Stainless steels and other corrosion resistant alloys exhibit strong passivity but are susceptible to localized corrosion in the presence of chloride or other aggressive ions. These alloys are often immune to attack in dilute solutions, but breakdown can occur during atmospheric or alternate immersion conditions by the following scenario. A droplet of salt solution on the surface loses water due to a temperature increase or a decrease in relative humidity (RH). The chloride concentration thereby increases until pitting corrosion initiates, which is accompanied by a sharp drop in the open-circuit potential (OCP).\textsuperscript{3,4}

Tsutsumi et al. exposed stainless steel 304 (SS304) samples to seashore and rural atmospheres.\textsuperscript{5} No pits were found on samples in the rural area, while pitting initiated between 35 and 75% RH in the marine environment. A humidity of 35% corresponds to a saturated magnesium chloride solution, and 75% RH relates to 3 M MgCl\textsubscript{2} (6 M Cl\textsuperscript{-}). According to these results, the chloride concentration for pit initiation under a thin electrolyte layer is around 6 M. This finding agrees with the results of other papers by the same authors.\textsuperscript{6,7} Tsutsumi et al. determined the onset of pitting, which is associated with a critical chloride concentration, from the sudden drop in the OCP of the stainless steel electrode measured vs an Ag/AgCl reference electrode (RE).\textsuperscript{8} The Cl\textsuperscript{-} concentration of the thin electrolyte layer was controlled by varying the RH. The initiation chloride concentration increased with increasing drying rate and with decreasing amount of salt on the surface. The same researchers also studied the influence of electrolyte drop size on the occurrence of the pitting and concluded that pitting is less likely under drops with a small diameter (<5 mm) due to a small cathode area.\textsuperscript{9}

The placement of the RE relative to the sample is complicated for a thin-film electrolyte. Vera Cruz et al. used an agar-filled hole coplanar with the sample surface to provide ionic connection to a remote RE.\textsuperscript{9} This approach suffers from problems associated with nonuniform current distribution for measurements in which the potential is applied.\textsuperscript{9,10} The problem of introducing an RE into the thin water layer responsible for atmospheric corrosion was solved by Stratmann and Streckel who demonstrated that a Kelvin probe (KP) vibrating above a sample provides a measure of the corrosion potential.\textsuperscript{11,12} Some KPs can control the distance between the tip and the sample, allowing simultaneous tracking of the sample topography or measurement of the thickness of an electrolyte layer as it dries.

In this study, the pitting corrosion behavior of SS304 under an electrolyte droplet was investigated using a height-controlled KP. It was thereby possible to determine the pit initiation time from the corrosion potential and the chloride concentration at initiation from the progression of the drop dimensions during drying.

**Experimental**

**Pitting measurements.**—Commercial grade SS304 plates (15 × 15 × 1 mm) embedded in epoxy resin were polished to 4000 grit and rinsed with ethanol. For the KP experiments, a micropipette was used to place a drop of MgCl\textsubscript{2} on the sample. The MgCl\textsubscript{2} solution had a concentration of 0.44 or 2.50 M. Three different volumes of 0.44 M MgCl\textsubscript{2} solution were used: 2, 4, and 6 µL. The KP was first calibrated with Cu/CuSO\textsubscript{4}. The MgCl\textsubscript{2} droplet was then applied to the surface of the sample, which was immediately placed in the KP chamber (21 × 19 × 21 cm). The KP tip was positioned on top of the drop, and the potential was monitored as a function of time. The KP tip was a type 304 stainless steel wire sharpened to a diameter of 189 µm. The air tight chamber door was closed, and the chamber was purged continuously with air of constant RH (33–34%), which was achieved by prebubbling the air through several columns containing saturated MgCl\textsubscript{2} solution. The solution drop on the sample surface with relatively low chloride concentration initially was not in equilibrium with the low RH in the air flowing through the chamber, causing the drop to lose water from evaporation and to decrease in height. The operation principles of the KP instrument (K&M SoftControl, Düsseldorf, Germany) were described previously.\textsuperscript{13} It has the ability to maintain a constant separation between the tip and the solution surface and so can track the drop height as well as the sample corrosion potential as a function of time (Fig. 1). When the MgCl\textsubscript{2} solution in the drop was in equilibrium with the RH in the chamber as indicated by no further change in drop height, the KP was used to map the drop topography to determine the final height and radius of the drop. The experiments were replicated many times (6–33) to develop sufficient statistics to discriminate the results.

