

# C06-I307: Effects of Applied Stress on Atmospheric Corrosion and Pitting Characteristics of 304 Stainless Steel

PRiME 2020

October 5<sup>th</sup> 2020



john9@unm.edu

John Plumley<sup>1,2</sup>, Christopher Alexander<sup>3</sup>, Zhenzhen Yu<sup>4</sup>, Nick Kemp<sup>1</sup>, Fernando Garzon<sup>2</sup>, Eric Schindelholz<sup>5</sup>, and Rebecca Schaller<sup>1</sup>



<sup>1</sup> Materials Science and Engineering, Sandia National Laboratories

<sup>2</sup> Center for MicroEngineered Materials, University of New Mexico

<sup>3</sup> Department of Civil & Environmental Engineering

<sup>4</sup> Center for Welding, Joining, & Coatings Research, Colorado School of Mines

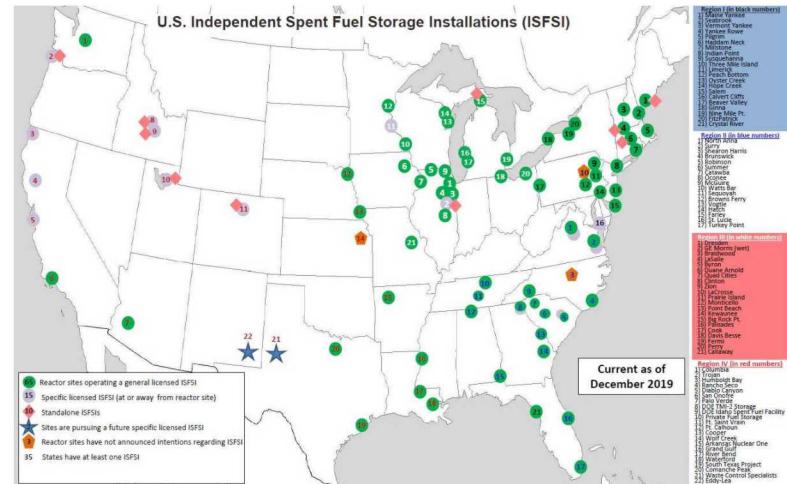
<sup>5</sup> Department of Materials Science and Engineering, The Ohio State University

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# Motivation

## Accumulation of spent nuclear fuel cannisters (SNF)

- 80 sites in 35 states
- Austenitic stainless steel (SS)
- Located in/near marine locations
- Salts can deliquesce on surface leading to corrosive environment
- Susceptible to pitting and subsequent stress corrosion cracking (SCC)



<https://www.nrc.gov/docs/ML1933/ML19337C178.pdf>



<https://blogs-images.forbes.com/jamesconca/files/2018/03/ENW-Dry-Cask-figure.jpg>

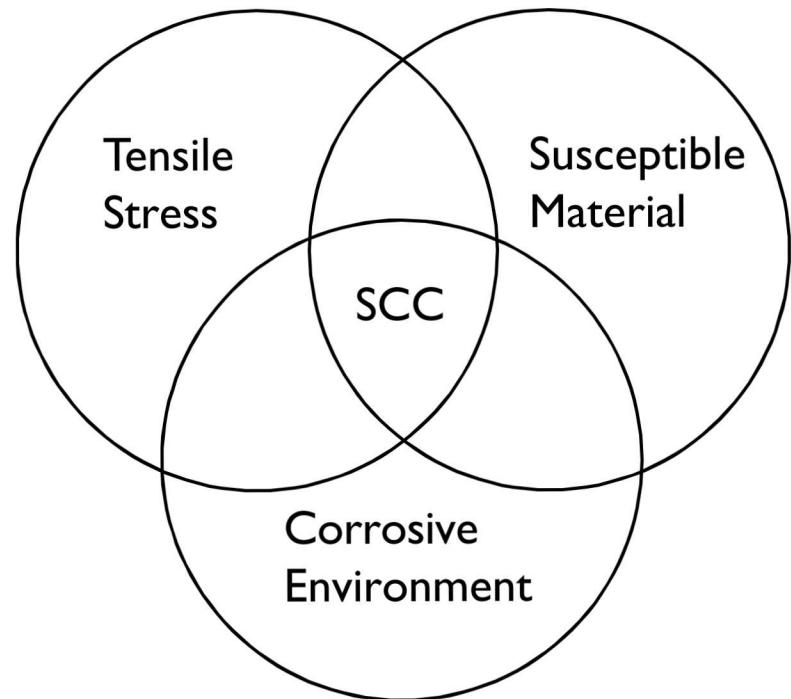
# Motivation

Remains a challenge to predict pitting and possible SCC

- Unknown effects of stress on corrosion and SCC due to canister formation and welding

# Stress Corrosion Cracking from Atmospheric Exposure

Both corrosion and tensile stress, be it applied or residual, are required for SCC to occur



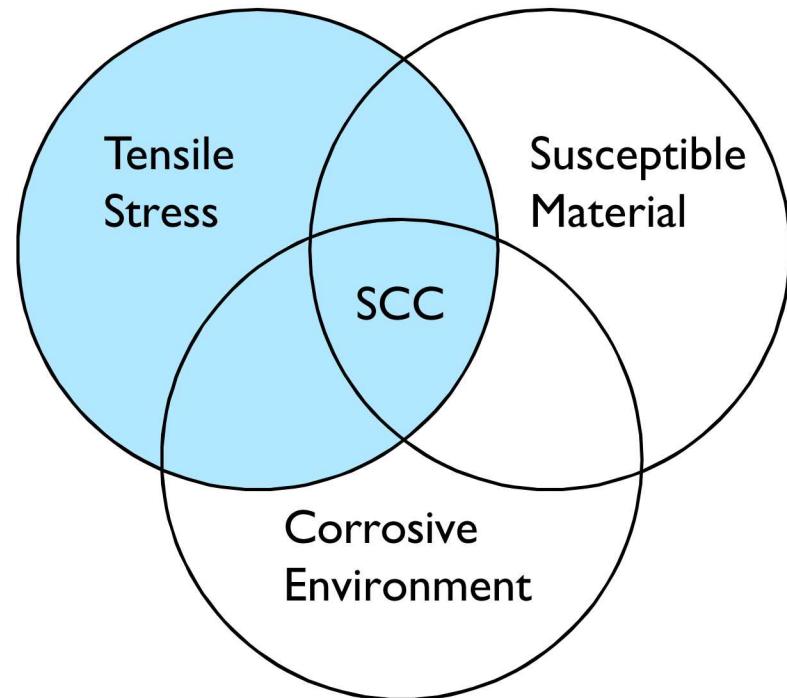
[https://www.researchgate.net/profile/Barry\\_Gordon/publication/257761781/figure/fig11/AS:668504487370754@1536395298091/Venn-Diagram-for-Stress-Corrosion-Cracking.png](https://www.researchgate.net/profile/Barry_Gordon/publication/257761781/figure/fig11/AS:668504487370754@1536395298091/Venn-Diagram-for-Stress-Corrosion-Cracking.png)

# Stress Corrosion Cracking from Atmospheric Exposure

Both corrosion and tensile stress, be it applied or residual, are required for SCC to occur

