Atmospheric Pitting Corrosion Studies of AA7075-T6 under Electrolyte Droplets: Part I. Effects of Droplet Size, Concentration, Composition, and Sample Aging

M. S. Thomson and G. S. Frankel∗,†
Fontana Corrosion Center, The Ohio State University, Columbus, Ohio 43210, USA

Pitting corrosion of AA7075-T6 was investigated in situ by Scanning Kelvin Probe (SKP) under droplets containing MgCl₂ or NaCl. The corroded samples were analyzed by optical microscopy and optical profilometry. The SKP results indicated that single regions of sustained pitting attack formed with preference at the edge of the droplets due to the evaporation of the MgCl₂ droplets. The pits at the sustained attack sites formed anodes with supporting cathodic reactions at the surrounding sample surface. As the pits grew, the cathodic region was observed to expand, leading to elevated potentials measured at the center of the droplets. Droplets with greater initial volume formed larger areas of contact with the sample surface and accelerated corrosion attack. Overall, sustained pitting attack was observed along groups of particles at the surface and oriented along the rolling direction. In many cases, pitting led to the formation of a secondary droplet at the periphery of the primary droplet. A mechanism is proposed for the pitting behavior of AA7075-T6 under the studied electrolyte droplets, as well as a new mechanism for the formation of secondary droplets.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.1051712jes] All rights reserved.

Because of its high strength to weight ratio, AA7075-T6 is an important material of construction in the aerospace industry but it is susceptible to various forms of localized corrosion attack, including pitting, intergranular corrosion, and crevice corrosion. Understanding this susceptibility is critical, particularly in atmospheric conditions typical of aerospace service environments. In atmospheric corrosion, sustained levels of relative humidity (RH) are required to maintain the electrolyte layer, but fluctuations of the humidity also play an important role in the chemistry of the thin layer. A droplet of salt solution on the surface of an aluminum alloy sample may not have the necessary Cl⁻ concentration to initiate attack, but at a low enough RH, the droplet will undergo evaporation resulting in an increase of salt concentration until the activities of water in the droplet and the water in air are in equilibrium. The elevation of Cl⁻ concentration could then be sufficient to promote breakdown of the passive layer and subsequently promote pitting attack.

The combination of high RH and atmospheric salts make marine environments ideal for atmospheric pitting corrosion by this mechanism. AA7075-T6 samples tested in coastal atmospheres suffered much greater loss of mechanical properties than those exposed to industrial or industrial-coastal atmospheres. In exposure tests performed in northern and eastern Australia, pitting attack was found to be the primary form of corrosion for 7075-T6 samples, with the most aggressive corrosion taking place at coastal sites. Coastal regions have been shown to deposit both MgCl₂ and NaCl on metallic sample surfaces. At relative humidity values equal to or greater than the critical RH values of these salts (35% RH for MgCl₂ and 75% RH for NaCl), liquid salt solutions can form on a sample surface. It is also important to note that, although the deposition rate of salts decreases with distance from the shore, it can remain elevated for a considerable distance from the shore. Chloride deposition rates as high as 10% of those observed at the shore were found as far as 52 km from the ocean.

Accelerated lab testing is not always successful in recreating behaviors that may be found in atmospheric corrosion, so it is necessary to develop new test methods. The Scanning Kelvin Probe (SKP) has been shown to be a promising technique for the study of corrosion behavior beneath thin electrolyte layers or droplets. The SKP provides a non-contact measure of corrosion potential beneath an electrolyte droplet in situ. This is an important capability when dealing with thin electrolyte layers, as the immersion of a probe in the electrolyte to measure potential can interfere with the corrosion behavior. Small electrolyte droplets provide a situation that is not identical to atmospheric corrosion conditions, but is similar enough to allow examination of the relevant phenomena. It can be assumed that small droplets reach a steady state that is in equilibrium with the controlled atmospheric conditions in the chamber.

