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Modeling the Effects of Crevice Former, Particulates, and the Evolving Surface Profile in Crevice Corrosion

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Crevice corrosion is an important mode of localized corrosion to be evaluated for the long-term performance of corrosion resistant alloys in high temperature, aqueous environments. This work focuses on the evolution of corrosion damage of Ni-Cr-Mo alloys in hot brines. For the initiation of crevice corrosion, a critical crevice chemistry must develop within the crevice to break down the passive film. The geometry of the crevice and particularly the height of the crevice gap is an important parameter, with tighter crevices being more aggressive. Crevice corrosion models mostly define a smooth walled crevice of uniform gap and do not account for the changing profile after crevice corrosion has initiated.

As a complement to our earlier models of the cathodic region¹, we focus here on the crevice (anodic) region and apply current and potential distribution models to examine the effects of the perturbed surface topography. The analysis focuses on three related issues: (i) the effects surface roughness of the metal and the crevice former, (ii) the effects of particulate within the crevice, and (iii) the evolution of the crevice profile in the active, anodic region.

Effects of surface roughness within the crevice

In practical systems, the crevice former and the metal substrate can have surface roughness of the order of or greater than the nominal crevice gap modeled presuming a smooth crevice. The narrow passages along the rough surface create constrictions to the current flow, as shown schematically in Fig. 1 (a). These constrictions can give rise to high localized IR drop. A goal of this work is to develop a methodology for representing a crevice with surface roughness in terms of an equivalent 'idealized' smooth crevice. We follow a procedure outlined by Lanzi and Landau for modeling porous electrodes², defining a constriction factor which can be determined from the cross sectional gap profile. A comparison of the constriction factor correction to a full 3-D numerical simulation using FEMLAB³, indicates the validity of the approach over a broad parameter range investigated.

Effects due to particulate matter filling the pit

Crevices may contain particulate matter from prior deposits on the metal surface or that form by precipitation during the corrosion process. These deposits and corrosion products would cause an increased ohmic resistance to current flow. A photomicrograph of corrosion products formed within a crevice are shown in Fig. 2 (a). Work is underway in a collaborative effort to determine the sequence and timing of the particulate formation, i.e. during active crevice propagation or during stifling and arrest. The current/potential distribution was modeled in the system depicted in Fig. 2 (b) to analyze the effects of the particulates on the propagation of the corrosion process.

Propagation of the anodic dissolution site

The surface profile of the dissolving anodic site has been modeled assuming a potential field driven current distribution. Concentration effects have not been considered in this work. Their impact will be considered

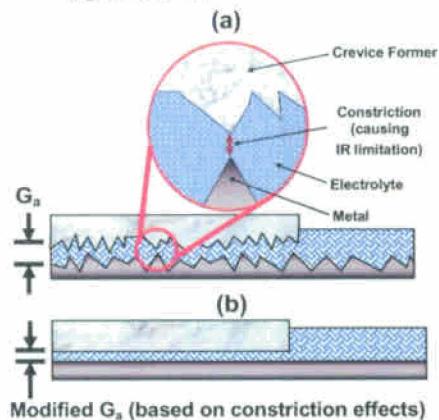
in future work. An electrochemical CAD program [Cell-Design⁴], has been used to simulate the evolving anodic region by time-stepping, updating the boundary geometry using Faraday's law. The active polarization behavior of the alloy in the critical crevice chemistry is an important input parameter. These kinetics are taken from experimental results in collaborative studies. Other model parameters include crevice gap, initiation length and distance within the crevice, potential at an external cathode, and solution conductivity. As the crevice corrosion proceeds, a tear shaped corroded region is formed due to the electric field, and the corrosion damage proceeds preferentially towards the crevice opening.

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References

1. A. S. Agarwal, U. Landau, Xi Shan and J. Payer, *ECS Trans.* 1, Oct. (2005).
2. O. Lanzi, and U. Landau, *J. Electrochem. Soc.* 137, 585-593, (1990)
3. "FEMLAB", multi-physics modeling package, COMSOL Ltd., Burlington, MA USA.
4. "Cell-Design", computer aided design software for electrochemical cells, L-Chem, Inc., Shaker-Heights, OH USA.



Modified G_a (based on constriction effects)

Fig. 1: Schematic diagram of (a) Crevice with rough surfaces of the crevice former and the metal substrate causing constrictions to current flow and (b) 'idealized' crevice model with an equivalent smooth gap

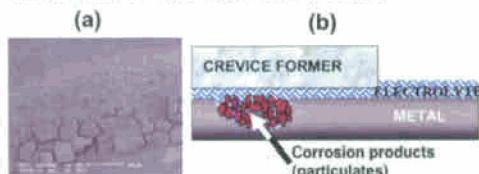


Fig. 2: (a) SEM micrograph of corrosion products observed in crevice corrosion region of Alloy 22 (b) Schematic of a modeled crevice with particulates (corrosion products) occupying the dissolved region.