## Factors that govern SCC susceptibility

- Magnitude of applied stress



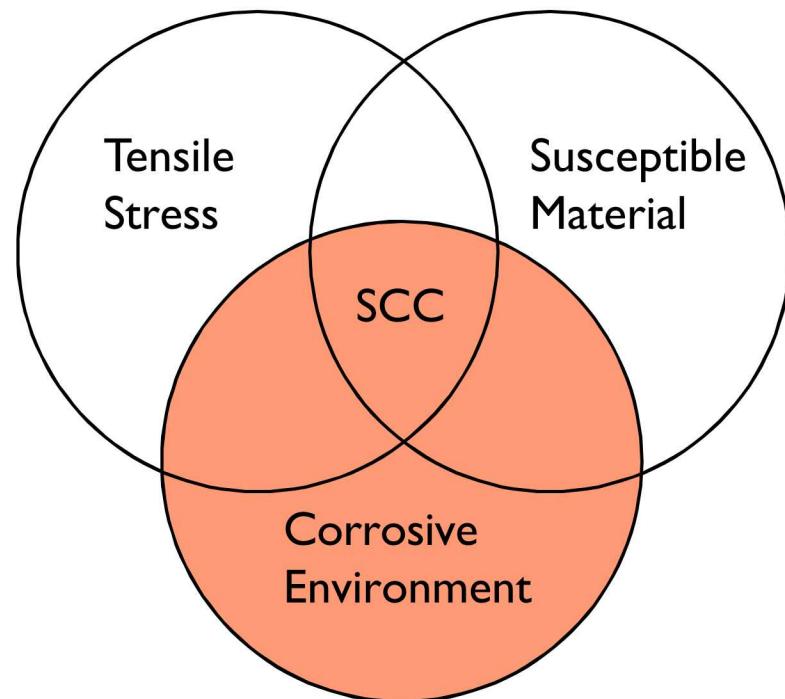
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# Stress Corrosion Cracking from Atmospheric Exposure

Both corrosion and tensile stress, be it applied or residual, are required for SCC to occur

## Factors that govern SCC susceptibility

- Magnitude of applied stress
- %RH
- Salt Loading



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\*D.T. Spencer, M.R. Edwards, M.R. Wenman, C. Tsitsios, G.G. Scatigno, P.R. Chard-Tuckey, *Corros. Sci.* 88 (2014): p. 76-88

\*\* G.G. Scatigno, P. Dong, M.P. Ryan, and M.R. Wenman, *Mater.* 8 (2019): p. 100509

# Stress Corrosion Cracking from Atmospheric Exposure

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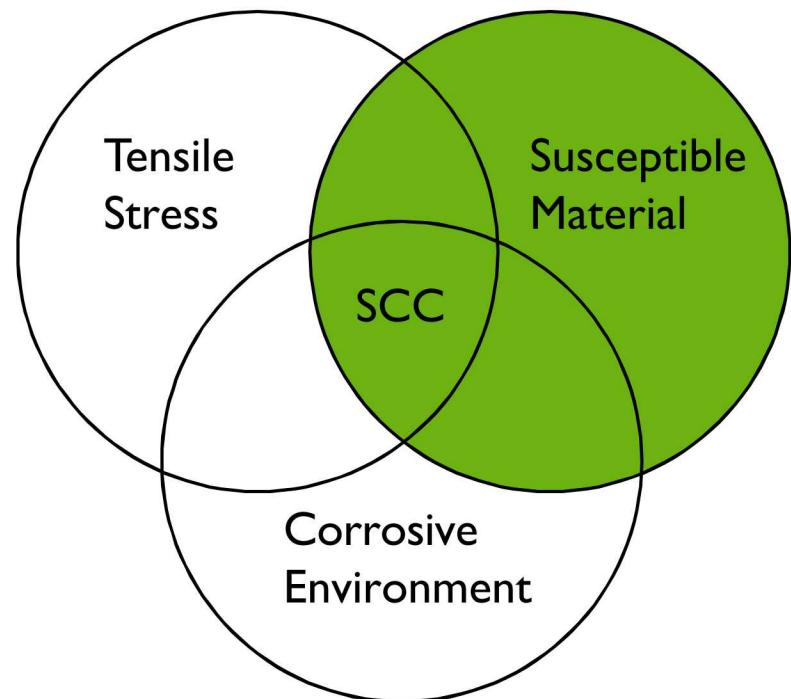
## Factors that govern SCC susceptibility

- **Magnitude of applied stress**

- **%RH**

- **Salt Loading**

- **Phase composition**



[https://www.researchgate.net/profile/Barry\\_Gordon/publication/257761781/figure/fig11/AS:668504487370754@1536395298091/Venn-Diagram-for-Stress-Corrosion-Cracking.png](https://www.researchgate.net/profile/Barry_Gordon/publication/257761781/figure/fig11/AS:668504487370754@1536395298091/Venn-Diagram-for-Stress-Corrosion-Cracking.png)

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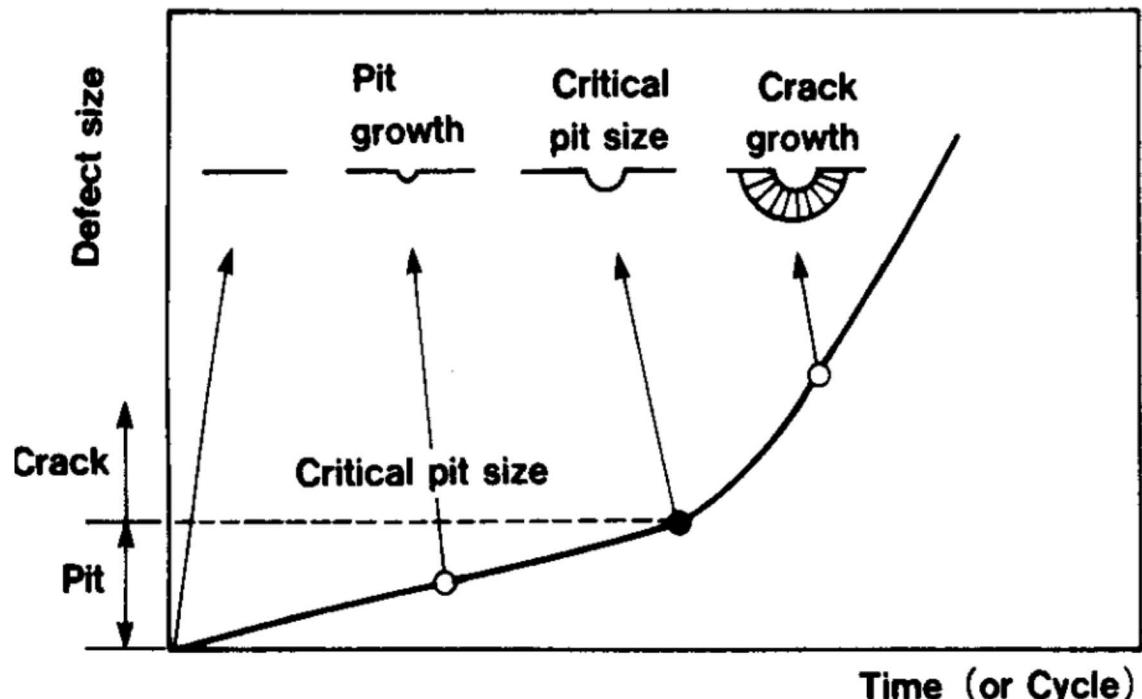
# Pit to Crack Transition

Pit to crack criteria proposed by Kondo\*

- Pit depth > threshold depth
- Crack growth rate > pit growth rate

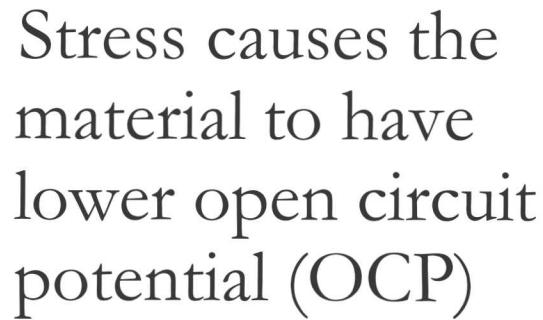
Applied stress can increase pitting susceptibility

