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Evaluating HEAC Possibility in RH-dependent Microcracking Observed in Austenitic Stainless Steels

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Research in Progress - EAC

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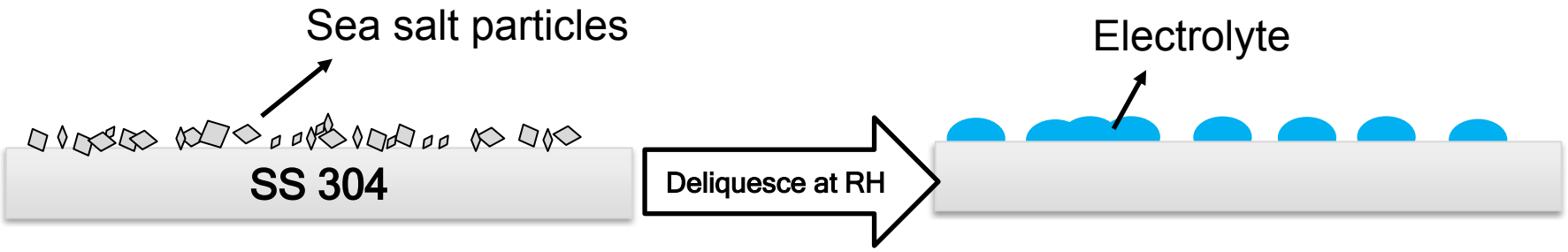
304 SS used for SNF storage exposed to corrosive atmospheres

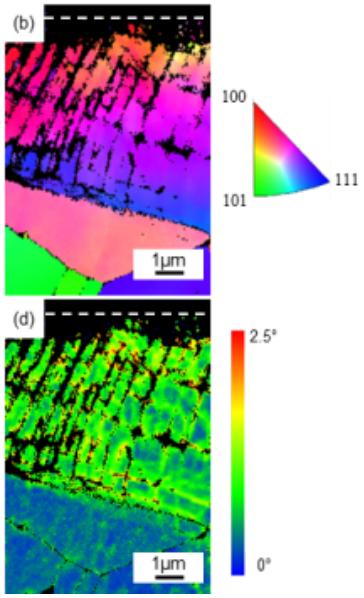


RH	$[Cl^-]$ $(mol \cdot kg^{-1})$	$[Na^+]$ $(mol \cdot kg^{-1})$	$[Mg^{2+}]$ $(mol \cdot kg^{-1})$
40%	10.45	0.18	5.33
76%	5.65	4.85	0.54

High chloride concentration in electrolyte leads to pitting risk

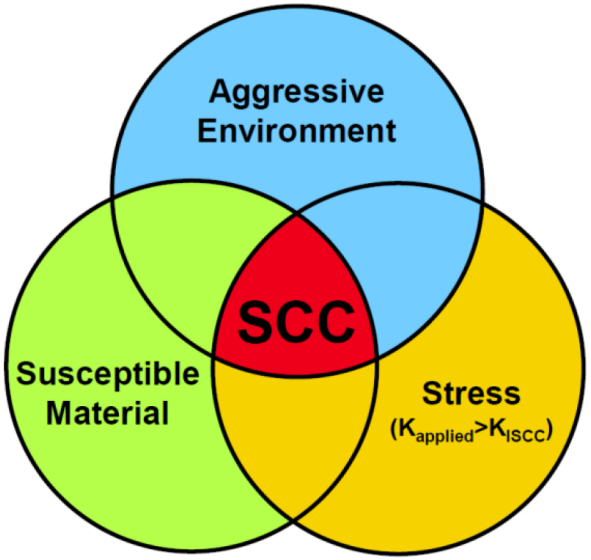
Weirich et al. JECS (2019).

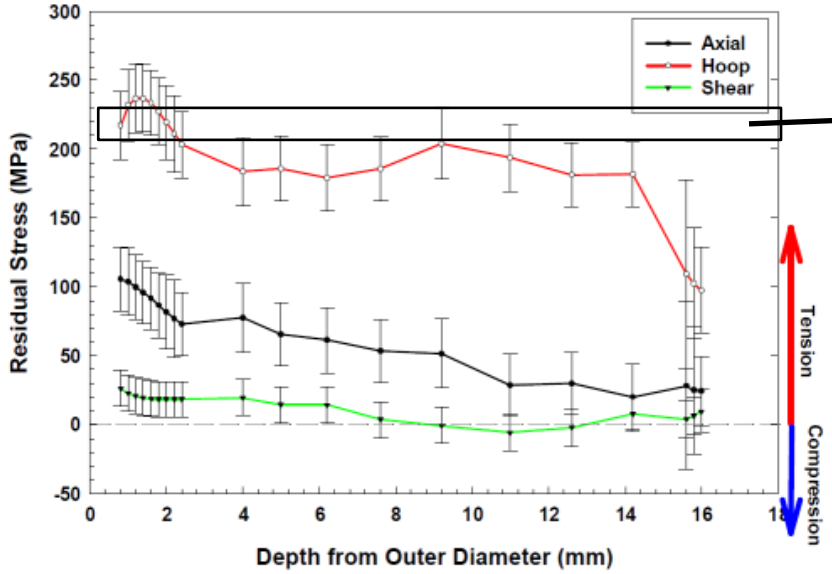
SCC risk present when 304 SS exposed to corrosive atmospheres



Weirich et al. JECS (2019).

Deformation from grinding may create susceptible subsurface microstructure





Enos and Bryan, SNL Report, 2016.

Yield strength for annealed 304 SS

Residual stress variation in SNF canister material shows through-crack propagation likely if initiation occurs

