

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

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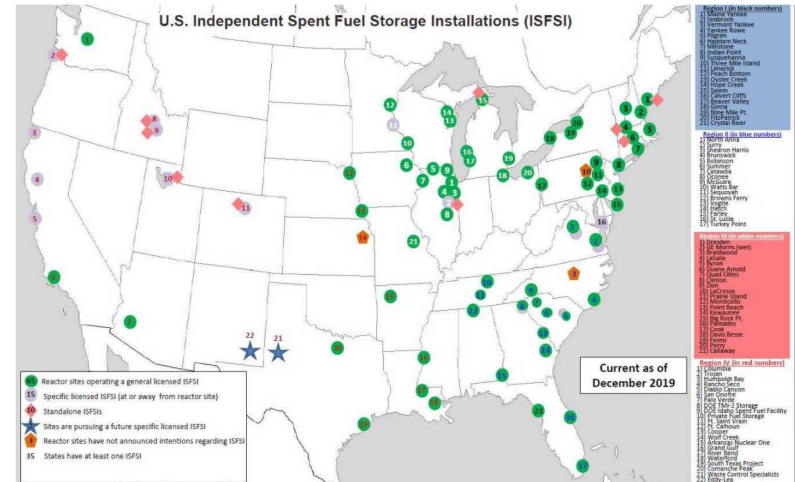
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# Motivation

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>

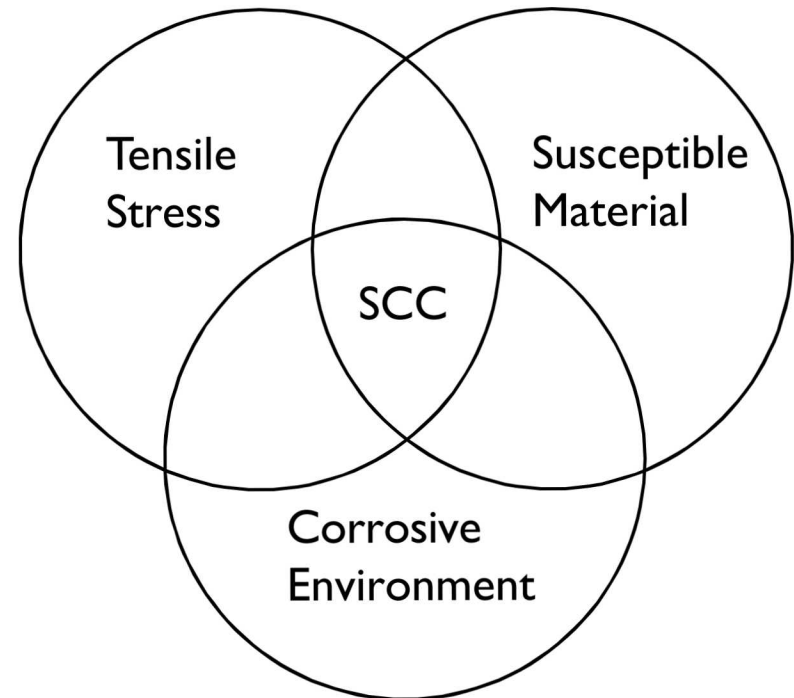
# Motivation

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/fig1/AS:668504487370754@1536395298091/Venn-Diagram-for-Stress-Corrosion-Cracking.png](https://www.researchgate.net/profile/Barry_Gordon/publication/257761781/figure/fig1/AS:668504487370754@1536395298091/Venn-Diagram-for-Stress-Corrosion-Cracking.png)

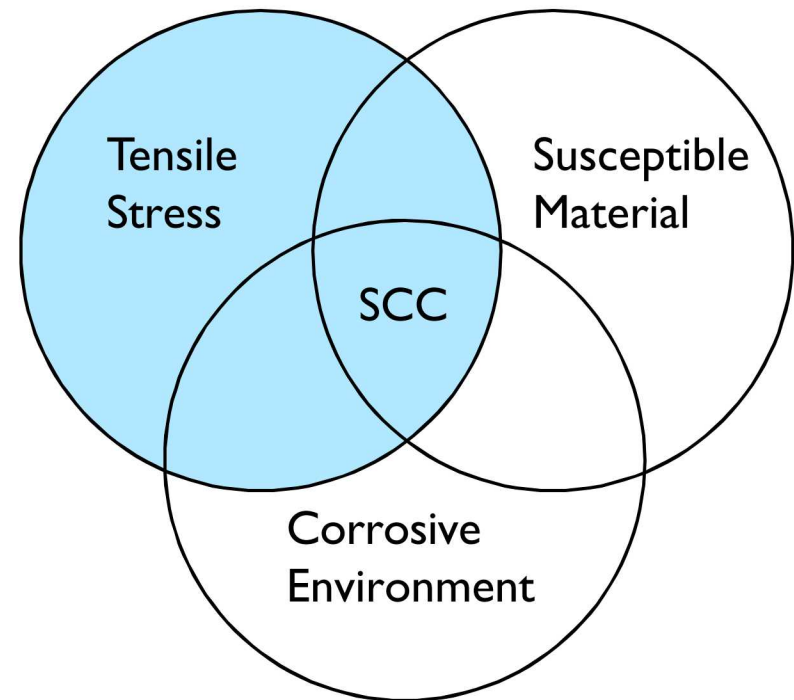


# Stress Corrosion Cracking from Atmospheric Exposure

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**



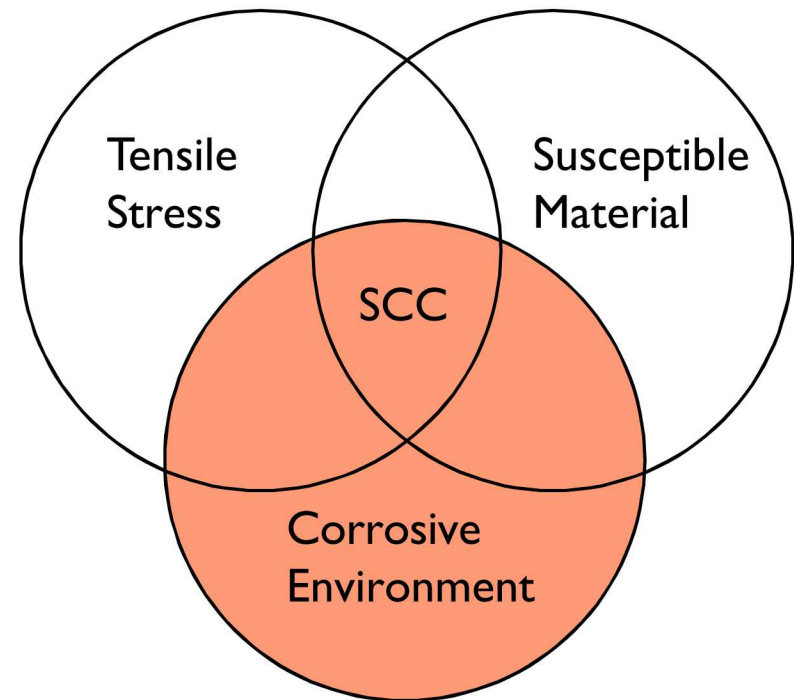
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# Stress Corrosion Cracking from Atmospheric Exposure