Utilizing the SKP, Maier and Frankel were able to study the pit initiation behavior on SS304 under droplets of varying initial volume and electrolyte concentration by monitoring the shape of and potential beneath the center of the droplets. Morton and Frankel used the same approach to study the pitting behavior of AA7075-T6 under NaCl droplets containing inhibitors. They found the formation of secondary droplets at the periphery of the initial droplets, under which accelerated corrosion attack took place by the large-scale separation of the anode beneath the secondary droplet and the cathode beneath the primary droplet. A mechanism was proposed for the creation of the secondary droplets. The diffusion of ions away from edge pits is restricted, leading to a local acidic environment caused by cation hydrolysis. The local acidity promotes stabilization of pitting attack in the area. The high concentration of ions generated by this pitting attack promotes deliquescent in the region, forming the secondary droplet. Secondary droplet formation was associated with a large jump in the potential observed at the droplet center, caused by the proposed large-scale cathode/anode separation. However, scans of the SKP probe tip across the droplet and secondary droplet at the end of the tests did not exhibit this same drastic potential increase, and this was attributed to evaporation of the droplet caused by a drop in humidity from opening the chamber to adjust the sample position for the scan.

The phenomenon and mechanism of secondary droplet formation are further investigated on AA7075-T6 in the present study, including the influence of initial droplet parameters such as volume, electrolyte, and electrolyte concentration.

Experimental

Samples used in these experiments were composed of rolled plate AA7075-T651 produced to meet ASTM B211, obtained with 6 mm thickness and cut into squares of 3 cm × 3 cm. The samples were abraded to 800 grit SiC paper in ethanol. The altered surface layer formed during abrasion was removed by etching the samples in 1 M NaOH solution at 60 °C for 45 s, followed by pickling in 70% HNO₃ for 10 s and finally rinsing with ethanol, which has been shown to be sufficient for removal of the layer. After etching, the samples were stored in a desiccator until use, typically for 3–7 days. Prior to testing, they were rinsed with ethanol and deionized water, and then dried with filtered, pressurized air.
Figure 1. Potential profiles for MgCl₂ droplet tests recorded with SKP for droplets with initial volumes of 3, 6 and 9 μL, and initial MgCl₂ concentrations of 0.1 M (top left), 0.25 M (top right), 0.5 M (bottom left) and 1 M (bottom right).

The SKP utilized in these experiments was a product of Wicinski-Wicinski GbR (Dusseldorf, Germany). The stainless steel 304L probe tip was 200 μm in diameter. Air was pre-bubbled through saturated KCl solution and flowed continuously into the SKP chamber to obtain an RH of 85%, as measured by a meter in the chamber. Before each experiment, the SKP tip was calibrated using a copper cup filled with saturated CuSO₄ solution, which is known to have a potential of 320 mV SCE. A 2 megapixel USB digital microscope inside the chamber was used for collecting images of samples once per min.

Electrolyte droplets were produced from solutions containing either MgCl₂ in concentrations of 0.1, 0.25, 0.5 and 1 M, or NaCl in concentrations of 0.25 M, 0.6 M (3.5% by weight), and 1 M. A droplet was deposited on a sample, which was then placed on the stage in the pre-humidified SKP chamber. Droplets of 3, 6 and 9 μL were tested for each solution composition, and every condition was repeated a minimum of four times. The stage and head were maneuvered to bring the probe tip above the center of the droplet. Measurement of the height and potential at that point was then initiated, recording both at 1 Hz for 20 h. During the tests, the distance between the probe tip and the droplet surface remained fixed, allowing for change of the droplet height with time to be determined. After 20 h, a line scan was performed across the diameter of the droplet, as well as across other areas of interest when necessary. The images of the droplet recorded with the digital microscope provided a time lapse of the droplet behavior.

After measurements in the SKP were completed, the samples were rinsed with DI water and ethanol, and the corrosion product was removed by immersion for 1 minute in a solution of 1.5 L DI water, 150 mL H₃PO₄, and 30 g CrO₃ at 80°C. Samples were then immersed in ethanol and placed in an ultrasonic bath for several min to remove any caps over pits. Images were recorded under an optical microscope after both stages of cleaning. Samples were then analyzed using a Contour GT-K1 optical profilometer to measure pit dimensions. It should be noted that any undercut would not be sensed by this line-of-sight technique.

