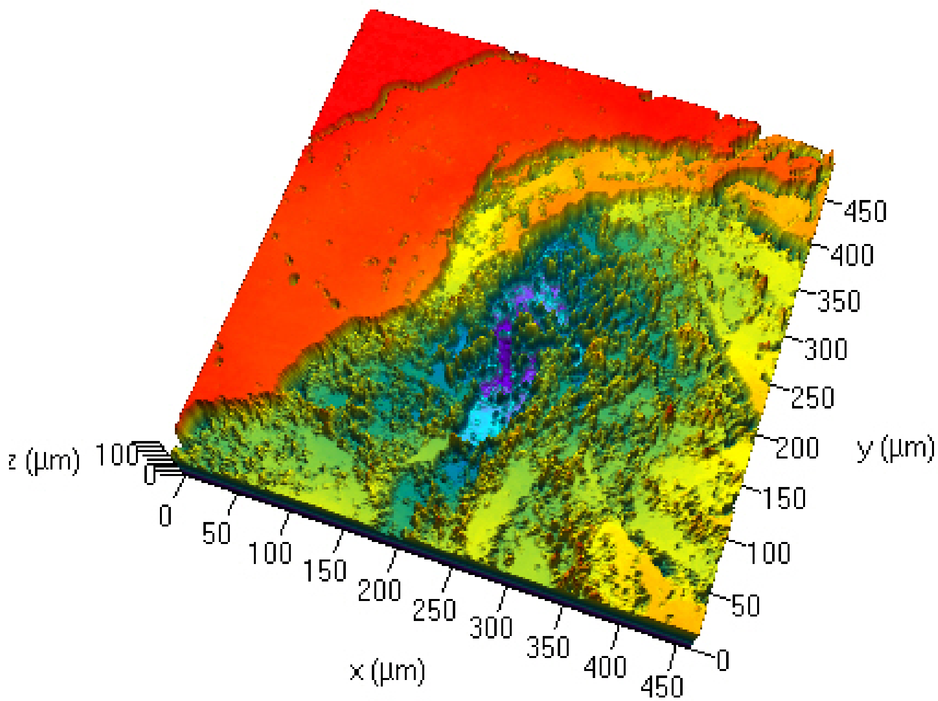
- **Laser scans horizontal planes at incremental depths, usually 0.5-2μm apart**
- **2D xy planes are then assembled to form 3D xyz solid**
- **Widely used in biological sciences to image cellular structures**



Examples of CLSM* Images of Corrosion

- **20x lens allows for about a 500μm x 500μm area to be scanned**





Alloy C-22 crevice: E = +0.1V (SCE), 6m NaCl + 0.9m KNO_3^-, 168 hrs
Courtesy of R. Rebak

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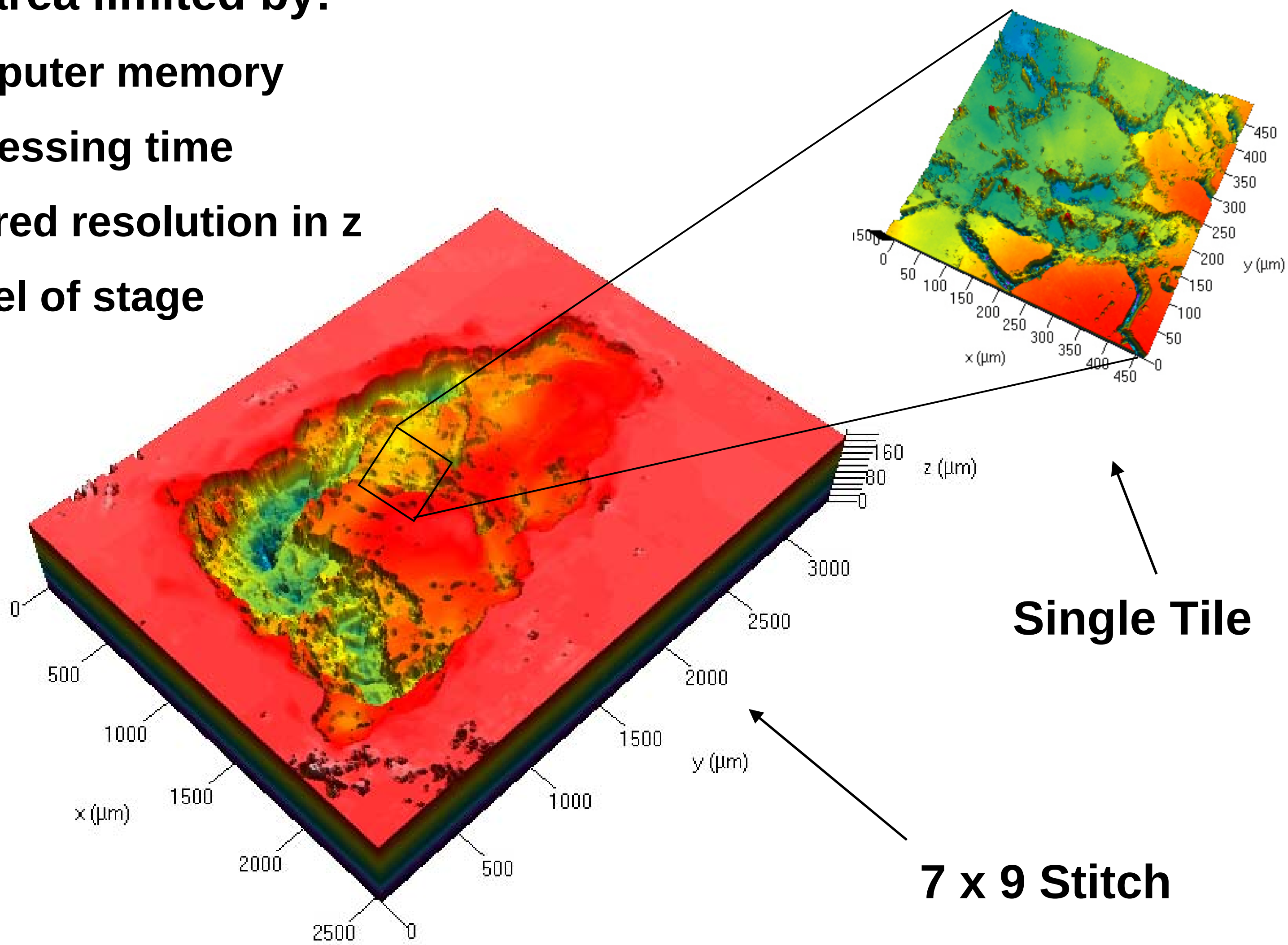
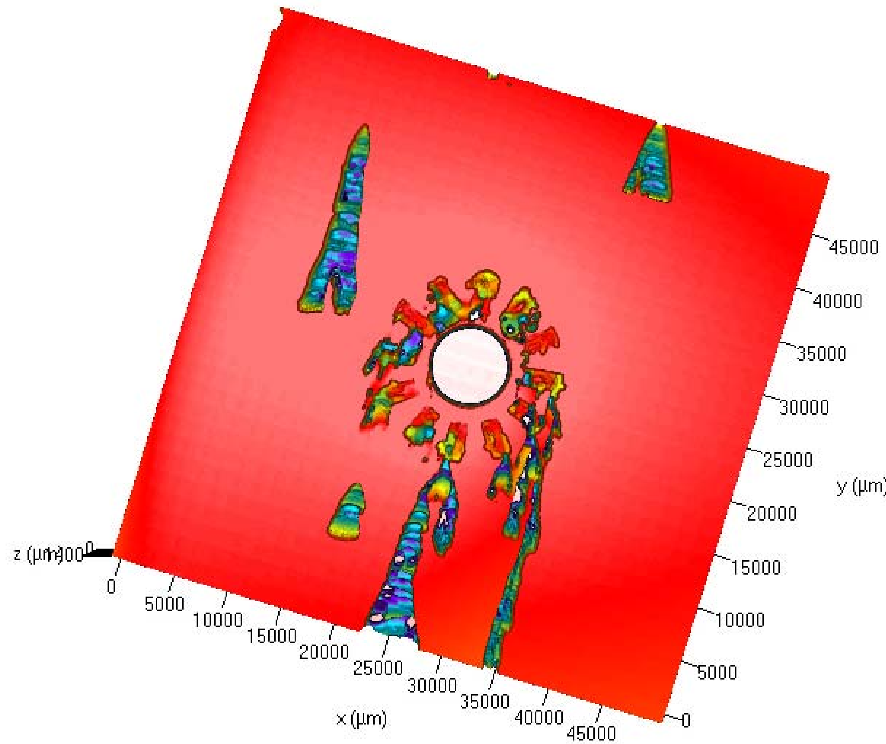
***Confocal Laser Scanning Microscope**