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

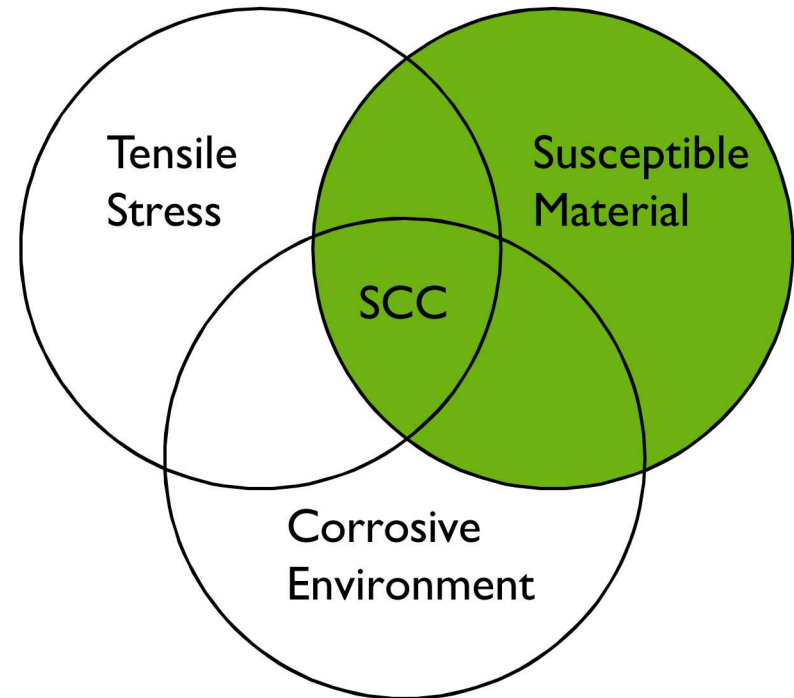
\*\* G.G. Scatigno, P. Dong, M.P. Ryan, and M.R. Wenman, *Mater.* 8 (2019): p. 100509

# Stress Corrosion Cracking from Atmospheric Exposure

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**
- **Phase composition**



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\*\*\* C. Örnek, X. Zhong, and D. L. Engelberg, *CORROSION*. 72, 3 (2016): p. 384-399