For comparison, samples with a surface area of ~72 mm\textsuperscript{2} were also immersed in bulk solutions with concentrations of 2.5, 3.0, 3.5, 4.0, 4.5, or 4.9 (saturated) M MgCl\textsubscript{2} for 22 h.

**Determination of dissolved oxygen in MgCl\textsubscript{2} solutions.**—The oxygen content of different MgCl\textsubscript{2} solutions equilibrated with air was determined by using the dissolved oxygen test kit model O-12 from CHEMetrics. Solutions with a volume of 100 mL and three different MgCl\textsubscript{2} concentrations were prepared: 0.42, 2.5, and 5.7 M. The test kit utilizes a glass ampule with Rhodazine D. Upon breaking the tip while submerged, the solution was sucked in. The Rhodazine D compound reacted with oxygen, leading to a blue coloration. The strength of the blue coloration depended on the oxygen concentration. The oxygen content of deionized (DI) water was measured as well.
Droplet volumes of 2 and 4 μL of 0.44 M MgCl₂ solution were used. Assuming stoichiometric dissolution of Fe, Cr, and Ni and a density of 7.93 g/cm³ of SS304, the current as the derivative of the charge can be calculated from the pit volumes for different pitting times.

### Results

Figure 2 shows a typical OCP transient during drying of a MgCl₂ droplet on an SS304 sample. The potential dropped by tens of millivolts, stabilized, and then exhibited a precipitous decrease. This decrease is considered to be associated with the initiation of pitting.

The form of this potential transient is identical to that observed using other techniques. Every sample exposed in this fashion exhibited a similar potential drop. Furthermore, upon examination of the surface afterwards, every sample contained a single pit that was randomly located relative to the droplet (i.e., pits were found at the center and toward the edge of the drop on different samples). More details on the pits are given below.

Also shown in Fig. 2 is the drop thickness or height change at the center of the drop. At the beginning of exposure, the drop thickness decreased linearly with time due to evaporation of water in the low RH environment. The evaporation rate gradually decreased until the height did not change anymore, at which point the drop was assumed to be in equilibrium with the RH in the chamber. At this point, the shape of the drop was determined by scanning across the entire drop surface with the KP tip. An example of the final drop shape as revealed by the KP scan is shown in Fig. 3.

A graphical software package was used to display the drop shape and to determine the radius (a) and thickness of the drop (h). With these data, the volume \( V \) of the drop as a function of time during drying was calculated from the thickness assuming that the drop resembled a spherical cap and that drop radius \( a \) was constant

\[
V(t) = \frac{1}{6} \pi h(t)[3a^2 + h(t)^2]
\]  

The assumption of constant radius with time was based on visual observation during drying and agrees with a similar study. By knowing the initial volume \( V_i \) and the concentration of the drop \( C_i \) and calculating the volume at time \( t \) \( V(t) \), the chloride concentration at any time can be determined from

\[
C_t = \frac{C_i(V_i/V)}{V}
\]

The chloride concentration at the time of pit initiation was obtained in this fashion using the droplet volume at the time of pit initiation.

Three different drop volumes of 0.44 M MgCl₂ solution (2, 4, and 6 μL) were used to investigate the relation between the drop size and the initiation chloride concentration, as well as pit initiation time. The final drop height exhibited considerable variability, but tended to increase with increasing initial volume. However, the drop area scaled linearly with drop volume. The time for pit initiation was lower for 2 μL drops, and no significant difference was observed for 4 and 6 μL drops (Fig. 4).

