

## Modeling of Crevice Corrosion Stability and Stifling of a NiCrMo Alloy and Stainless Steel

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Damage of structural significance from crevice corrosion of corrosion resistant alloys requires that at least a portion of the creviced area remain active over a sufficiently long period. Stifling results when the aggressive chemistry required inside the crevice to keep the material depassivated, *i.e.*, actively corroding, cannot be maintained. This loss of critical chemistry occurs when the rate of mass transport out of the crevice exceeds the rate of dissolution and subsequent hydrolysis of metal ions inside the crevice. For the treatment considered here, the mass transport conditions are constant for a given geometry and potential. What then controls the stability of the internal chemistry is the interaction between the electrochemical kinetics at the interface and the crevice chemistry composition.

This work focuses on the parameters that control the stability of crevice corrosion by modeling the evolution of the chemical and electrochemical conditions within a crevice open only at one end (*e.g.* the mouth) in which the entire crevice is initially filled with the Critical Chemistry Solution (CCS) or filled with chemistries slightly less or more aggressive than the CCS. The crevice mouth is in contact with a weak acid solution (pH 3) that provides the boundary conditions at the crevice mouth. The potential at the mouth was held constant at  $+0.1$  V<sub>sce</sub> in most instances with selected cases held at 0.0 V<sub>sce</sub>. The material selected was Ni-22Cr-6Mo alloy. The electrochemical kinetics at the pH values of interest have been recently characterized via potentiodynamic polarization. Figure 1 shows the polarization curves for Ni-22Cr-6Mo samples tested at room temperature in various HCl solutions. These data were used in all calculations. That is as the pH changed, a new polarization curve was applied to the position in the crevice. E, pH was calculated at each position and from this data, current at each position was determined. The effects of the crevice gap and the crevice length on stabilization were studied by conducting calculations on samples of various gaps and lengths. In addition, the importance of the increase in the activity coefficient for hydronium ion with high ionic strengths is shown to be critical for stabilizing crevices of the investigated Ni-22Cr-6Mo.

Figure 2 shows the evolution with time of the total current demanded by the crevice (normalized to a 1-cm wide crevice), for cases with different initial solution pH. Three distinct behaviors were observed: 1) for cases with the higher pH solution there was a monotonic decay in current, suggesting that repassivation is taking place, 2) for the case with initial solution of -0.24 pH: the total current had a similar monotonic decay, but after ~40 seconds the current began to increase, suggesting that stabilization is taking place, 3) when the solution pH is <-0.4, there is a small current drop at very early time (< 2 s) but the currents remain high during the duration of the simulation. Thus stabilization appears to be possible for the last two situations.

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These results were compared with results based on similar calculations considering crevice corrosion of Type 316L stainless steel. It was found that the solution pH of the initial critical chemistry that allows stabilization was considerably more negative for the Ni-22Cr-6Mo system, in agreement with what was expected based on what has been reported in the literature [1,2].

### Reference

- [1] A. J. Sedriks, in *Corrosion of Stainless Steels 2<sup>nd</sup> Ed.*, New York, Wiley, (1996).
- [2] R.S. Lillard, M.P. Jurinski and J.R. Scully, *Corrosion* 50 (4): p251 (1994)

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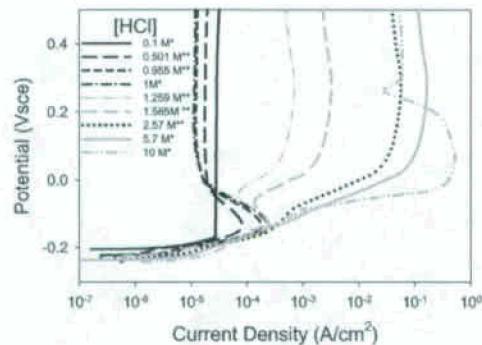


Figure 1. Polarization curves for Ni-22Cr-6Mo (in the indicated HCl molarity) coded into the model to describe the interfacial kinetics at different chemistries. \*Fitted to experimental, \*\* Interpolated.

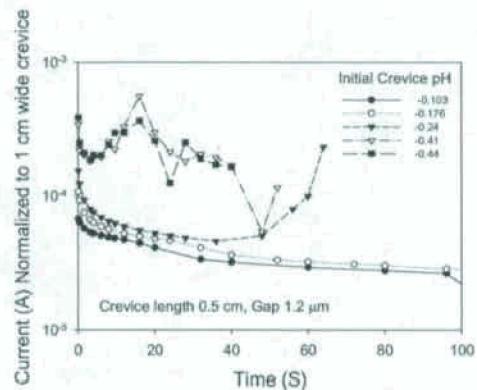


Figure 2. Total current demanded by the crevice vs. time. Crevices had a 1.2  $\mu$ m gap and 0.5 cm length. Initial crevice solution pH values ranged from -0.44 to -0.103.