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Quantifying Alloy 625 Crevice Corrosion Using an Image Differencing Technique: Part I. Initiation and Propagation

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An image differentiating technique was used to analyze optical images from an alloy 625 crevice made using an acrylic window. In these experiments, crevices were immersed in ASTM artificial ocean water and held potentiostatically in the passive region while the current was monitored with time. The technique quantified the change in pixels between successive images due to corrosion damage. By calibrating the number of pixels per unit area we calculated the active area and, from this, the crevice current density. It was found that the crevice propagated in the current density range between 3 mA cm\(^{-2}\) at initiation and 100 mA cm\(^{-2}\) at steady state. It is shown that the mass loss as a function of position calculated from the current density accurately reproduces the damage profile inside the crevice. By knowing the location of the active front and the crevice current, we are also able to calculate the wall potential as a function of time and distance. It is shown that the initiation site has a wall potential that is within millivolts of the applied anodic potential and decreases as the active front moves towards the mouth. Finally, we derive an expression for the crevice shape factor which was used to show that the crevice is under diffusion control at later times in the propagation stage.

**Background**

Variables describing crevice initiation in Ni alloys.—As detailed below, the critical variables for crevice corrosion initiation have typically been determined using potentiostatic and potentiodynamic methods. In those studies, a remote crevice (or a multiple crevice assembly) of the material of interest is held at a series of constant potentials and the corresponding current vs time data are recorded.\(^1\) The minimum potential that results in an increase in current is designated as the critical potential for initiation. In general, for nickel alloys, it has been found that increasing temperature and chloride concentration of the bulk solution decrease crevice initiation potentials.\(^2,\)\(^2\)\(^3\)\(^4\) In comparison, pH of the bulk in the range of 2 to 7, has not been shown to have an effect.\(^2\)\(^5\) However, the addition of inorganic inhibitors to the bulk solution, such as nitrate, sulfate and phosphate, increase crevice corrosion initiation potentials.\(^2,\)\(^2\)\(^3\)\(^4\)

Kehler et al. investigated the influence of solution composition and temperature on the critical potentials for crevice initiation in nickel alloys 625 and C22.\(^2\) In that study, it was found that, for the same solution, the initiation potential for alloy C22 was on the order of 100 mV higher than that of alloy 625 (taken when the cumulative distribution function was equal to 0.5). In addition, for both 625 and C22, bulk pH (2.5 vs 7.75) had no effect on the critical potential for crevice initiation. Inhibitor concentration in the bulk solution (in this case nitrate) also influenced the crevice initiation potential with higher bulk concentration being associated with higher initiation potentials. With respect to the effect of temperature, Kehler et al. found that the critical potential for crevice initiation decreased with increasing temperature for both 625 and C22. Similar results were found by Ilevbare et al. for C22 in NaCl.\(^2\) In that study, higher sulfate concentrations and lower temperatures resulted in higher crevice initiation potentials. Ortiz et al. investigated the relationship between chloride concentration in the bulk solution and the initiation potential in alloy C22.\(^2\)\(^6\) Over the Cl\(^-\) range of 0.1 to 10 M, the critical potential for crevice initiation decreased by 100 mV with increasing concentration. Bocher et al. developed a model to predict the critical potentials for crevice corrosion initiation in “lab-made” Ni-Cr-Mo alloys based on activation controlled Tafel kinetics.\(^5\) The critical potential for crevice initiation was calculated from a Nernstian relationship based on the corrosion potential and corrosion current density of the alloys in simulated crevice solutions (10 M HCl solution and a LiCl-HCl solution) at 50° C. For the lab made 625 alloy, the critical potential was on the order of 0.4 V SCE. It may be noted that potential is quite high in comparison with potentials reported for the Flade potential.

Unlike studies using potential control to initiate creviced corrosion, Jakupi et al.,\(^6\) and later Misra and Shoesmith,\(^7\) used a galvanostatic method to investigate the variables controlling crevice corrosion initiation in alloy C22 in chloride solution at elevated temperature and pressure. In these experiments, a constant current (ranging from 4 × 10\(^{-5}\) to 2 × 10\(^{-3}\) A) was applied to the specimen and the resulting potential was measured as a function of time. At early times, the potential increased rapidly, reaching a maximum value that was proportional to the applied current, approximately 0.45 V vs Ag/AgCl at 2 × 10\(^{-4}\) A and 0.2 V at 4 × 10\(^{-5}\) A. Once the maximum current density was reached, the potential decreased rapidly to a steady-state “propagation” potential (approximately 0 V AgCl) that was independent of applied current. While the precise mechanism resulting in these transients was not determined, the authors did note that initiation potentials exceeded the Cr(III) to Cr(VI) potential, that is, the transpassive potential for Cr oxidation.
Models of localized corrosion propagation.—Crevice corrosion is usually defined as one of the two subsets of localized corrosion, the other being pitting corrosion. However, the models for crevice corrosion initiation and propagation that have been proposed in the literature are not consistent with those that have been proposed for pitting. If in fact crevice and pitting are both forms of localized corrosion, there should be commonalities in their mechanisms and a unified model would be more cogent than what has been proposed for crevice corrosion.