Stitch Together Adjacent Fields of View to Image Larger Areas of Sample

- **Size of area limited by:**
  - **Computer memory**
  - **Processing time**
  - **Desired resolution in z**
  - **Travel of stage**



With Patience, Even Large Samples Can Be Scanned



- 30 tiles x 30 tiles scanned
- Sample ~1.5 mm thick
- Took about 2 days to scan

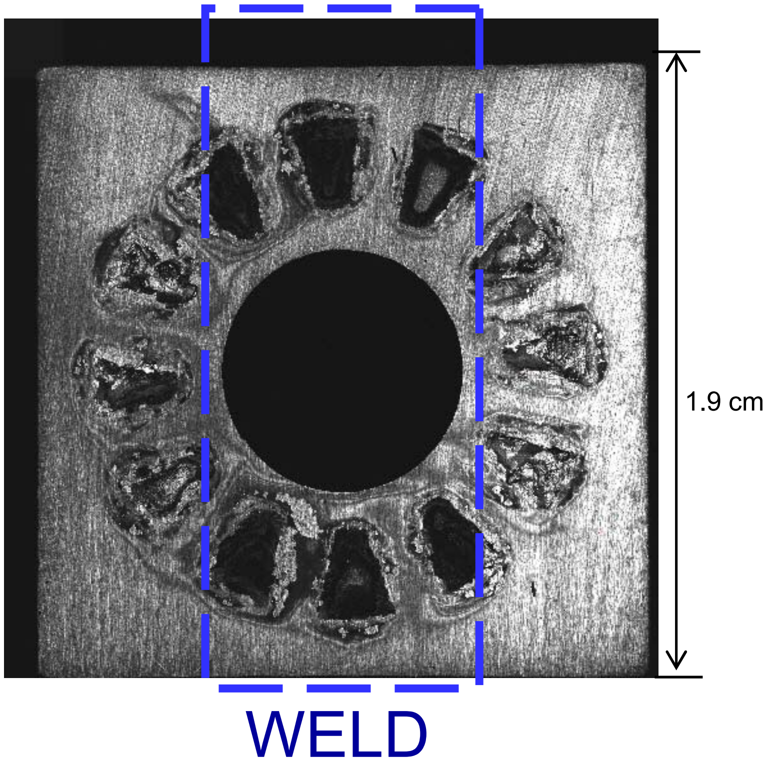
Examples of Use in Crevice Corrosion

- **Quantified topography of crevice corrosion**
  - **Welded C-22**
    - **R. Rebak, Lawrence Livermore Natioal Lab (LLNL)**

- **Quantification of growth geometry of crevice corrosion**
  - **Annealed C-22**
    - **B. Kehler, J. R. Scully, University of Virginia (UVa)**

Quantified Topography of Crevice Corrosion

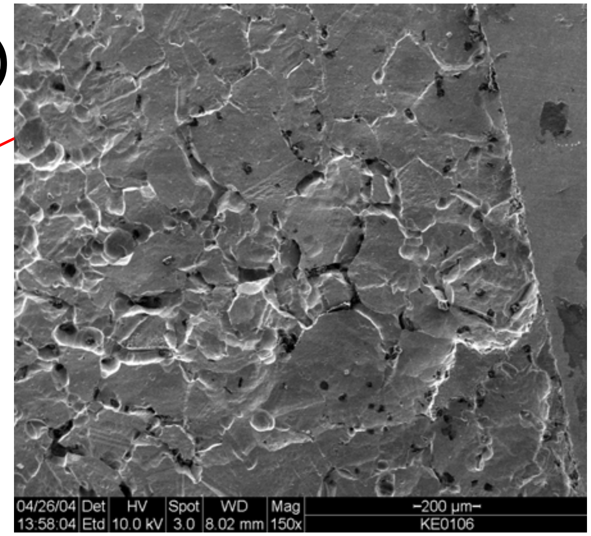
- Crevice corrosion of Welded C-22[1]
- Multiple Crevice Assemblies (MCA)
- Welds through majority of width
- Potentiostatic tests for 168 h
- Explored {NaCl}, E, NO_3^-/Cl^-
  - T = 100 C
- UVa: Image individual feet
  - Damage morphology
  - Damage quantification

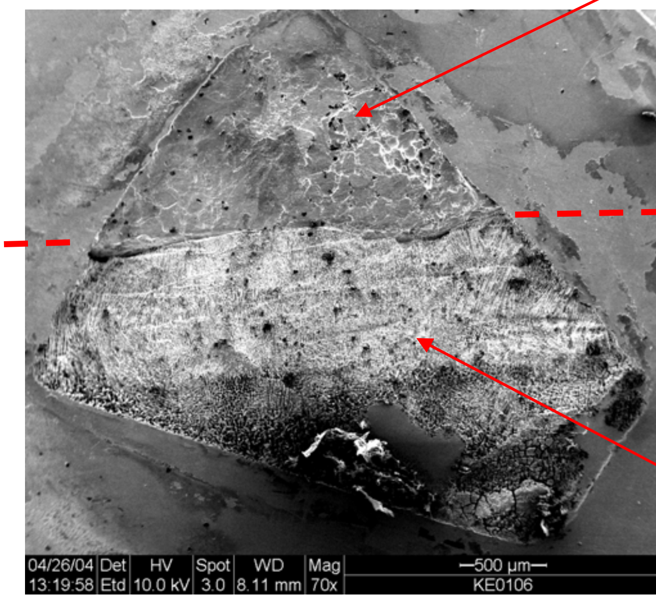


[1]K. Mon, G. Gordon, R. Rebak, “Stifiling of Crevice Corrosion in Alloy 22.” 12th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors, Salt Lake City, UT, 8/14/05-8/18/05.