- Higher pitting density and higher probability of deeper pits
- More cracking

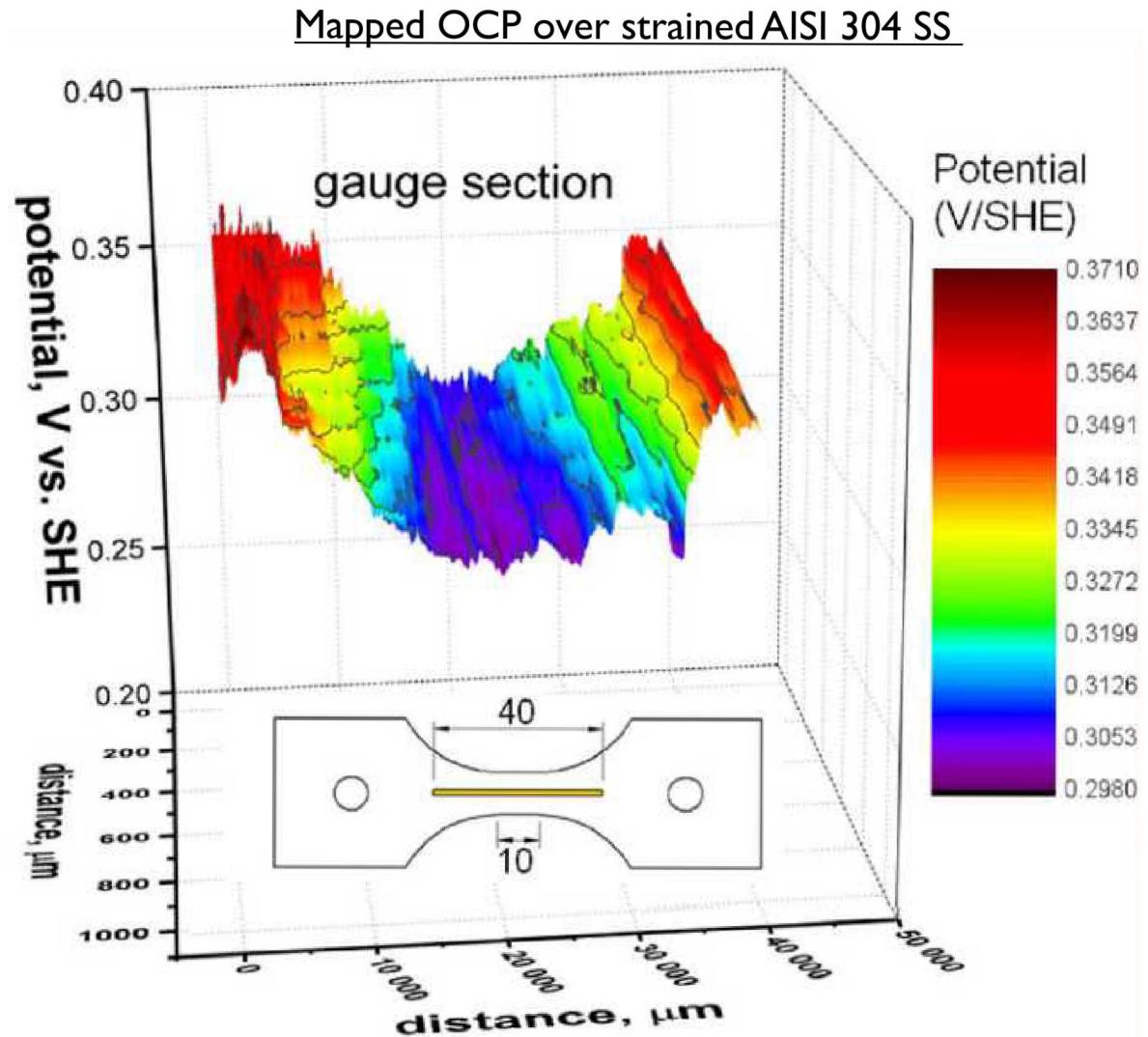


\*Y. Kondo, Corrosion, 45, 1 (1987): p. 7-11.

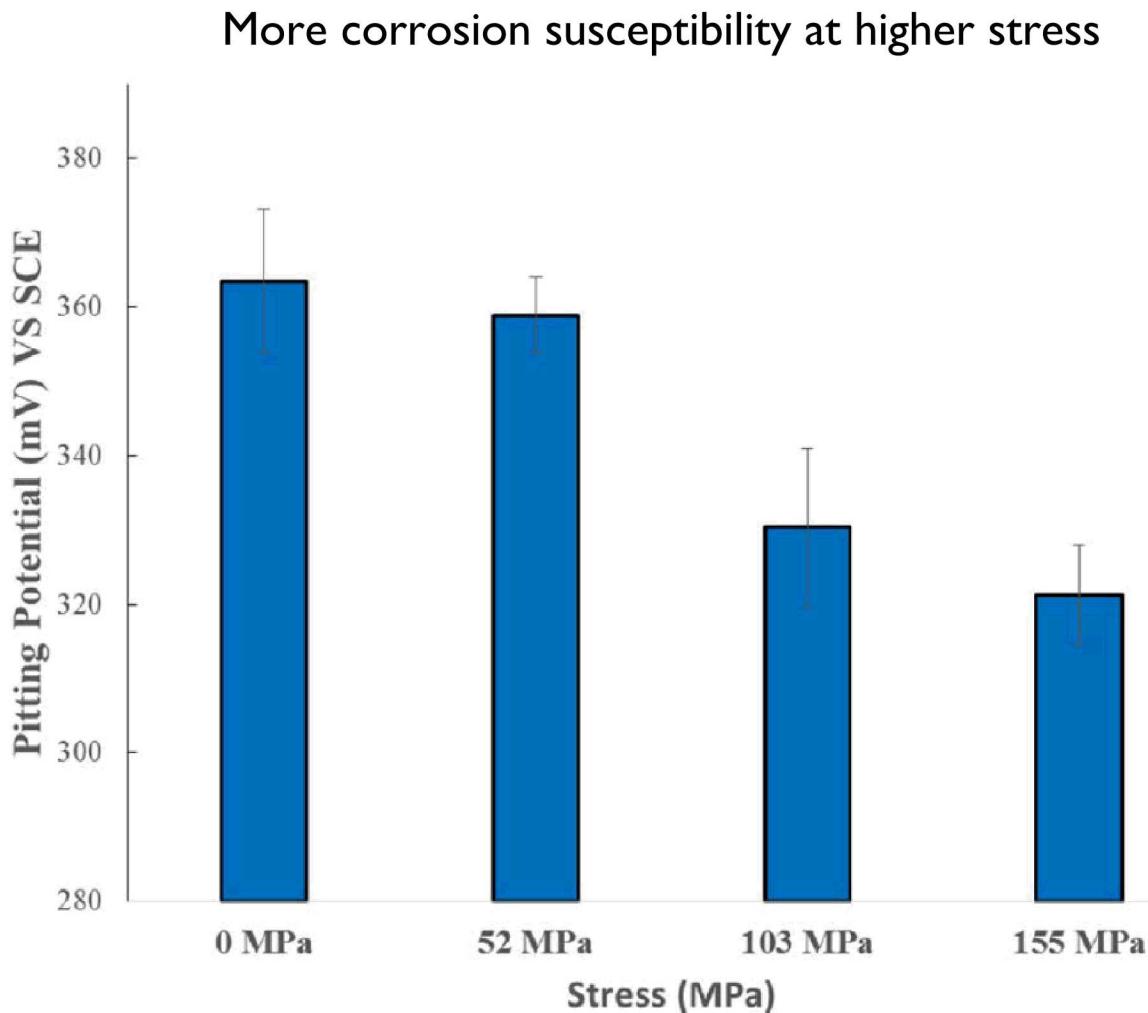
# Influence of Stress on Corrosion



Lower OCP  
signifies a greater  
corrosion  
susceptibility



# Influence of Stress on Corrosion



# Research Questions



It's been observed that stress has an effect on pitting, what about in canister relevant environments...

- Under atmospheric exposure what dependence does stress have on pit distribution, pit size, and pit morphology in 304L SS?
- What are some of the more localized effects stress can have on pitting?