Exposure to high and low RH leads to different pit morphology in 304 SS

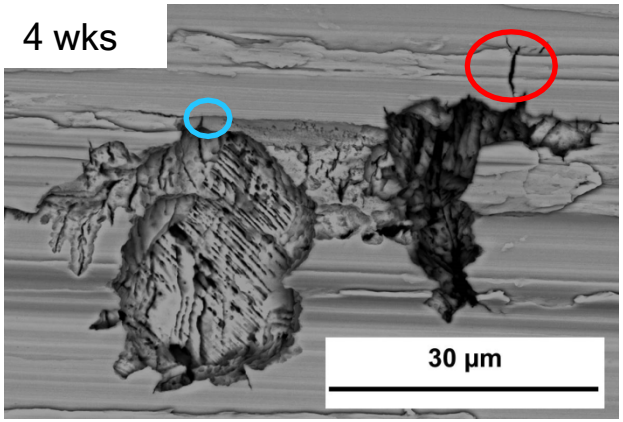
40% RH

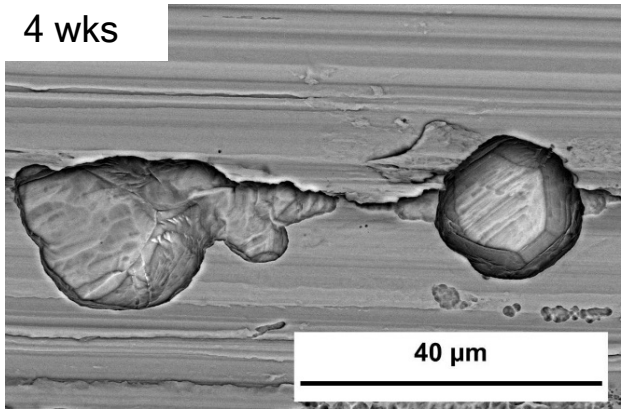
76% RH

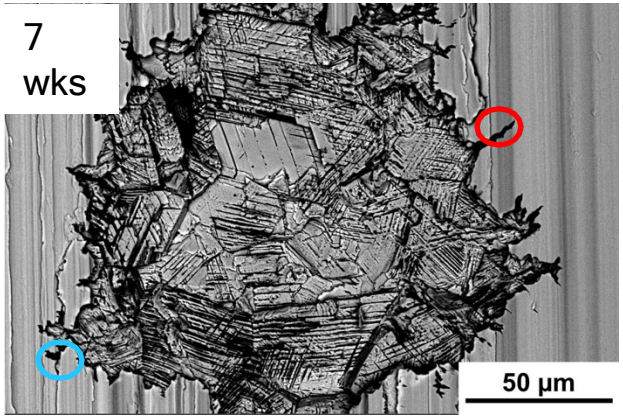
Atmospheric exposures

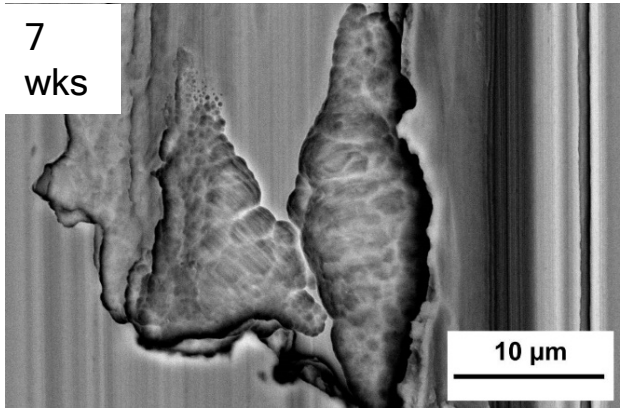
35 °C

Full immersion exposures in eq. brines









cross-hatched pits, microcracks, fissures

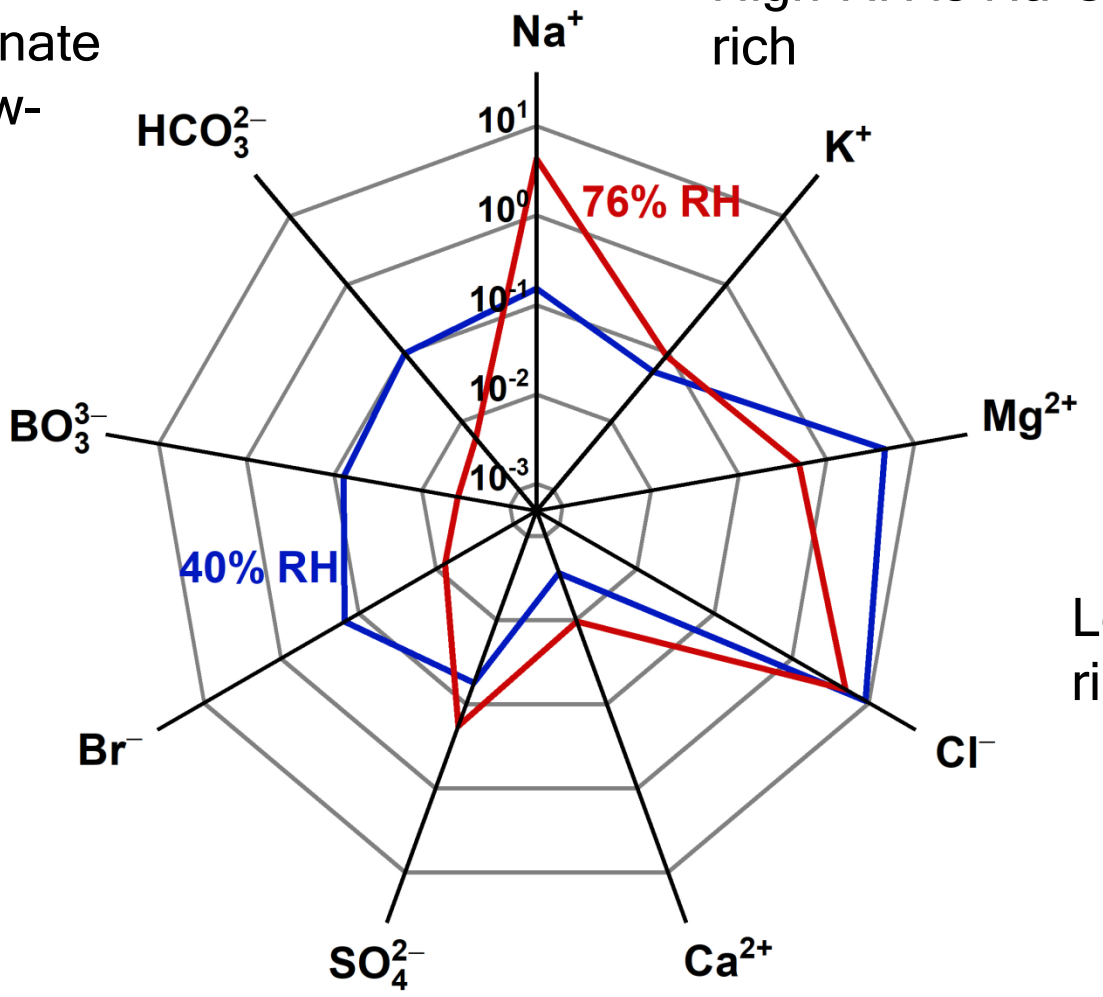
Ellipsoidal, faceted pits

[1]Weirich et al., J. Electrochem. Soc. 166 (2019).
[2]Srinivasan et al., J. Electrochem. Soc. 168 (2021).

Differences in electrolyte chemistry may be responsible for morphology differences

Higher carbonate species in low-RH brines

High-RH is Na-Cl-rich



Low-RH is Mg-Cl-rich

Full immersion exposures performed at 35 °C in simulated sea salt brines

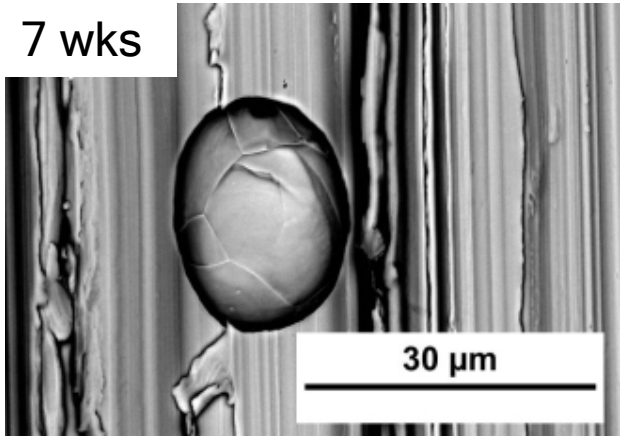
Solution	$[Cl^-]$/M	$[HCO_3^-]$/M
40% RH equivalent sea salt brine	9.003	9.79×10^{-2}
0.566 M $MgCl_2$	1.132	1.37×10^{-5}
2.61 M $MgCl_2$	5.22	1.60×10^{-5}
4.47 M $MgCl_2$	8.94	3.08×10^{-5}
76% RH equivalent sea salt brine	5.009	5.73×10^{-3}

Note: These are model-calculated values of ionic concentrations. Actual measured values may be lower due to repeated filtering of precipitates prior to use in testing.