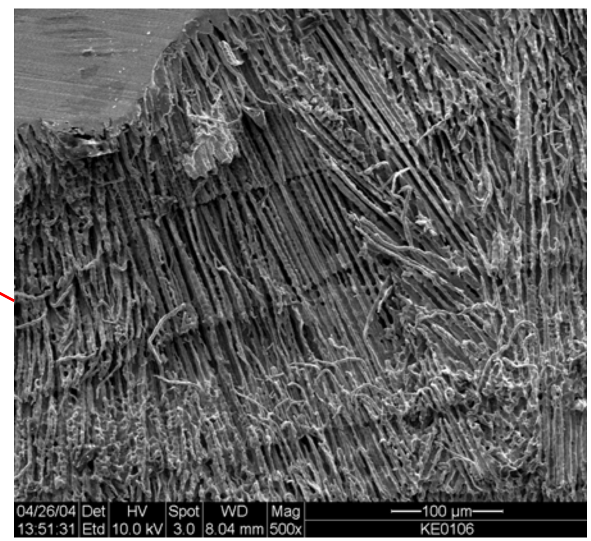
SEM Examination of Attack (by LLNL)

Base Metal Heat Affected Zone (HAZ) (Intergranular Attack)





Weld Metal (Interdendritic Attack)

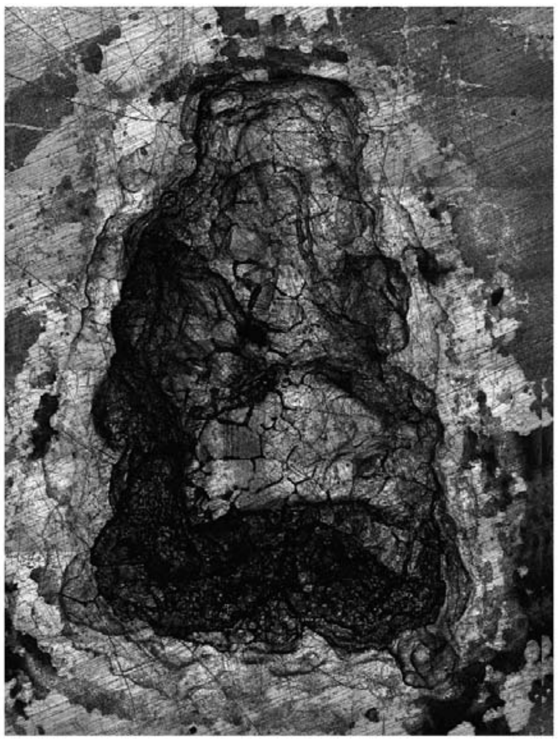


500 microns

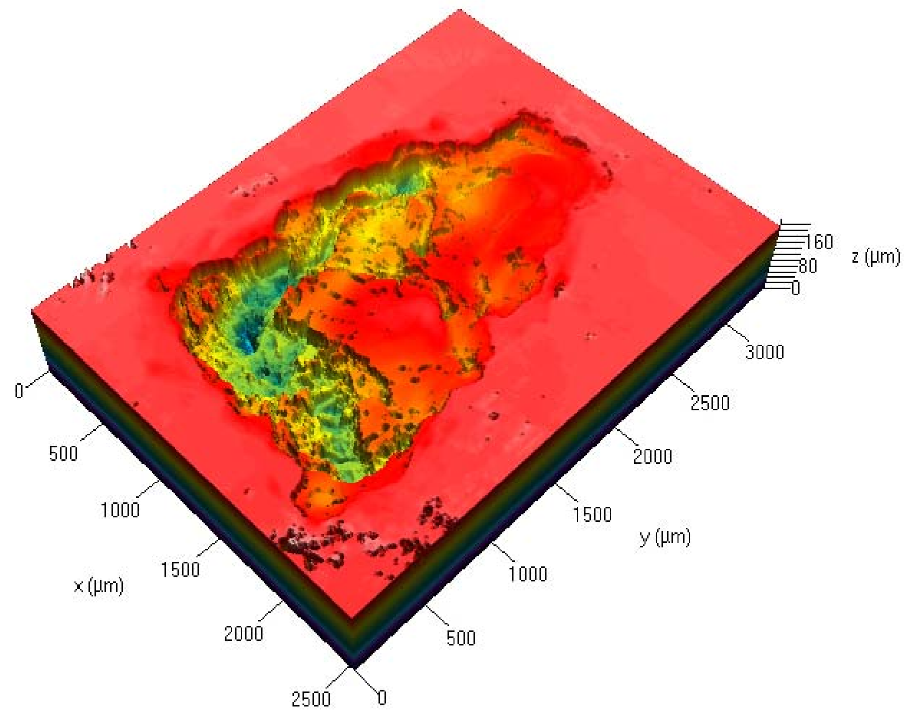
Courtesy R. Rebak

Comparison of Optical and CLSM

- **Staining and differences in reflectivity can be differentiated from differences in topography**



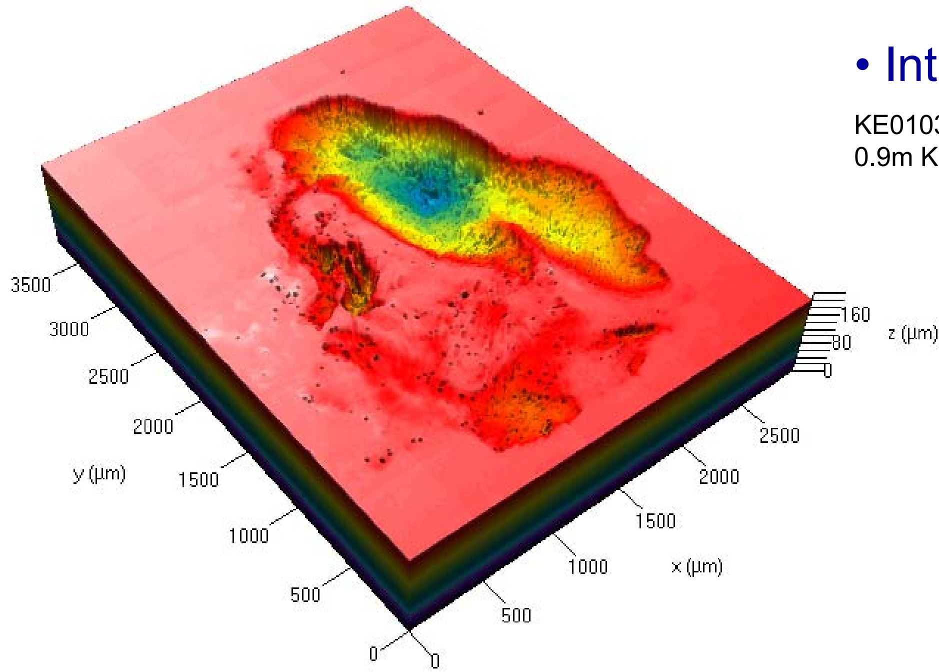
2-D image



3-D Topography

KE0103: 6 m NaCl, $NO_3^-:Cl^-$ =0.15, E=+0.1 V(SCE)