Tests were performed to investigate the influence of time spent in the desiccator after active surface layer removal. These samples were prepared in the same manner described previously, but they were either used immediately after etching, or after aging in the desiccator for 1–6 days. Tests were repeated at least four times for samples at each aging time. A droplet of 9 μL 3.5% NaCl was placed on the sample, which was then placed in the SKP chamber at 85% RH for 20 h. Droplets were chosen to be 9 μL to make changes in wetting diameter as large as possible. Samples were then tested in the same manner described in the previous section, cleaned and imaged by optical microscope, and analyzed by optical profilometer.

Results

SKP point measurements.—Potential values were recorded by the SKP during the point measurement tests and representative results are displayed as profiles in Figures 1 and 2 for MgCl₂ and NaCl droplets, respectively. During the initial stages of all tests, the droplets partially evaporated in the 85% RH air, leading to increased concentration of electrolyte and initiation of pitting. This evaporation period, typically lasting between 1–5 h depending on the initial droplet volume and concentration, was consistently associated with a rapid decrease in its height.
Figure 2. Potential profiles for NaCl droplet tests recorded with SKP for droplets with initial volumes of 3, 6 and 9 μL, and initial NaCl concentrations of 0.25 M (top left), 3.5 wt% (top right) and 1 M (bottom).
Figure 3. Representative example of secondary droplet formation found under 6 μL droplet of 3.5 wt% NaCl. a) Pit initiation observed after 2 hours. b) Pit growth at 6 hours. c) Secondary droplet initiation at 12 hours. d) Secondary droplet growth after 20 hours. The scale of these images as well as the other images of droplets in this paper taken by the digital microscope can be assessed by the probe diameter, which is 200 μm.

Line scans.—After the point measurement experiments were completed, the SKP was then utilized to perform a line-scan across the center of the droplet starting on the bare sample surface and making sure to scan the entire diameter of the droplet. During the line-scans, the height and potential were recorded at 10 μm intervals, providing height and potential profiles across the droplet. The droplet heights for different conditions of concentration, volume and salt cation are shown in Figure 4. As expected, droplets with higher initial salt concentration exhibited greater equilibrium droplet thicknesses. Variation in observed droplet heights for droplets of the same starting conditions could be attributed to random differences in droplet diameter.

The droplets were effectively spherical caps and the droplet profiles had the shape of a circular arc. Examples of these line scans obtained for droplets with initial concentration of 0.1 M MgCl₂ and varying initial volume are provided in Figure 5. Assuming a perfect spherical cap, the arc radius could be calculated from the width and height of the droplet. From the calculated arc radius, a perfect arc of the appropriate height and width could be simulated and compared to the observed profile of the droplet height measured by the SKP, permitting the assumption that the droplets behave as spherical caps to be verified. An example of this is shown in Figure 6. The assumption was found consistently to be true for droplets except in a few cases where the buildup of product resulted in the formation of bulges that distorted the droplet. It appeared that the bulges were formed by a collection of hydrogen bubbles extending higher than the rest of the droplet, such as in the height profile in Figure 7. In experiments where this occurred, the bulge was much higher than the expected droplet thickness, and the remainder of the droplet was found to be thinner than was observed for other droplets of the same test conditions, suggesting that more solution was allocated to these regions. Because the droplets behaved as spherical caps in nearly all tests, their volumes could be calculated using Eq. 1.

\[
Volume = \frac{\pi H}{6} \left(3a^2 + H^2\right)
\]

where a is the radius of the base of the cap and H is the height of the cap. When calculating the volume, the droplet diameter measured was reduced by 200 μm to compensate for the diameter of the probe tip. As the probe tip approached the droplet edge during line scans, the height of the probe was not at the height of the bare metal surface until it was completely beyond the edge of the droplet. Because the probe had a diameter of 200 μm, this was not the case until the center of the probe tip was 100 μm away from the actual droplet edge. This occurred at both points that the probe was passing the droplet edge, so the measured droplet diameter was 200 μm greater than the actual droplet diameter.