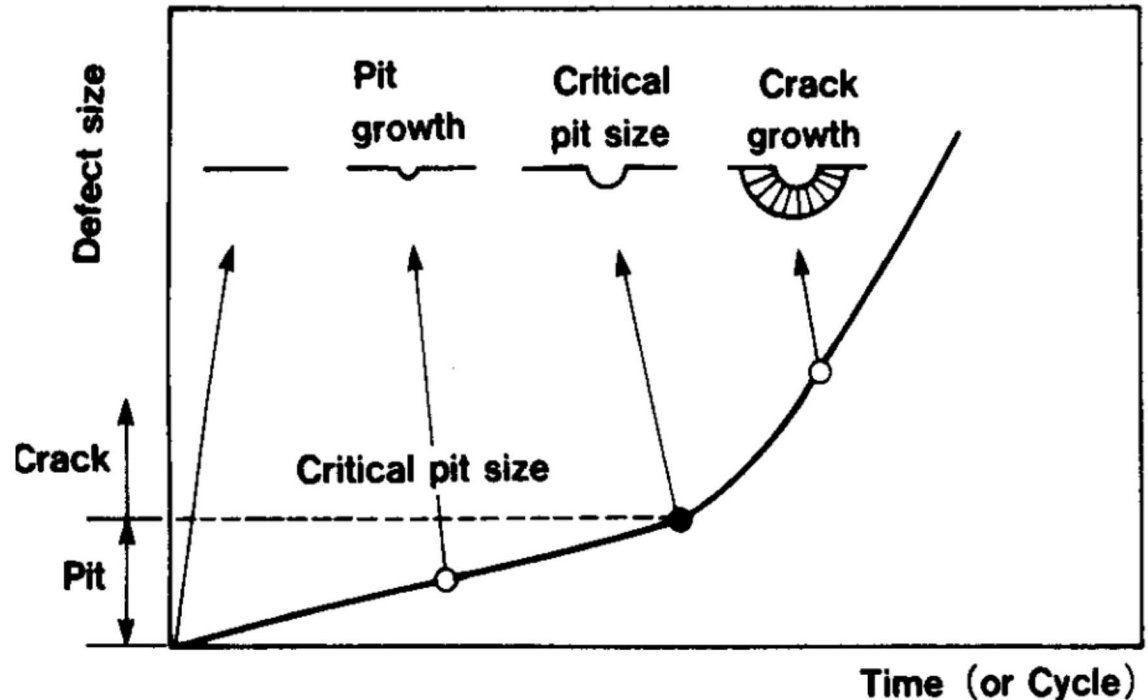
# Pit to Crack Transition

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



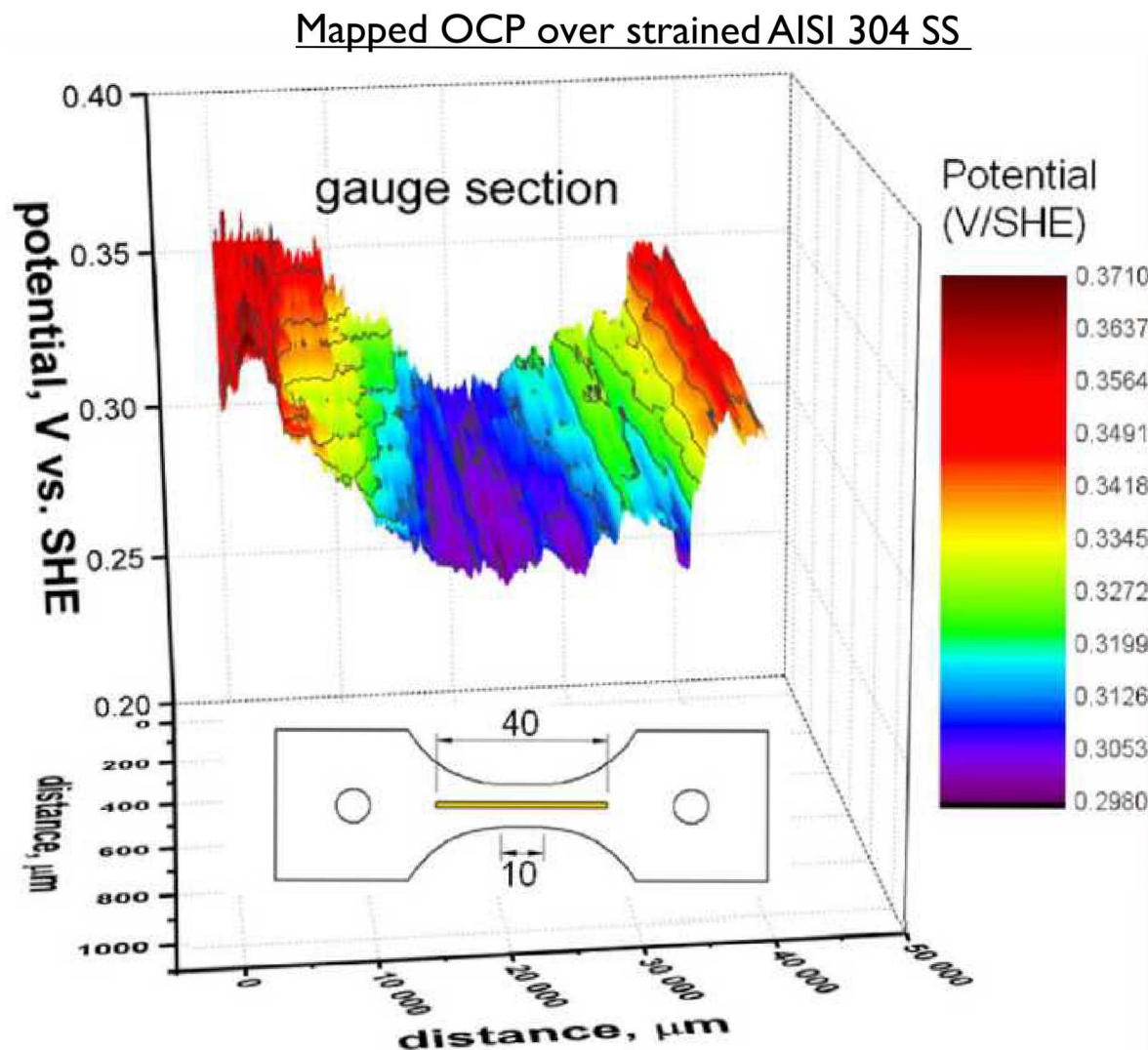
\*Y. Kondo, Corrosion, 45, 1 (1987): p. 7-11.



# Influence of Stress on Corrosion

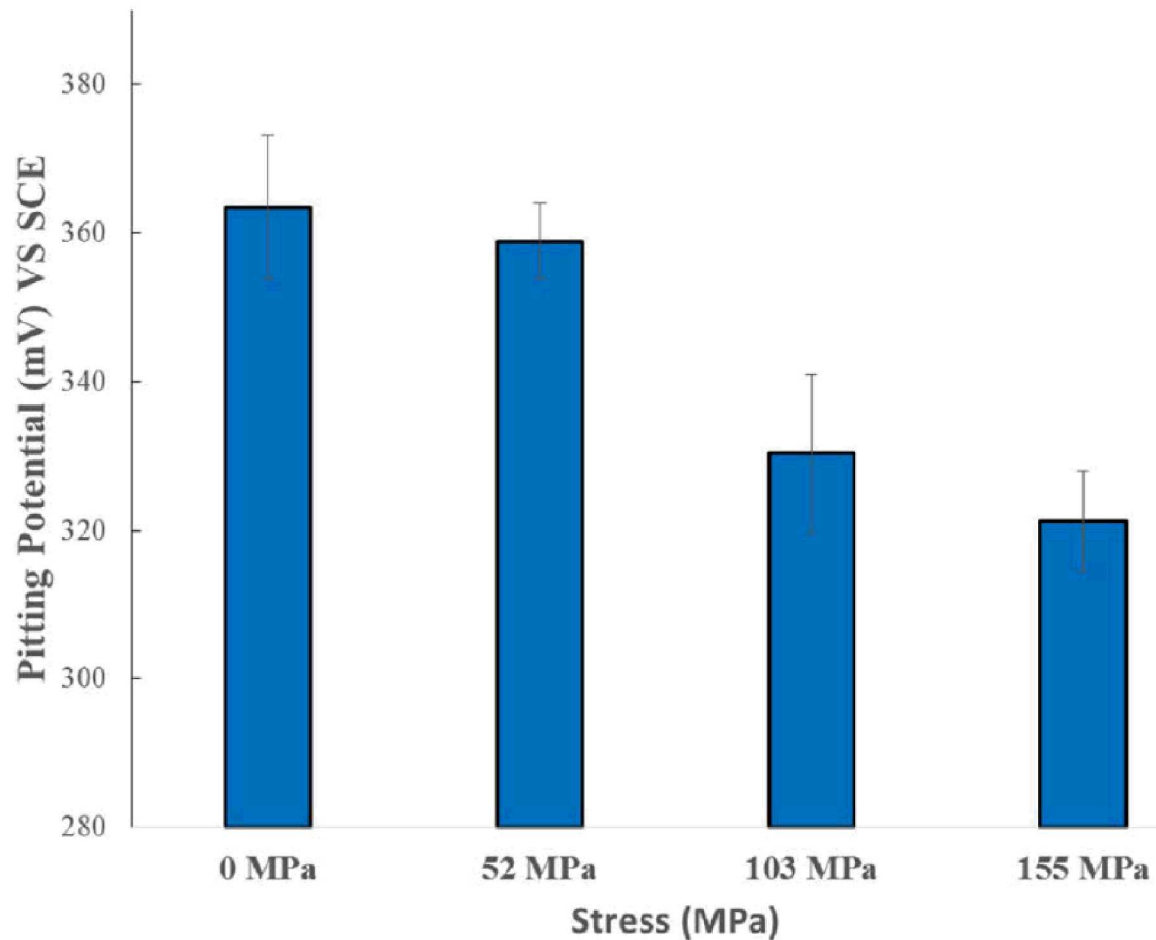
Stress causes the material to have lower open circuit potential (OCP)

Lower OCP signifies a greater corrosion susceptibility



# Influence of Stress on Corrosion

More corrosion susceptibility at higher stress



# 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 ( $0.1 \text{ Ra } \mu\text{m}$ )

Artificial seawater (ASW) Loading density ( $4 \text{ g/m}^2$  chloride)

Atmospheric exposure in humidity chamber (50 days at  $50^\circ\text{C}$  and 35 % RH)

- Accelerated corrosion
- Cleaning Procedure (submerged in 0.6 M diammonium citrate solution at  $70^\circ\text{C}$  for 24 hours (ASTM-G1))



# Analysis

Optical profilometry

- Pitting analysis

Scanning electron microscopy (SEM)

- Interrogate pits further

Electron backscatter diffraction (EBSD)