Tester and Isaac and later Newman and Isaac investigated diffusion-coupled active dissolution in one-dimensional (1D) pits in stainless steel.8,9 At high enough applied potentials (and current densities) they found that the rate of oxidation and cation production exceeded the diffusive transport. At sufficient depths and current densities, the concentration of cations within the pit exceeded the saturation limit resulting in the precipitation of a salt film at the interface stabilizing propagation. During this stage, they found that the current density varied inversely with the square root of time. More recently, Srinivasan and Kelly have shown that propagation may occur below the saturation limit.10 In their work, results from 1-D stainless steel pits were used to develop a transport model. Experimental results found that the limiting current densities within the pit varied with the reciprocal of pit depth while their transport model showed that pit propagation could occur at 50% of the saturation limit. Li Scully and Frankel published a series of papers with the goal of a unified model of pitting corrosion that considered the passive film, pit growth kinetics and salt film formation.8,11,12 In these papers, the concept of \( i_{\text{diss, max}} \) was introduced to represent the maximum current density that a pit can achieve at a given applied potential and temperature. The authors compared \( i_{\text{diss, max}} \) with the diffusion current density, to determine the boundaries for pit propagation and repassivation. It was shown that, if the environment exceeds a critical concentration of metal cations then it was able to propagate, else repassivation ensues. If \( i_{\text{diss, max}} \) exceeded the limiting current density, the pit solution saturated resulting in the formation of a salt film.

With respect to the models used to describe crevice corrosion, traditionally they have been based on the Fontana and Green model13 and the formalizations of Oldfield and Sutton.14,15 Within those frameworks, crevice corrosion begins with the deoxygenation of the crevice and shifting of the cathodic reactions to the bulk surface. Anodic reactions within the crevice, specifically passive dissolution, and transport restrictions caused by the geometry of the crevice result in a buildup of metal cations within the crevice. To preserve electroneutrality, chloride ions from the bulk solution migrate into the crevice. Metal hydrolysis reactions cause the pH to drop and crevice corrosion initiation was proposed to occur once the crevice solution pH and \([\text{Cl}^-]\) increased the current density above a threshold, typically viewed as being \(10 \times 10^{-6} \text{ A cm}^{-2} \). Up until this point, the description of crevice corrosion has parallels with that described for pitting. However, the mechanisms as described in the literature diverge at this point. With respect to crevice corrosion, a model based solely on IR-drop for the initiation and propagation, the IR\(^e\) model, was proposed by Pickering.16 In that model, crevice occurs when the crevice IR causes a portion of the wall to fall to a potential value that is “within the active peak of the polarization curve.” This requires the crevice material to have an active-to-passive transition in the bulk solution and most corrosion resistant alloys do not. Shaw and Moran17 and later Lilard and Scully18 unified the concepts of the Oldfield-Sutton and Pickering models to explain the crevice corrosion mechanism in metals that are spontaneously passive in the bulk solution, such as alloy 625 in seawater. Those authors proposed that crevice corrosion in alloy 625 occurs in two stages: (i) the initiation stage, during which the development of a critical crevice solution (CCS) inside the crevice results in a polarization curve with an active-to-passive transition not present in the bulk, and (ii) the propagation stage, which occurs if the geometry of the crevice is such that it places a portion of the crevice in the active-to-passive transition of the polarization curve in the crevice environment.

In our opinion, the divergence of the pitting and crevice corrosion models in the literature owes to the lack of a method for obtaining the active crevice area and, thus, crevice current density and wall potential. To date, crevice current data have traditionally been normalized by the total crevice area or some arbitrary fraction thereof.19,20 While Pickering has published a number of papers imaging crevices through a crevice, as well as measuring the potential and pH profiles within crevices in an attempt to describe the crevice corrosion mechanism21-24, the crevice current density has remained elusive. With knowledge of the true crevice current density, a direct comparison between pitting and crevice mechanisms is possible. This is one of the goals of this study.

Experimental

The remote crevice assembly (RCA) used in this study consisted of a bolt a nut, and a washer made of nickel alloy 625 and a crevice former made from acrylic. The alloy washer was fabricated from a 1.5” rod (Metalmen, Table I). The rod was machined into washer-shaped specimens with the geometry and dimensions shown in Fig. 1 with care to ensure that the two faces were parallel. These specimens were polished using successive grits of SiC paper 320, 400, 600, 800, and 1200 on the two faces and the outside edge of the washer. As a final cleaning step, the polished surfaces were degreased with acetone and ethanol followed by rinsing in DI water.