Effect of Welding on Damage Morphology:
C-22 Weld Metal

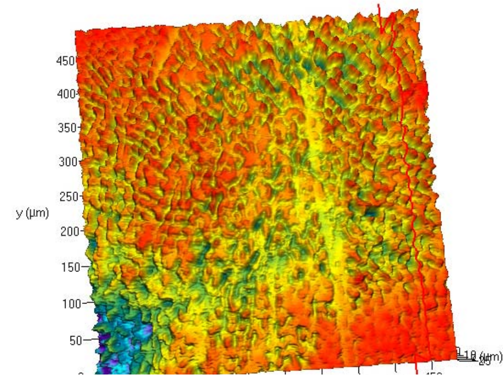


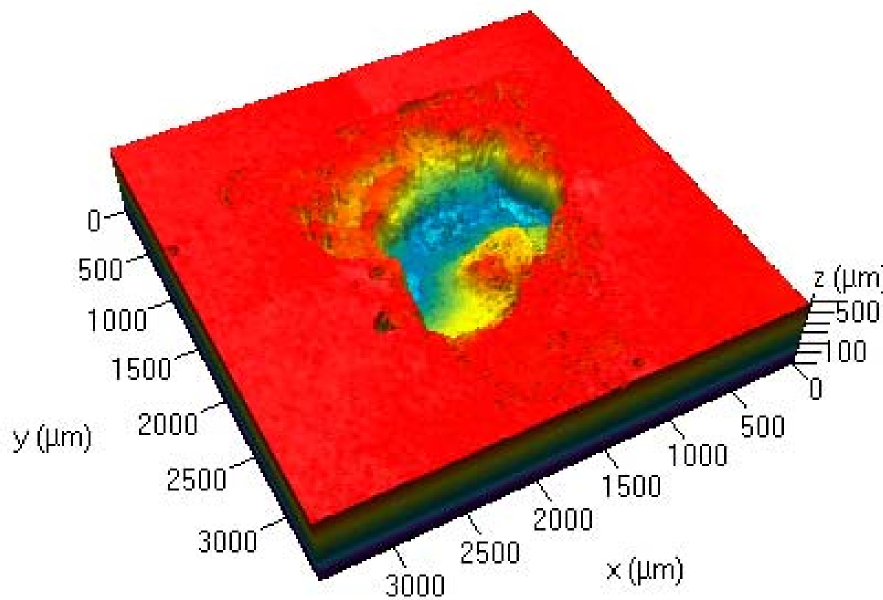
KE0104: E=+0.1V (SCE), 3.5m NaCl + 5.25m KNO3-, 168 hrs

- Large, wide volumes dissolved

- Interdendritic attack

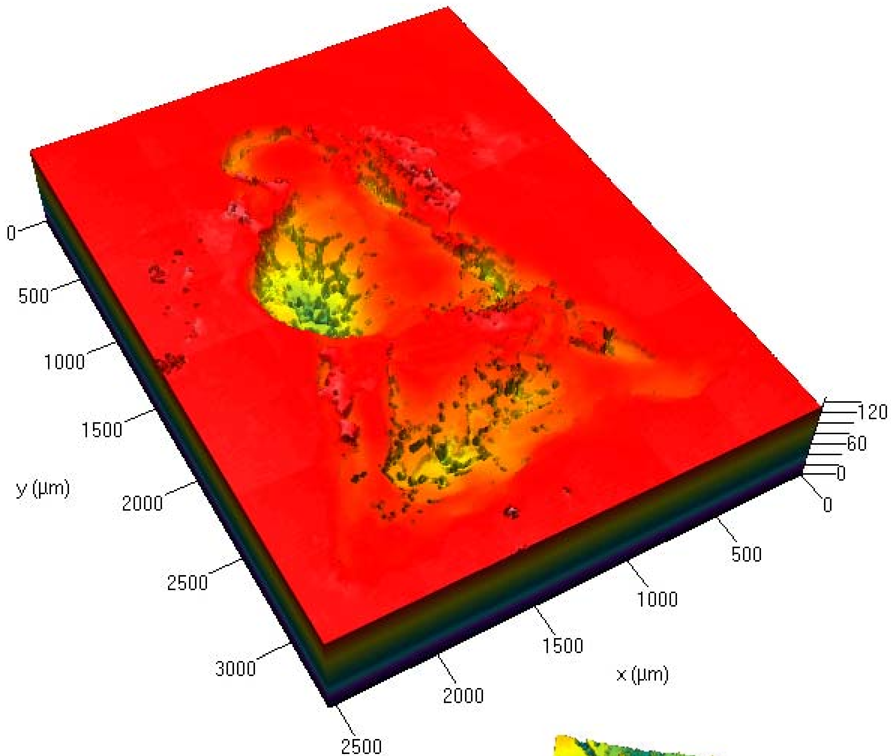
KE0103: E=+0.1V (SCE), 6m NaCl + 0.9m KNO3-, 168 hrs



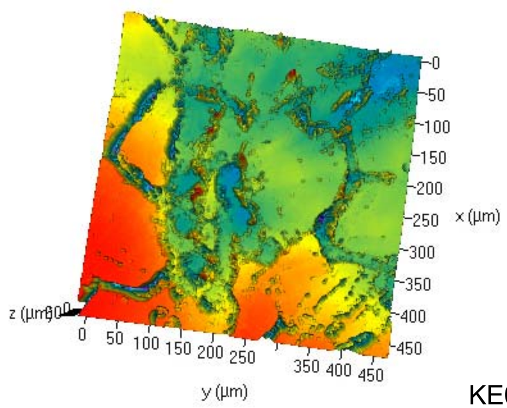


KE0104: E=+0.1V (SCE), 3.5m NaCl + 5.25m KNO3-, 168 hrs

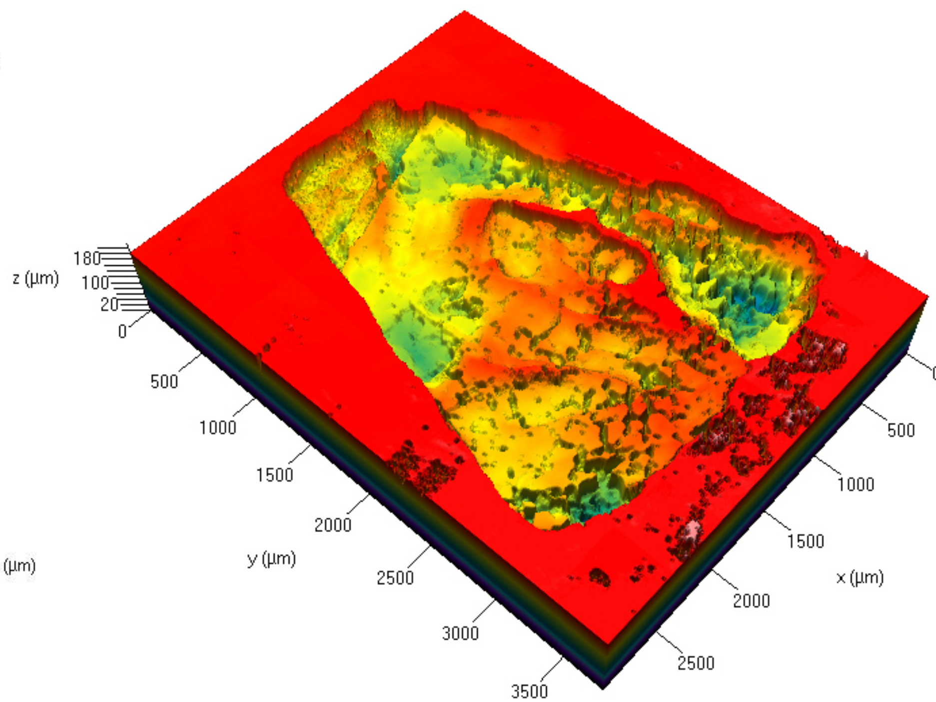
Effect of Welding on Damage Morphology:
C-22 Base Metal/HAZ



