

ORIGINS OF PERSISTENT INTERACTIONS AMONG LOCALIZED CORROSION SITES

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It is often believed that pitting events are stochastic without any spatial or temporal effect on each other. However, as pits begin to form, the local environment changes [1]. Solution concentration and potential gradients develop that can affect pitting susceptibility on adjacent surfaces. These factors can also affect nearby oxide film and non-metallic inclusions to produce more permanent interactions. Taking into account these local changes, pitting can have a significant influence on the susceptibility of adjacent surfaces to localized corrosion. However, the time constant associated with each of these interactive processes differs [2-4]. Moreover, the origin or cause of persistent pit interactions is unknown. The goal of this study is to identify the source of persistent interactions.

Evidence of spatial interactions has been seen visually in the form of satellite pits that tend to form patterns around larger primary pits. Visual evidence of these pits can be seen on AISI 316 stainless steel that was anodically polarized in dilute chloride solution. As seen in Figure 1, a large pit has developed and formed circular zones indicating different degrees of pitting susceptibility on the nearby electrode surface. A region of suppressed pitting corrosion is observed in a concentric ring around a central large pit. Surrounding the suppressed region, a concentric ring of enhanced pitting corrosion is seen. These visual patterns indicate that interactions are occurring, but further investigations are required to determine their sources.

The visual patterns that are formed from pitting event interactions can be examined using spatial point pattern analysis techniques [5]. Spatial point pattern analysis methods analyze patterns of points on a surface and determines if they are random, aggregated, or regular. Figure 2 shows the output of spatial point pattern analysis indicating the regions of regular, random, and aggregated populations. Shown is a 316 SS electrode pitted in 0.05M NaCl and the L_2 curve indicates that interactions are taking place. Inclusions can be analyzed to determine if they are randomly located on the electrode surface. If they are not randomly located what processing mechanism (such as drawing) can cause aggregated inclusions. Pitting events can also be analyzed by point pattern analysis to determine if pitting events are random, aggregated, or regular. If spatial point pattern analysis results indicate an aggregated population this indicates that interactions are occurring.

Interactions were also studied using AISI 316 stainless steel in the form of one hundred 250 μm wires fashioned into a multi-electrode array. The MEAs were configured in a 5x20 close packed rectangle that was used to simulate the surface of a planar electrode. The use of the MEA allowed both spatial and temporal measurements to be acquired simultaneously. In order to simulate pits on the surface, two centrally located rows were anodically polarized to initiate large primary pits that approached the size of the wire by pit coalescence. The remainder of the electrodes in the MEA were

evaluated to determine their susceptibility. The pitting potential (E_{pit}) was used as a measure of susceptibility throughout the study. Statistical analysis such as cumulative probability was used to unambiguously distinguish interactions from variability. Since MEAs also allow spatial measurements, evaluation of E_{pit} as a function of distance from the initiated rows was enabled.

Three of the hypothesized interactions were evaluated using MEAs. Ohmic potential shielding, aggressive species concentration enhancement, and persistent surface damage were all evaluated. Careful experimental design allowed the separation of these hypothesized interactions. MEAs were evaluated in a low halide concentration (0.05 M NaCl (pH 6.8) at 47°C) solution to allow significant potential and concentration gradients to develop during pit propagation. After initiating active pits on the centrally located rows the interactions were studied. By keeping the initiated rows active a potential field was created and pit susceptibility of rows close to the active row were suppressed by ohmic potential shielding. When initiated rows were deactivated (IR free) and the remainder of the electrodes were evaluated for susceptibility it was found that susceptibility was enhanced adjacent to active electrodes associated with aggressive species accumulation due to the acid pitting mechanism associated with primary pits [1]. During the acid pitting mechanism, high concentrations of H^+ and Cl^- ions accumulate and increase the pitting susceptibility of adjacent electrodes. High concentrations of H^+ ions, which would occur adjacent to active pits, have also been shown to cause persistent surface damage. Persistent surface damage was evaluated by allowing aggressive species concentrations to form and dissipate prior to determining the susceptibility of adjacent electrodes. Even after allowing aggressive species concentrations to dissipate for five hours persistent surface damage was still present (Figure 3).