With the volume calculated, and the known initial chloride content, the chloride concentrations could be determined as well by dividing the initial chloride content by the calculated droplet volume. From the height data gathered during the point measurements, and assuming the droplet radius remained constant, the chloride concentration of the droplet could be determined through the duration of the experiment. Typical chloride concentration profiles during evaporation and approaching equilibrium are shown in Figure 8. In Figures 8a and 8c, the concentrations of the droplets are shown for 0.5 M MgCl₂ and 3.5 wt% NaCl, respectively, for each initial droplet volume. For droplets containing NaCl, the equilibrium concentration of chloride fell between 3.6 M and 4.2 M, and for MgCl₂ it was found in the range of 3.5–4.5 M. For droplets with the highest starting chloride concentration, the equilibrium chloride concentration was found to be higher. This can be seen in Figures 8b and 8d, which show Cl⁻...
Droplet height profiles obtained by line scans for 0.1 M droplets of MgCl$_2$ at initial volumes of 3, 6 and 9 μL. The axes are scaled differently so as to allow the droplet height to be clearly observed.

Concentration profiles for MgCl$_2$ and NaCl respectively, with starting volumes of 9 μL and each concentration tested. It is possible that the corrosion products that developed increased the volume of the droplets, perhaps by possessing a lower critical RH for deliquescence and absorbing more water from the atmosphere. This would have the most noticeable effect on droplets with the lowest starting concentrations, as they would also have the lowest equilibrium volume, so assuming similar amounts of corrosion product in the first hours of all of the tests would mean a greater addition of volume relative to the equilibrium volume. Also evident in Figures 8a and 8c, the concentration increased faster for smaller droplets, and also reached equilibrium sooner. This was observed for all droplet conditions, and was likely a result of the relationship between the surface area and volume of the droplets. The rate of evaporation of a water droplet on a glass surface was found to be constant with time, but dependent on a, the radius of the base of the spherical cap.17 Droplets of smaller initial volume have smaller a, leading to the accelerated increase in concentration of smaller droplets. Also, for droplets of the same starting volume, those with higher MgCl$_2$ concentration reached equilibrium concentration fastest, Figure 8b. For 6 and 9 μL droplets of NaCl, however, equilibrium was found to be achieved fastest for droplets with lower starting salt concentration, Figure 8d. It is not clear what causes this discrepancy, but it could be related to the factor causing the much greater equilibrium chloride concentrations in droplets of MgCl$_2$ with greater starting salt concentrations.

The chamber of the SKP was not opened prior to the line-scans performed after the point measurements to avoid altering the droplet by evaporation. Line scans were restricted to movement along the x-axis direction, however, so in addition to scans over the center of the droplets, scans were also performed at different regions on the droplets if necessary to ensure that regions of pitting and product buildup were inspected. Due to technical issues with the SKP, scans were not possible in some instances when the change in droplet height was too steep, as this would cause the probe tip to come into contact with the droplet surface, rendering further measurements inaccurate.

The potential beneath the droplet was steady across regions where no obvious product buildup was observed and elevated outside of the droplet on the bare surface, as shown in Figure 9. However, for a variety of corrosion product and droplet formations, the potential profiles exhibited different fluctuations related to the location of the pit and product buildup. In previous work,13 the formation of secondary
Figure 8. Chloride concentration profiles of droplets derived from the known starting chloride content and the volume calculated from the diameter and observed droplet height. a) Droplets with initial MgCl\textsubscript{2} concentration of 0.5 M. b) Droplets with initial volume of 9 \textmu L and varied MgCl\textsubscript{2} concentration. c) Droplets with initial NaCl concentration of 3.5 wt\%. d) Droplets with initial volume of 9 \textmu L and varied NaCl concentration.