KE0165: E=+0V (SCE), 6m NaCl + 0.9m KNO3-, 168 hrs

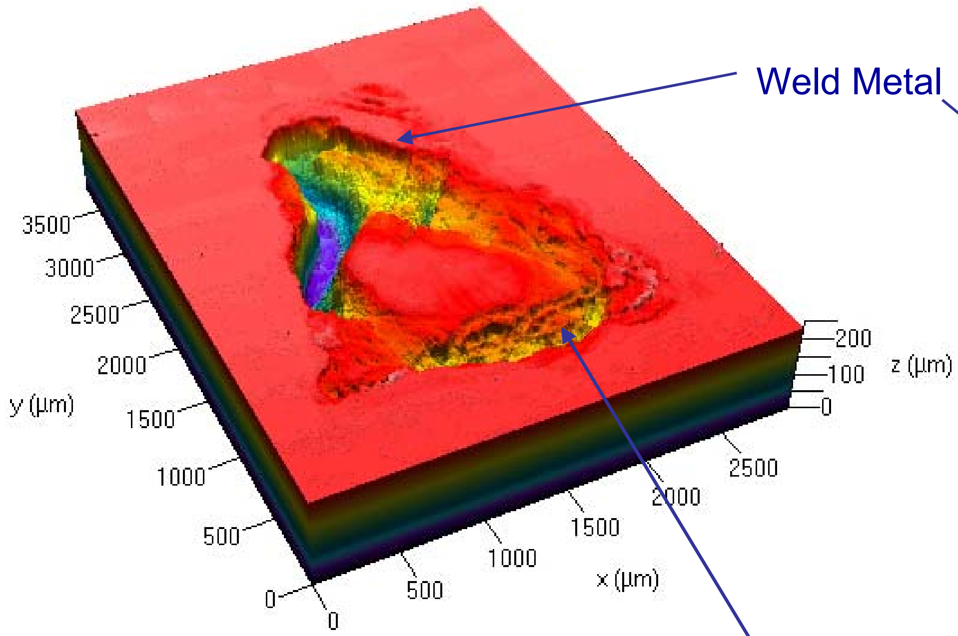


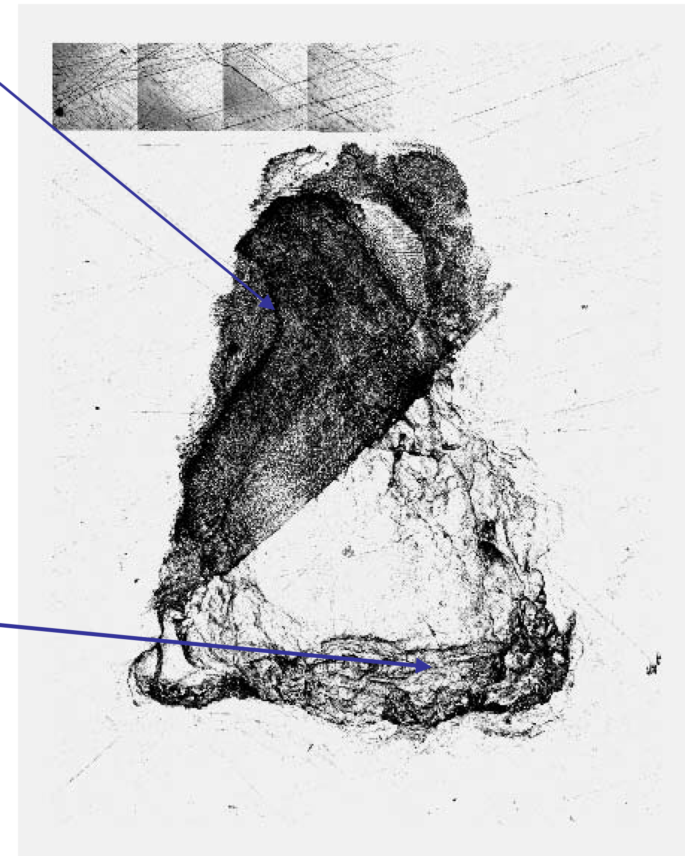
- Base metal in Heat Affected Zone (HAZ)
- Intergranular attack shown by clearly defined grain boundaries in images



KE0103: E=+0.1V (SCE), 6m NaCl + 0.9m KNO3-, 168 hrs

Effect of Welding on Damage Morphology:
C-22 Weld and HAZ/Base Metal



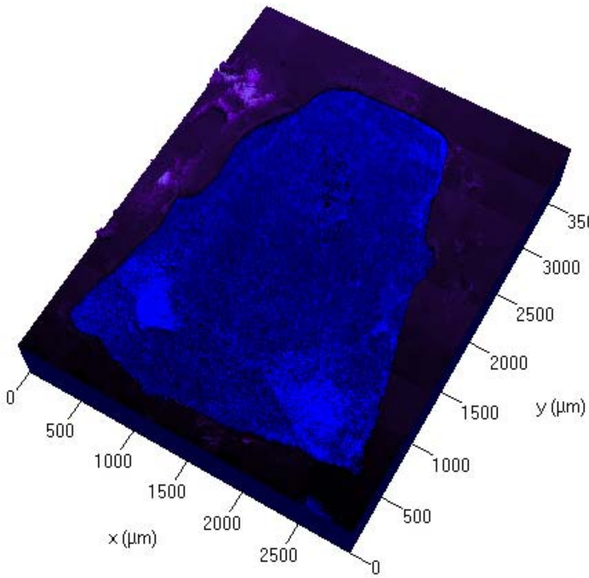


KE0104: E=+0.1V (SCE), 3.5m NaCl + 5.25m KNO3-, 168 hrs

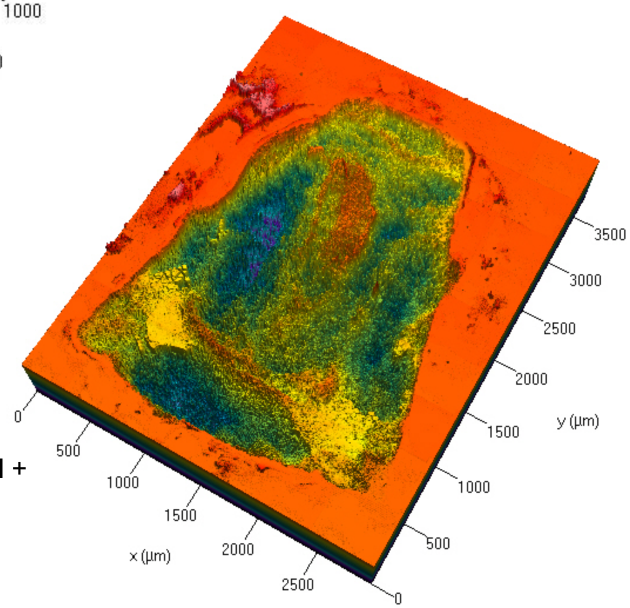
- Well-defined change in corrosion morphology at transition between base metal and weld metal

Volume and Depth Profile Quantification

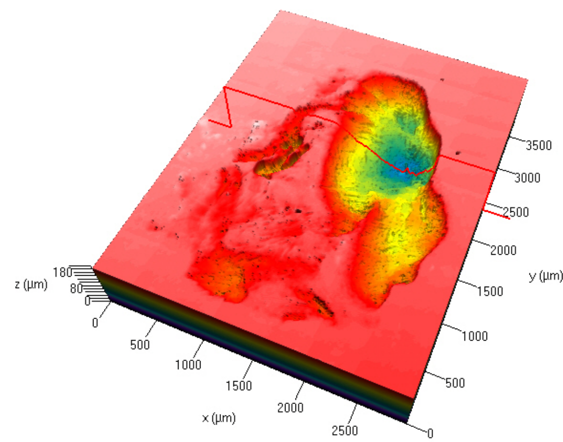
- **Volume Lost**
- **Profile of Damage**