- Composition analysis

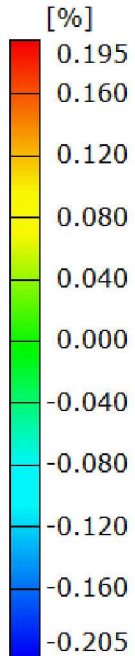
Micro-electrochemical cell

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

# Material and Stress Application

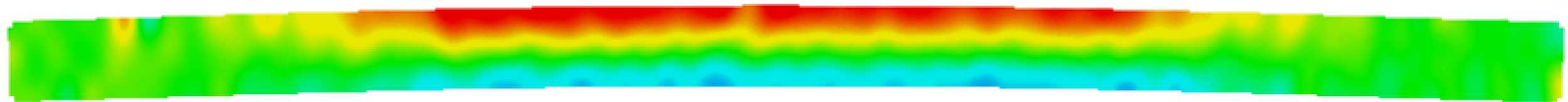
A four-point bend bar was atmospherically exposed to explore a full stress gradient, from tensile to compressive stresses, across the thickness of the bar

Strain (%)



Stressed, Corroded  
304L Stainless Steel

Digital Image Correlation

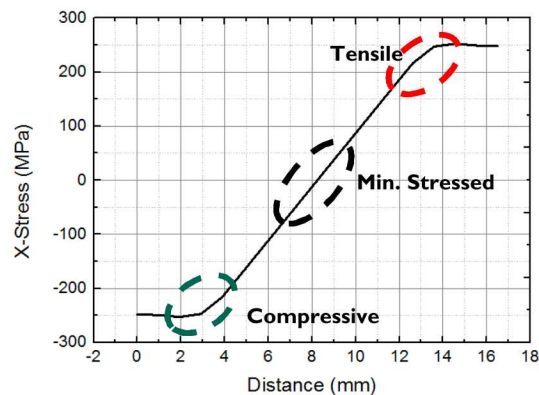
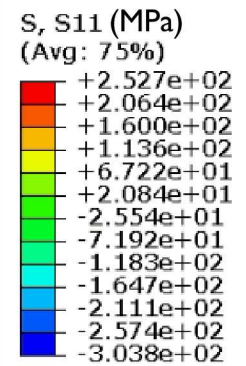
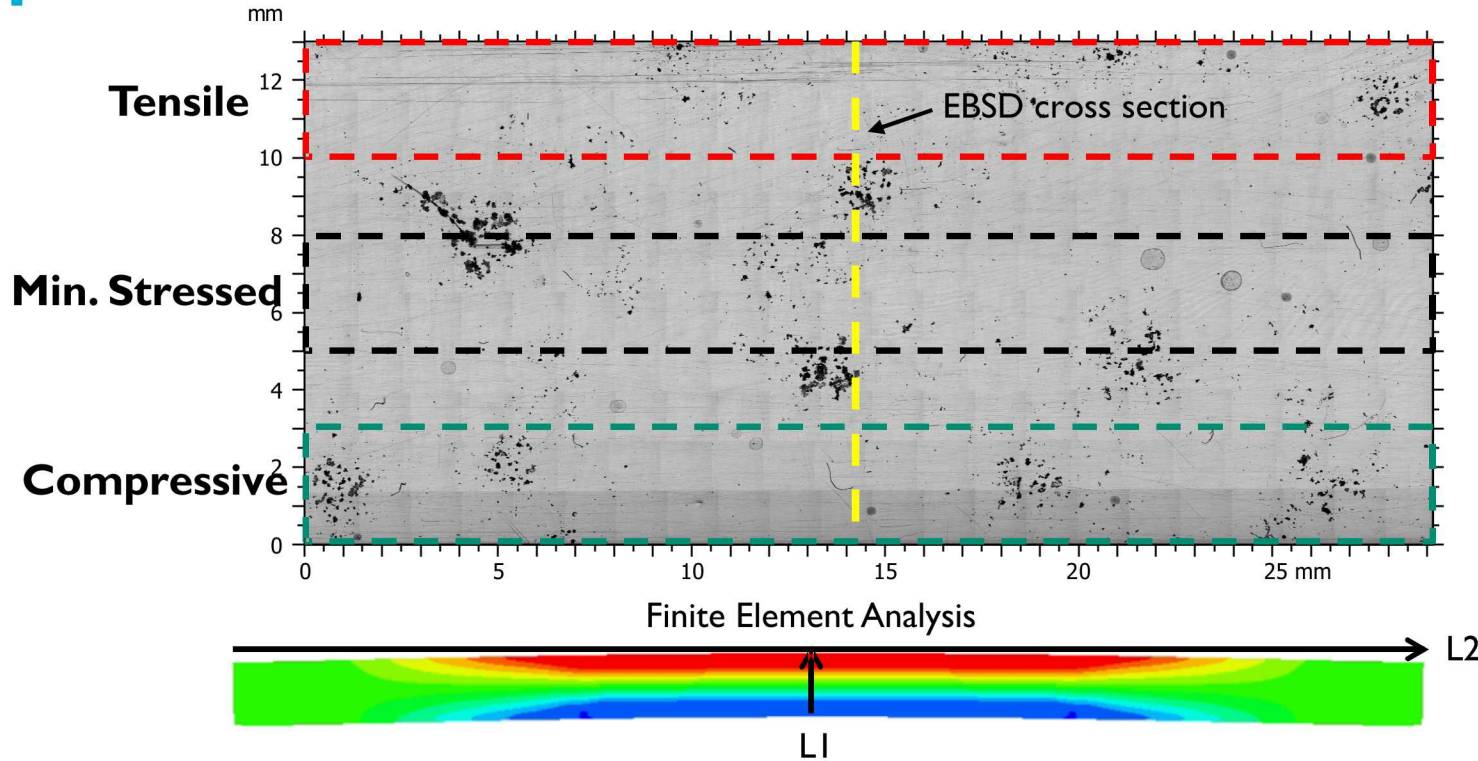


Base metal composition of the 304L stainless steel bar

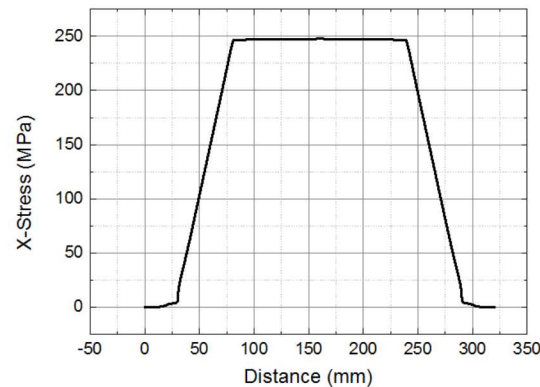
## SS304L bar composition (wt. %)

