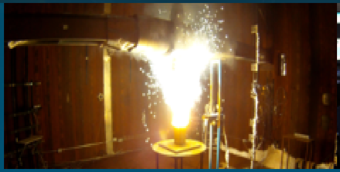
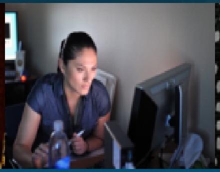
THE OHIO STATE UNIVERSITY

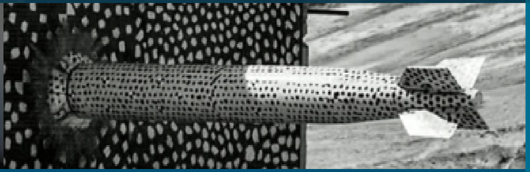
Sandia National Laboratories

SAND2020-11739C

Pit-to-Crack Transition in Stress Corrosion Cracking of Type 304 Stainless Steels Under Marine Exposure Conditions







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Practical Background of Investigating SCC of Stainless Steels

Austenitic stainless steels (SS) are susceptible to localized pitting in marine environments

SS is currently being used for spent nuclear fuel dry cask storage

- Containers intended for interim storage beginning relicensing period

Canisters in overpacks may develop a Cl- rich brine on the surface

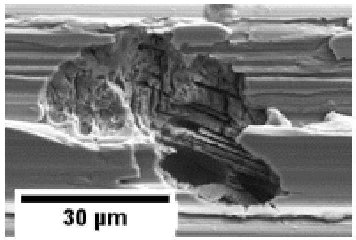
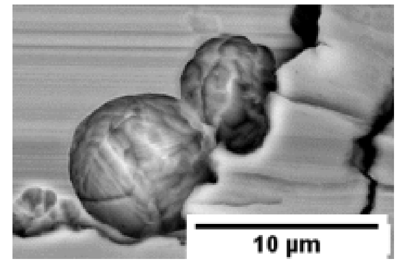
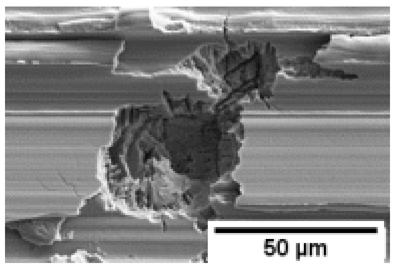
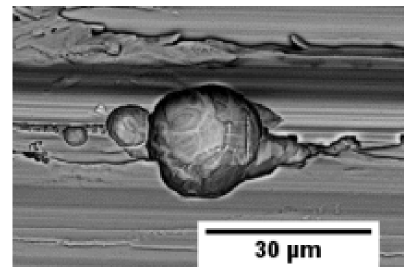
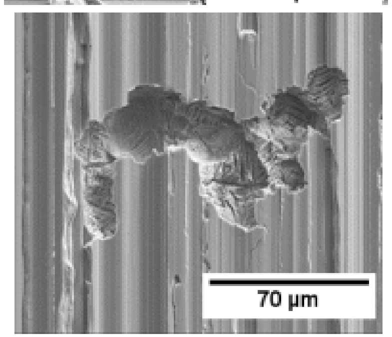
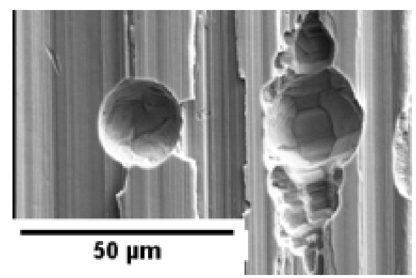
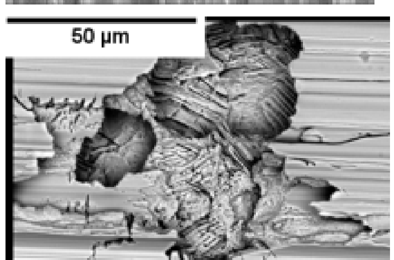
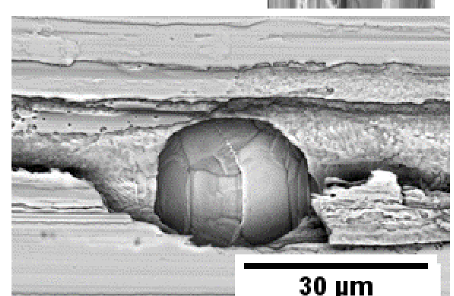
- Develops from accumulated dust that deliquesces on surface
- Sea salt responsible for chloride presence

Brines form in droplets on the surface when the RH and T on the surface exceeds the deliquescence RH of a particular salt

Knight, Andrew et al. Corrosion-Resistant Coatings for Mitigation and Repair of Spent Nuclear Fuel Dry Storage Canisters. 2020. Web. doi:10.2172/1646742.