# Experimental Approach

Applied stress to 304L SS bar using 4 pt. bend

- Finite element analysis (FEA)
- Direct image correlation (DIC)

Polished (0.1 Ra  $\mu$ m)

Artificial seawater (ASW) Loading density (4 g/m<sup>2</sup> chloride)

Atmospheric exposure in humidity chamber (50 days at 50 °C and 35 % RH)

- Accelerated corrosion
- Cleaning Procedure (submerged in 0.6 M diammonium citrate solution at 70 °C for 24 hours (ASTM-G1))

# Analysis

Optical profilometry

- Pitting analysis

Scanning electron microscopy (SEM)

- Interrogate pits further

Electron backscatter diffraction (EBSD)

- Composition analysis

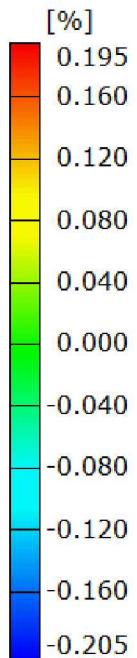
Micro-electrochemical cell

- On unexposed 4-pt bend bar
- Localized electrochemical parameters

# Material and Stress Application

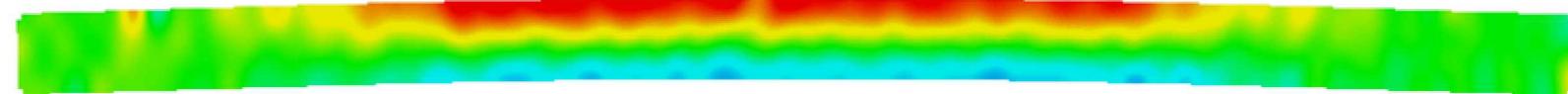
A four-point bend bar was atmospherically exposed to explore a full stress gradient, from tensile to compressive stresses, across the thickness of the bar

Strain (%)



Stressed, Corroded  
304L Stainless Steel

Digital Image Correlation

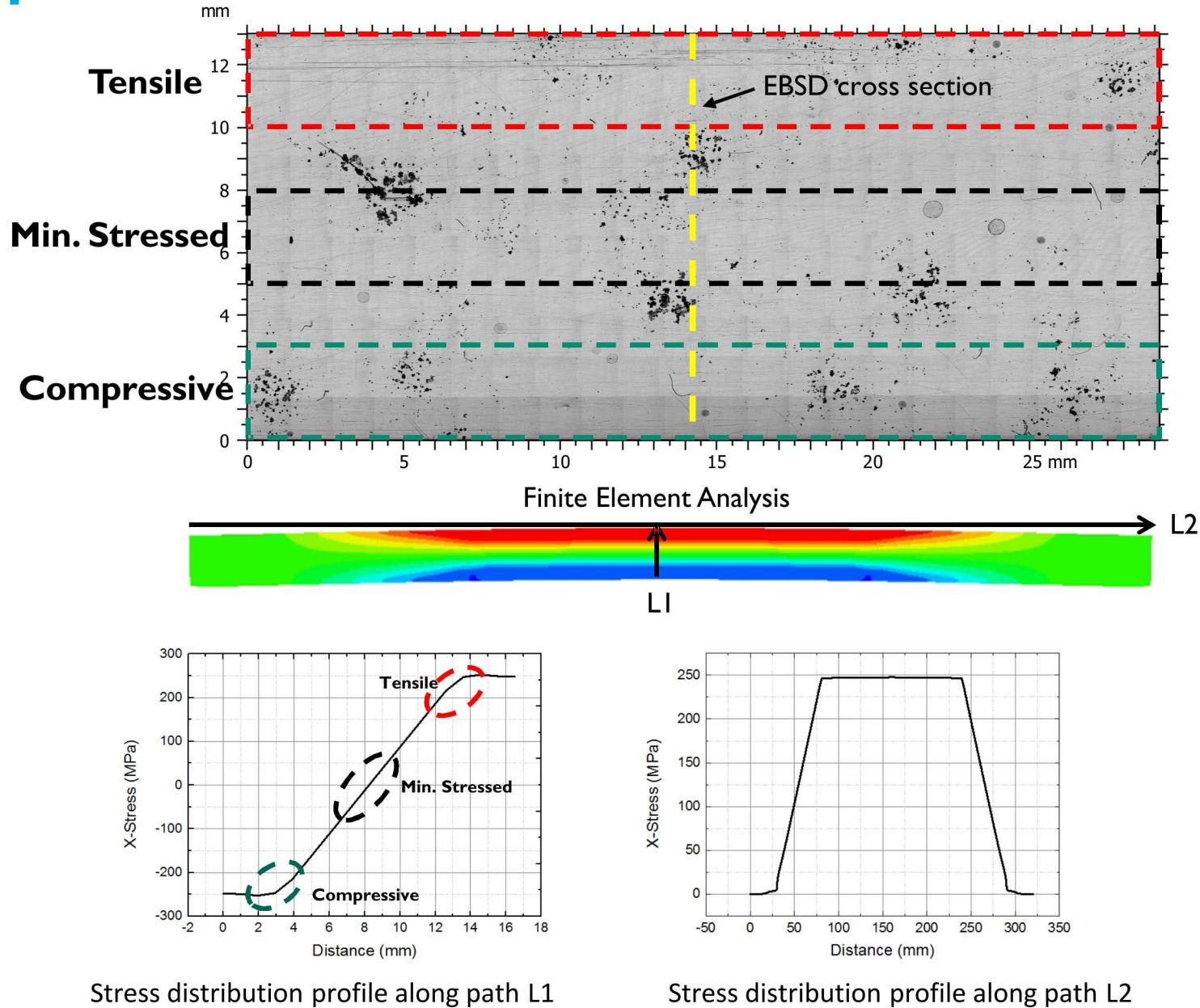


Base metal composition of the 304L stainless steel bar

**SS304L bar composition (wt. %)**

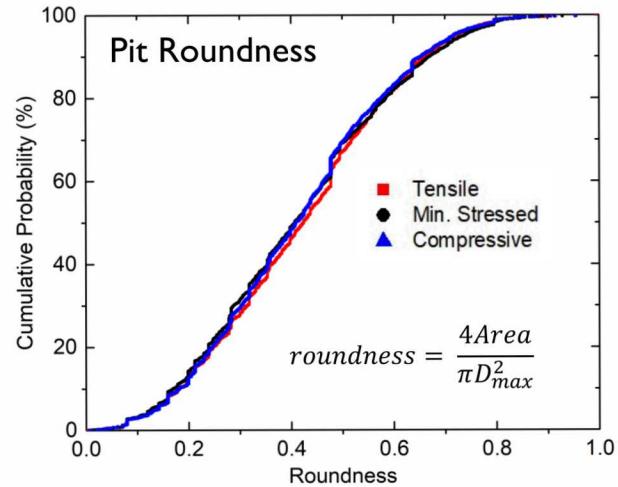
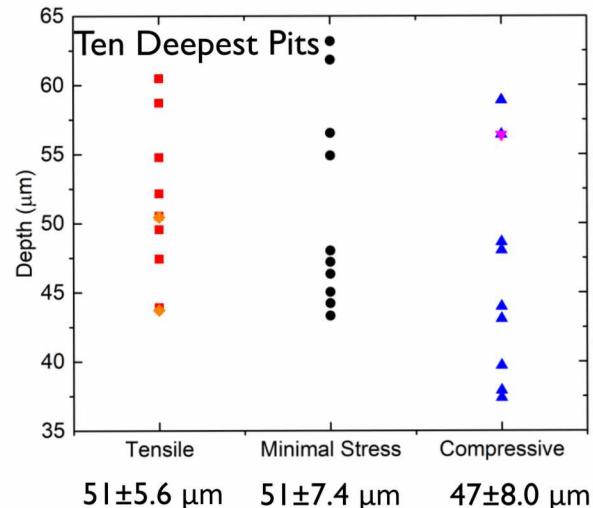
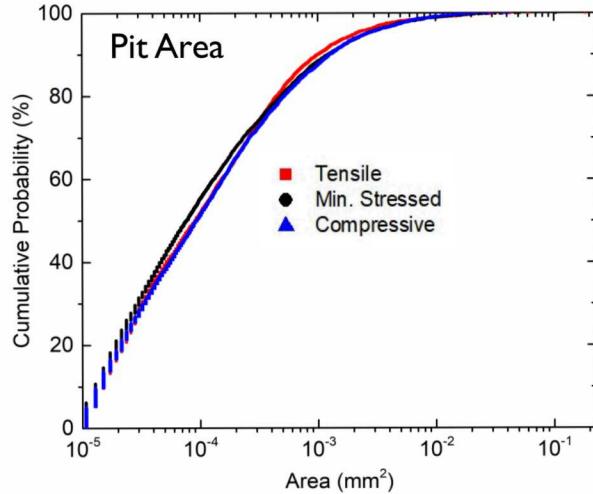
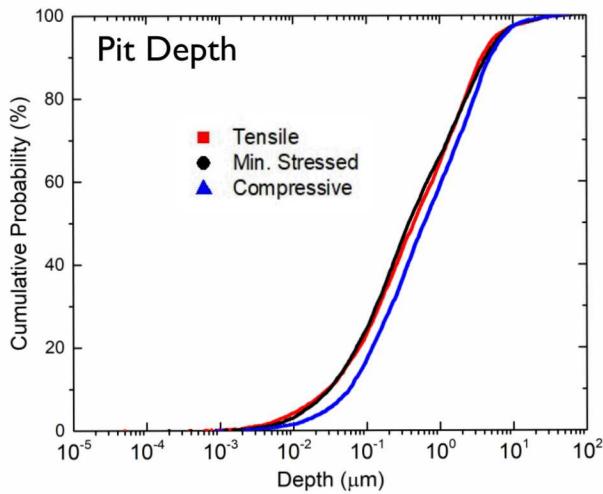
C	Co	Cr	Cu	Mn	Mo	N	Ni	P	S	Si	Fe
0.0216	0.198	18.3	0.392	1.83	0.286	0.0889	8.11	0.325	0.001	0.251	Bal.