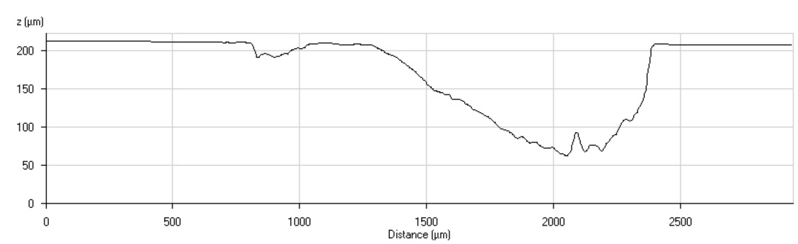


Vv(z) 0.1606 mm3



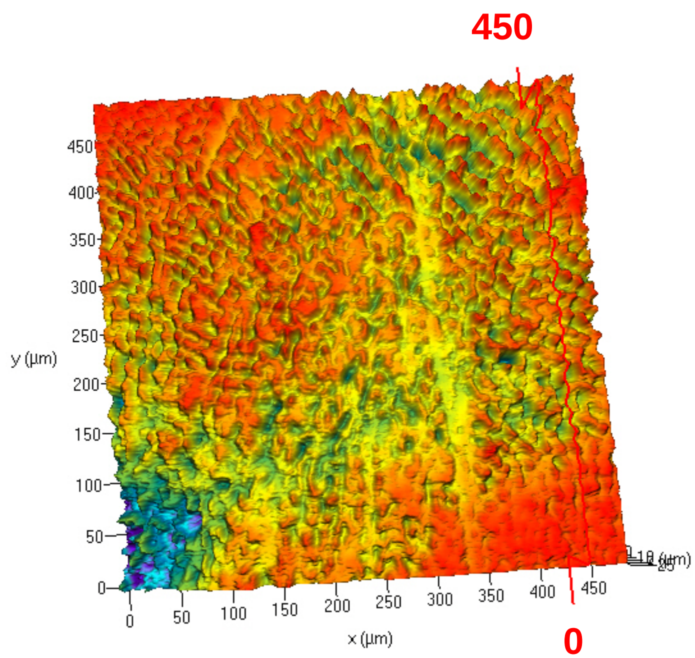
KE0108: E=+0.1V (SCE), 3.5m NaCl + 0.175m KNO3-, 168 hrs

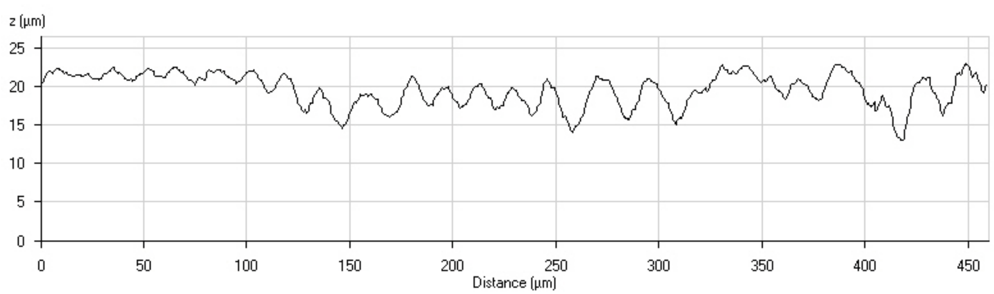




KE0104: E=+0.1V (SCE), 3.5m NaCl + 5.25m KNO3-, 168 hrs

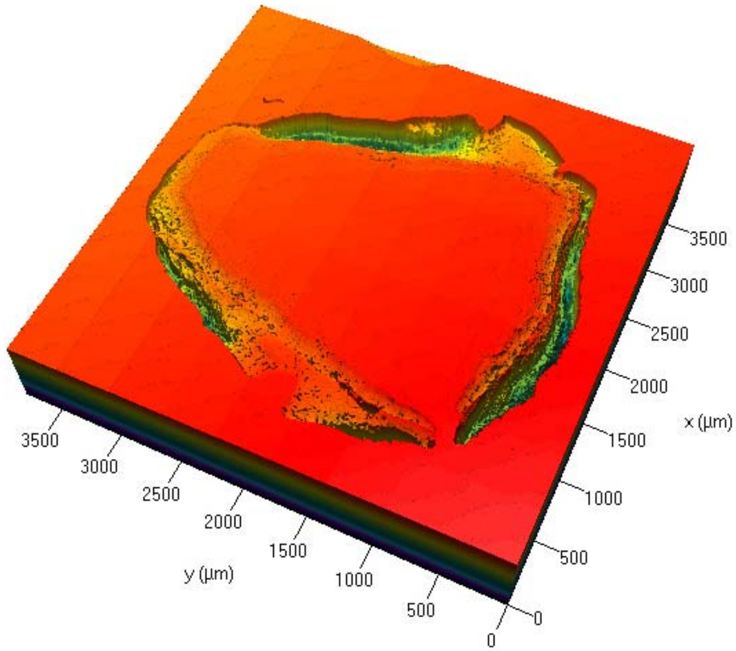
Measurements of Size and Spacing of Corroded Dendrites





KE0103: E=+0.1V (SCE), 6m NaCl + 0.9m KNO3-, 168 hrs

Quantification of Growth Geometry of Crevice Corrosion

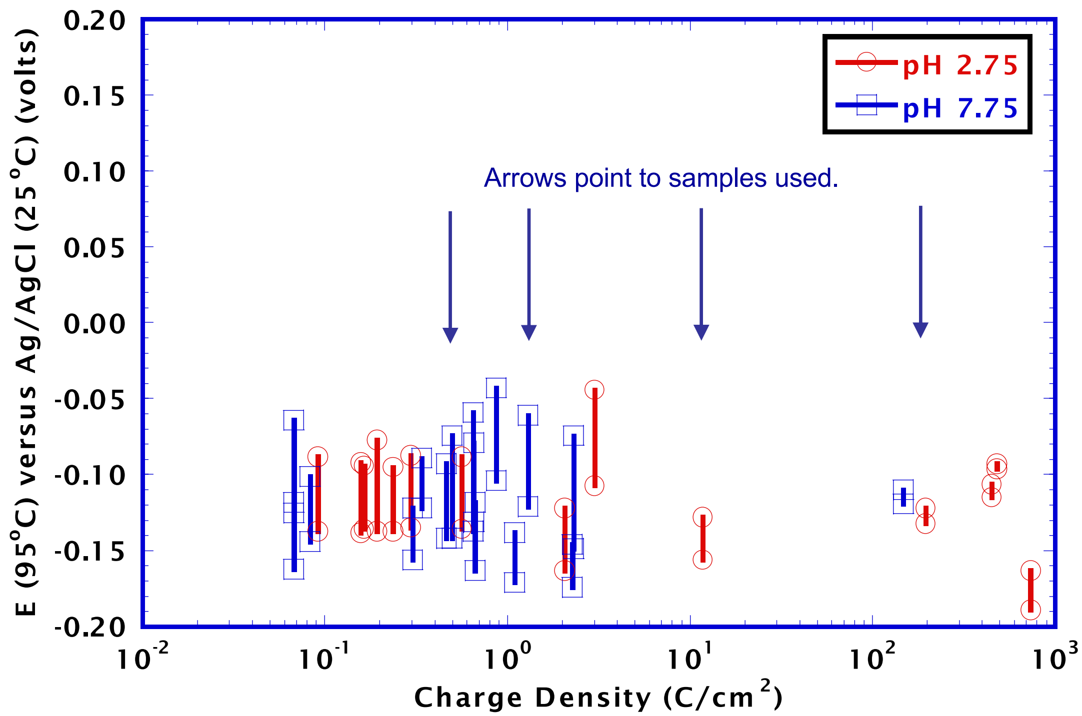


Sample	T °C	Chemistry	Charge (C/cm^2)
UVAC22-76	95	pH 2.75, 100:1	0.529628
UVAC22-75	95	pH 7.75, 100:1	1.5989
UVAC22-68	85	pH 2.75, 100:1	12.5818
UVAC22-26	95	pH 2.75, 100:1	305.05