Previous Work: Strong Correlation between Relative Humidity and Morphology under Droplets

Sea Salt Particles Deposited on Stainless Steel

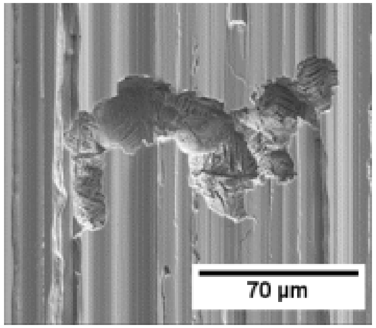
	40% RH		76% RH
		1 week	
		4 weeks	
		52 weeks	
		78 weeks	

Crosshatching, Microcracking

Ellipsoidal Shape

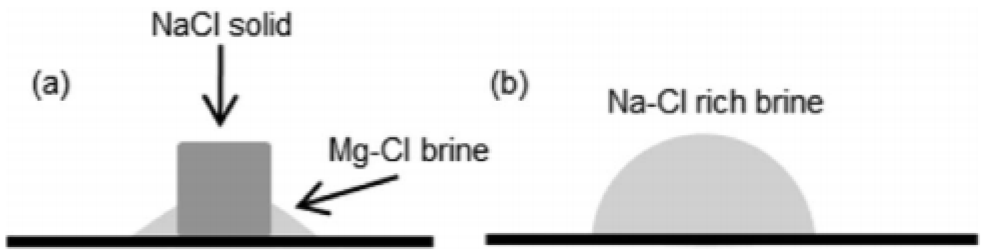
Weirich et al. JECS (2019).

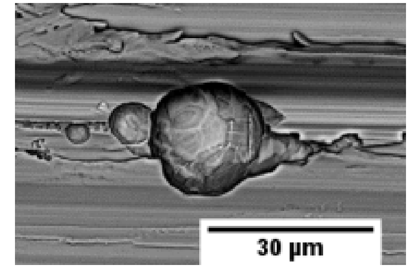
Significant Compositional Variations Between Brines at Different Relative Humidities



40% RH

76% RH





40% RH

Salt	Moles / kg Water
Cl^-	10.18
Mg^{2+}	5.187
Br^-	0.166
BO_3^{3-}	0.0915
HCO_3^-	0.166
Na^+	0.179
SO_4^{2-}	0.0815
K^+	0.00466
Ca^{2+}	0.00259

4.47 M $MgCl_2$

76% RH

Salt	Moles / kg Water
Cl^-	5.72
Mg^{2+}	0.576
Br^-	0.00800
BO_3^{3-}	0.00441
HCO_3^-	0.00683
Na^+	4.88
SO_4^{2-}	0.206
K^+	0.105
Ca^{2+}	0.0129

0.566 M $MgCl_2$

5.22 M NaCl

Weirich et al. JECS (2019).

Experimental Purpose: Determining Conditions for SCC

Goal: determine why the difference in pit shape, pit morphology, and presence of microcracking occurs in marine atmospheric environments. These factors will contribute to the initiation of SCC.

Hypothesis:

- **Species at lower relative humidities will exhibit more irregular pits, crosshatching, and increased microcracking due to the presence of Mg^{2+} ions.**