The arrangement of the RCA is shown in Fig. 1. Before the assembly was tightened, the crevice area was wetted with ASTM ocean water which was also used as the bulk electrolyte (Lake Products). Once wetted, a fixed applied torque of 13.6 N-m (10 ft-lb) was used to tighten the RCA in attempt to create a reproducible crevice gap in each experiment. All experiments were carried out at room temperature.

Once assembled, the RCA was used to study crevice corrosion damage during potentiostatic holds. In these tests, the RCA was held at the OCP for 1 h, followed by a potentiostatic hold for a predetermined period of time. To study the effect of applied potential on crevice corrosion phenomena, four different anodic potentials were used: 100, 200, 250 and 300 mV vs SCE. These potential values were chosen because they are in the passive region of the alloy 625 polarization curve in ASTM ocean water at room temperature. More importantly, these potentials are below the transpassive potential for alloy 625 in this solution which is equal to approximately 375 mV SCE.25 In these potentiostatic holds, the RCA was exposed for times up to 60 h. Corresponding current vs time data were collected at a rate of 1 point/s (3600 points/h).

Crevice corrosion damage evolution was recorded in time lapse images using an Olympus SZX16 stereoscope, a magnification of 0.7 X and the manufactures image capture software. The experimental set up is shown in Fig. 1. This setup allowed us to image approximately 40% of the crevice though, for symmetry reasons, we chose to analyze only 26% of the total crevice area (yellow lines in Fig. 1b). Capture rates were varied between 55 s\(^{-1}\) and 264 s\(^{-1}\). These rates were varied to optimize surface detail and image storage volume. The effect of image capture rate on our calculations of crevice corrosion damage rate was studied and it was found that, for

Table I. Nominal composition of alloy 625 rod used to create the RCA washers in mass%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass %</th>
</tr>
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<tbody>
<tr>
<td>Ni</td>
<td>60.56</td>
</tr>
<tr>
<td>Cr</td>
<td>22.36</td>
</tr>
<tr>
<td>Fe</td>
<td>3.74</td>
</tr>
<tr>
<td>Mo</td>
<td>8.76</td>
</tr>
<tr>
<td>Nb</td>
<td>3.56</td>
</tr>
<tr>
<td>Ti</td>
<td>0.03</td>
</tr>
<tr>
<td>Al</td>
<td>0.18</td>
</tr>
<tr>
<td>Si</td>
<td>0.06</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05</td>
</tr>
<tr>
<td>C</td>
<td>0.05</td>
</tr>
<tr>
<td>Co</td>
<td>0.03</td>
</tr>
<tr>
<td>P</td>
<td>0.02</td>
</tr>
<tr>
<td>Ta</td>
<td>0.01</td>
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image capture rates greater than 1 image every 600 s, the calculated rate was unaffected.

**Results**

*Observations of damage evolution.*—Typical current vs time data for an RCA held at 300 mV SCE is shown in Fig. 2. The results are typical of this system as we have reported previously where we identified three stages of crevice corrosion: Stage I—Initiation, Stage II—Propagation; Movement of an active front, and Stage III—Propagation at the limiting current. In our images, we first detect corrosion damage at 1536 s and the response in the current is seen soon after at 1716 s as seen in Fig. 2. A sequence of images of the crevice during this experiment is presented in Fig. 3. The capture times for each image are indicated in the current vs time data shown in Fig. 2 by arrows. As seen in this sequence of images, crevice corrosion initiates near the tip of the crevice (closest to the bolt) and moves towards the mouth (the interface with bulk solution) with increasing time. Once 65.3 ks was reached, the crevice corrosion stopped moving towards the mouth. It is interesting to note that this time corresponds to the transition from Stage II crevice propagation to Stage III in the current vs time data. No matter how long the RCA was held at this potential, the damage did not move any closer to the mouth though it continued to propagate. This “stopping” distance between the mouth and the active front, which we have previously identified as $x_{crit}$, appears to be potential dependent as shown in Fig. 4. As seen in this figure, for small applied potentials $x_{crit}$ is large and decreases with increasing applied potential. One may also note that, at 100 mV vs SCE, crevice corrosion is not uniform about the central bolt and a patch of uncorroded area is observed in the region between 9 and 10 o’clock in the image. In this sequence of images, we also note plumes of corrosion product in the crevice solution between the damage area and mouth (arrows). The current vs time curves for these images recorded just prior to concluding experiment are presented in Fig. 5. As seen in this figure, the limiting current associated with our Stage III increases with increasing applied potential.