# Optical Profilometry



# Analysis From Optical Profilometry Measurements

- **No apparent contribution from stress on physical pitting characteristics**



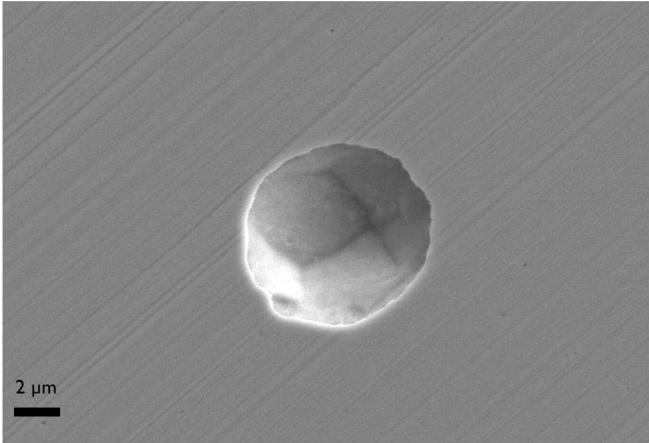
## Pitting Density:

Tensile: 1020 pits/ $\text{cm}^2$

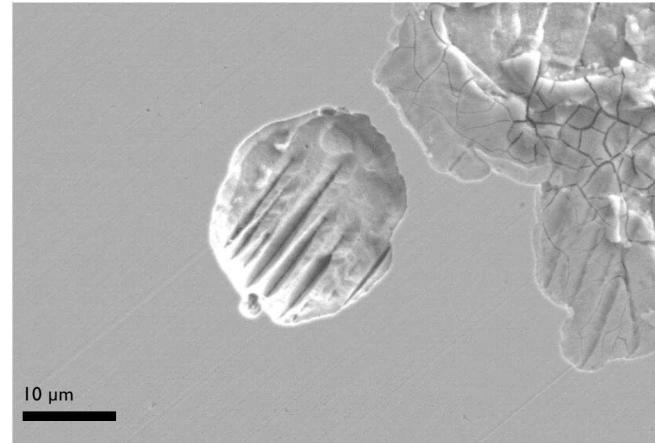
Min. Stressed: 1270 pits/ $\text{cm}^2$

Compressive: 1020 pits/ $\text{cm}^2$

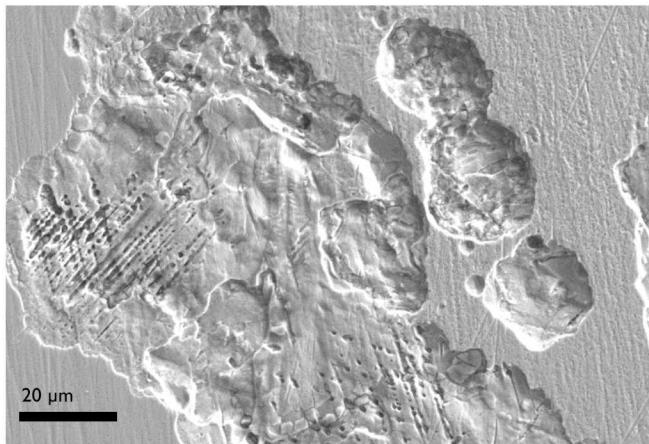
# SEM Images (Four Prominent Pit Types)