Testing Conditions Across Entire Set

Full Immersion

cathodic area is maximized

35 ºC

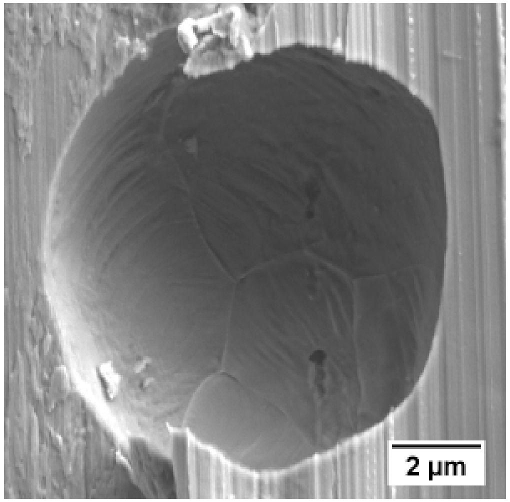
Ground Surface Finish

SS 304L

Summary of Chloride Equivalents and Indication of Pitting

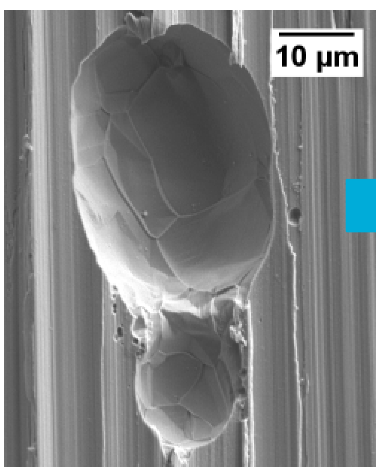
Salt Type	Salt Conc.	Equiv. RH	Equiv Salt	Time	Pitting?
Seawater	-	76%	-	2 Weeks	Yes
Seawater	-	40%	-	1 Week	Yes
Seawater	-	40%	-	2 Weeks	Yes
Seawater	-	40%	-	4 Weeks	Yes
NaCl	5.22 M	76%	NaCl	1 Week	Yes
NaCl	5.22 M	76%	NaCl	2 Weeks	Yes
NaCl	5.22 M	76%	NaCl	7 Weeks	Yes
$MgCl_2$	0.566 M	76%	$MgCl_2$	1 Week	No
$MgCl_2$	0.566 M	76%	$MgCl_2$	2 Weeks	No
$MgCl_2$	0.566 M	76%	$MgCl_2$	4 Weeks	No
$MgCl_2$	0.566 M	76%	$MgCl_2$	7 Weeks	Yes
$MgCl_2$	2.61 M	76%	NaCl	1 Week	No
$MgCl_2$	2.61 M	76%	NaCl	2 Weeks	Yes
$MgCl_2$	2.61 M	76%	NaCl	7 Weeks	Yes
$MgCl_2$	4.47 M	40%	$MgCl_2$	2 Weeks	Yes

NaCl Dominant Tests all Exhibit Similar Morphologies

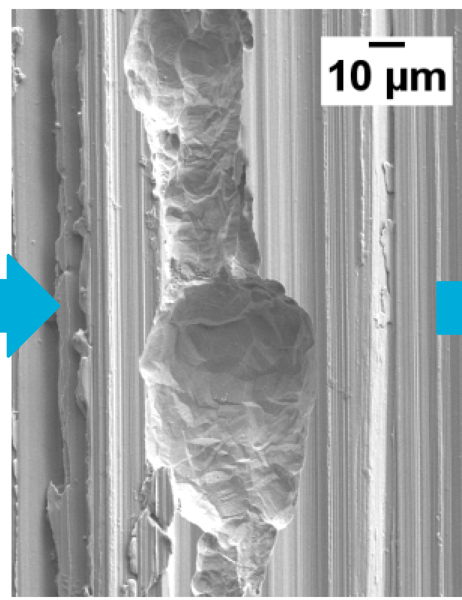


76% RH, 2 Weeks

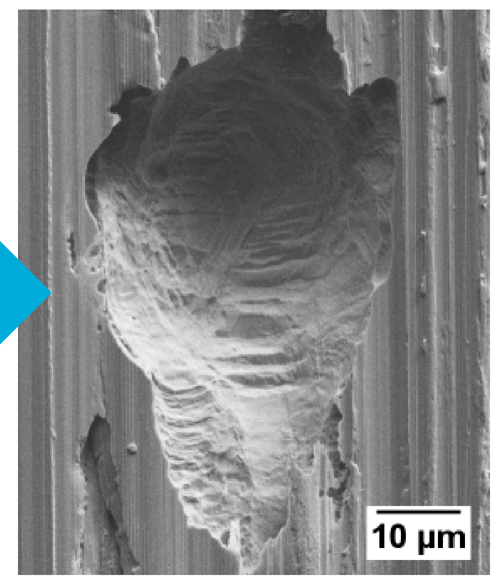
All pits appear ellipsoidal, becoming larger as test duration increases