The calculated chloride concentration at the time of pit initiation varied from 3.0 to 8.4 M (Fig. 5). Other authors reported a range of 4.9–6.2 M. It is apparent from Fig. 5 that the median initiation concentration decreases with increasing initial drop volume. The probability of pitting at a lower chloride concentration is higher under a large drop than under a small drop.

The final drop height exhibited considerable variability, and there was no relationship between the final drop height and the critical chloride concentration for pitting.

Figure 6 shows a distribution plot of the initiation chloride concentration for pitting of SS304 exposed to droplets with two different initial MgCl₂ concentrations (0.44 and 2.50 M), which equates to initial chloride concentrations of 0.88 and 5.0 M, respectively. For a starting chloride concentration of 0.88 M, pits initiated at concentrations of as low as 3.5 M, and the mean pit initiation concentration was ~6 M. However, for a starting concentration of 5.0 M, the lowest pit initiation concentration was 6.5 M. It seems that the initiation time is influenced strongly by the time needed for the breakdown of the passive film as well as achieving a sufficiently high chloride concentration in the droplet. The wide range of initiation chloride concentrations suggests that there is no single critical chloride concentration for pit initiation.

### Pit morphology

Figure 7 shows scanning electron microscope (SEM) images of pits grown for different amounts of time. There was always only one pit under each droplet, and the pit site was not at a specific location. The drop diameters ranged between 3 and 4
mm depending on the initial volume and were, therefore, approximately 50 times larger than the pit diameters, which were on the order of 70–120 \( \mu \text{m} \).

The pits in Fig. 7 are seen to be almost perfectly circular, particularly for those grown for only a short period. Figure 7a shows a pit that grew for 1.6 min after initiation. In the center of the pit, there was a small hole that was likely the initiation site. Other researchers saw similar features and assumed they were associated with MnS inclusions,\textsuperscript{6,8} which are well-known initiation sites for pitting corrosion on stainless steel.\textsuperscript{15-17} The pits grew uniformly in all directions from the initiating defect resulting in circles. The pits started out as a shallow “V” shape of depth \(-950\) nm after 1.6 min with the defect in the center, as shown in Fig. 8a. They then developed into a “U” shape of depth \(-1500\) nm after 39 min (Fig. 8b). After some time, the pits stopped growing in the lateral direction and then grew in depth but only in a certain area forming an ear-shaped hole, as can be seen in Fig. 7b-d. Further discussion of the ear formation is given below.

The pit volume and active pit area were determined with an atomic force microscope, an optical microscope, and imaging software. Pits were allowed to grow for various times after initiation and then removed from the KP chamber, rinsed, and dried. The charge associated with pit volume was calculated assuming congruent dis-

---

**Figure 3.** Topographic map of a droplet after equilibration with the low RH environment. The units on the axes and color scale bar are in micrometers.

**Figure 4.** Distribution plot of pitting initiation times for the three different initial drop volumes.

**Figure 5.** Distribution plot of initiation chloride concentration for the three different initial drop volumes.
solution of SS304 and is shown in Fig. 9 as a function of growth time. For the determination of the active pit area, it was assumed that the entire circular disk was active at the beginning, and later on, only the ear-shaped region was active, as shown in Fig. 10. The active areas of pits grown for various times under 2 μL droplets are shown in Fig. 11 as a function of growth time. No clear trend can be seen. Similar results were obtained for pits under droplets with a volume of 4 μL.

Discussion

Pitting under droplets.— As shown in Fig. 4, the time needed for pit initiation was lower for 2 μL drops than for 4 and 6 μL drops. The volume and therefore the chloride concentration at every time during the experiment can be calculated by Eq. 1 and 2. Such calculations show that drops with a volume of 2 μL have a steeper increase in chloride concentration than drops of 4 and 6 μL (Fig. 12). As a result of the faster decrease in volume and increase in chloride concentration for the smallest drop size, higher chloride concentrations are reached quicker and pitting initiates earlier. The higher drying rate probably originates from a larger surface area to volume ratio of the 2 μL droplet in comparison to 4 and 6 μL. Assuming the drop resembles a spherical cap, the surface area is given by