The origin of persistent surface damage was speculated to be caused by MnS inclusions damage by acidic local environments generated from active primary pits. This was studied by modifying the electrode surface prior to testing with reducing acids that were designed to damage (1M HCl) and oxidizing acids designed to remove the inclusions (20% HNO_3). When electrodes were pretreated with HCl, susceptibility increased (Figure 4). This mimics proximity to primary pits and confirms that aggressive species damages adjacent electrode surfaces. HNO_3 pretreatments showed little effect compared to non-treated MEAs (Figure 4). MEAs that were treated first with HNO_3 followed by HCl, also showed little deviation from non-treated MEAs. By removing inclusions with HNO_3 prior to damaging treatments (HCl), susceptibility is not changed drastically from non-treated MEAs. These results indicate that treatment with 1M HCl, which approximately simulates the solution that would form around active pits, causes surface damage that increases susceptibility. However, when inclusions are removed prior to exposure to reducing acids, damage effects are not observed. These results implicate MnS inclusion damage as the origin of surface damage caused by aggressive acidic environments generated around active primary pits.

As a final experiment to confirm the origins of persistent surface damage, MEAs were pretreated with HNO_3 prior to persistent interaction MEA tests. After MEAs were subjected to pretreatment in HNO_3 , active rows of pits were again initiated, deactivated,

and the concentration gradient was allowed to dissipate prior to determining the susceptibility of the surrounding electrodes. Results of MEAs pretreated with HNO_3 showed that the persistent surface damage was eliminated (Figure 5). The origin of persistent interactions was concluded to be damage to MnS inclusion caused by the aggressive species concentration developed around active pits. Removal of these inclusions prior to pitting eliminated such interactions.

References

1. J. R. Galvele, *J. Electrochem. Soc.*, **123**:464 (1976).
2. T. T. Lunt, V. Brusamarello, J. R. Scully, and J. L. Hudson, *Electrochem. Solid-State Lett.*, **3**:271 (2000).
3. T. T. Lunt, S. T. Pride, J. R. Scully, J. L. Hudson, and A. S. Mikhailov, *J. Electrochem. Soc.*, **144**:1620 (1997).
4. T. T. Lunt, J. R. Scully, V. Brusamarello, A. S. Mikhailov, and J. L. Hudson, *J. Electrochem. Soc.*, **149**:B163 (2002).
5. L. J. Young and J. H. Young, *A Population Perspective-Statistical Ecology*, Kluwer Academic Publishers, Boston, 1998.

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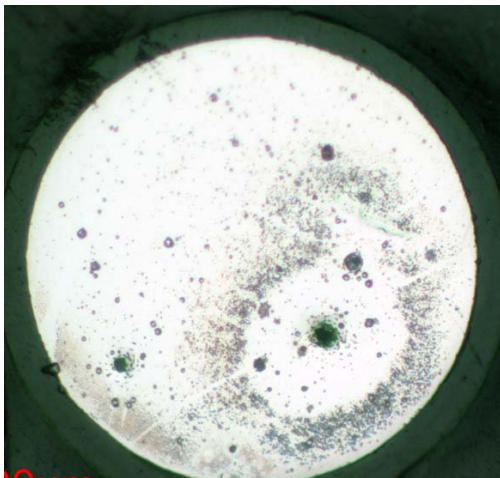


Figure 1. Visual observations of regions of enhanced and suppressed localized corrosion around large primary pits on AISI 316 stainless steel potentiodynamically scanned in 0.05 M NaCl