A surface profile, from white-light interferometry, of the washer after the experiment in Figs. 2 and 3 is presented in Fig. 6. In this figure, the mouth of the crevice is located at position $x = 0$, to the right of the plot. Although it is not obvious from this plot, in this line scan the initiation site was located 0.81 cm from the mouth (confirmed using optical metallography). The curvature between 1.2 cm and 0.8 cm and the spikes near the washer hole appear to be
artifacts and are not related to crevice corrosion damage. Similarly, the spikes in depth between 0.67 and 0.49 cm also appear to be artifacts and are not related to changes in the surface profile.

None-the-less, between 0.81 cm and 0.49 cm the surface damage increases to a maximum value of approximately $8.7 \times 10^{-6}$ m. In general, the profile differed from location to location around the

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**Figure 3.** An image sequence from the RCA experiment in Fig. 2 at an applied potential of 300 mV vs SCE. Times presented here are represented by the arrows in Fig. 2.

**Figure 4.** Images from RCA experiments as a function of potential. The images depict the closest that the damage front came to the crevice mouth ($x_{\text{crit}}$) for each applied potential. Arrows indicate regions of visible corrosion product (soluble and insoluble). Images recorded just prior to concluding experiment, 100 mV: 210 ks; 200 mV: 137 ks; 250 mV: 137 ks; 300 mV 65 ks.
for a specimen that was held at 300 mV SCE. In that figure we present images at two times ($t_1$ and $t_2$) and their difference ($\Delta A$). To generate this figure, we have chosen a time step that is large (3600 s) in comparison to what we use for our quantitative analysis (192 s) so that the difference may be easily observed. As seen in the difference sequence, the only active corrosion area on the specimen surface is a front that is moving towards the crevice mouth. The corroded area behind this front appears to have repassivated or, is corroding at such a low rate that it cannot be detected by our method.

From our MatLab image processing routine, we can calculate the number of new pixels in subsequent images. Calibrating for the number of pixels cm$^{-2}$, we can calculate the change in area from frame to frame in the image ($\Delta A_{\text{image}}$). This is the actively corroding area in the image during that time. To calculate the total active area across the entire washer, it was assumed that the un-imaged portion of the specimen was oxidizing at the same rate as the area being imaged. Any experiments where we could not confirm this visually over the course of the experiment were rejected. This is another way of saying that those specimens that were not corroding symmetrically about the bolt were not used in our calculations. For each time step (192 s) we calculated the fraction of area corroding in the image:

$$p = \frac{\Delta A_{\text{image}}}{A_{\text{image}}}$$

Where $A_{\text{image}}$ is the total area in the image and is equal to:

$$A_{\text{image}} = \frac{\theta \pi r_w^2}{360}$$

where $\theta$ is the angle that defines our experimental area in the MatLab routine and was typically in the range of 60° to 80° (Fig. 1) and $r_w$ is the radius of the washer and is equal to 1.91 cm. The extrapolated active area across the entire specimen ($\Delta A$) is then calculated by multiplying $p$ in Eq. 1 by the total area that would have been imaged if the field of view was wider ($A_{\text{total}} = 11.4$ cm$^2$):

$$\Delta A = p \times A_{\text{total}}$$

Figure 8 presents the active area, $\Delta A$, calculated from Eq. 3 as a function of time for the data presented in Figs 2, 3, 6 and 7 which are all from the same experiment. As seen in this figure, $\Delta A$ remains relatively unchanged up to 15,360 s when a large increase in $\Delta A$ occurs. Between 15,360 s and 57,878 s $\Delta A$ appears to be erratic though the general trend is decreasing. While it appears that there is an abrupt decrease after 57,878 s, we believe that this owes to our inability to measure $\Delta A$ once $x_{\text{crit}}$ has been reached. For this reason, in our analysis we will not consider times greater than 57,878 s. Once $\Delta A$ for each time step was calculated, the current density of the active front was calculated by dividing the measured current at that time step by $\Delta A$:

$$i_{\text{active front}} = \frac{I_{\text{meas}} - I_{\text{pass}}}{\Delta A}$$

Where $I_{\text{meas}}$ is the measured current and $I_{\text{pass}}$ is the passive current corresponding to the boldly exposed surface. As we show in Fig. S1 (available online at stacks.iop.org/JES/167/021511/mmedia) of the Supplemental Material, the passive current is negligible at all times. In addition, we recognize that there is damage owing to penetration depth (out-of-plane area) that the technique cannot quantify. However, as seen in Fig. 6, the additional out-of-plane depth is on the order of 0.001% of the total length making it negligible in our calculation. The corresponding calculated current density of the active front for times up to 57,878 s is presented in Fig. 9. The fluctuation in current density seen in this plot are a direct consequence of the changes in $\Delta A$ seen in Fig. 8.