\[ S = \pi (a^2 + h^2) \]

where \( a \) is the drop radius and \( h \) is the drop height. The surface to volume ratio thus has an inverse dependence on height. Drops of volume 4 and 6 μL show similar drying rates. The RH at the beginning of the experiments was not well controlled because the chamber door of the KP was open during the insertion of the sample. As a result, around 5 min were required to achieve a constant RH of 33–34%. However, the solution height as a function of time in Fig. 2 does not show a different slope at the beginning and after 5 min. Thus, lack of RH control at the beginning of the experiment did not affect the initial drying rate.
Figure 12 also shows that the final chloride concentration in equilibrium with the environment was \(8\) M. The RH in the chamber was controlled by presaturating the purge air using a series of wash bottles filled with saturated pure \(\text{MgCl}_2\) solution. The concentration of the saturated pure \(\text{MgCl}_2\) solution was calculated to be \(4.9\) M \(\text{MgCl}_2\) or \(9.8\) M \(\text{Cl}^-\) based on the solubility of \(\text{MgCl}_2\) in water \(\text{g} \cdot \text{MgCl}_2/100 \text{ mL water}\) and the measured density of the saturated solution \(\text{g/mL}\). The concentration of a pure \(\text{MgCl}_2\) droplet in equilibrium with the test humidity was measured by placing a \(0.44\) M \(\text{MgCl}_2\) drop on a gold substrate and mapping the steady-state volume with the KP. The chloride concentration for a droplet on Au at equilibrium was \(9.6\) M, which closely agrees with the calculated saturation concentration. The lower concentration of chloride for the droplet on stainless steel indicates that the products of the corrosion process influenced the equilibrium between the concentrated salt solution and the humidity in the environment. It is likely that the critical humidity of the salts in the droplet after the corrosion process was lower than that for the pure \(\text{MgCl}_2\) because, for example, ferrous chloride has a critical RH of \(20\%\). As discussed below, the other salts in the solution might also affect the physical properties of the solution.

Figure 5 shows that the chloride concentration at the time of pit initiation varied from \(3.0\) to \(8.4\) M and that the initiation critical concentration decreased with increasing initial drop volume. The wide range of initiation chloride concentrations suggests that there is no single critical chloride concentration for pit initiation. On the other hand, the increase in chloride concentration associated with
drying was clearly critical to the stability of pits, as shown in an experiment where the RH was increased from 34 to 90% after the potential drop associated with pit initiation was observed, as shown in Fig. 13. The droplet height immediately increased, indicating that the higher humidity caused the droplet to take up water, which resulted in dilution of the dissolved salts. Within ~100 s, the potential started increasing, eventually almost reaching the value observed before pit initiation. This increase in potential indicates that the pit repassivated as a result of the dilution of the droplet solution.

Simple immersion experiments in bulk solutions with different chloride concentrations were performed for comparison with the experiments under thin droplets. No corrosion of any form was observed on the sample immersed in bulk 5.0 M chloride solution (2.5 M MgCl₂). For samples immersed in bulk solutions with 6.0 and 7.0 M chloride concentration, crevice corrosion was observed at one site along the epoxy mount edge. The samples immersed in 8.0, 9.0, and 9.8 (saturated) M chloride solutions exhibited pitting and not crevice corrosion. These concentrations are in the same range as the critical chloride concentrations observed for pitting in the thin droplet. However, direct comparison of the two environments is complicated. A drying droplet is very dynamic in that the chloride and oxygen concentrations and the viscosity are changing until saturation occurs. During the bulk experiments, these parameters remain constant. Figure 6 shows that, by just increasing the initial chloride concentration of an electrolyte drop, the pitting initiation concentration distribution increased to higher values.