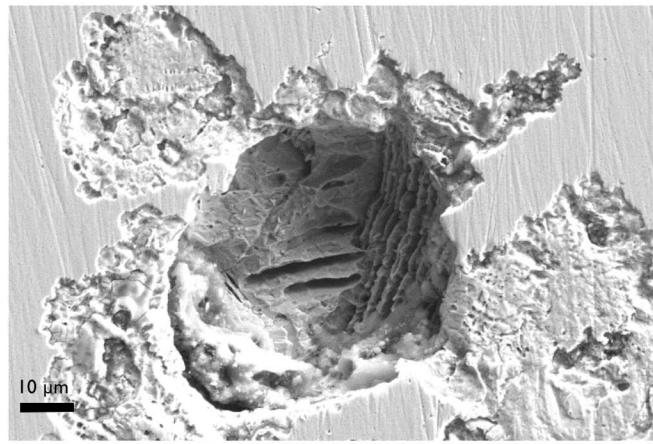
Hemispherical with smooth interior



Hemispherical with interior microstructural attack

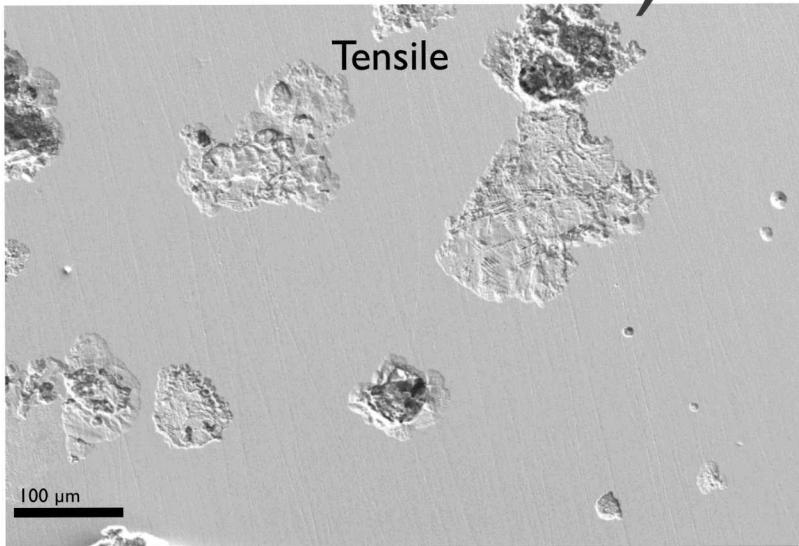


Irregular shaped with shallow microstructural attack

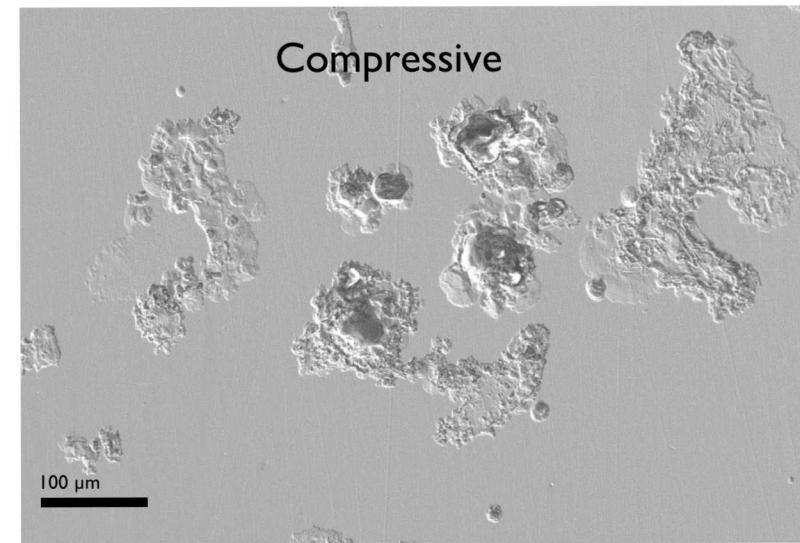
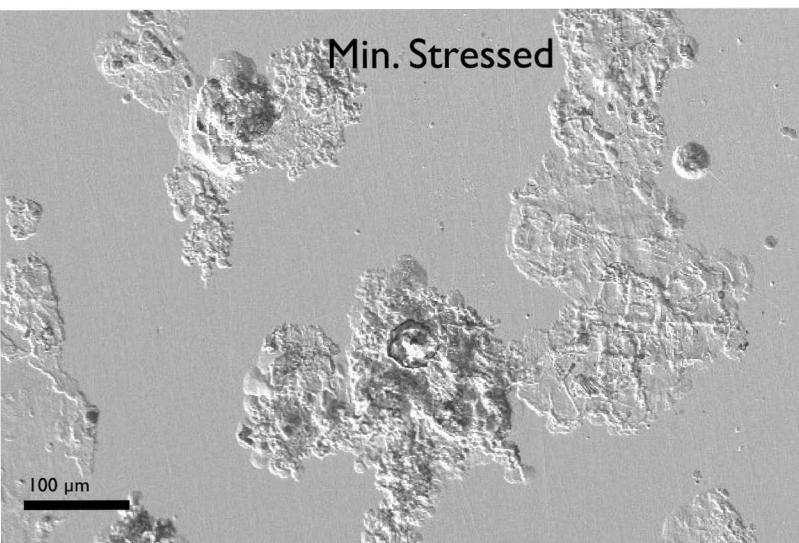


Irregular shaped with deep microstructural attack

# Low Magnification SEM (Pitting Distribution)

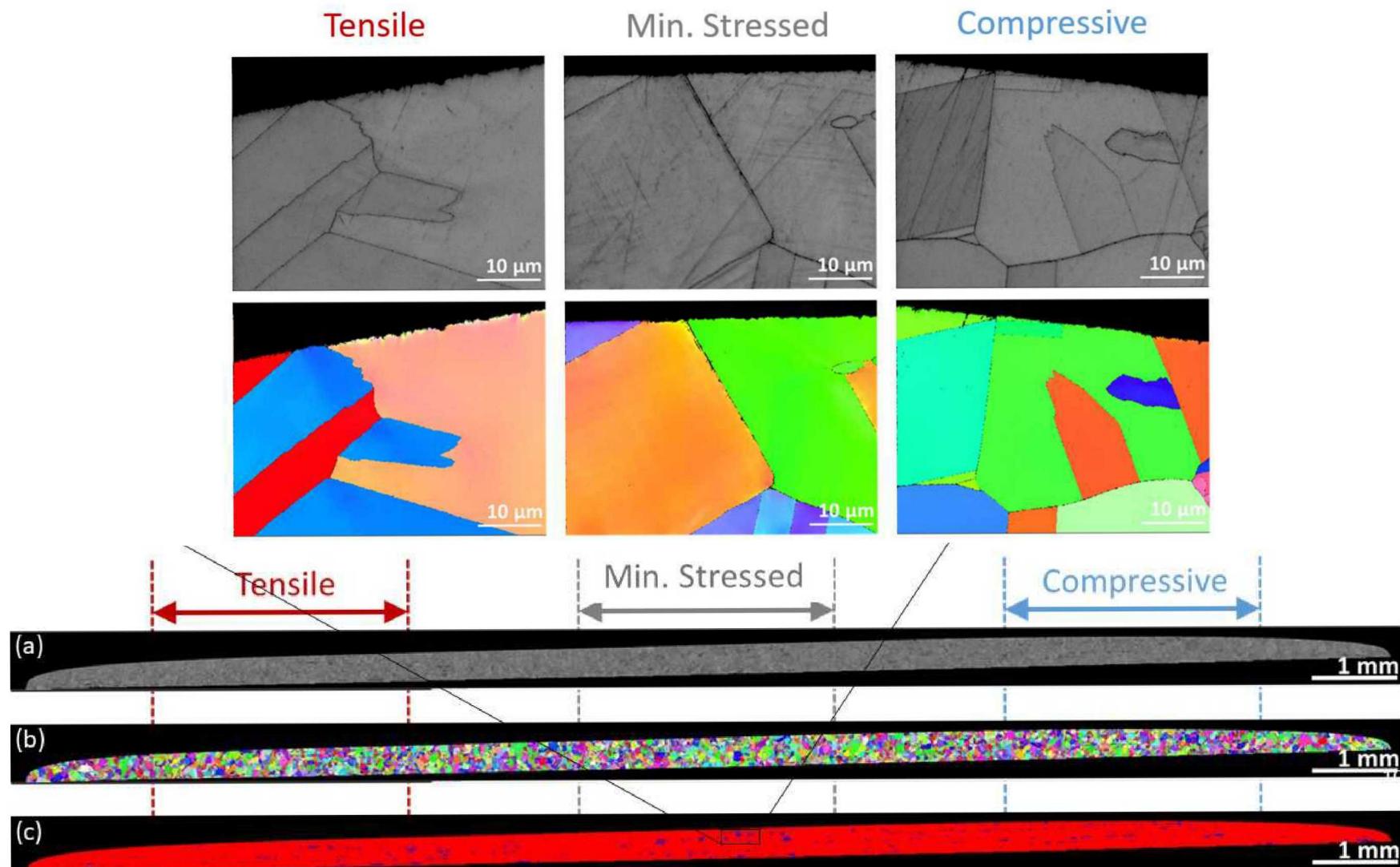


- No obvious effect from stress
- Pitting distribution appears random
- Mixture of hemispherical and irregular pits



# Microstructural characterization

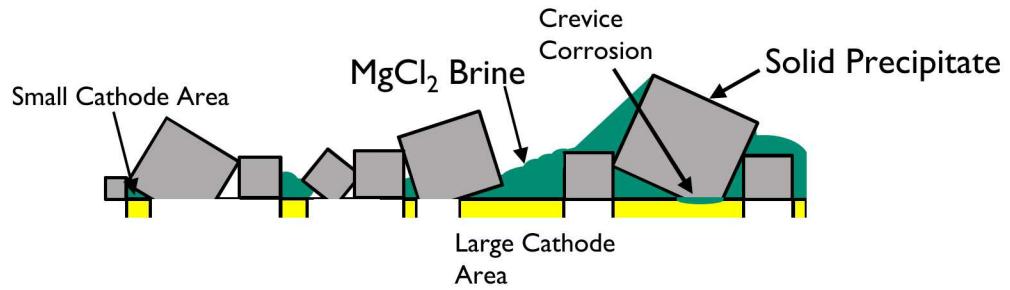
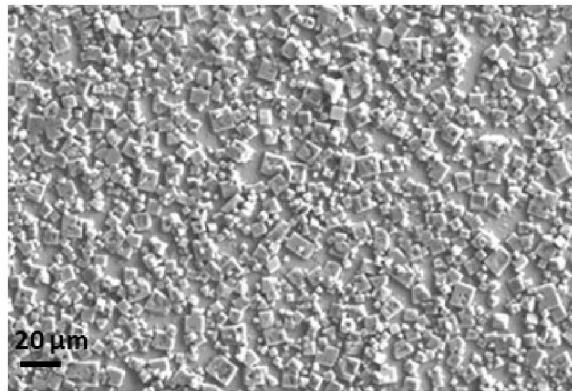
## Electron Backscatter Diffraction (EBSD)