The total corroded area with time, $\Sigma \Delta A$ (actively corroding + inactive) is presented in Fig. 10. As seen in this figure the change in corroded area with time is a sigmoidal shaped curve, reaching a

washer and, for this specimen, $x_{\text{crit}}$ varied between 0.4 cm and 0.5 cm and the maximum depth due to crevice corrosion was on the order of $10 \times 10^{-6}$ m.

**Image analysis and calculation of current density.**—One of the critical parameters in the discussion of the mechanism of crevice corrosion is the current density of the active area. While we have time lapse images of the crevice and can see the damage evolution, it is not immediately obvious from those images what the active area is. To determine the active area within the crevice we have employed a differential imaging technique. In this method, we have used the Image Analysis package that accompanies MatLab (MathWorks) to develop a code that generates the difference (pixels) between two sequential images. An example of the results is presented in Fig. 7.
Figure 7. Typical output from our image difference routine. The figure shows images from two times on the left and their difference, right. Corrosion damage in the difference image appears brighter while black indicates no change between images $t_1$ and $t_2$ (e.g., no new damage).

Figure 8. Change in corroded area with time calculated from Eq. 3. Data is the newly corroded area due to the movement of the active front and correspond to the experiment presented in Fig. 2 ($E_{\text{app}}$ 300 mV vs SCE).

Figure 9. Surface current density calculated from Eq. 4 as a function of time for the RCA experiment in Fig. 2.
limiting value on the order of 2.6 cm$^2$. Knowing $\Sigma \Delta A$ as a function of time, we can approximate the distance between the active front and the mouth of the crevice ($x$ in Fig. 11). Further, we can represent the corroded area as an annulus with an inner and outer radii, $r_1$ and $r_2$. The outer radius, $r_2$, is a function of damage ($\Delta A$) and can be calculated from the relationship:

$$\sum \Delta A = \pi (r_2^2 - r_1^2)$$ \[5\]

where the inner radius, $r_1$, takes the value from the previous time step. The distance between the active front and the mouth ($x$) is equal to $r_w - r_2$ or:

$$x = r_w - \sum \frac{\Delta A}{\pi} + r_1^2$$ \[6\]

In this manner, the current density plotted as a function of distance from the mouth, $x$, is presented in Fig. 12. As before, we have terminated our calculations at 57,878 s. As seen in this figure, the current density of the active front increases as it approaches the mouth of the crevice. This relationship is consistent with that observed in 1D pitting experiments (pencil electrodes), where the current density is inversely proportional to the distance from the pit mouth.\[11,27\]

For comparison with these results, it is instructional to consider alternative methods for area normalization. For example, one might argue that, owing to surface roughness, the technique is not sufficiently sensitive to detect cumulative damage in the area behind the active front. As such, we have considered two normalization methods in which, once initiated, the crevice area stays active. The results are presented in Figs. S2 and S3 of the Supplemental Material. As shown in the Supplemental Material, these methods incorrectly predict the damage profile. As shown in Fig. S2, when the entire damage area is used, the maximum damage is always predicted to be closest to the tip even for current densities as low as $5 \times 10^{-4}$ A cm$^{-2}$. This occurs because the time in which the area near the tip remains active is long (50 ks) in comparison with the area closer to the mouth (100 s to 1,000 s). This is inconsistent with the experimental data in Fig. 6 and elsewhere in the literature where it is observed that the maximum damage occurs nearest the mouth. This is additional evidence that the area behind the crevice either repassivates (possibly due to the precipitation of corrosion product) or is corroding at a rate that is too slow to be perceived in the experimental times used here.
Calculation of IR and wall potential.—In addition to current density, another critical parameter in the discussion of the crevice corrosion mechanism is potential drop (IR). To calculate IR, we need an expression for solution resistance between the active front and the mouth ($R_{crev}$). If our geometry was a parallelepiped, the resistance of the crevice solution volume would be given as, $R = \rho (L/A)$, where $(L/A)$ is a geometric shape factor with $A$ being the cross-sectional area of the parallelepiped, $\rho$ is solution resistivity and $L$ is its length.