The effect of droplet size shown in Fig. 4 can partly be explained by the fact that a drop of larger radius has a higher probability of covering an area that includes a more susceptible defect, such as an MnS inclusion, so pitting has a higher chance of initiation at a lower chloride concentration. No direct evidence linking MnS inclusions to pit initiation sites was found. For instance, energy-dispersive spectroscopy (EDS) analysis in an SEM found no evidence of surface contamination by S. However, the amount of S associated with a single inclusion is likely too small to be observed by EDS. The distribution of susceptible sites was studied using a sample that was polished to 0.05 μm and then etched in 10% FeCl₃. Figure 14 is an optical micrograph of an area after etching. The dark spots are as-
sumed to be MnS inclusions that were dissolved in the FeCl$_3$ solution. The field of view in these images is approximately equal to the size of the pits formed in the concentrated MgCl$_2$ solution, showing that there are many MnS inclusions available in the area of a droplet to act as initiation sites. The pit initiates at the most susceptible site, and the rest of the area is, apparently, cathodically protected from attack.

Another issue to consider is the effect of the droplet size on the available cathodic current. Tsutsumi et al. suggested that there is a decreased likelihood of pitting under small drops because the smaller exposed area supports a less cathodic current.$^6$ Stable pit growth at open circuit requires sufficient cathodic reaction to meet the anodic current demand, which typically increases with time as a pit increases in size even though the rate of growth decreases.$^{21,22}$ For this near neutral chloride solution, the dominant cathodic reaction is oxygen reduction. Therefore, continued pit growth requires a sufficient supply of oxygen to support the anodic current needed to sustain the concentrated local environment necessary for pit stability. Assuming that the oxygen reduction reaction is diffusion limited, the available cathodic current is given by

$$I_{\text{cath}} = \frac{nFDC_{\text{ox}}}{\delta \pi a^2}$$

where $n = 4$ is the number of electrons in the oxygen reduction reaction, $F$ is the Faraday constant, $D$ is the O$_2$ diffusion coefficient, $C_{\text{ox}}$ is oxygen concentration, $a$ is the radius of the area covered by the droplet, and $\delta$ is the diffusion layer thickness for O$_2$ in the droplet.

The concentration of oxygen in the electrolyte decreases drastically with time during exposure to the low humidity atmosphere because of a decrease in solubility associated with the increase in magnesium chloride content. Figure 15 shows the oxygen concentration as a function of chloride concentration for MgCl$_2$ solutions from the literature$^{23}$ and also from the dissolved oxygen test kit.

The oxygen diffusivity can be determined from the Stokes–Einstein equation, which indicates that the diffusion coefficient varies with the inverse of the viscosity.$^{24}$ The viscosity of MgCl$_2$ solutions increases with increasing MgCl$_2$ concentration,$^{25}$ as shown in Fig. 16. Knowing the diffusivity of oxygen in pure water (2.2
times. The anodic current demand for growing pits can be calculated from the derivative of the charge vs time curves. For droplet volumes of 2 or 4 μL, the current demand of pits growing at the OCP decrease with time according to these fitted equations

\[
2 \, \mu L: I = 7.18 \times 10^{-7} t^{-0.336} \tag{5}
\]

\[
4 \, \mu L: I = 5.97 \times 10^{-7} t^{-0.320} \tag{6}
\]

This decrease in pit current with time is in contrast to other papers of increasing pit current with time.\textsuperscript{28-30} The pits in this study grew at the OCP under a thin electrolyte layer, whereas the other involved anodic polarization in bulk solution\textsuperscript{28,29} or exposure to a bulk solution containing oxidizing agents.\textsuperscript{30} Pits in stainless steel formed at high potentials in bulk solution tend to grow deeply into the metal, whereas the pits in the droplet with high chloride concentration were extremely shallow. This geometrical effect controlled the pit current as discussed presently.

To compare the anodic current demands (Eq. 5 and 6) with the available cathodic current, it is necessary to assume a pit initiation time. The available cathodic current starts decreasing immediately upon exposure to the low humidity environment as drying occurs, but the anodic demand only commences with pit initiation. Therefore, the anodic currents in Fig. 18 were offset in time by amounts equal to the mean values of the pitting initiation time for 2 and 4 μL droplets shown in Fig. 4, 748 and 1400 s, respectively. Also shown in Fig. 18 are the available cathodic currents from the low current region of Fig. 17. The available cathodic current decreases quickly and then levels off and remains constant. The current demand for a growing pit is smaller than the available cathodic current, which is a requirement for pit stability. This agrees with the observation that repassivation was never observed for any experiment unless the RH was increased as described above. However, the suggestion that pits do not initiate under very small drops due to insufficient cathodic current\textsuperscript{6} cannot be explained by this calculation.