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



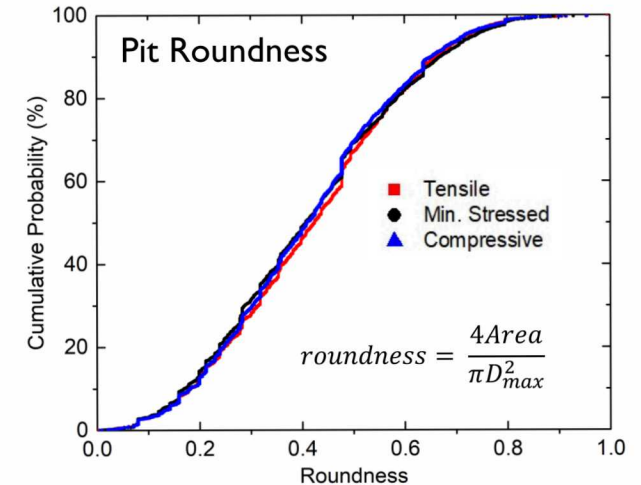
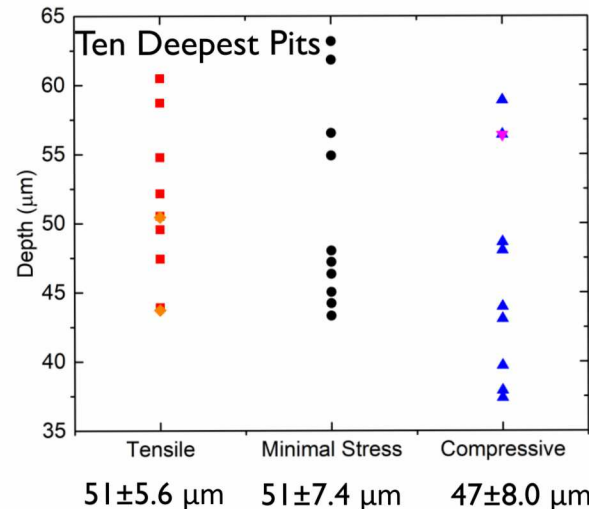
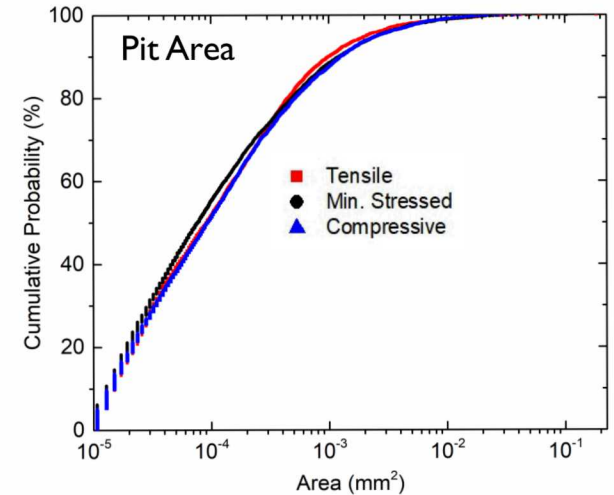
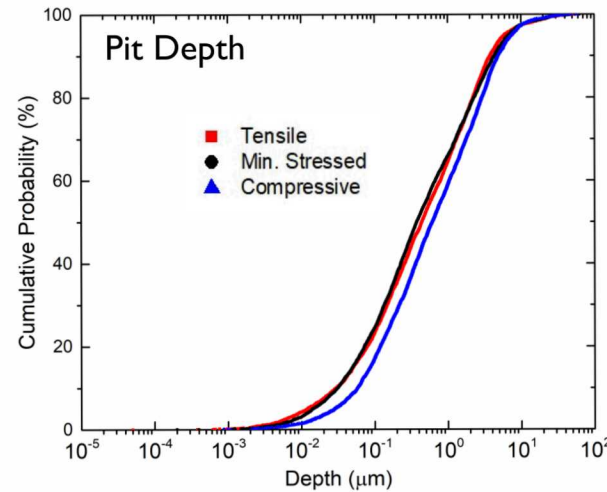
Stress distribution profile along path L1



Stress distribution profile along path L2

# Analysis From Optical Profilometry Measurements

- No apparent contribution from stress on physical pitting characteristics



## Pitting Density:

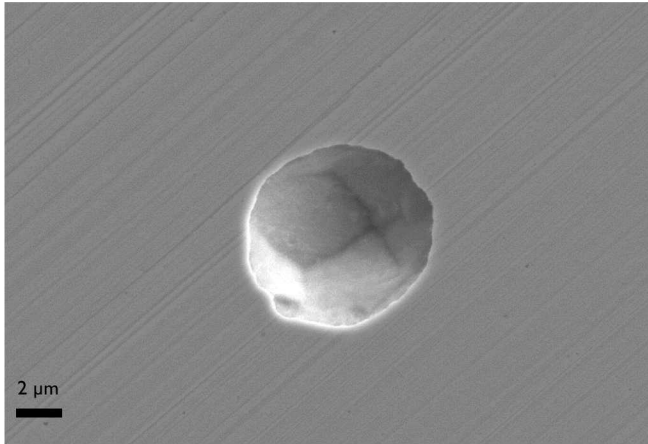
Tensile: 1020 pits/ $\text{cm}^2$

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

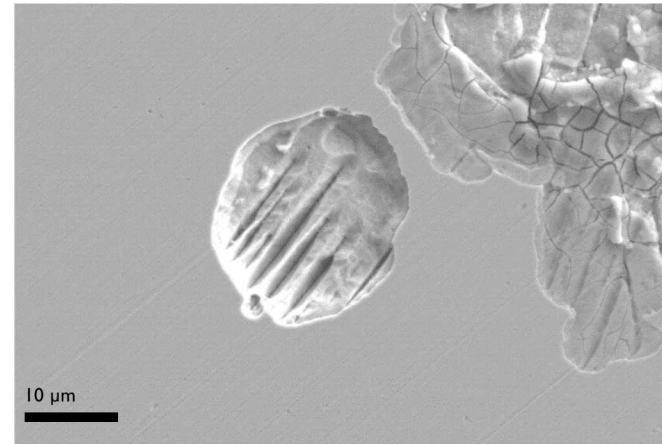
Compressive: 1020 pits/ $\text{cm}^2$



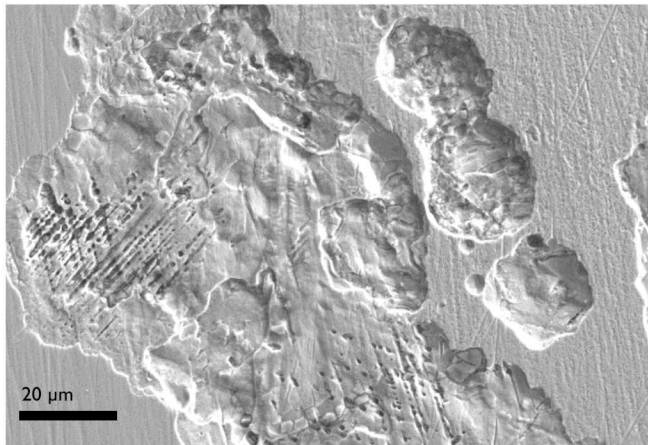
# SEM Images (Four Prominent Pit Types)