For the resistance of the toroid of solution that forms between the 625 washer and the acrylic crevice former used here, $R_{crev}$ can be calculated by first considering a small volume of solution ($v$) defined by $\delta$ (crevice gap), $dr$ and $rd\theta$ (Fig. 14, left). For small values, this geometry approximates a parallelepiped. In this configuration, the current is normal to the surface area defined by $\delta \cdot r d\theta$ and the resistance of $v$ ($R_v$) is equal to:

$$R_v = \frac{\rho dr}{\delta \cdot r d\theta} \tag{7}$$

To calculate the resistance of the toroid ($R_T$), we first sum $R_v$ between the time dependent radius associated with the active front $r_2(t)$ and $r_w$ as shown in Fig. 14. Recognizing that the resistances from the innermost radius ($r_2(t = 1)$) to $r_w$ are in series:

$$R_S = \int_{r_2(t)}^{r_w} 1/R_v = \int_{r_2(t)}^{r_w} \frac{\rho dr}{\delta \cdot r d\theta} \tag{8}$$

integrating the right side of the expression with respect to $r$ we find:

$$R_S = \frac{\rho}{\delta \cdot d\theta} \ln \frac{r_w}{r_2(t)} \tag{9}$$

To find the total resistance of the toroid ($R_{crev}$) we sum $R_S$ in parallel over $2\pi$ (Fig. 14, right):

$$1/R_{crev} = \int_0^{2\pi} 1/R_S = \int_0^{2\pi} \left( \frac{\rho}{\delta \cdot d\theta} \ln \frac{r_w}{r_2(t)} \right)^{-1} \tag{10}$$

solving for $R_{crev}$:

$$R_{crev} = \frac{\rho \cdot \left( \ln \frac{r_w}{r_2(t)} \right)}{2\pi \delta} \tag{11}$$

As $R_{crev} = 1/kS_{crev}$, the two-dimensional shape factor for the toroid that defines the crevice gap ($S_{crev}$) is equal to:

$$S_{crev} = \frac{2\pi \delta}{\ln \frac{r_w}{r_2}} \tag{12}$$
The solution resistance between the active front and the mouth of the crevice as a function of time was calculated from Eq. 11 and is presented in Fig. 15. As might be expected, \( R_{crev} \) decreases with time, e.g. it decreases as the active front moves closer to the mouth of the crevice. Also, in this figure we present the corresponding IR (\( I_{tot} \cdot R_{crev} \)). Please note that these calculations of IR are for fixed times. As such, the IR profile shown in this figure never exists in the crevice. Rather, this is the IR between the active front and the mouth at fixed times. As seen in Fig. 15 the IR between active front and the mouth increases as the front moves toward the mouth. This occurs because the experimental current increases by two orders of magnitude over the course of time while \( R_{crev} \) decreases only by a factor of two during this same time. Subtracting the IR from the applied potential (\( E_{app} = I_{tot} \cdot R_{crev} \)), we calculated the wall potential at the active front in V vs SCE at fixed times (equivalent to distance from the mouth) and present the results in Fig. 16. Because these wall potentials are for fixed times, as before, the profile shown never exists in the crevice. The dashed lines are linear extrapolations to \( E_{app} = 0.30 \) V at the mouth for fixed times to aid the reader in understanding what the trend in potential down the length of the crevice may look like and do not represent actual potential profiles. We make no claim about the wall potential at greater depths for these fixed times.

\[ \frac{dm}{dt} = D\Delta C \left( A(r) \frac{d}{dr} \right) \]  

where \( \Delta C \) is the concentration difference between the CCS at the active site and the bulk and \( A(r) = \delta \cdot r \cdot d\theta \) as in Fig. 14. Substituting this relationship for \( A(r) \) into Eq. 13 and recognizing that:

\[ 1/S_{crev} = \int \frac{d\theta}{\delta \cdot r \cdot d\theta} \]  

we find that:

\[ \frac{dm}{dt} = D\Delta C S_{crev} \]  

Substituting for:

**Discussion**

In our previous paper on alloy 625 crevice corrosion, we studied the progression of crevice corrosion damage with time using a crevice assembly made from two 625 washers, e.g. a metal-metal crevice assembly. We found that initiation occurred exclusively at the tip as observed in this study. It was proposed that, early on, the IR down the length of the crevice is minimal and initiation occurs when the chemistry inside the crevice changes sufficiently to lower the breakdown potential (such as the transpassive potential) below the potential of the boldly exposed surface (or applied potential in the lab). Once initiated, we found that the actively corroding area moved from the tip towards the mouth as observed here. However, the mechanism of propagation was not clear as the wall potential was not known, nor was the crevice current density. In the following discussions, we will attempt to shed light on the mechanism of crevice propagation as well as role of IR.