droplets was shown to be associated with large-scale separation of the anode in the secondary droplet and the supporting cathodic region observed under the adjoining primary droplet. Such behavior was again observed in this study. Figure 10 shows the line scan measurement of a 9 \textmu L droplet of 0.25 M MgCl\textsubscript{2}. Figure 10a shows the direction of the line scan, beginning on the bare surface and progressing across the secondary droplet and the primary droplet. The secondary droplet was found to overlap considerably with the primary droplet. In Figure 10b, it can be seen that the potential beneath the primary droplet far from the secondary droplet remained similar to what would be expected in regions without corrosion product as was shown in Figure 9. However, a lower potential associated with the pit was observed beneath the secondary droplet, and the potential was elevated beneath the primary droplet near the secondary droplet, showing the location of the primary cathode. This was also observed in previous studies.\textsuperscript{13} Similar behaviors were also found when sustained pitting occurred under the primary droplet without the formation of a secondary droplet, as seen in Figure 11, showing the results from a 6 \textmu L droplet of 0.1 M MgCl\textsubscript{2}. Again, the region of pitting was found to have a lower potential relative to the bulk, and the immediate surrounding region in the droplet was at an elevated potential. The region of bare surface just outside of the droplet near the pit was also at a potential elevated relative to what is expected. Farther away from the pitting region, the potential returned to values expected in regions without pitting. This scan exhibited the same 50–60 mV difference between the pitting region and the immediate surrounding area as was seen in cases of secondary droplets. Such behavior contradicts the previously reported results that suggested a larger potential difference was observed in cases of secondary droplet formation.\textsuperscript{13}

Figure 9. Potential profile obtained by SKP line scan across droplet of 0.1 M MgCl\textsubscript{2} with initial volume of 9 \textmu L after 20 hour test in SKP chamber.
To observe the development of the regions of potential differences during point measurements, line scans were performed at intervals of five hours during point measurement tests performed under the same conditions as presented, with a 6 μL droplet of 3.5 wt% NaCl. Figure 12 shows that a pit formed near the far edge of the droplet, and repeated line scans were performed over this region. Between line scans, the probe was returned to the center of the droplet, and measurement of the potential at that point continued. Results of this test are given in Figure 13. In Figure 13a, the potential at the center of the droplet is reported. The intervals during which line scans were performed can be observed as breaks in the profile. The accompanying potential profiles obtained from the line scans are shown in Figure 13b. In the initial line scan, performed 5 h after the start of the test, the potential profile was similar to that shown in Figure 9, consistent with the lack of an observed pitting region. In the following potential profiles, recorded at 10, 15 and 20 h into the experiment, a region of elevated potential formed and grew laterally, extending beneath the center of the droplet where the probe was located. The extension of the elevated potential region beneath the probe was consistent with the increase of potential observed in the point measurements. This suggests that the fluctuations in potential observed during the other point measurements performed in this study were a result of growth and changes in the shape of the cathodic region surrounding the pitting regions. The failure to observe a lowered potential during the interval line scans suggests that the anodic pit was not below the SKP probe tip as it scanned across the surface.

Optical microscopy and profilometry.—After measurements were completed in the SKP, samples were cleaned and observed by optical microscopy and optical profilometry. A typical pattern was observed on the surface beneath the droplet for all conditions, and examples of representative behavior are shown for NaCl and MgCl₂ droplets in Figure 14. As shown in Figure 14a, regions of sustained pitting attack were observed in 3.5 wt% NaCl, with buildup of corrosion product directly on top of and in the immediate vicinity of the pit.
Breaks during line scans

Figure 13. On top, the potential profile against time measured by SKP at the center of the droplet shown in Figure 11. On bottom, potential profiles recorded during line scans by SKP performed after 5, 10, 15 and 20 hours.