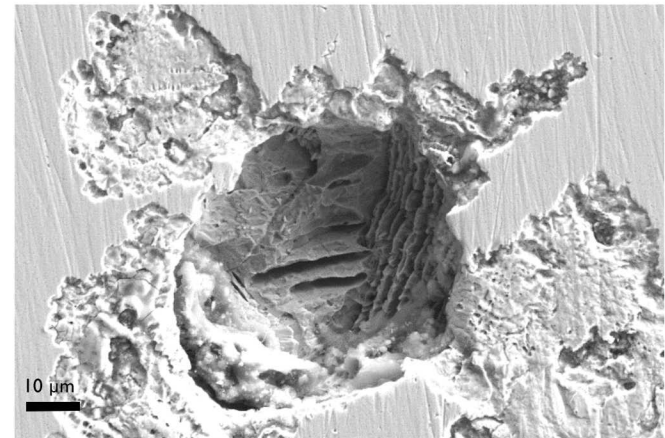
Hemispherical with smooth interior



Hemispherical with interior microstructural attack

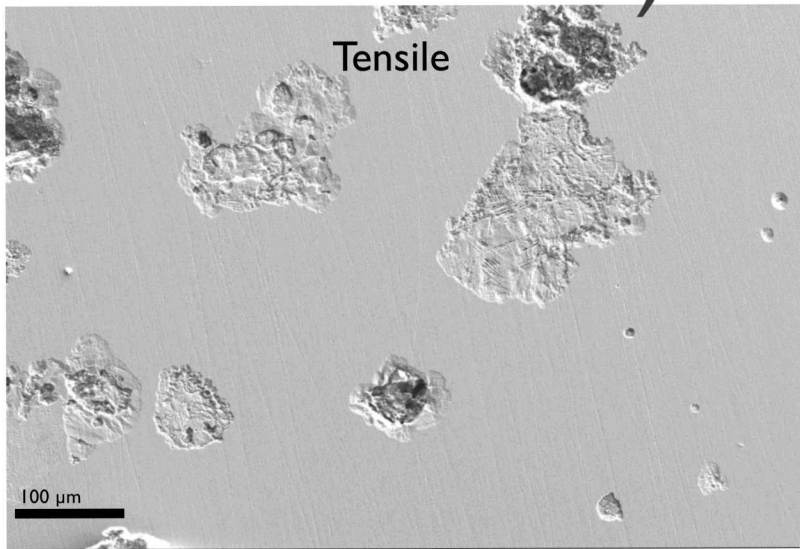


Irregular shaped with shallow microstructural attack

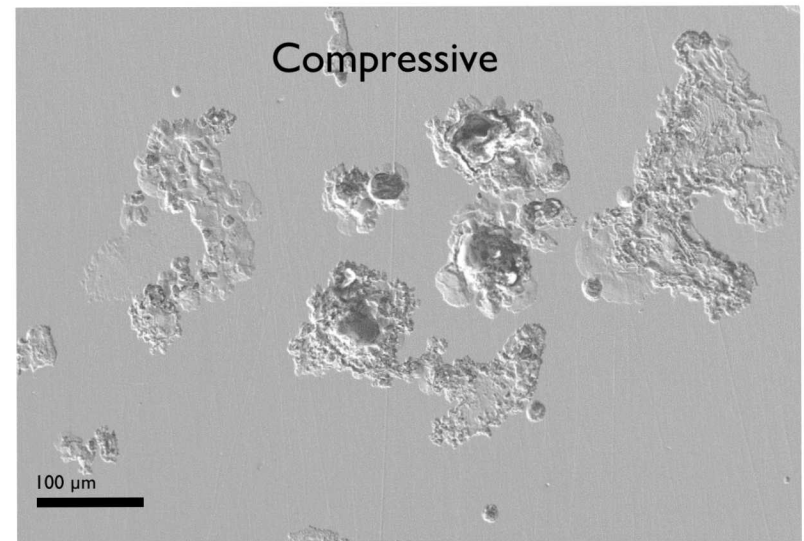
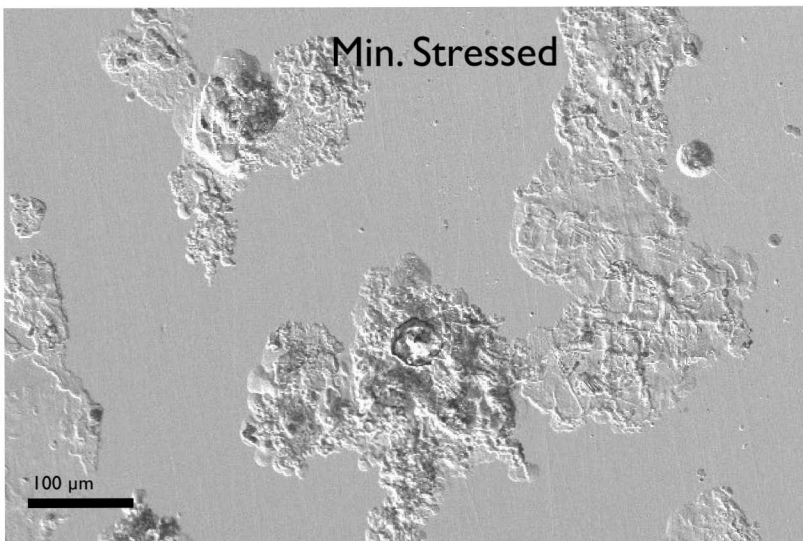


Irregular shaped with deep microstructural attack

# Low Magnification SEM (Pitting Distribution)



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



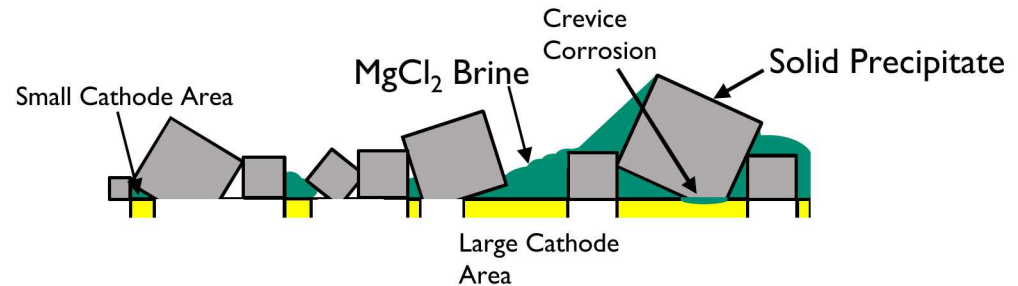
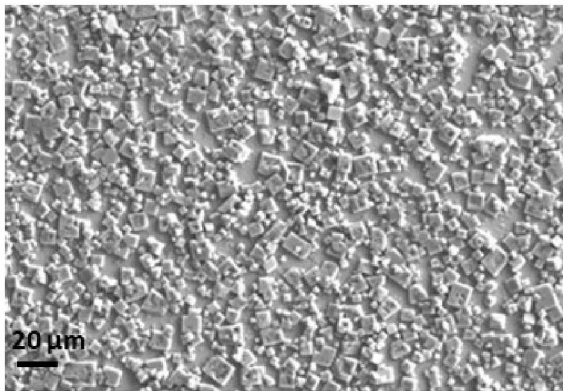