**Crevice propagation.**—Corrosion propagation may occur via diffusion control, activation control, or ohmic control. The diffusion rate due to mass transport \((dm/dt)\) from the crevice is given by:

\[ \frac{dm}{dt} = D\Delta C \left( A(r) \frac{d}{dr} \right) \]  

\[ \frac{dm}{dt} = D\Delta C S_{crev} \]
\[
\frac{dm}{dt} = \frac{I_{\text{meas}}}{nF} \quad [16]
\]
where \( n \) is the equivalent charge for alloy 625 equal to 2.12 we find:

\[
I_{\text{meas}} = 2.12DF\Delta C_{\text{crev}} \quad [17]
\]

Thus, a plot of \( I_{\text{meas}} \) vs \( S_{\text{crev}} \) should be linear with slope equal to \( 2.12DF\Delta C \). The reader may note that, in 1D pits it is convenient to normalized both sides of Eq. 17 by the surface area, that is, in a pencil electrode experiment pit flux is equal to surface current density. In addition, for hemispherical pits such a normalization also allows for simplification of the shape factor. For the crevice geometry here, crevice flux is not equal to surface current density.

A plot of \( I_{\text{meas}} \) vs \( S_{\text{crev}} \) is presented in Fig. 18. As seen in this figure, there are two distinct regions in the plot, one prior to 15 ks and one after. The implication of these results being that there are two different values of \( 2.12DF\Delta C \) in Fig. 18a, one before 15 ks and one after. For constant diffusion coefficient, at times greater than 15 ks this would mean a decrease in concentration between the active site and the mouth, possibly due to the precipitation of a salt film. In pitting corrosion, salt films form when the dissolution current density exceeds the diffusion-limited current density as described by Li. \(^{10}\) It has been shown that a salt film is not necessary for pit growth, rather, a consequence of diffusion-controlled growth. Prior to Ni salt film precipitation, there is a period of supersaturation, followed by crystal nucleation as shown by Hammons. \(^{30}\) As nucleation and growth processes proceed a salt containing layer is formed in solution and the concentration of Ni\(^{2+}\) begins to decrease. Upon salt film formation and steady state, Ni\(^{2+}\) concentration is maintained at a value below saturation. Thus, from Fig. 18a, one could conclude that the concentration of metal cations in solution reaches a supersaturated value just prior to 15 ks, where upon salt film formation occurs, and at times greater than 15 ks crevice corrosion is propagating beneath a salt film. While we have not measured limiting current densities \( \text{pencil} \), a key indicator of salt film formation, there is an interpretation of Fig. 17 that is consistent with this idea. As we have noted, the limiting current density observed in 1D pits is inversely proportional to distance from the pit mouth. \(^{9,11}\) Similarly, the \( x \)-axis in Fig. 17 also represents distance. Therefore, as the potential decreases due to IR and the active front moves forward, the current density must increase to the limiting current density associated with this shorter distance. This would also explain what appears to be different limiting currents as a function of distance in Fig. 5.

Additional evidence of diffusion control is a diffusion length that is proportional to the square root of time:

\[
x = \sqrt{4Dt} \quad [18]
\]
where \( x \) is distance from the mouth in cm, \( D \) is diffusion coefficient in \( \text{cm}^2 \text{s}^{-1} \) and \( t \) is time in s. In Fig. 19 we have plotted the distance between the crevice mouth and the active front as a function of time (propagation rate). As seen in Fig. 19a, there are two distinct propagation rates, a rate prior to approximately 15 ks and one after. While we are uncertain about the rate at times less than 15 ks, after 15 ks the rate is fit by a quadratic equation, specifically \( t^{1/2} \) (Fig. 19b) consistent with Fick’s second law. From the coefficient of \( t \) in Fig. 19b, 0.00249 cm \( \text{s}^{0.5} \), we calculate the average diffusion coefficient for the alloy (\( D_{\text{aveg}} \)) as \( 1.6 \times 10^{-6} \text{cm}^2 \text{s}^{-1} \) (assuming propagation and diffusion rates are equal). For comparison, the diffusion coefficient of Ni\(^{2+}\) calculated from pencil electrode experiments has been reported to be \( 3 \times 10^{-6} \text{cm}^2 \text{s}^{-1} \). \(^{30}\)
We shall return to the topic of crevice species and salt film formation in our papers on transport and crevice repassivation.