[$MgCl_2$] influences pit morphology

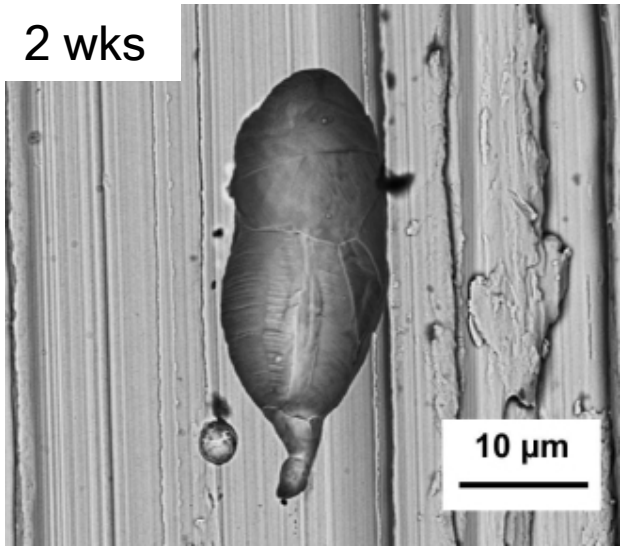
0.566 M $MgCl_2$

7 wks



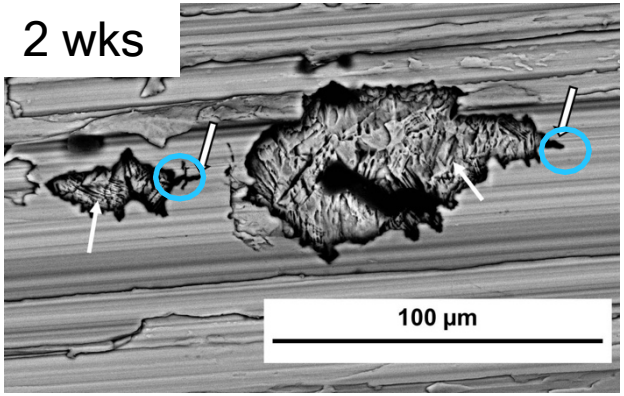
2.61 M $MgCl_2$

2 wks



4.47 M $MgCl_2$ (satd.)

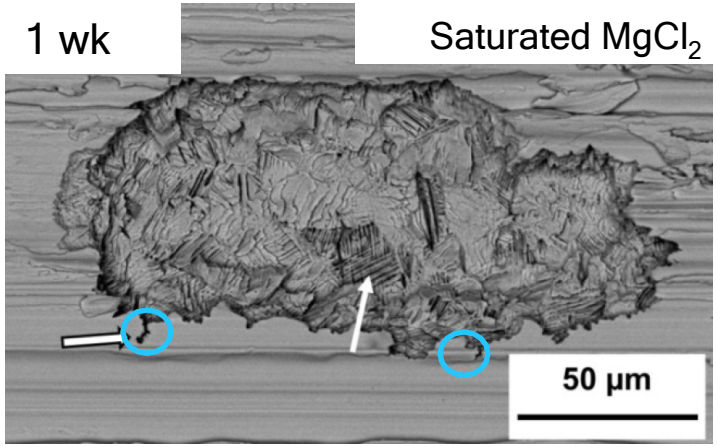
2 wks

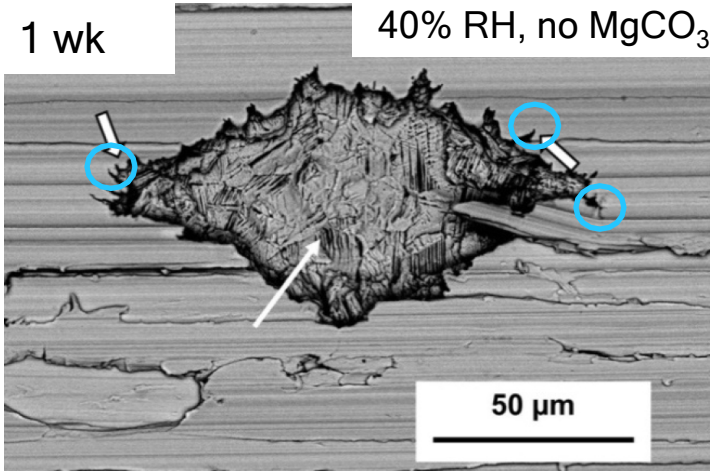


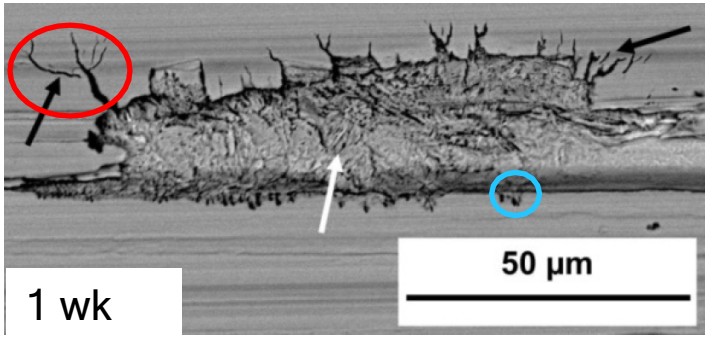
Concentrations < saturation show ellipsoidal, faceted pits

Saturated $MgCl_2$ shows cross-hatching, fissures

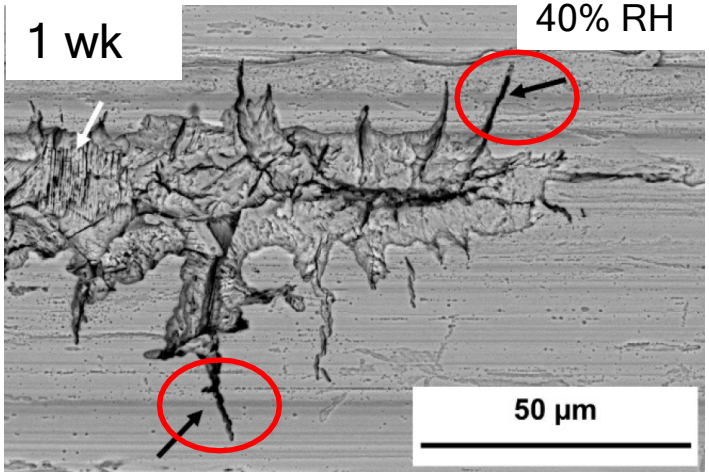
High level of dissolved carbonates may be necessary for microcracks