The fact that only one pit is always formed under each droplet area, but not the entire sample surface in bulk electrolyte. However, the progression of pit morphology described below indicates that cathodic limitation eventually occurred in the small droplets. The
calculated available cathodic current is assumed to be an overestimation because of the values used for oxygen concentration and diffusivity.

It is of interest to determine the anodic current density, which can be calculated using the active pit areas shown in Fig. 11. The anodic current density for pits under droplets of an initial volume of 2 μL is shown in Fig. 19. The results for the 4 μL droplet were very similar. At short pitting times, the anodic current densities varied over a wide range. However, for pitting durations longer than ~160 min, the current density was almost constant at ~6 × 10^{-4} A/cm². This value is quite small compared to other reported pit current densities for stainless steels. Szklarska-Smialowska and Janik-Czachor obtained pit current densities between 1 and 2.5 A/cm² for a Fe-16Cr alloy in a 0.7 N NaCl + 0.7 N Na₂SO₄ solution. Frankel et al. calculated stable pit current densities between 2 and 4 A/cm² for SS302 in different bulk electrolytes. Pistorius and Burstein reported current densities between 1 and 6 μI for stainless steels. Szklarska-Smialowska and Janik-Czachor obtained pit current densities between 1 and 8 A/cm² in a 6% NaCl solution. However, all of these results were obtained with pits grown under anodic potential control, not at the OCP, and applied potential can have a large effect on pit current density.

Knowing the anodic current density, it is possible to calculate the pit stability product \( i d \), where \( i \) is the current density and \( d \) is the pit depth or radius. Pistorius and Burstein found that the critical value of \( i d \) for a pit to grow and not repassivate was between 0.3 and 0.6 A/m for SS304. Frankel et al. calculated a critical \( i d \) value of 0.4 A/m. The necessary pit current density to maintain pit stability is large for a small pit and decreases as the pit grows. Assuming this value of pit stability product is applicable to the pits under droplets observed in this study, the expected pit radius associated with the calculated current density \( (6 \times 10^{-4} \text{ A/cm}^2) \) is ~5 cm, which is orders of magnitude larger than the size of the pits. Clearly, the stability criterion for the pits in this study is much different than for potentiostatically controlled pits at higher potentials in bulk dilute chloride electrolytes. Using a pit radius of ~50 μm for the pits under droplets (Fig. 7) and a current density of \( 6 \times 10^{-4} \text{ A/cm}^2 \), the \( i d \) value is 3 × 10^{-6} A/cm, which is 3 orders of magnitude lower than the values reported previously.

Galvele modeled the transport of ions in a 1D pit geometry. He found a critical value of \( i x \) (\( i \) is 1D pit depth) for pH change inside the pit, which was related to pit stability. The calculated values of \( i x \) for Fe, Ni, and Cr were on the order of 10^{-6} A/cm, which is close to the values determined in this study. However, Galvele calculated the conditions to achieve a metal ion concentration in equilibrium with the metal oxide and arbitrarily used the value of 10^{-6} mol/L. Today, the ion concentration in a stable pit is known to be considerably higher, namely in the molar region. The low \( i d \) value determined in this study results from the lower current density required to stabilize pitting in the concentrated MgCl₂ droplet solution, which ends up being similar to that required to achieve a relatively low ion concentration in pits grown in a dilute bulk electrolyte as calculated by Galvele.