identified as region “1” in the image. This pitting product was in several cases also observed to be present in the shape of a dome. Beyond this region of corrosion product, an area of clean sample surface was found surrounding the pitting region (region “2”) with a ring of corrosion product buildup along its perimeter. Beyond that, the remainder of the area beneath the droplet was covered in a dark corrosion product (region “3”). The same regions formed for droplets of MgCl$_2$, Figure 14b; however, the product in region “3” for these tests was much lighter in color and the product buildup at the edge of the clean region “2” was less noticeable. Across the droplet area, small pits were observed, typically less than 5 $\mu$m in depth. The small pits were observed to initiate at intermetallic particles, found dispersed in the rolling direction. Regions of sustained pitting appeared to be a series of pits aligned in the rolling direction. However, upon placing the samples in an ultrasonic bath for several minutes, corrosion product and material covering the pits were removed, revealing that the pits were connected. This agglomeration of pits was always observed to have grown laterally in the rolling direction. When the sustained pit was oriented such that the nearest droplet edge was parallel to the rolling direction, the pit agglomeration extended parallel to the droplet edge. However, when the pit initiated in a region where the rolling direction was perpendicular to the nearest edge, lateral growth of the pit would extend toward the droplet edge. A schematic displaying these pit orientations is presented in Figure 15. The perpendicular orientation, case ‘a’ in Figure 15, was found in all tests that developed secondary droplets, with the laterally growing pit extending beneath the secondary droplet region.

Analysis with the optical profilometer allowed for the areas of sustained pitting attack to be characterized. In Figures 16 and 17, the volume and maximum depth of the large pit agglomeration are presented for all droplet experiment conditions for NaCl and MgCl$_2$, respectively. Considerable scatter was observed for both salts, which might result from inaccuracies in measurement associated with undercut of the surface as mentioned above. Nonetheless, there was a trend of increased pit depth and pit volume with increased initial droplet volume. This may have been caused by an increase in the available area for cathodic reaction, while the area of the anodic pits stayed roughly the same. It is also possible that, because the droplets of larger volume covered a greater area of the sample, they were more likely to cover regions susceptible to more aggressive pitting attack. Considering droplets of the same volume but different starting salt concentration, there is no clear trend regarding the pitting depth and pitting volume. In other words, it does not appear that initial droplet concentration had any clear, direct relation to the severity of pitting attack. It seems likely that a combination of factors, such as equilibrium height of the droplet, area of contact, and concentration of chloride ions, interacted to influence the variations in pitting attack observed between the various droplet conditions.

Aging tests.—For all samples prepared for the droplet tests conducted in this study, samples were etched after polishing to remove

![Image](https://example.com/image.png)

**Figure 14.** Optical microscope images of representative examples of behavior under droplets in SKP tests. a) Droplet of 3.5 wt% NaCl with initial volume 6 $\mu$L. b) Droplet of 0.5 M MgCl$_2$ with initial volume 6 $\mu$L. Regions consistently observed are identified in both images.

![Image](https://example.com/image.png)

**Figure 15.** Schematic of the surface under a droplet with rolling direction (and subsequently lateral pit growth direction) identified. a) Sustained pitting growing laterally toward droplet edge. b) Sustained pitting growing laterally parallel to droplet edge.
the active surface layer,\textsuperscript{18} and then placed in a desiccator until use. During droplet tests in the SKP, droplets of the same initial conditions were found to have different diameters, possibly from variability inherent in the droplet application process, but also possibly a result of differing surface conditions. One possible condition variable could be the aging of the oxide layer as the sample sat in the desiccator for increasing times. To investigate the influence, if any, of time spent in the desiccator before use on the behavior observed in testing, experiments were conducted on samples at different amounts of time after etching. The initial droplets were 9 μL and 1 M NaCl.

The observed diameters of the droplets, recorded from line scans performed by the SKP, and the total pitting volumes of the sustained pits and maximum pit depths are given in Figure 18. Droplets tested immediately after etching showed greater wetting of the sample surface, resulting in droplets spreading to a larger diameter. This effect decreased with time after etching, leveling out at three days and beyond, Figure 18a. This same trend was found for the volume of pitting attack, which also leveled out after three days, Figure 18b. Although it exhibited more scatter, the maximum pit depth also decreased with increasing time after etching, Figure 18c. The depth of pits appears to be sensitive to the aging process due to the decreased droplet area with increased aging time, however this relationship does not appear to be as strong as that found between pitting volume and aging time. These results show that increased aging after etching influences the droplet diameter, especially immediately after etching. However it is still unclear if it is the less mature oxide layer in these early tests that makes the sample susceptible to more aggressive pitting attack, or if it is simply a product of the droplet diameter being greater. The increased droplet diameter is probably the more influential factor.