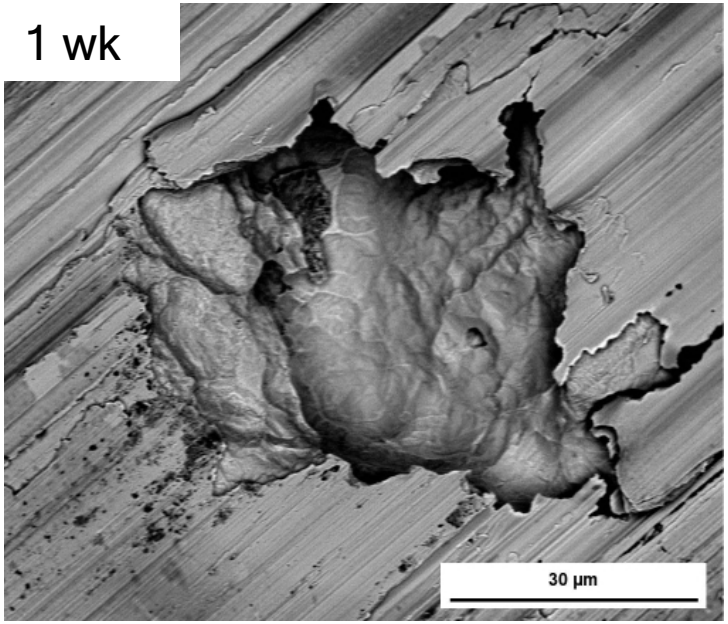
Saturated $MgCl_2$ + $MgCO_3$



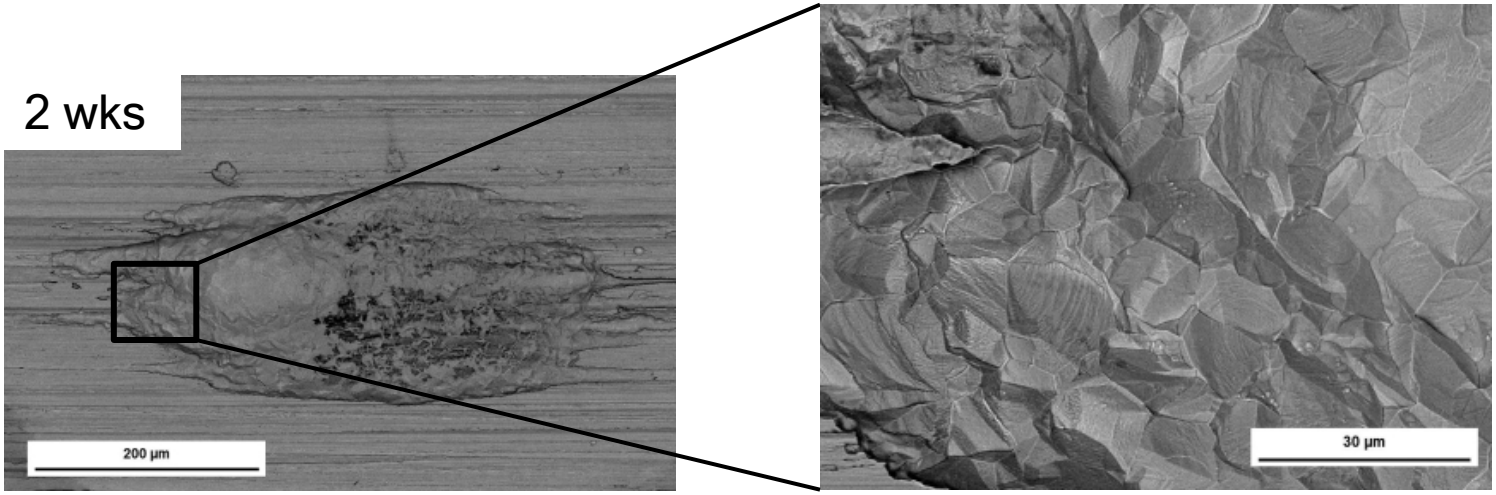
Microcracking may be linked to high levels of dissolved carbonates
Insufficient dissolved carbonate → no prominent microcracking

Dissolved carbonate alone does not produce microcracks, sat. $MgCl_2$ also necessary

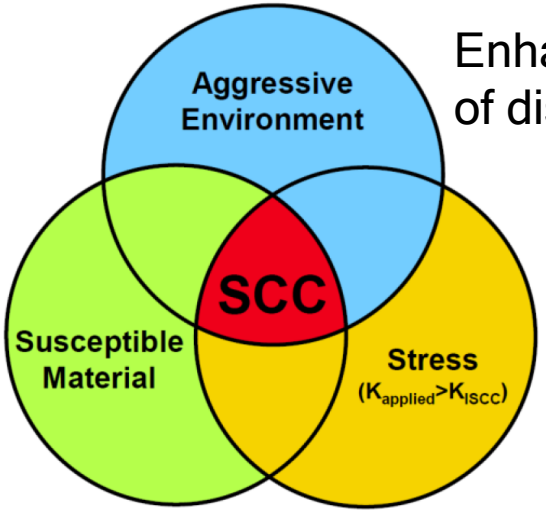
2.61 M $MgCl_2$ + $MgCO_3$



Cross-hatching resulting from sat. $MgCl_2$ may be synergistic with microcracking



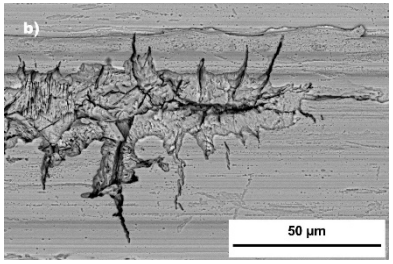
Can micro-cracking occur via HEAC at low RH?



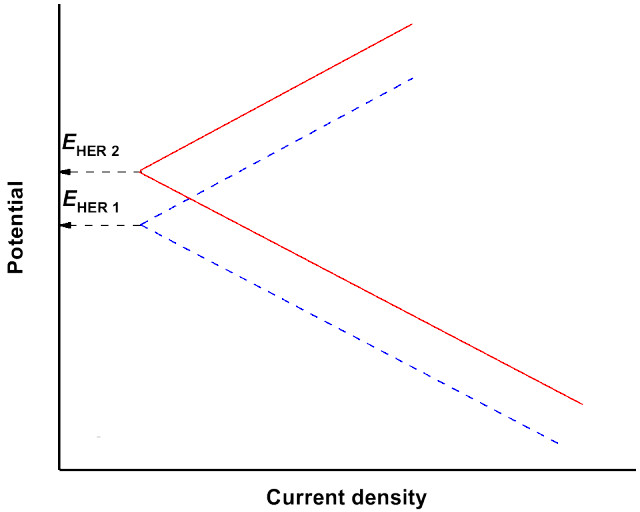
Enhanced HER due to action of dissolved carbonate

Strain-induced martensite from surface grinding

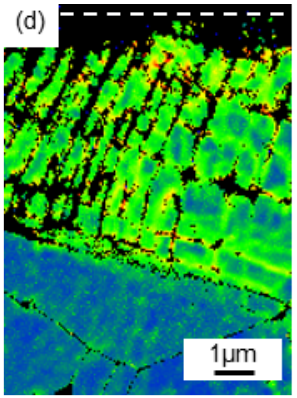
Residual stress, cross-hatching may act as stress concentrator