5.22 M NaCl, 1 Week



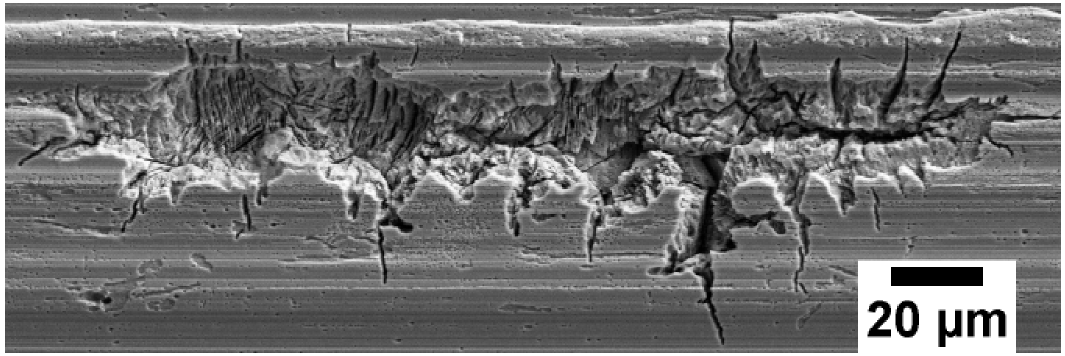
5.22 M NaCl, 2 Weeks



5.22 M NaCl, 7 Weeks

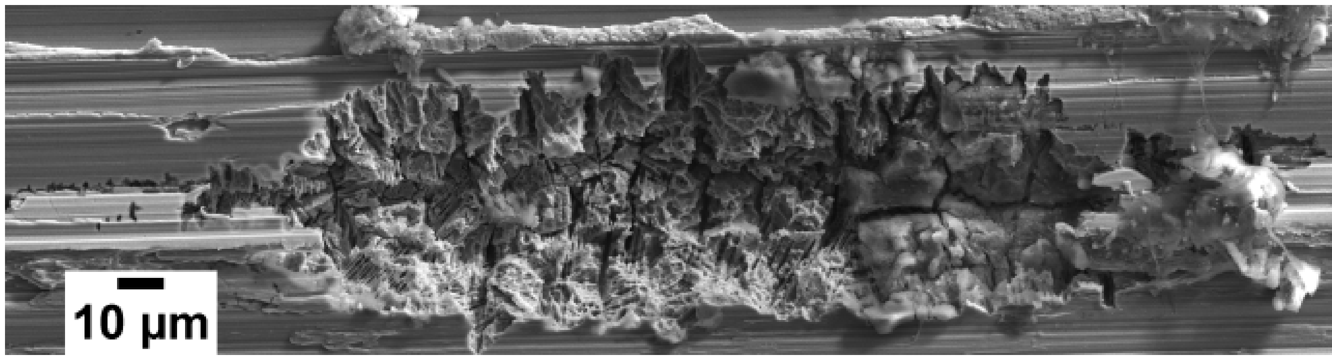
40% RH Tests all Exhibit Microcracking, Cross-hatching