# Pitting Morphology and Distribution

Electrolyte, exposure environment, and the underlying material play a role in the pit size and morphology

- Maximum pit size is governed by the electrolyte rather than stress
- Pitting is assumed to behave according to Chen-Kelly model\*
- Precipitated salts disrupt the continuous brine layer at low 35% RH



1. Larger liquid electrolyte volumes = larger available cathodic area
2. Smaller liquid electrolyte volumes = reduced cathodic current

\*Z.Y. Chen and R.G. Kelly, *J. Electrochem. Soc.* 157, 2 (2010): p. C69-C78

# Microstructural Attack May be a Function of Pre-Existing Phase Composition

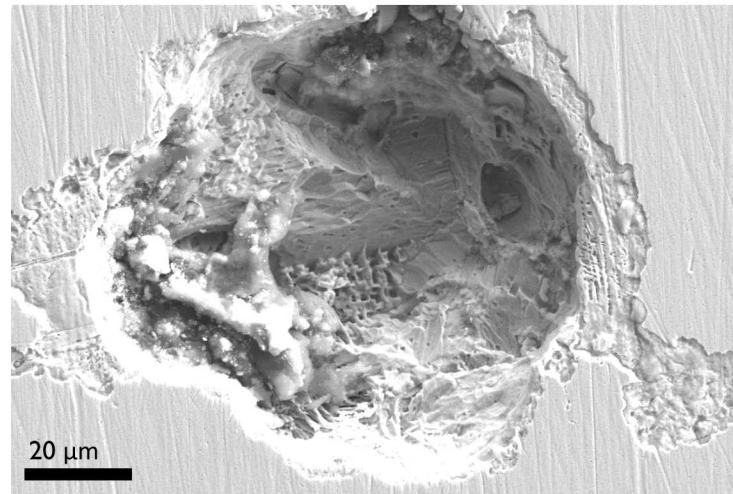
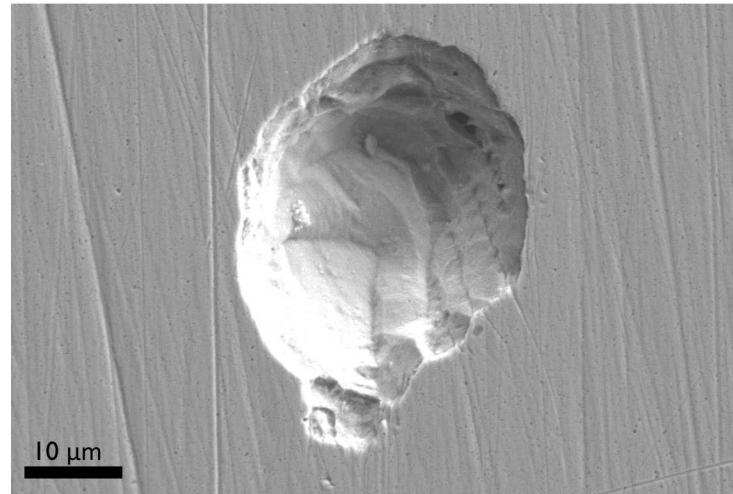
Likely favorable dissolution of martensite within the primary FCC austenitic phase

Smooth hemispherical pit

- Sufficient cathode area
  - Enough current to corrode both phases at the same rate

Microstructural Attack

- Less cathode area
- Both phases corroding at different rates



# Approach (Microelectrochemical Cell Measurements)

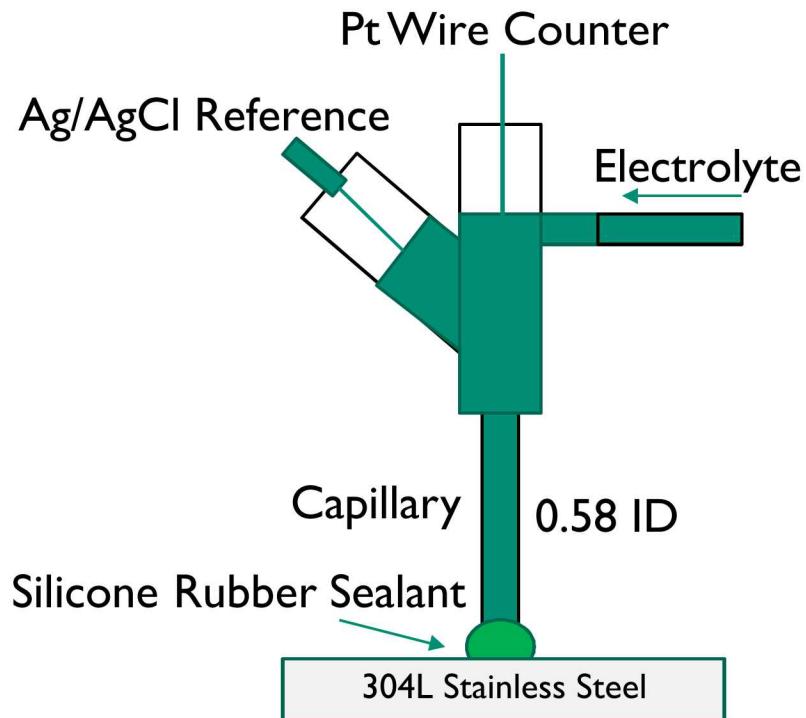
## Motivation

- Believed that aggressive, high chloride environment dominates pitting susceptibility
- Overrules any effects by localized stresses

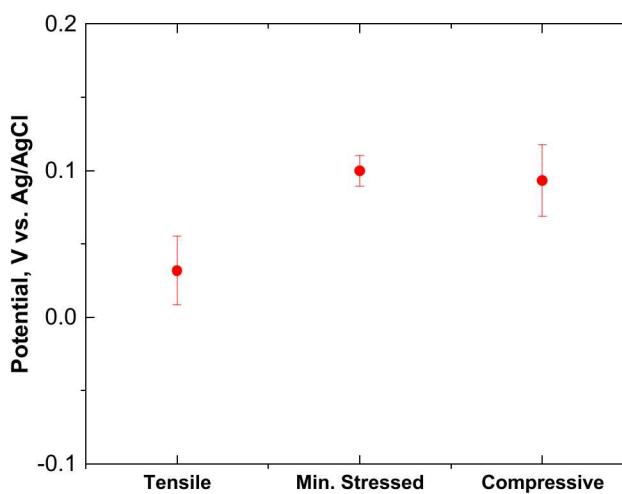
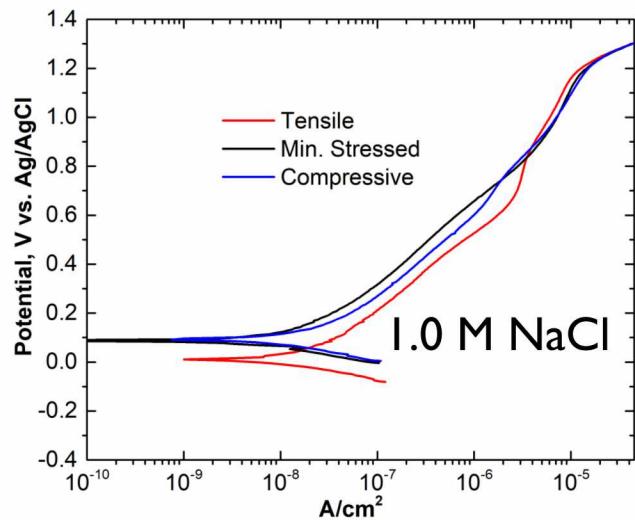
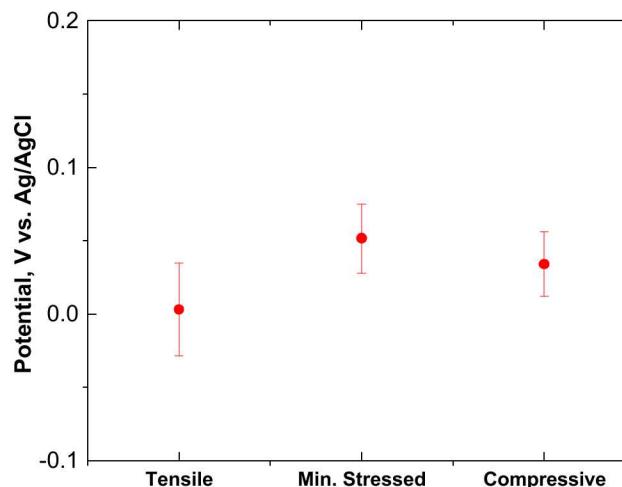
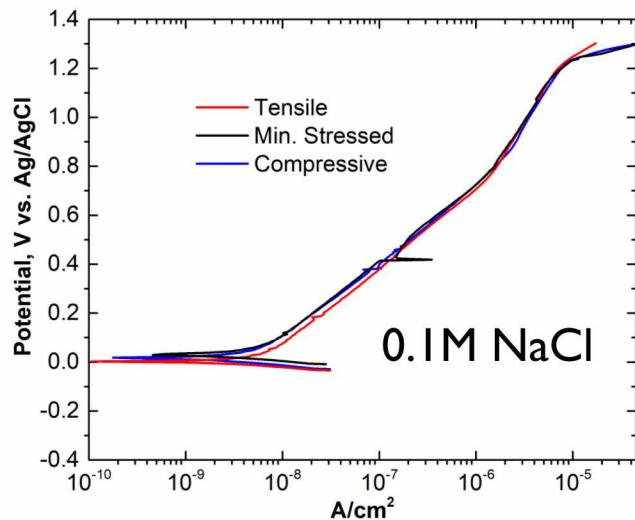
Local, spatially selective electrochemical investigations were carried out in both aggressive and benign chloride solutions