Stress concentration from cross-hatching



Accelerated HER from high carbonate level

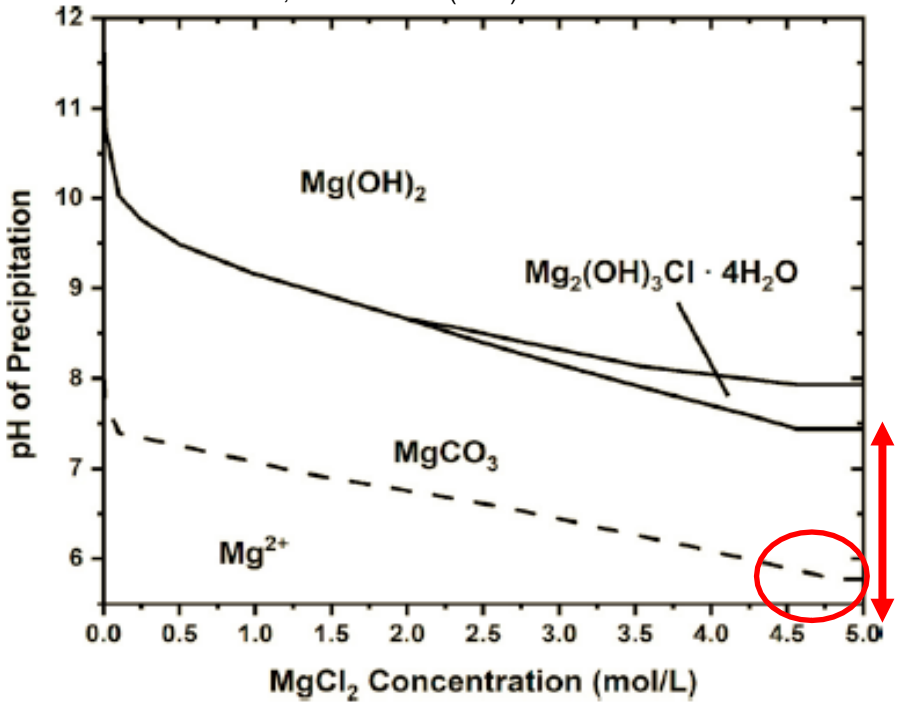


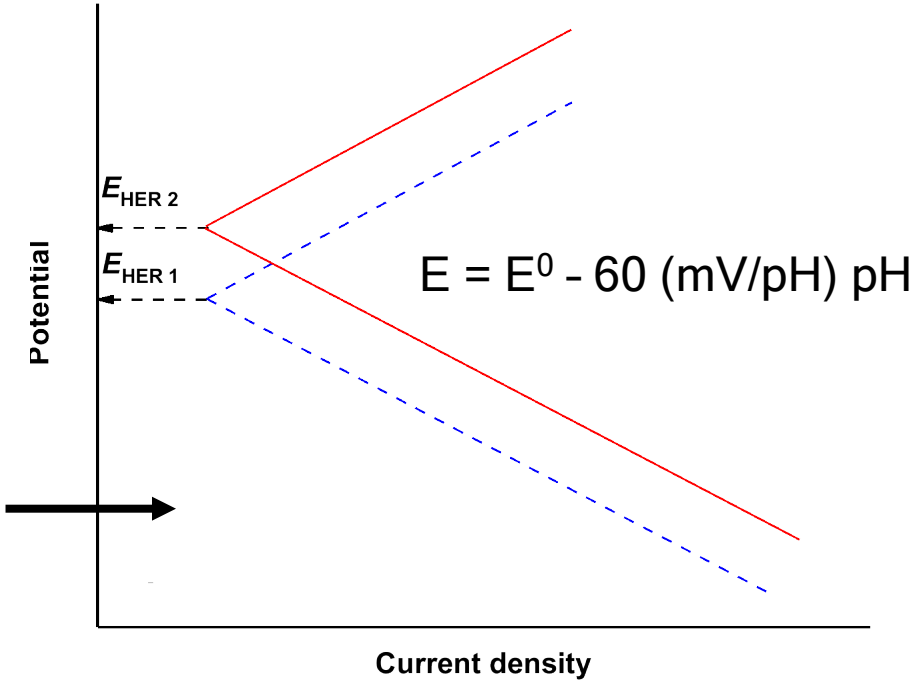
Weirich et al. JECS (2019).

Sufficient residual stress, SI martensite

HER kinetics may be accelerated by precipitate buffering action of magnesium-hydroxide-carbonate phases

[1]Katona et al., Corr. Sci. 177 (2020).





Dissolved carbonate species to precipitate at cathodic sites buffering to lower pH

Lower pH raises HER Nernst potential, enhances kinetics

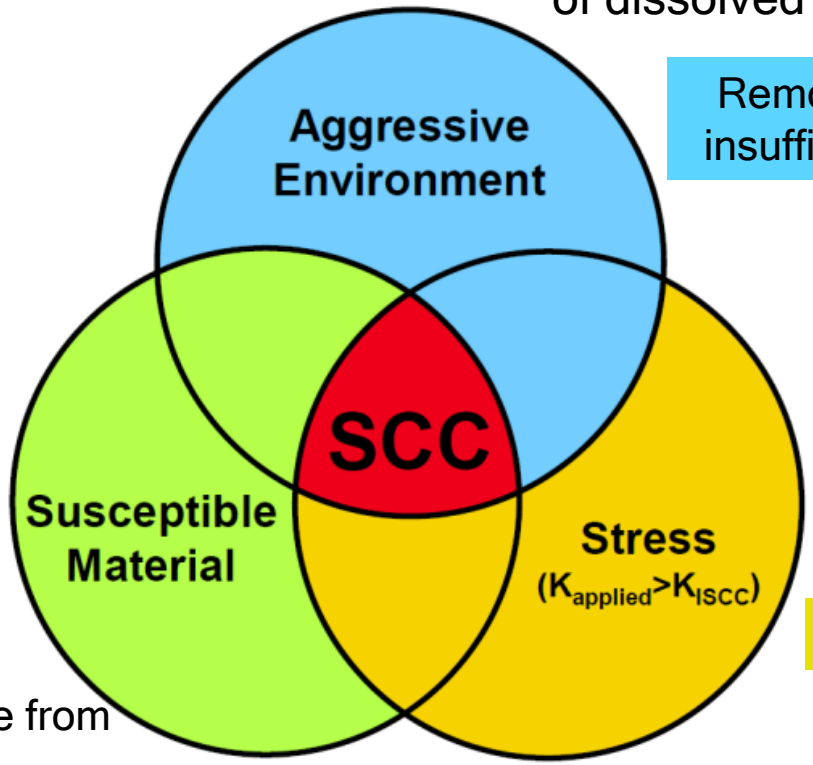
Exact species precipitating/buffering is kinetics-dependent – $MgCO_3$ precipitation kinetically hindered[2,3]

[2]Katona et al., Echem. Comm. 118 (2020).
[3]Swanson et al., PCCP 16(42) (2014).