- Solution annealed at a minimum of 1,121 °C
- 100:1 = 5 M LiCl + 0.024 $NaNO_3$ + 0.026 M Na_2SO_4

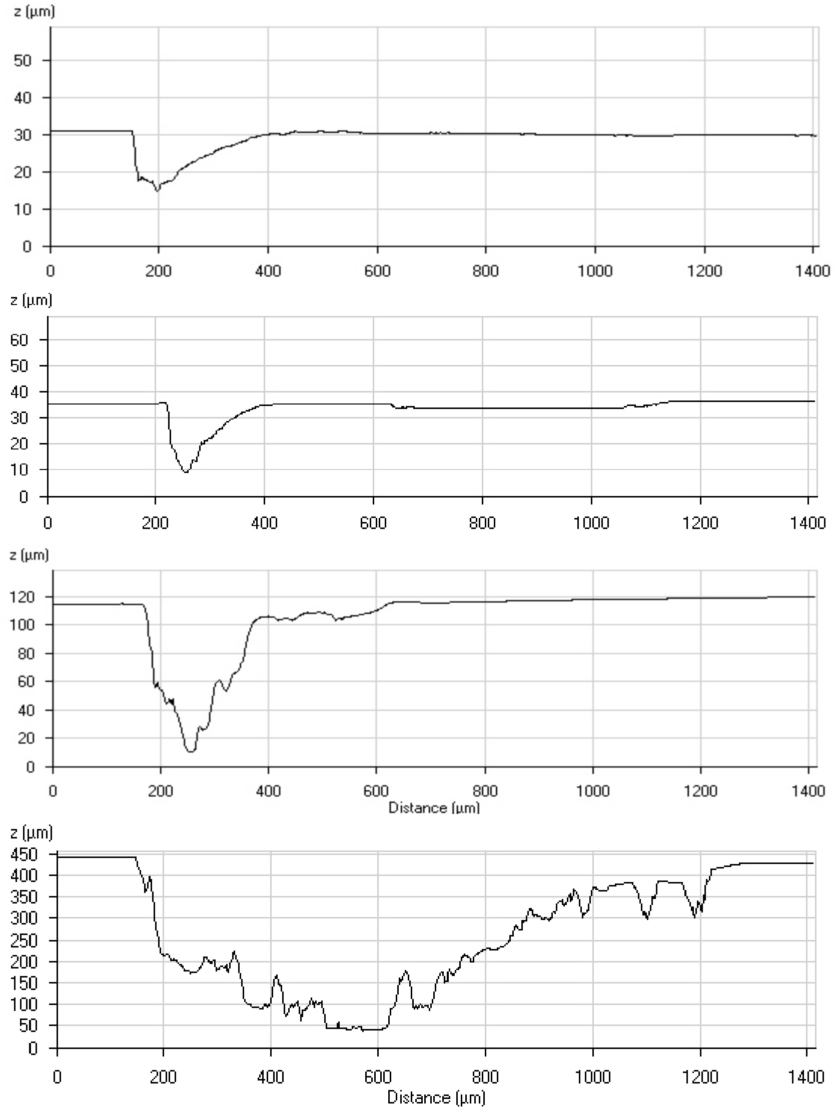
Quantification of Growth Geometry of Crevice Corrosion: $E_{r,crev}$ as a Design Parameter

- **Sridhar, Cragnolino, and Dunn showed that $E_{r,crev}$ was independent of the charge passed <u>above a mininum amount of charge</u>**
  - **Demonstrated utility of repassivation potentials for engineering design**
- **Kehler and Scully showed $E_{r,crev}$ was independent of charge and bulk pH for C-22**
- **How does the geometry of the damage change with increased charge such that the $E_{r,crev}$ remains constant?**



$E_{r,crev}$ = crevice repassivation potential

Effect of Charge Passed on Crevice Damage Profile

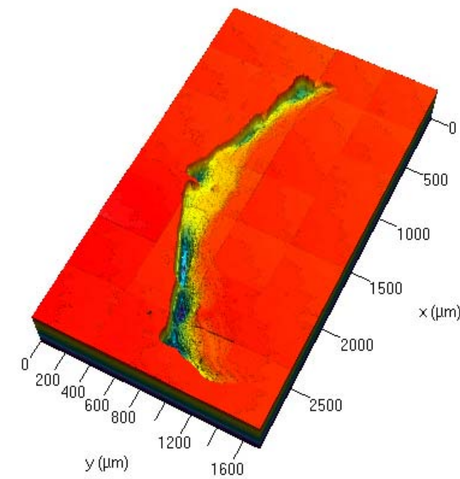


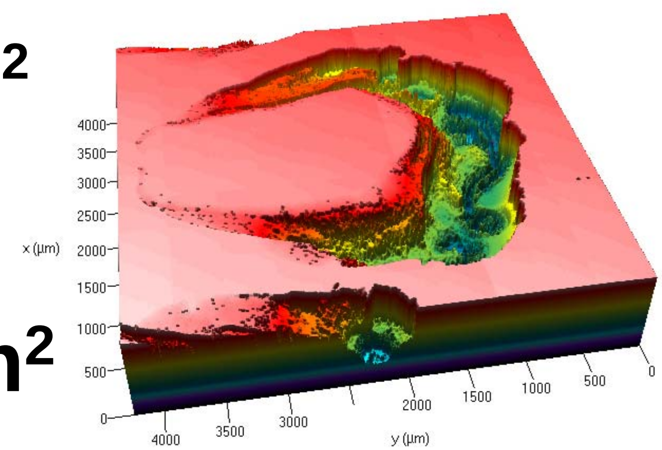
0.530 C/cm²

1.60 C/cm²

12.7 C/cm²

305 C/cm²



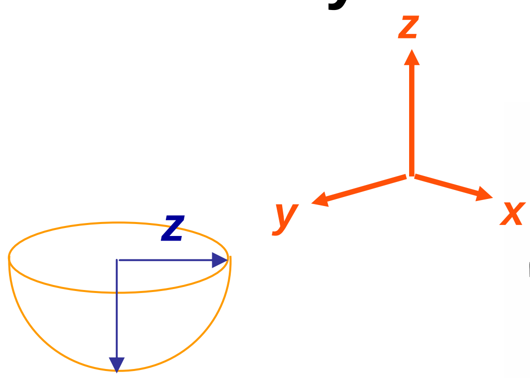


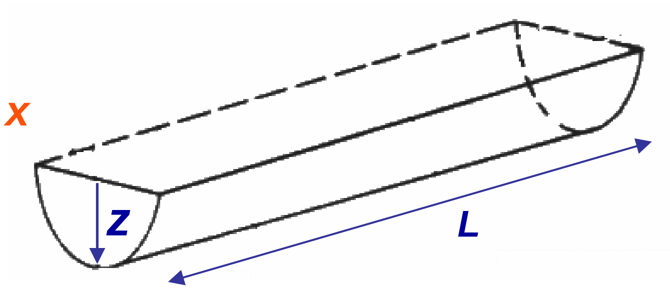
C/cm² = Coulombs/cm²

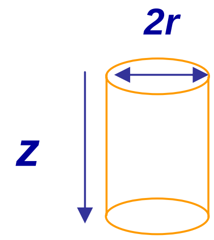
Crevice Corrosion Growth Laws

- **Geometry of damage determined by growth law**

V = volume lost   *z* = Maximum depth







3D growth	2D growth (*x* and -*z* directions)	1D growth (-*z* direction)
$V_{3D} = \iiint \frac{1}{2}(2*\pi*z)d\theta d\phi dz$	$V_{2D} = \iint \frac{1}{2}(2*\pi*z)dzdy$	$V_{1D} = \int \pi r^2 dz$
$V_{3D} = (\frac{2}{3})*\pi*z^3$	$V_{2D} = (1/2)*L*\pi*z^2$	$V_{1D} = \pi r^2 * z$
$V_{3D} = C*z^3$	$V_{2D} = C*z^2$	$V_{1D} = C*z$