- 0.1 and 1 M NaCl
- 0.05 and 0.5 M MgCl<sub>2</sub>

## Microelectrochemical Setup



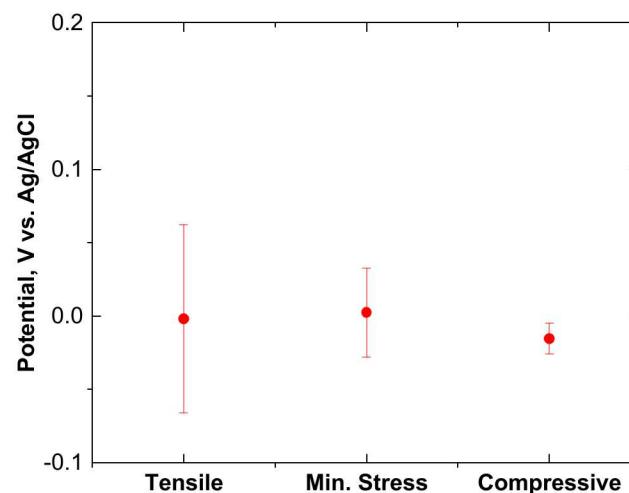
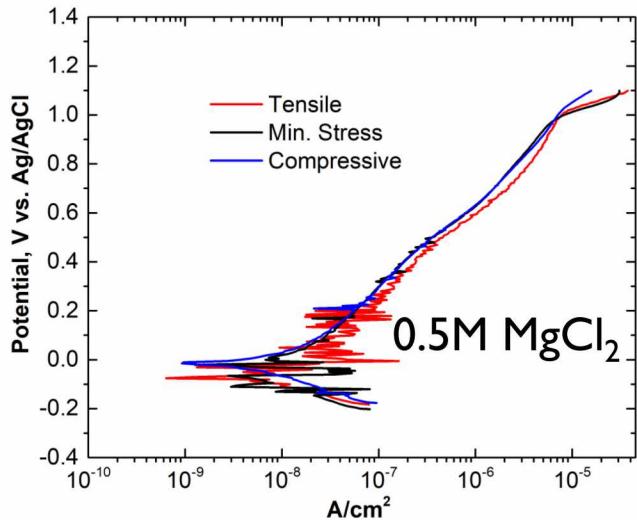
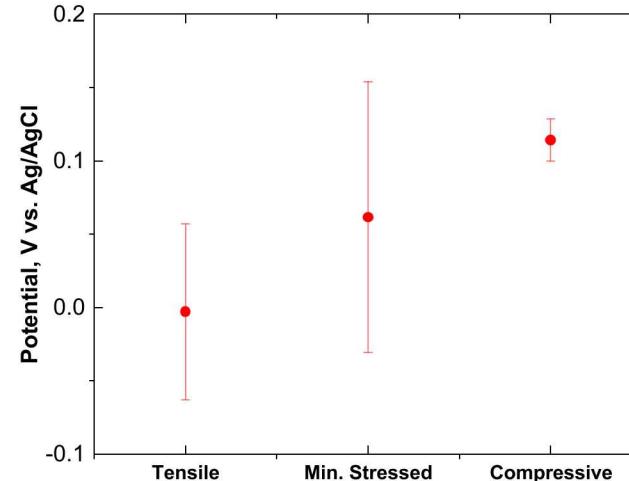
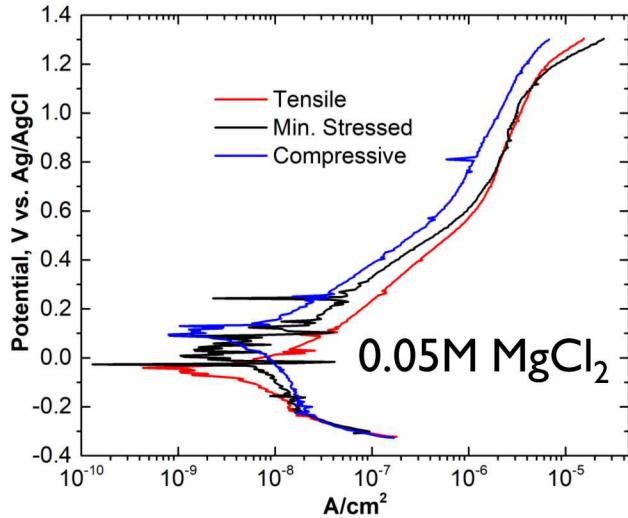
# Microelectrochemical Cell Potentiodynamic Scans of Stressed 304L Bar Exposed to NaCl



Potentiodynamic Scans

OCP Averaged Over 5 Scans

# Microelectrochemical Cell Potentiodynamic Scans of Stressed 304L Bar Exposed to $\text{MgCl}_2$



Potentiodynamic Scans

OCP Averaged Over 5 Scans

# Conclusions

- 1) Atmospheric exposure conditions explored herein were highly aggressive
  - Dominated effects from applied stress on resultant pit morphology
- 2) High salt load and low RH resulted in irregularly distributed brine and brine concentration
- 3) Dominated by
  - pre-existing phase composition of the SS
  - cathodic availability of the heterogeneous brine
  - crevice formation from precipitated salts
- 4) Effects of applied stress on the electrochemical polarizations were enhanced in more benign (lower chloride concentration) environments

# Conclusions and Future Work

- **Still want to understand:** What are the mechanisms of pitting under stress and how does pitting initiate cracks during atmospheric exposure?
- **From current study:** severity of brine environment played a larger role in governing pit distribution, morphology, and size than applied stress
- **Future work:** Determine effects of varied deposition densities, brine concentrations, exposure conditions, etc. in combination with applied stress at various levels on resultant pitting and pit-to-crack transition

# Acknowledgments

## SNL:

Dr. Charles Bryan

Alana Parey

Sara Dickens

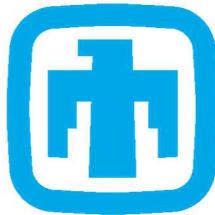
Bonnie McKenzie

Ryan Katona

## UNM:

Dr. Lok-kun Tsui

Dr. Thomas Peng



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