Systematic evaluation of factors

Enhanced HER due to action of dissolved inorganic carbon

Removed by [$MgCl_2$] < satn. + insufficient dissolved carbonate



Residual stress, cross-hatching may act as stress concentrator

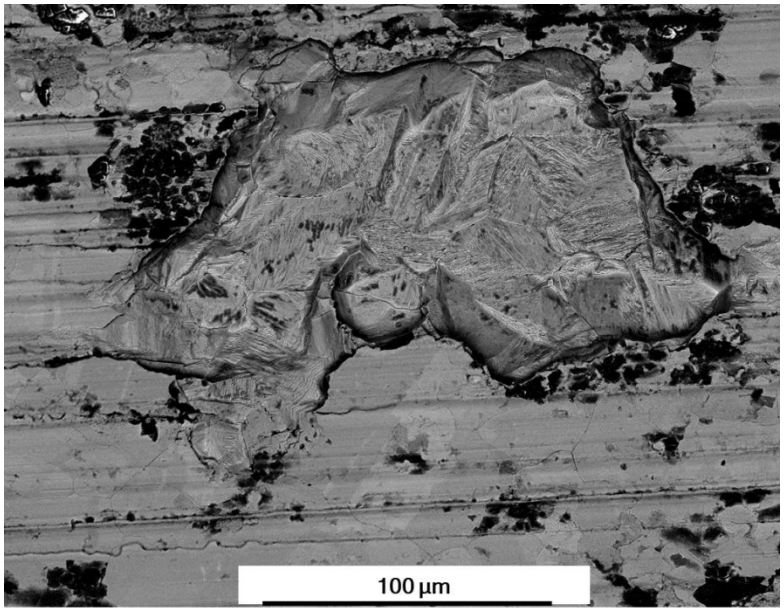
Removed by Annealing

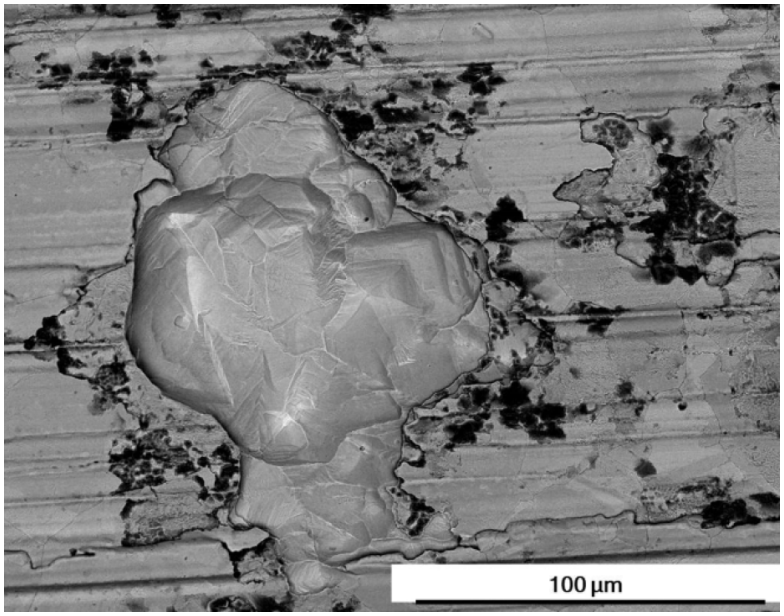
Removed by Annealing

Strain-induced martensite from surface grinding

Microcracking not seen in annealed samples

Samples solutionized at 1050 °C for 1 h and then exposed to 40% RH for 1 week at 35 °C

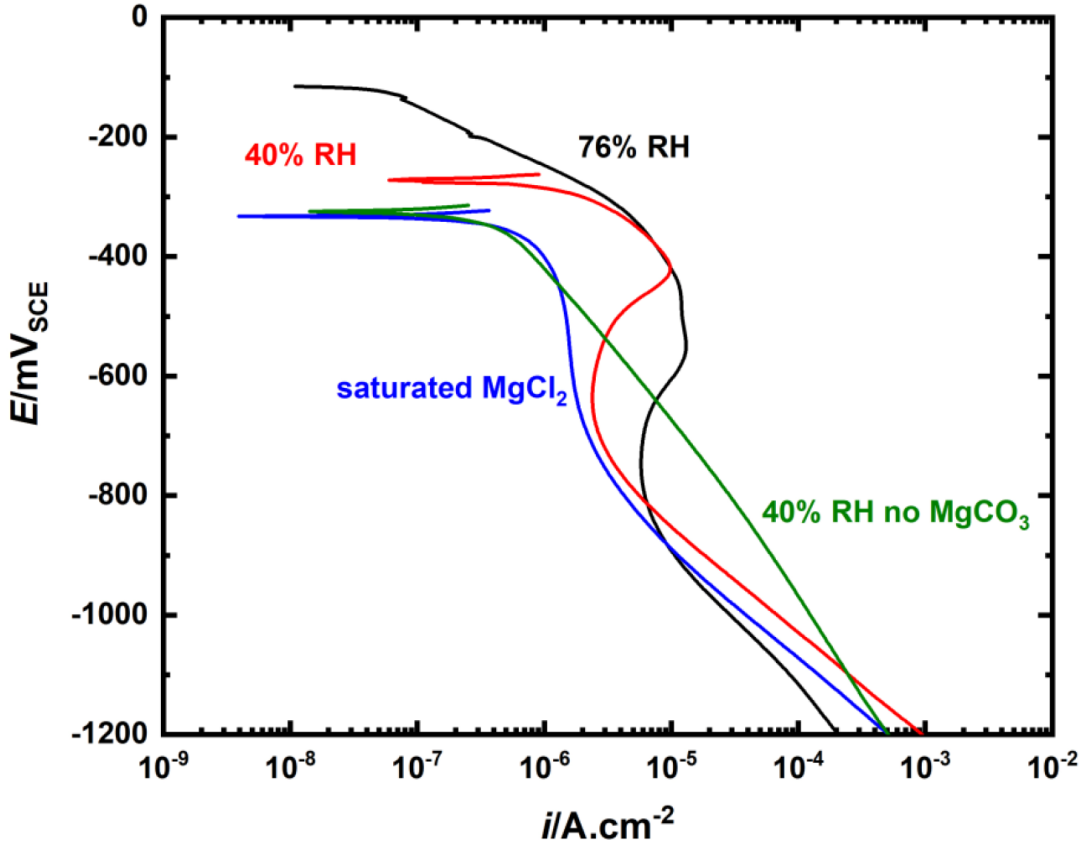




Few pits seen, occasionally in clusters, typically ellipsoidal and faceted

NO microcracks observed

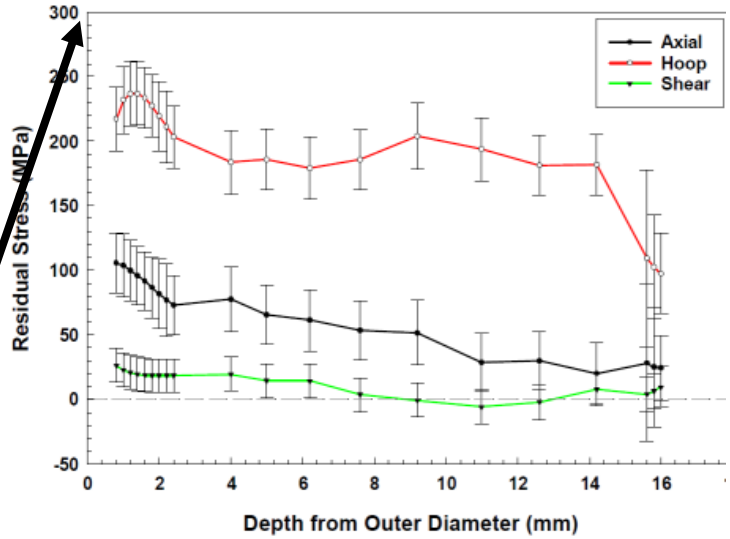
Cathodic kinetics may suggest precipitation in carbonate-rich brines

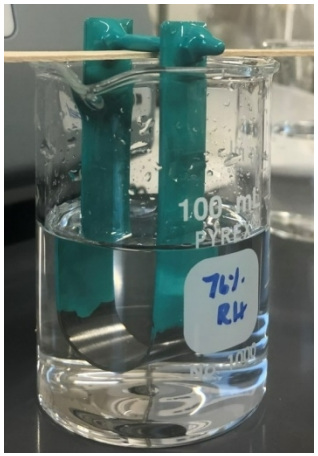


HER effects on morphology may be slow-acting, long-term - not likely captured by short scan duration

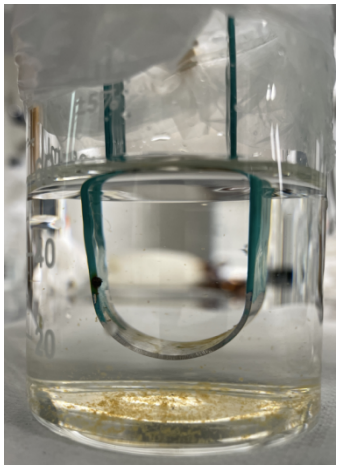
U-bend tests ongoing - can large-scale cracking result from immersion in seawater brines?

304SS at 35 °C
Strain on outer bend = 4% (ASTM G-30)
Stress on outer bend ≈ 300 MPa

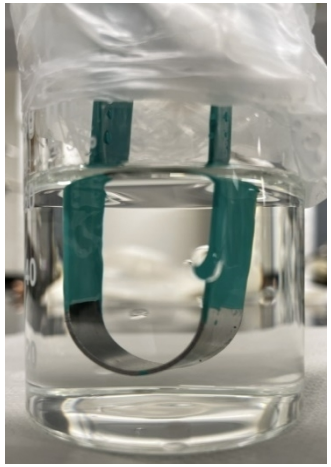




Enos and Bryan, SNL Report, 2016.