The role of IR in crevice corrosion initiation and propagation.—As seen in Fig. 15, the ohmic drop in the crevice between the mouth and the active site is lowest at early times (initiation) and, as a result, the wall potential at the initiation site is within a few millivolts of \( E_{\text{applied}} \). In addition, our observations do not show any evidence of gas bubbles or corrosion product forming between the initiation site and the crevice mouth or any other “constriction” which may increase the resistance and decrease the local potential. Thus, initiation is most likely associated with some type of breakdown event at potentials more positive than the passive region such as transpassive breakdown of the oxide film or pitting as we have discussed previously. Further, this result rules out the possibility that initiation occurs when the crevice IR causes a portion of the wall to fall to a potential value that is “within the active peak of the polarization curve” in the CCS. Recall, the Flade potentials for alloy 625 in simulated CCS are on the order of \(-0.2\) V to \(0.0\) V vs SCE. As such, for the case of alloy 625, breakdown most likely owes to transpassivity. There is a wealth of literature on the transpassivity of nickel alloys and these investigations typically focus Cr(III) oxidation to soluble Cr\(^{6+}\) in the transpassive region and little attention is given to the role of other alloying elements. Recently, Henderson reported on transpassive dissolution of Cr and Mo at applied anodic potentials from four nickel base alloys; BC-1 (15 mass% Cr, 22 mass% Mo), C-22 (22% Cr, 13% Mo), G-35 (33% Cr, 8% Mo) and G-30 (30% Cr, 5% Mo). Using atomic emission spectroelectrochemistry it was shown that, for all four alloys, the dissolution rates of alloying elements were incongruent with respect to Ni, that is, in each alloy the rate of dissolution of Ni was greater than that of Cr, or Mo. This implied a surface enrichment of these species during transpassive dissolution. Upon stepping the potential down from the transpassive state, the alloy with the greatest crevice corrosion resistance, BC-1 retained the surface enriched Mo while the least crevice corrosion alloy (G-30) released Mo into solution. The implication being, that Mo retention improves crevice corrosion resistance “when an oxide is compromised, either due to transpassive dissolution” or another localized event.

With respect to propagation, Fig. 15 also shows that the IR between the active front and the mouth of the crevice increases as the front moves closer to the mouth. That is, the crevice is not propagating at a constant potential. Further, the current potential relationship (Fig. 17) is non-linear. As such we rule out ohmic controlled propagation for the times being considered here, although it is possible that during steady state (\( t > 57 \) ks in Fig. 2) that the crevice may be propagating under ohmic control.

A final comment on the experimental damage profile shown in Fig. 6 and the role of IR in alloy 625 crevice corrosion. We are not the first to report such a profile, they are observed routinely in crevice corrosion for many different metals and geometries. Investigators commonly associate this characteristic profile with IR drop down the length of the crevice and the active-to-passive transition. That is, a mapping out of the active-to-passive region of the polarization curve on to the crevice wall. This idea appears in the earliest papers on the IR* model and, in fact, the profile is used as justification for the model. From our current density calculations, however, there is now an alternate explanation for the damage profile in Fig. 6 as we show in the calculated profile presented in Fig. 13. The damage profile that is observed during crevice corrosion is the consequence of the movement of an active front from the tip to the mouth and the associated increase in current density, not a mapping of an active to passive transition onto the crevice wall. In addition, as indicated by Fig. 16, the damage at deeper depths occurred at more positive potentials, further evidence that this is not a mapping of the active to passive transition on to the crevice wall.

Conclusions

An image differencing technique was used to analyze optical images from an alloy 625 crevice made using an acrylic window. Crevices were immersed in ASTM artificial ocean water and held potentiostatically in the passive region of ASTM artificial ocean water while the current was monitored with time. The differencing technique allowed for the active area to be determined and, thus, the crevice current density.

With respect to initiation, calculation of the crevice resistance allowed the IR drop between the active front and the mouth to be calculated as a function of time. The wall potential at the time of initiation was high, for all purposes equal to the applied potential (0.30 V SCE). In comparison, by the time the active front approached the mouth, the wall potential had dropped to approximately 0.07 V vs SCE. From this result we concluded that initiation was most likely associated with some type of breakdown event at potentials above the passive region such as transpassive breakdown of the oxide film or pitting. Further, this result rules out the possibility that initiation occurs when the crevice IR causes a portion of the wall to fall to a potential value that is “within the active peak of the polarization curve” in the CCS as the Flade potentials for alloy 625 in simulated CCS are \(-0.07\) V vs SCE. From this result we concluded that initiation was most likely associated with some type of breakdown event at potentials above the passive region such as transpassive breakdown of the oxide film or pitting. Further, this result rules out the possibility that initiation occurs when the crevice IR causes a portion of the wall to fall to a potential value that is “within the active peak of the polarization curve” in the CCS as the Flade potentials for alloy 625 in simulated CCS are \(-0.07\) V vs SCE.

Once initiated, crevice propagation moves as an active front from the crevice tip towards the mouth and, during the course of this movement, the current density increases. The veracity of this conclusion is supported by the observation that the theoretical damage profile calculated from this model agrees well with the experimental one. Further, the increasing current density and corresponding increase in total current results in a decrease in wall potential even though the crevice resistance is decreasing as active front moves towards the mouth. These observations rule out the possibility that the damage profile is the result of a mapping of the active-to-passive transition onto the crevice wall.

Finally, we introduced a geometric shape factor for the volume of solution that exists within the crevice. The shape factor was used to find a finite solution to Fick’s law of diffusion and illustrate that crevice propagation is controlled by mass transport at later times.

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