# Pitting Morphology and Distribution

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

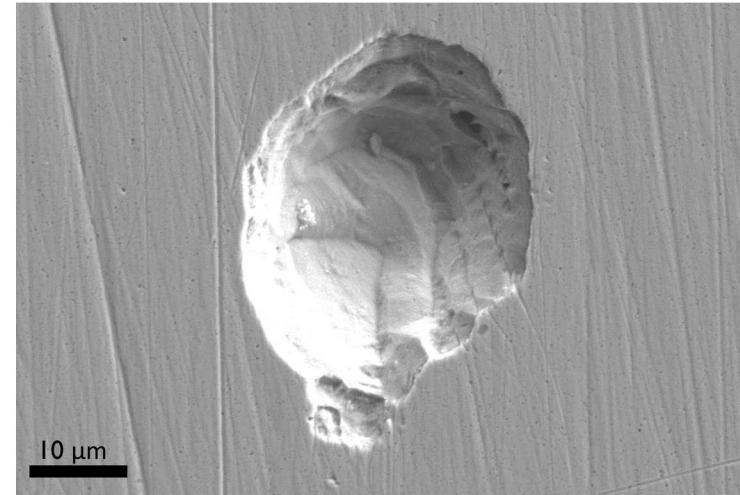


# Microstructural Attack May be a Function of Pre-Existing Phase Composition

Likely favorable dissolution of martensite within the primary FCC austenitic phase

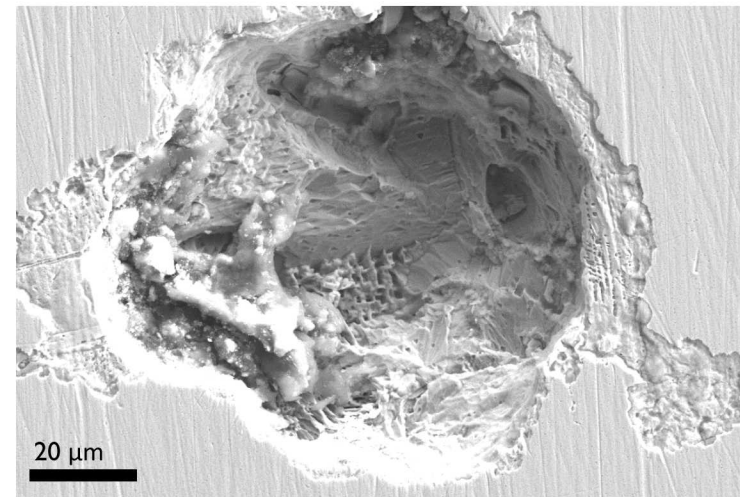
Smooth hemispherical pit

- 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)