76% RH after 5 days



40% RH after 5 days

Key takeaway points

- Microcracking observed in low-RH brines correlates with subsurface SI martensite + residual stress + cross-hatching + dissolved carbonates
- HER may be enhanced at cathodic sites as Mg-species ppt buffer near-surface pH to lower values
  - Cathodic kinetics in carbonate-rich $MgCl_2$ solutions suggest precipitation effects
- Annealing removes microcracking tendency
  - Removal of SI martensite, residual stress results in no microcracking

Next steps

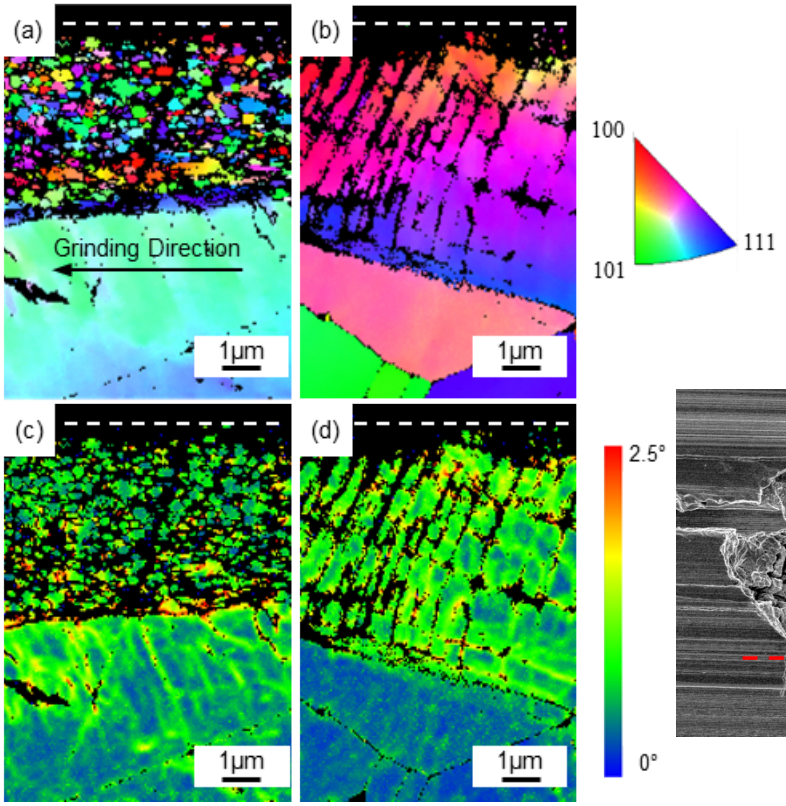
- Cathodic kinetics after longer-term exposure to evaluate if HER acceleration is time-dependent
- Continuing U-bend immersion tests

Acknowledgments

- This work is supported at the Ohio State University by Sandia National Laboratories (SNL). SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.
- The support of the Momental Foundation through the Mistletoe Research Fellowship 2020-2021 in purchasing equipment used in the study is acknowledged.
- Thanks to Andrew Knight, SNL, for assistance in calculation of ionic concentration using the EQ 3/6 software and the Pitzer parametrization.
- Thanks to Rashed Alazemi, graduate student, Fontana Corrosion Center, OSU for assistance with monitoring U-bend immersion experiments.

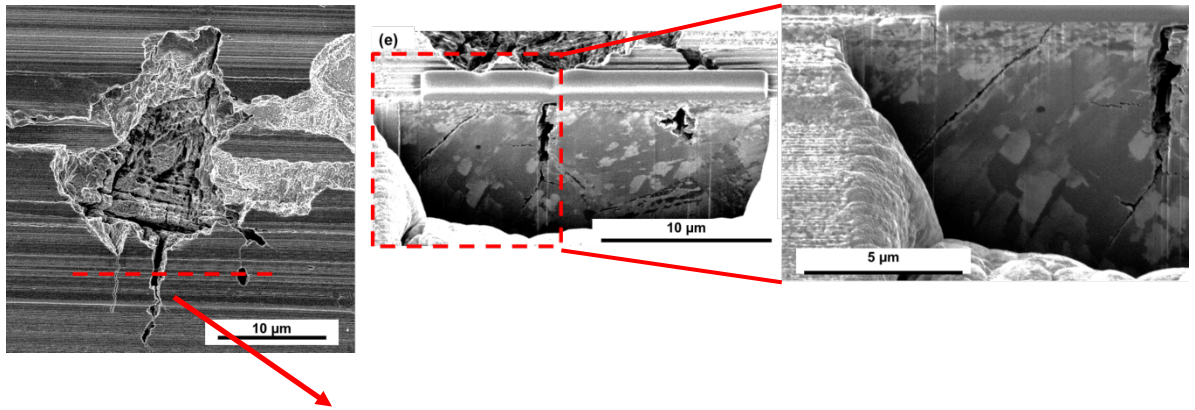
SUPPLEMENTAL

Deformation substructure may contribute to susceptible morphology



Deformation from grinding may create susceptible microstructure

FIB-SEM of small pits show long cracks

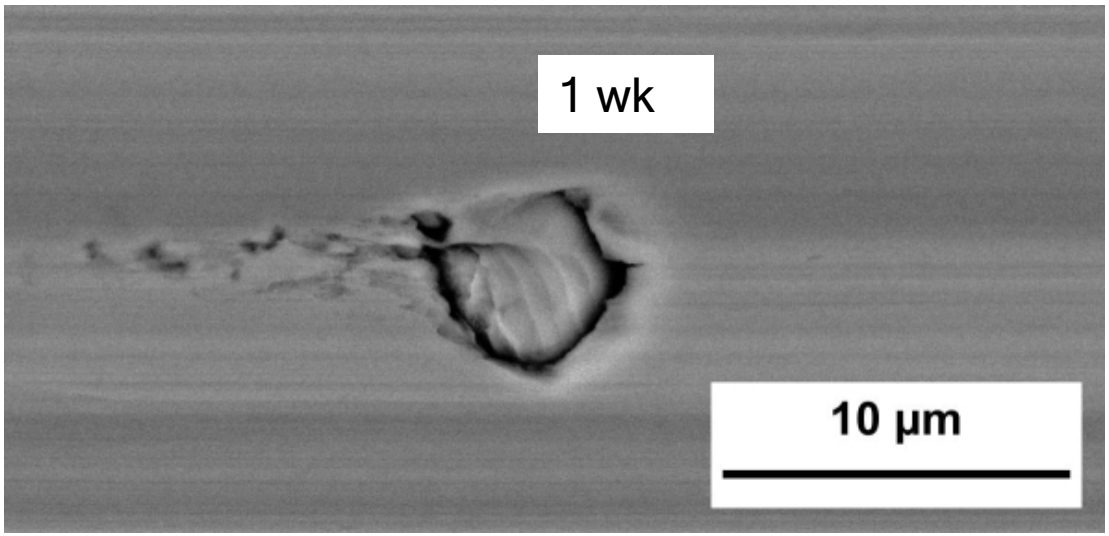


SCC initiator?

Weirich et al. JECS (2019).