**Discussion**

The monitoring of the corrosion of 7075-T6 under electrolyte droplets by SKP conducted in this study has shown many behaviors consistent with previously reported results. However, some key differences are evident. SKP line scans across the surface of droplets have shown that anodic pitting regions form near the edge of the droplets, and that the pits are surrounded by supporting cathodic regions. This behavior is similar to that described by Evans drop experiments on iron,\textsuperscript{19} but for Al the anode is not limited to the center of the droplet.
because of the role of the microstructure in pit initiation. Morton and Frankel monitored the potential at the center of droplets of 3.5 wt% NaCl on AA7075-T6 and observed large jumps (as large as 500 mV) in some cases corresponding to the formation of secondary droplets.  

When line scans after the point measurements were completed, less drastic potential profiles were observed, often exhibiting a potential change less than 100 mV. The smaller potential change was attributed to evaporation of the droplet caused by a humidity drop during opening of the chamber to adjust the sample position before performing the line scans. In this study, however, no such large potential jumps were observed during point measurements under any conditions. On the other hand, similar potential profiles were observed from line scans performed without opening the SKP chamber. This suggests that there was a difference somewhere in the acquisition of the potential data.

It is important to consider the resolution of the potential that is achievable by the SKP. The Volta potential measured by the SKP between the probe and the electrolyte surface is directly proportional to the corrosion potential. It is assumed that the Volta potential observed is essentially a reflection of the potential at the interface of the metal and solution. In the present study, it is not clear how large an area under the droplet is sensed by the probe. It is possible that, if the signal is weak enough, the observed potential could be an average produced from the potential over a large area. Preliminary investigations using probe tips with smaller diameters appeared to collect stray signal from surrounding areas. This was particularly an issue when the probe tip was located near the edge of a droplet where signal gathered from the side of the probe influenced the recorded potential. The SKP used in this study is the same used by Morton et al. It also underwent repairs during this investigation due to an insufficient signal, and later encountered a malfunction again that weakened the signal. It is possible that degradation of the SKP signal caused the probe to collect signal from a larger area. This could lead to an observed potential produced from the average of a larger area and could also explain the failure to observe the spikes in potential previously observed.

Although not large, changes in the observed potential during point measurements were observed, as shown in Figures 1 and 2. By supplementing the point measurements with interval line scans, Figure 13, these potential changes were found to take place during expansion of the pitting region, most visibly the agglomeration of H2 bubbles, beneath the SKP probe tip. This, in combination with the observed growth of the cathodic region during interval line scans presented in Figure 1, is suggested to be the cause of the elevations in potential observed in many of the point measurement experiments. The lateral resolution described in the previous paragraph could also influence this potential change, by blurring the boundary of the cathodic region and increasing the observed potential before the cathodic region actually extends beneath the probe. Optical analysis of the pits after testing showed that they underwent lateral growth along the rolling direction, shown schematically in Figure 15. This lateral expansion could cause propagation toward the center of the droplet, resulting in the observed growth of the cathodic region in that direction as it pushed out ahead of the anodic pit. The area of cathodic reaction may have also increased as a result of the increased size of the anodic pitting area, and expansion toward the center of the droplet promoted due to the limit posed by the droplet edge.

Conclusions

The pitting behavior of AA7075-T6 has been investigated by application of electrolyte droplets under varying initial conditions and analysis by Scanning Kelvin Probe measurement, optical microscopy and profilometry. Studies of the influence of droplet volume, salt cation, and initial concentration were performed, as well as the influence of the etching procedure on droplet behavior. The following conclusions can be made.