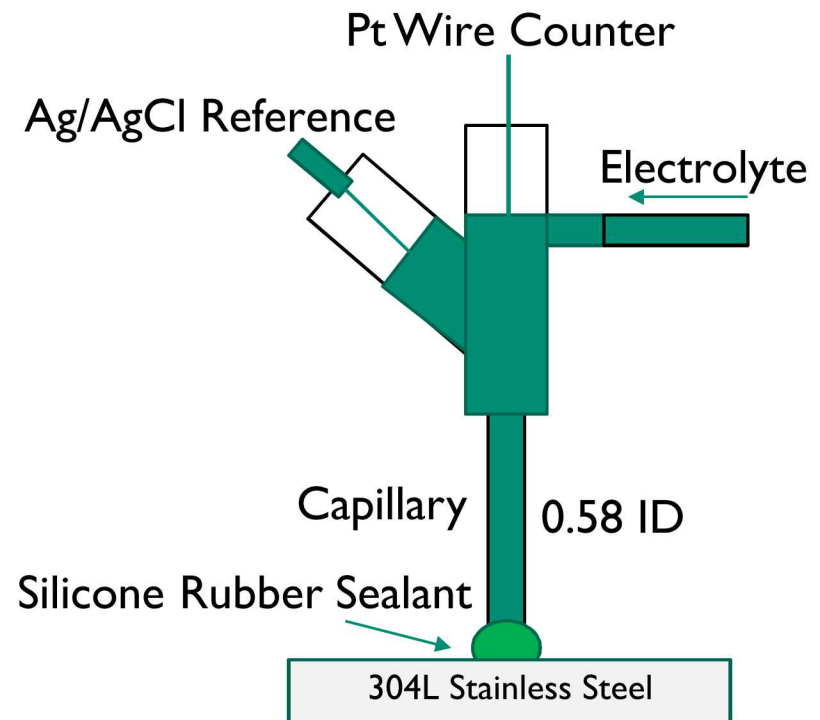
## Motivation

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

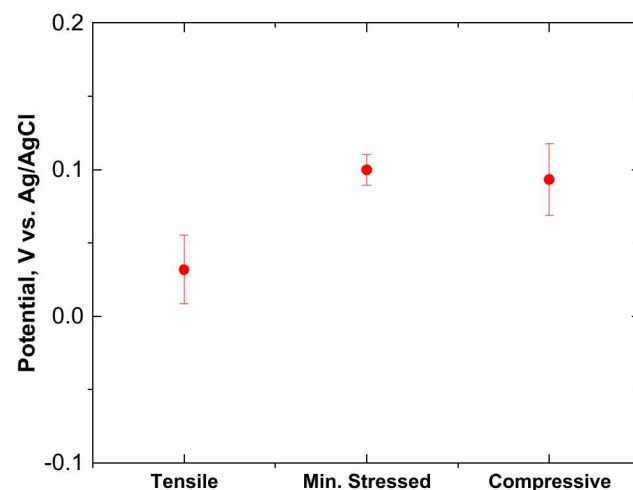
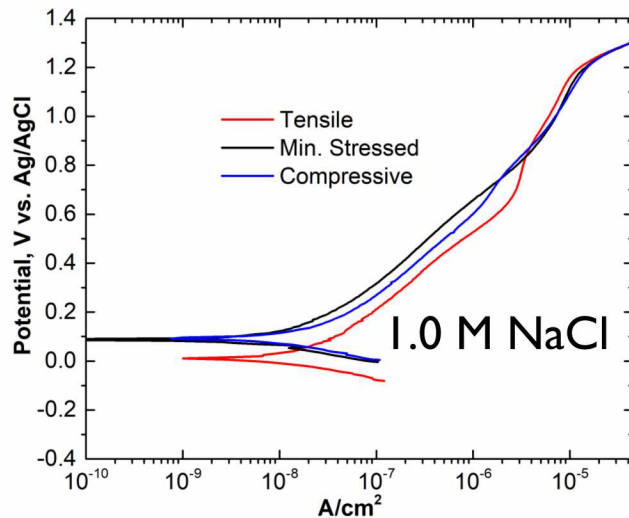
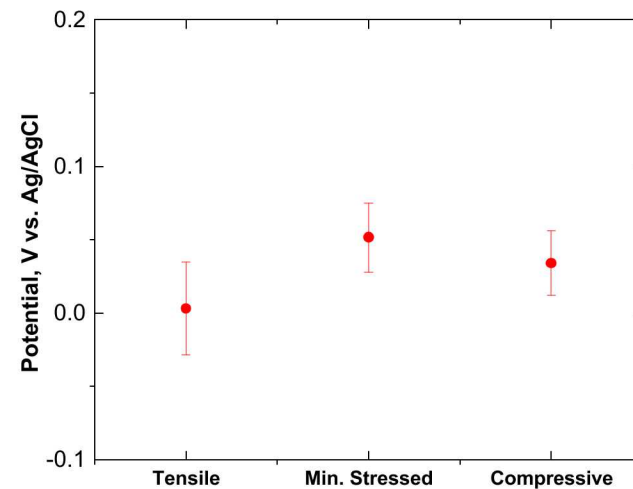
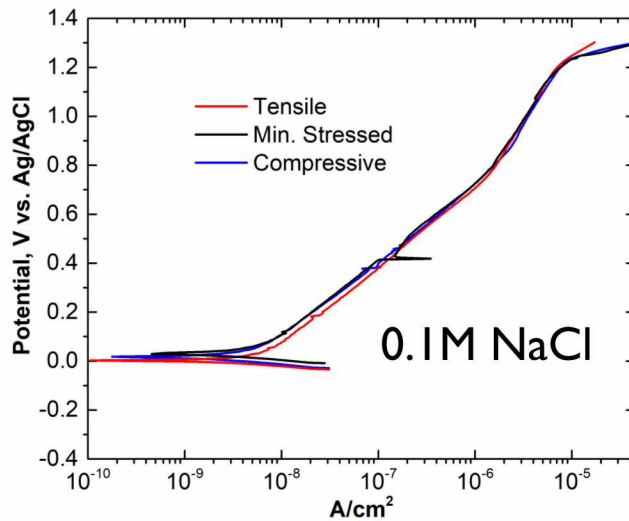
Local, spatially selective electrochemical investigations were carried out in both aggressive and benign chloride solutions

- 0.1 and 1 M NaCl
- 0.05 and 0.5 M  $\text{MgCl}_2$

## Microelectrochemical Setup



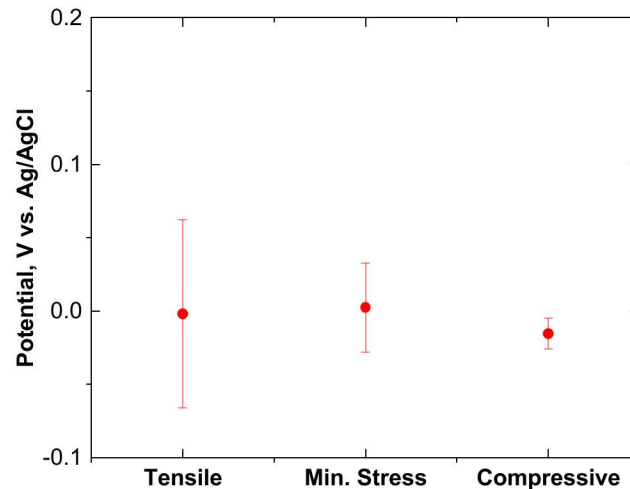
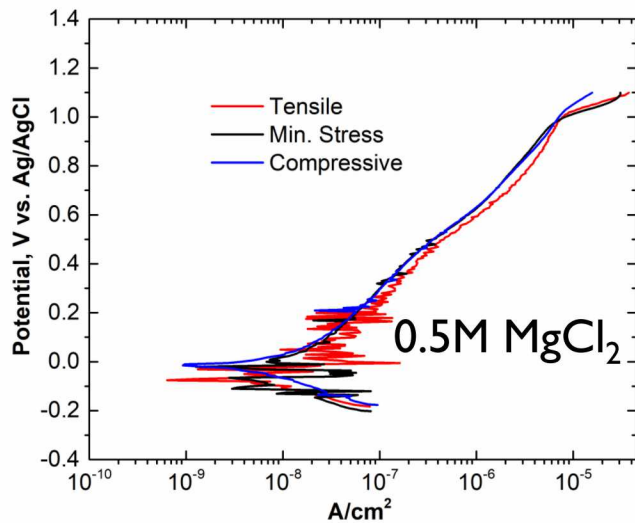
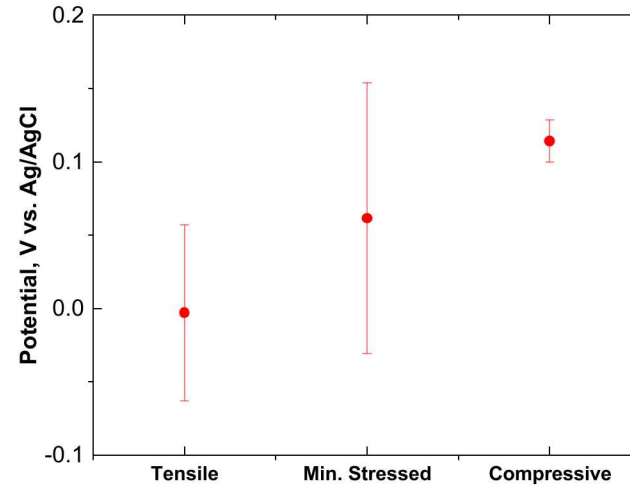
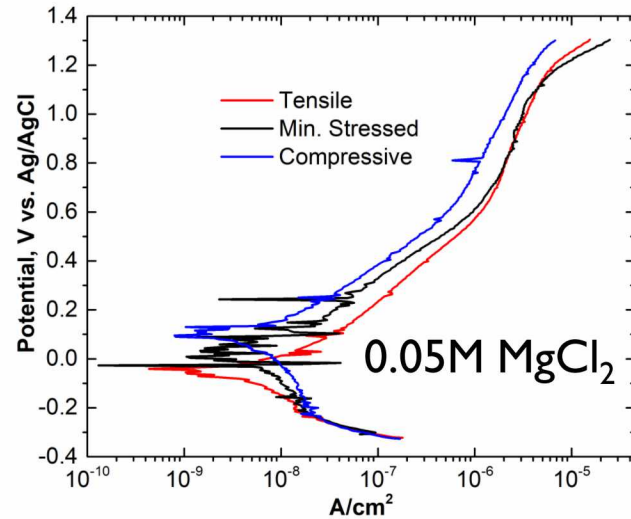
# Microelectrochemical Cell Potentiodynamic Scans of Stressed 304L Bar Exposed to NaCl



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:

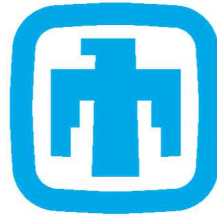
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