Dissolved inorganic carbon by itself does not produce microcracks, likely synergistic with cross-hatching

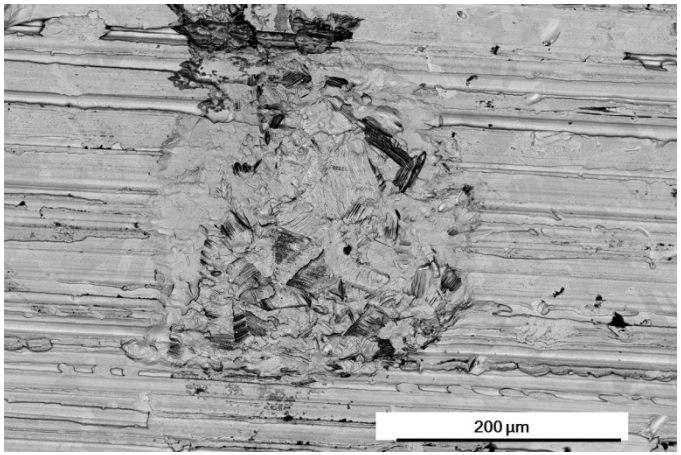
Saturated NaCl + $MgCO_3$

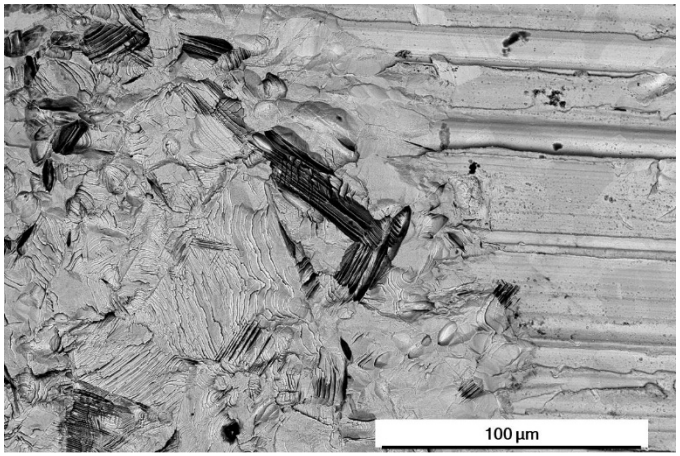


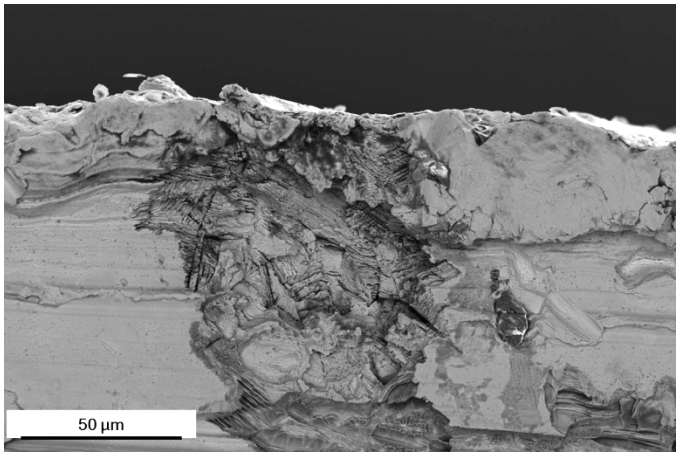
40% RH sea salt brine without $MgCO_3$ addition	3.39	9.003	2.82×10^{-5}

5.22 M NaCl	5.187	5.22	5.09×10^{-6}
5.22 M NaCl + added $MgCO_3$	8.61	5.22	7.29×10^{-3}

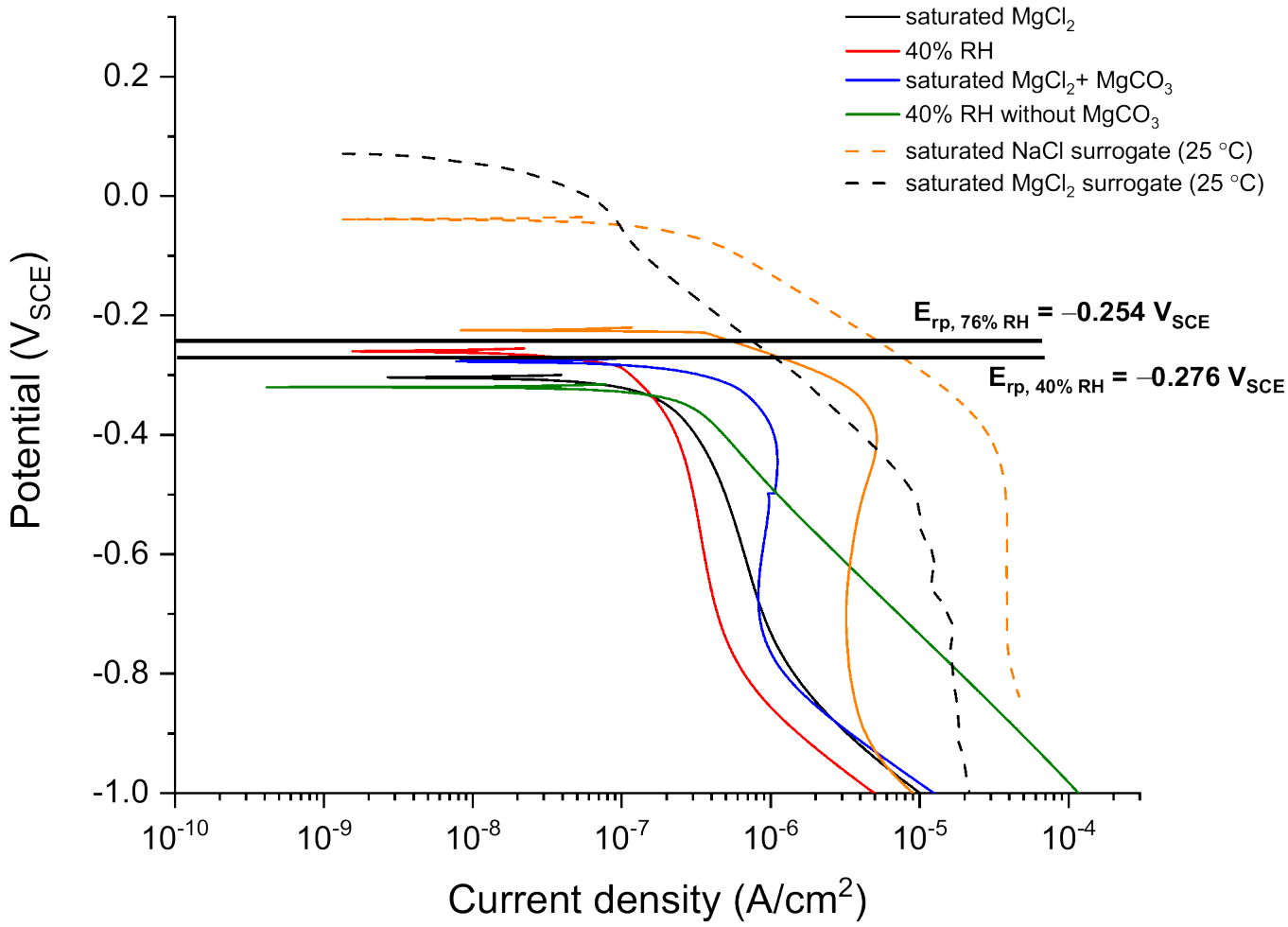
4.47 M $MgCl_2$ + added $MgCO_3$	7.07	8.94	4.55×10^{-2}


200 µm


100 µm


50 µm

Solutions containing sat. $MgCl_2$ have an OCP very close to E_{rp} at 40% RH, cathodic kinetics trend not conclusive of HER acceleration



Cathodic current availability determines polarization levels, morphology