1. Regarding the initial droplet conditions, the area of the droplet/sample interface had the greatest influence on corrosion behavior. Increasing the area led to increasing pitting attack, likely because areas more susceptible to accelerated attack are more likely to be covered by a larger droplet.
2. Higher initial salt concentration in droplets of the same initial volume, which resulted in greater droplet thickness at a given RH, did not have a direct relationship with the severity of attack. It seems likely that additional variable conditions played a role, possibly in combination with droplet thickness, to influence the severity of corrosion attack. These factors, however, were not identified.

3. Aging time after etching to remove the active surface layer was shown to affect the wetting of the sample surface, changing droplet diameters and corrosion behavior. This should be carefully monitored in future studies to ensure consistent conditions.

4. Sustained attack initiated at a cluster of secondary particles at the surface and propagation followed an anodically favorable pathway oriented in the rolling direction.

5. Differences in the magnitude of potential fluctuations observed here and in a previous study were attributed to operational issues with the SKP that could have influenced the potential resolution of the instrument. It is possible that the potentials measured by the SKP in the current study were an average of potentials collected over a larger area.

Acknowledgments

This work was supported by Office of the Secretary of Defense Technical Corrosion Collaboration through the United States Air Force Academy under award FA7000-12-2-0015.

References

1. J. E. Hatch, *Aluminum: properties and physical metallurgy*, ASM International, Metals Park, OH (1984).
2. Q. Meng and G. S. Frankel, *J. Electrochem. Soc.*, 151, B271 (2004).
3. R. P. V. Cruz, A. Nishikata, and T. Tsuru, *Corrosion Science*, 40, 125 (1998).
4. D. A. Jones, *Principles and prevention of corrosion*, Prentice Hall, Upper Saddle River, NJ (1996).
5. S. Hu, S. Sun, A. Guo, X. Jia, and Y. Geng, *Corrosion*, 67 (2011).
6. B. S. Smith, E. J. Duxbury, and B. T. Moore, “Atmospheric Corrosivity of Defence Bases in Northern and Eastern Australia”, DSTO Aeronautical and Maritime Research Laboratory, Melbourne, Australia, 1997.
7. Y. Tsutsumi, A. Nishikata, and T. Tsuru, *Journal of the Electrochemical Society*, 153, B278 (2006).
8. J. R. Duncan and J. A. Ballance, in *Degradation of Metals in the Atmosphere*, STP965, S. W. Dean and T. S. Lee, eds., ASTM International, West Conshohocken, PA, (1988).
9. C. Legraf and T. E. Graedel, *Atmospheric Corrosion*, Wiley-Interscience, New York, NY (2000).
10. G. S. Frankel, M. Stratmann, M. Rohwerder, A. Michalik, B. Maier, J. Dora, and M. Wicinski, *Corros. Sci.*, 49, 2021 (2007).
11. J. F. Li, B. Maier, and G. S. Frankel, *Corrosion Science*, 53, 2142 (2011).
12. B. Maier and G. S. Frankel, *J. Electrochem. Soc.*, 157, C302 (2010).
13. S. C. Morton and G. S. Frankel, *Materials and Corrosion-Werkstoffe Und Korrosion*, 65, 351 (2014).
14. in *Annual Book of ASTM Standards*, Vol. 2.02, ASTM, Philadelphia, PA, (2000).
15. Z. Zhao and G. S. Frankel, *Corr. Sci.*, 49, 3064 (2007).
16. C. Vargel, *Corrosion of Aluminium*, Elsevier, Amsterdam (2004).
17. K. S. Birdi, D. T. Vu, and A. Winter, *Journal of Physical Chemistry*, 93, 3702 (1989).
18. Z. Zhao and G. S. Frankel, *CS Corrosion Science*, 49, 3064 (2007).
19. U. R. Evans, *An introduction to metallic corrosion*, E. Arnold; American Society for Metals, London; Metals Park, Ohio (1982).
20. M. Stratmann and H. Streckel, *Corrosion Science*, 30, 681 (1990).