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An Investigation of the Formation of Crack-Like Intergranular Fissures in 7000 Series Aluminum by Grain Boundary Galvanic Corrosion

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ABSTRACT

The present study builds upon the work of Maitra and English, and postulates that anodic polarization of a galvanic couple falling between two breakdown potentials could cause significant intergranular corrosion but minimal general pitting of the matrix of 7000 series aluminum alloy. The crack-like intergranular fissures, visually similar to stress corrosion cracking (SCC) or intergranular cracking (IGC), would be difficult to detect and independent of applied or residual stress. Component failure initiating from the fissures could be incorrectly identified as SCC. SCC mitigation by the introduction of surface compressive residual stresses would be ineffective against a failure mechanism indifferent to applied or residual stress fields.

In this study, the Maitra-English grain boundary attack mechanism was observed in potentiodynamic testing of a proprietary 7000 series aluminum alloy, producing both crack-like fissures along grain boundaries and more general pitting. Galvanic couple testing of the shot peened aluminum alloy and a more noble Al-bronze material exposed to the vapor phase of 3.5 wt% NaCl solution was also performed. In only 20 days, crack-like attack along grain boundaries developed and grew through the compressive layer, where it could then propagate as a fatigue crack to failure under in-service operating stresses.

Galvanic corrosion driven grain boundary attack is shown to be a possible cause of material failure in the absence of SCC conditions. The presence of residual compression is shown not to impede the galvanic grain boundary attack mechanism.

Key words: Galvanic Corrosion, Intergranular Cracking (IGC), Stress Corrosion Cracking (SCC), 7075 Aluminum, 7000 Series Aluminum Alloy

INTRODUCTION

The susceptibility of 7000 series aluminum alloys to stress corrosion cracking (SCC) is well known to be affected by the aging treatment, microstructural, and galvanic state conditions. The conventional peak aged T6 condition is considered to be more vulnerable to intergranular attack than the overaged T7 condition.[1] Although no sustained SCC has been documented in the form of da/dt vs ΔK plots for 7000 series alloys, observed intergranular attack has been initially characterized as SCC. Localized intergranular corrosion (IGC) attack has been reported in AA7075 alloy[2] and attributed to anodic polarization behavior. Similarly, sharp crack-like IGC fissures were reported in AA7178 alloy.[3] Similar selective IGC attack has been reported in these and numerous other studies of 7000 series aluminum alloys. In all of these studies, the overaged T7 temper condition was found to be more resistant to sharp IGC attack than the peak aged T6 condition.

In the 1981 paper titled "Mechanism of Localized Corrosion of 7075 Alloy Plate," authors Maitra and English document a phenomenon of localized corrosion along grain boundaries of various tempers of 7075 aluminum. By studying the anodic polarization behavior, the authors were able to demonstrate distinct breakdown potentials attributable to local variations in the microstructure around grain boundaries resulting from heat treatment and aging. The authors concluded that, among the two breakdown potentials observed in the potentiodynamic polarization scan of 7075-T651, the more active breakdown potential corresponds to preferential corrosion attack of the grain boundary region, while the more noble breakdown potential infers general corrosion attack and pitting of the matrix.

The goal of this report is to document the potentiodynamic polarization response of various heat treatments of a proprietary 7000 series aluminum alloy as well as the effects of galvanically induced anodic polarization. The formation of very fine crack-like fissures along grain boundaries is attributed to galvanic corrosion effects between the 7000 series alloy and a more noble Al-bronze material. The crack-like grain boundary fissures are observed even in the presence of a deep surface layer of compressive residual stress with no externally applied tensile stress.

EXPERIMENTAL PROCEDURE

Material and Sampling

All aluminum test samples were cut from a single forged section of a shot peened 7000 series aluminum component. The material had been previously manufactured with a T6 heat treat before shot peening, but enough time, as is suspected in this case, can naturally age the material to a T7 condition. A cross section, perpendicular to the shot peened surface and etched to show the forging flow, is shown in Figure 1. The flow pattern of the grains resulting from the forging and other processing of the material is evident in this figure. Of particular significance is the directionality of the elongated grains slightly declined away from the surface. As shown later in this report, all of the fine crack-like IGC fissures observed for various test conditions were also found to be oriented in the same direction as these elongated grain boundaries.