Pit growth progression under droplets.— The SEM pictures in Fig. 7 show pits that were grown for different amounts of time. The pits that were only propagated for a short time have a disk-shape appearance with a small hole at the center. Other researchers saw a similar defect and suggested it to be a MnS inclusion, which is a well-known initiation site for pitting corrosion on stainless steel. From the defect, the pits grew uniformly in all directions resulting in circular shapes. Eklund calculated a potential pH diagram of reactions between H₂O, Cl⁻, and MnS. According to this, MnS is not thermodynamically stable at an initial OCP between 400 and 300 mV vs standard hydrogen electrode (Fig. 2) and neutral pH. The predominant species are Mn²⁺ and SO₄²⁻. Due to an increase in pH during the formation of these two species, H₂S and elemental sulfur can be formed. Hydrogen sulfide was reported to shorten the time to the breakdown of the passive film and to decrease the pitting potential on SS304 in chloride solution. The dissolution of MnS leads to sulfur precipitation on the alloy surface adjacent to the inclusion. This adsorbed layer increases the dissolution of the metal due to a decrease in metal/metal bond strength and impedes repassivation. These observations can be used to explain the circular shape of the pit. Activating S-containing species as well as H⁺ are transported radially in the thin electrolyte layer, which has a high Cl⁻ concentration. Consequently, a circular area around the initial defect is activated and the active area grows radially and downward slowly at a constant current density. This growth continues until reaching a critical condition. When the current demand exceeds the available cathodic current, the active pit area must decrease to maintain current density on the order of \( 6 \times 10^{-4} \text{ A/cm}^2 \). The decrease in the anodic area is accomplished by partial repassivation and the formation of an active “ear” where the current is focused. Figure 7b-d shows the ear formation for pits grown for different times. Figure 11 reflects this behavior in a slight decrease in the active area with increasing pitting time. Careful observation of a series of pits indicated that a depression inside the disk started forming between 90 and 100 min after the initiation of pitting under 2 μL droplets.
and between 130 and 140 min under 4 μL drops. Thus, critical conditions are reached earlier under smaller drops than under larger ones.

Conclusions

In this study, the pitting corrosion behavior of SS304 under an evaporating electrolyte droplet was investigated with a KP. The effect of the drop size and concentration on the pit initiation time and initiation chloride concentration was determined. The following was found:

1. Pits initiated sooner under small droplets than under large drops because of a faster evaporation rate and a steeper increase in the chloride concentration during drying.

2. The initiation chloride concentration was between 3.0 and 8.4 M for droplets with a starting concentration of 0.88 M Cl\(^-\). The pitting initiation concentration was higher for drops with a higher starting concentration.

3. The probability of pitting at a lower chloride concentration was higher under a large drop than under a small drop, possibly because of the larger electrolyte-covered area and higher chloride concentration.

4. Available cathodic current decreases with time. Required anodic current is less than the calculated cathodic current. However, several observations indicate cathodic limited pit growth.

5. Pit stability criterion (id) is much lower than for potentiostatically controlled pits in dilute bulk chloride solutions.

Appendix

Support by the Science & Technology Program of the Office of the Chief Scientist (OCS), Office of Civilian Radioactive Waste Management (OCRWM), U.S. Department of Energy (DOE) is gratefully acknowledged. The work was performed under the Corrosion and Materials Performance Cooperative, DOE cooperative agreement no. DE-FC28-04RW12252.

The Ohio State University assisted in meeting the publication costs of this article.

The droplet area is given by

\[ A = \pi R^2 \]

where \( R \) is the radius of the droplet.

The second term on the right side of Eq. A-9 was determined by numerical integration to result in the total available cathodic current shown in Fig. 16.

\[ I = \frac{c}{200 \mu m} \pi \delta^2 + \int_{r_1}^{\infty} \frac{2\pi x}{\sqrt{R^2 - x^2} + (h-R)} dx + \frac{c}{10 \mu m} \pi \delta^2 \]

which can be differentiated for later integration

\[ dI = 2\pi dx \]

The droplet area is given by

\[ I_{10-200} = \frac{c}{\delta(x)} \int_{r_1}^{\infty} \frac{2\pi x}{\sqrt{R^2 - x^2} + (h-R)} dx + \frac{c}{10 \mu m} \pi \delta^2 \]

References