Modeling of the Effect of Crystallographic Orientation on
Pit Growth and Shape

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Multiple studies have shown that corrosion pit initiation and growth behavior in metals depends upon the crystallographic orientation of the exposed surfaces at the corrosion front. Changes in pit density and polarization behavior with respect to orientation have been observed in various metals, including: pure aluminum and aluminum alloys [1], beryllium [2] and stainless steels [3]. Packing characteristics of crystal atomic planes, microscale defect density and reaction rate variation have been described as some of the possible reasons for this behavior. While many microstructural features can affect pit initiation and growth kinetics, it is apparent from the diversity in experimental data on pure metals, for example in aluminum and beryllium, that crystallographic orientation is one of the most dominant features. Both the extent of growth and the ensuing shape can lead to pit geometries that give rise to regions of stress concentration in loaded structures; therefore, an investigation into how pits may evolve due to this effect can improve the understanding toward causes of mechanical failure.

The objective of the current modeling effort is to quantify the effect of crystallographic orientation on stable growth and resulting tortuosity in shapes by performing a parametric study in terms of microstructural and polarization behavior variations, respectively. The modeling is unique in the sense that the actual microstructure of the material is incorporated into the simulations. The model material is chosen to be 316 stainless steel. For simplicity, 2D geometry and maximum corrosion conditions are assumed, the later of which implies the absence of convective and diffusive modes of transport in the pit due to rapid mixing of the electrolyte. This assumption represents an upper bound on the corrosion rate for a given set of boundary conditions and leads to the reduction of the balance of species relation to the familiar Laplace equation for the electric potential in the electrolyte.

The high-resolution microstructure is obtained through orientation image microscopy (OIM) and image-processing techniques in the form of voxel datasets with assigned grain and orientation identifiers for each voxel. This dataset is imported in the finite element models through an interpolation scheme based on very fine grid resolution. An initial idealized pit form is assumed and the corrosion front movement is simulated with the help of the arbitrary Lagrangian-Eulerian (ALE) meshing technique provided as part of the commercial partial-differential equation solver COMSOL. The front speed, or the material dissolution rate, is approximated with a linearized Butler-Volmer relationship that relates the dissolution current density to the electrode and corrosion potentials (fixed) and electrolyte potential (evolving).

The dependence of the corrosion potential on the crystallographic orientation introduces the effect of the exposed surface orientations on pit growth. Based on reported data on aluminum with a similar FCC structure, 2.5% and 5% variations in the corrosion potential from the mean value are assumed for 316 steel, as a function of crystallographic orientation. Ten initial pit locations are randomly chosen in the microstructural sample dataset for the parametric study on the effect of microstructural variance. The results show that crystallographic orientation at the corrosion front controls pit growth kinetics and causes tortuous shapes commonly observed in experimental studies (Figure 1).
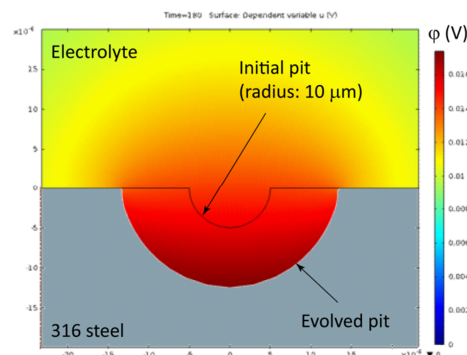
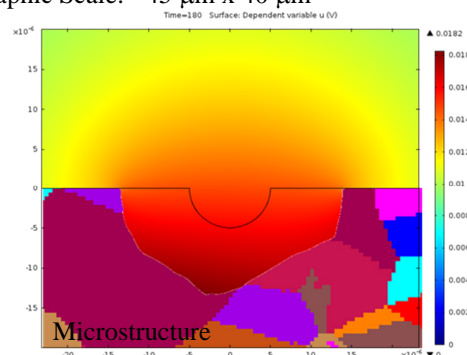
Graphic Scale: ~45 μm x 40 μm

Figure 1. Stable pit growth at a given location without microstructure (top) and with microstructure (bottom) for an assumed variation of 5% in corrosion potential with respect to cyrstallographic orientation. The colored contours in the top halves show electric potential variation in the electrolyte.

While the pit shape provides a visual confirmation of the effect of crystallographic orientation, quantifiable parameters provide a better representation when evaluating a large number of pits. Consequently, natural metrics like changes in depth, width, area and perimeter are calculated for the grown pits. Similarly, tortuosity parameters incorporated from the medical industry to describe retinal diseases are also incorporated and measured. The effect of variation in corrosion potential as a function of orientation on these metrics over all ten locations show that increasing the corrosion potential variation increases the variations in pit shape and tortuosity quantifiers. Efforts are underway to link these geometric descriptions to measures of stress concentration in load bearing components.

References:
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[3] Shahryari, A., Szpunar, J. A., and Omanovic, S., 2009, *Corrosion Science*, 51(3), pp. 677-682.