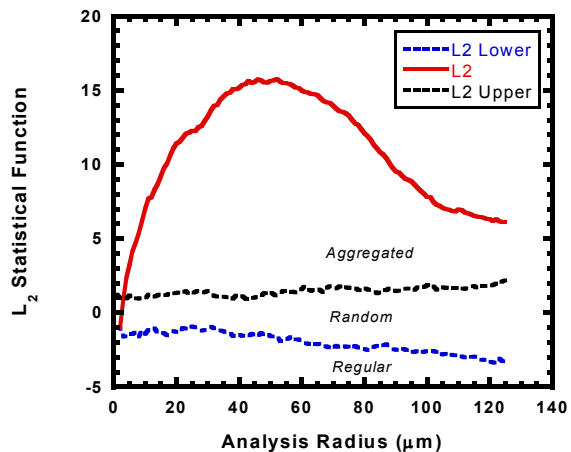


Figure 2. Point pattern analysis results for AISI 316 stainless steel potentiodynamically scanned in 0.05 M NaCl (pH 6.8) at 47°C. Figure indicates regions of regular, random, and aggregated populations.

(pH 6.8) at 47°C.

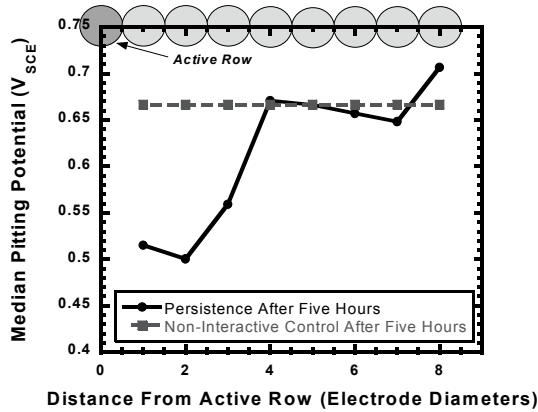


Figure 3. Median IR-free E_{pit} , as a function of MEA row, for AISI 316 SS in 0.05 M NaCl (pH 6.8) at 47°C, as affected by 5-hour exposure to dissipating aggressive species from primary pits.

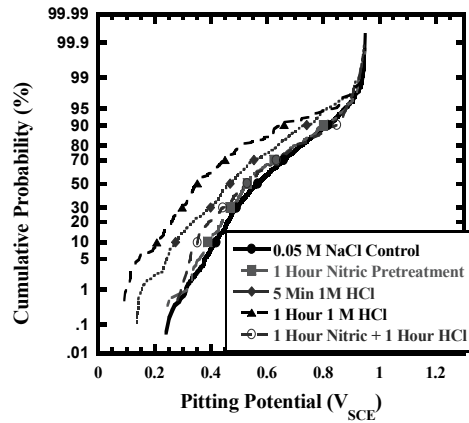


Figure 4. Cumulative probability of pit stabilization for AISI 316 SS in 0.05 M NaCl (pH 6.8) at 47°C after HCl and HNO_3 pretreatment of electrodes.

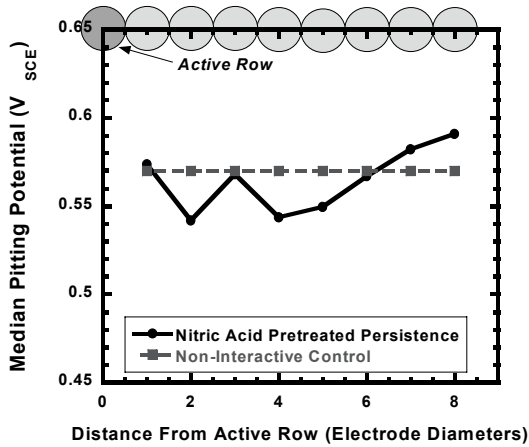


Figure 4. Median-IR free E_{pit} , as a function of MEA row, for AISI 316 SS in 0.05 M NaCl (pH 6.8) at 47°C pretreated with nitric acid prior to aggressive species induced surface damage from primary pits.