40% RH, 1 week

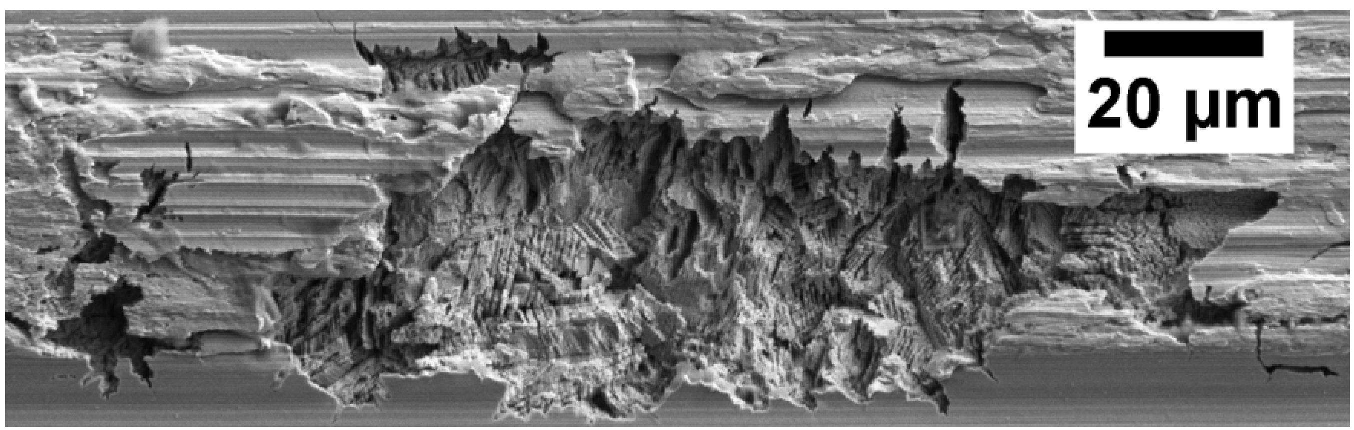


Cross-hatch morphology present, elongated pits

40% RH, 2 weeks

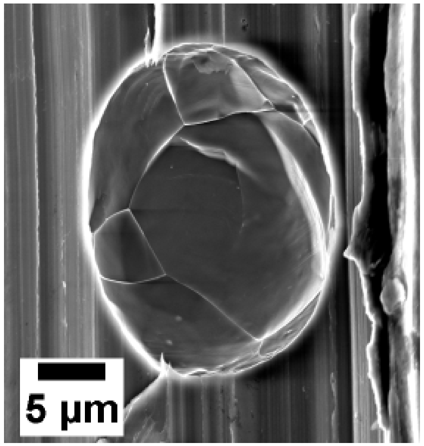


40% RH , 4 weeks

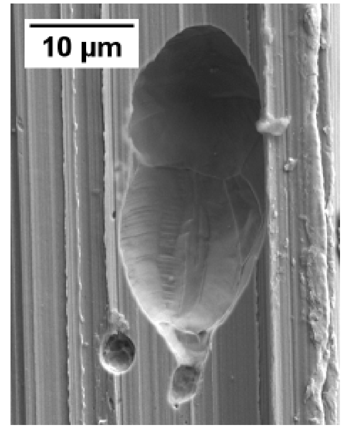


As exposure time increases, microcracks widen

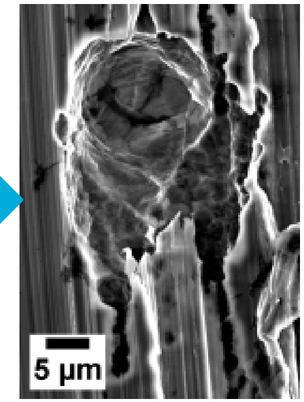
Other $MgCl_2$ Dominant Tests Show No Microcracking and Less Aggressive Pitting