All result in power law relation between V and z

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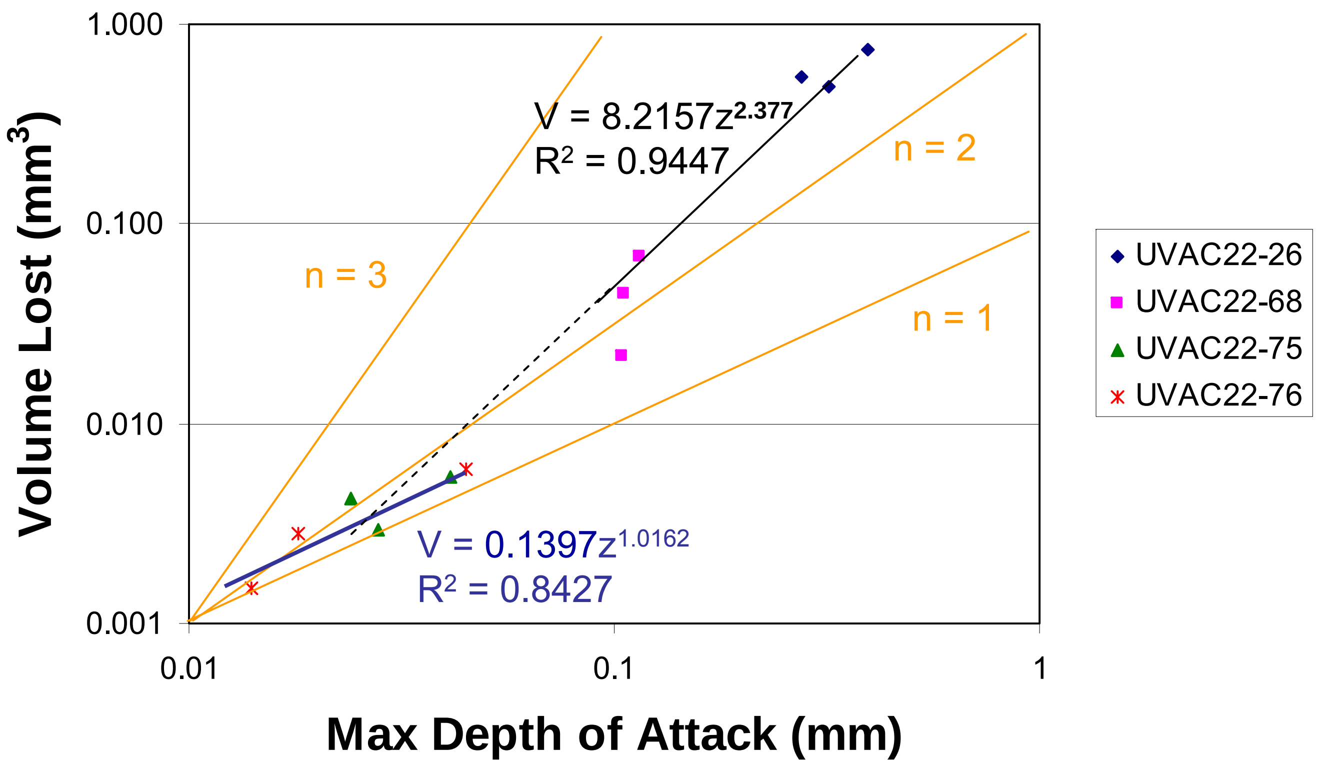
Crevice Growth Law for Annealed C-22

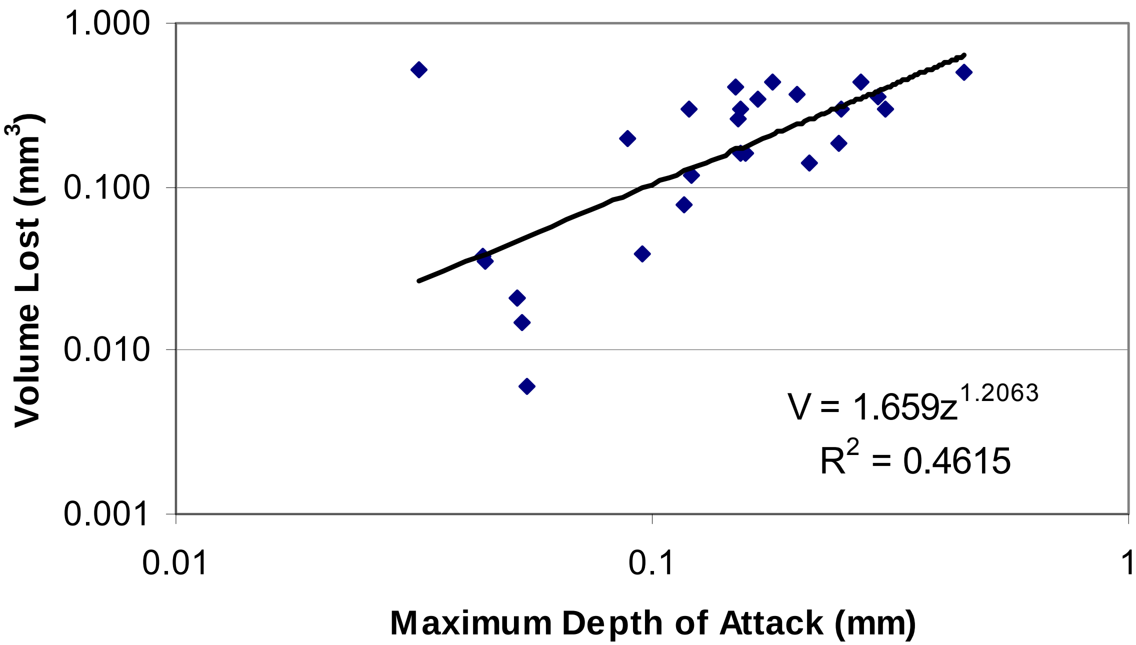
Power Law applied to solution-annealed C-22 samples of Kehler and Scully



- **Overall match to 2D growth, but at small volumes, n=1 fits as well**
- **Evidence for crevice corrosion initiating as tunnels**
  - **Larger growth is more like a channel**

Crevice Growth Law for Welded C-22

• **Power Law applied to welded C-22 samples of Rebak et al.**



- **Does <u>not</u> fit, possibly due to different <u>types</u> of crevice corrosion**
  - **Interdendritic on the weld metal**
  - **Intergranular on the base metal**

Summary

- **Confocal Laser Scanning Microscopy offers avenue for quantitative descriptions of crevice corrosion**
- **In welded C-22 samples with crevices, dendrite structure was revealed in the weld metal and grain boundaries were etched in the HAZ/base metal**
- **In annealed C-22 samples, the damage can be described as classic crevice corrosion**
- **Crevice corrosion of solution-annealed C-22 appears to:**
  - **Initiate as tunnels (1D growth)**
  - **Grow as a channel (2D growth)**
- **Welded samples do not obey a simple growth law, apparently due to a more complex surface texture.**