0.566 M $MgCl_2$, 7 weeks

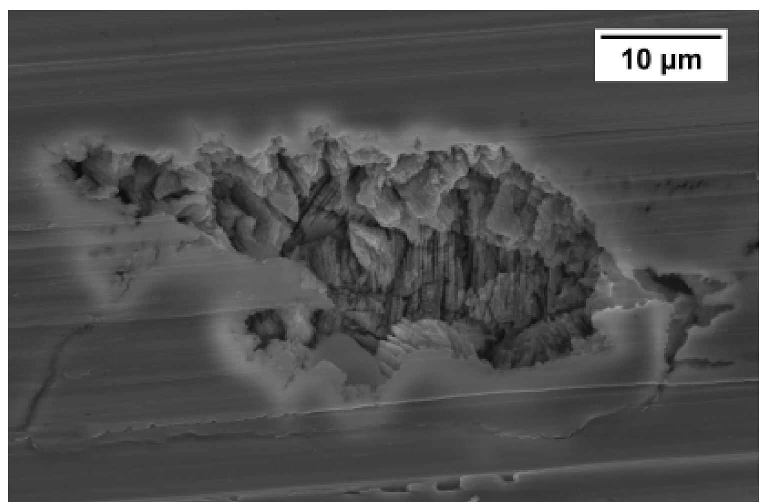


2.61 M $MgCl_2$, 2 weeks



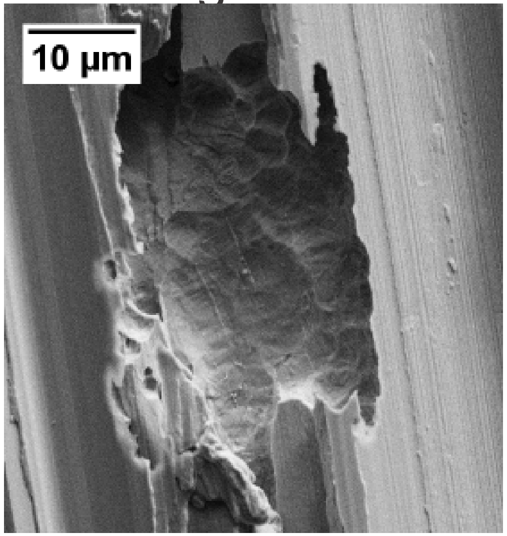
2.61 M $MgCl_2$, 7 weeks

At the equivalent $MgCl_2$ concentration at 40% RH, cross-hatching visible, but no microcracking

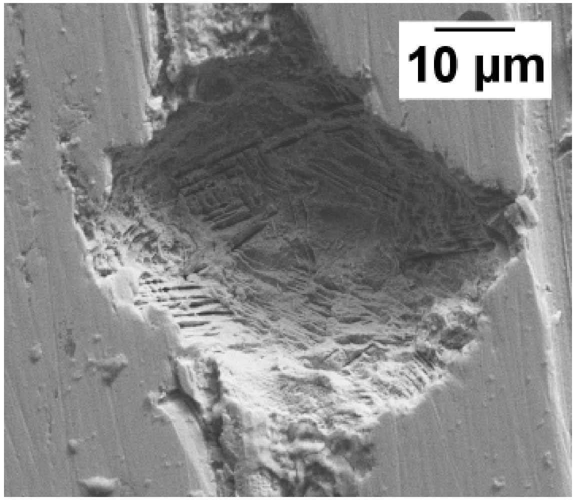


4.47 M $MgCl_2$, 2 weeks

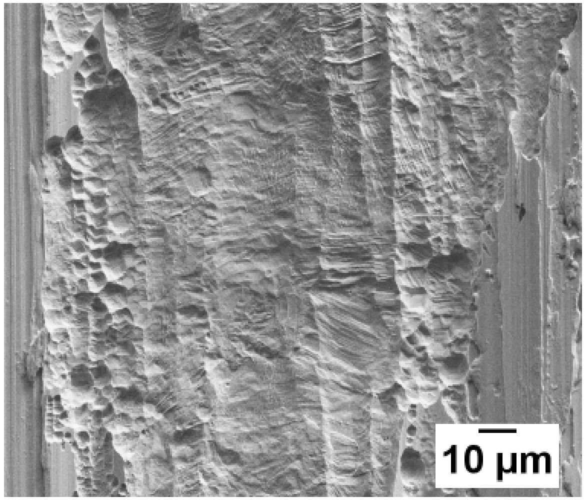
Replicable Results with SS 304H, More Aggressive Pitting



0.566 M $MgCl_2$, 7 weeks



2.61 M $MgCl_2$, 7 weeks



5.22 M NaCl, 7 Weeks

At each respective chloride concentration, morphology mirrors 304L tests but exhibits more aggressive pitting

Conclusions: $MgCl_2$ has an Influence on Pit Morphology, Not on Microcracking

Current research indicates that brine chemistry is the primary factor behind differences in morphology

- This may explain part of why SS experiences SCC more quickly under certain conditions
- Determines under what conditions future SCC work will take place to observe more severe potential scenarios

- Immersion tests under similar conditions and with similar chemistries exhibit similar pit morphologies
- Mg^{2+} influences pit morphology in short-term testing but does not cause severe microcracking seen in 40% RH
- Microcracking promoted by some chemical species or chemical concentration present in 40% RH artificial seawater
  - pH changes may also increase microcracking susceptibility
- In 40% RH solutions, pitting seems to grow at a faster rate than microcracking, possibly due to a lack of residual stress in the sample

Future Work

What is the role of residual stresses on pit morphology, specifically cross-hatching?

How do pH and other minor species present in the brine affect the presence of microcracking?

How does droplet size affect pit morphology?

How do differences geometries or morphologies of the pit affect crack initiation?

How will applying stress affect the continued initiation of microcracking?