Three heat treat conditions of the 7000 series aluminum were studied and are defined as: "as-received" (assumed naturally aged T7), "re-heat treat" (T6), and "re-heat treat + artificial age" (T7). The re-heat treat condition was solution treated to 900 °F (482 °C) for 60 minutes then water quenched. This was followed by a T6 heat treatment of 250 °F (121 °C) for 24 hours with an air cool. The re-heat treat + artificial age condition was re-heat treated as just described, then exposed for 30 hours at 325 °F (163 °C) to achieve a T7 condition.

Figure 1: Etched cross section of forged material showing grain orientation and flow near the shot peened surface

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Electrochemical Testing

Samples were prepared and tested per guidelines established in ASTM G61[4] and ASTM G5.[5] Experimental setup and technique was validated per ASTM G5.

Potentiodynamic polarization testing was conducted in a 3.5 wt% sodium chloride (NaCl) electrolyte solution with ASTM D1193 type IV purified water at a temperature of 25 ±1 °C. Testing was performed using a Gamry Interface 1010B potentiostat along with an Avesta style polarization cell specially designed to minimize crevice effects when testing flat samples. The tested region was a circular patch of area 0.59 in^2 (380 mm^2). Platinum was used as a counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode (RE). The RE was separated from the bulk solution via a Luggin probe and salt bridge connection. After immersion, samples were allowed to rest in solution for 1 hour with a nitrogen gas (N_2) purge prior to initiating the polarization scan. A scan rate of 0.6 V/hr was used for all potentiodynamic tests.

Potentiostatic polarization testing was performed in the manner described above, but instead of a dynamic scan, the potential was held constant at a fixed value for a predetermined time duration.

Galvanic Exposure

Galvanic exposure testing was designed to simulate a condition in which an aluminum component not properly electrically isolated from a more noble Al-bronze component is exposed to a salt water environment. To preclude the possibility of SCC, no external stress was applied.

Four shot peened 7000 aluminum sections in the as-received condition and four sections of Al-bronze material were cut for galvanic exposure testing. The aluminum samples had nominal shot peened surface dimensions of 4.5 x 0.9 in. (114 x 23 mm). The Al-bronze sample surface areas, while not measured, were estimated to be more than double that of the exposed shot peened areas of the aluminum. The aluminum surfaces were tested in the as-received condition – no additional heat treat or aging processes were performed.

All edges of the aluminum sections except the shot peened surface were electrically isolated from the corrosion environment with a stop-off coating. The aluminum sections were then mated with their corresponding Al-bronze sections and secured with insulated binding wire. No external loads were applied to the samples.

Each of the four galvanic couple samples were suspended in the vapor phase above a 3.5 wt% NaCl electrolyte solution maintained at 90 °F (32 °C) in individual Erlenmeyer flasks. The solution in each flask was aerated, and evaporation was contained through the use of glass condenser tubes. An additional shot peened section sample, electrically isolated with stop-of coating as described above, but without the addition of an Al-bronze galvanic couple, was also exposed to provide a control in order to characterize the galvanic influence.

A galvanic couple sample was removed for inspection and imaging after exposure of 20, 40, 80, and 100 days. At each inspection interval, the aluminum samples were cross sectioned to expose the plane shown previously in Figure 1. Samples were then mounted and polished for metallographic imaging in a Phenom XL scanning electron microscope. The uncoupled control sample underwent inspection at 20 days.

Residual Stress

Residual stress measurements were made by the x-ray diffraction technique in accordance with SAE HS-784,[6] on the as-received shot peened aluminum surface to characterize the residual stresses resulting from the shot peening process. Measurements were made in a 0 and 90 degree direction as a function of depth from the surface to a maximum depth of 0.1 in. (2.5 mm).

Material was removed electrolytically for subsurface measurement in order to minimize possible alteration of the subsurface residual stress distribution as a result of material removal. All data obtained as a function of depth were corrected for the effects of the penetration of the radiation employed for residual stress measurement into the subsurface stress gradient.[7] Corrections for sectioning stress relaxation and for stress relaxation caused by layer removal[8] are applied as appropriate.

RESULTS

Electrochemical Testing

The polarization response curves are plotted graphically in accordance with ASTM G3.[9] Figure 2 shows the anodic polarization response of the 7000 series material in the three heat treat conditions previously described. Of particular note are the two distinct breakdown potentials evident in each curve; the first between -0.84 V and -0.82 V, and the second between -0.80 V and -0.78 V.

Maitra and English showed how different metallurgical phases present after various heat treatments of 7075 aluminum alloy have corresponding and unique breakdown potentials. The authors concluded that the more active breakdown potential corresponds to attack of the grain boundary region, while the more noble breakdown potential corresponds to pitting of the matrix. At potentials between these two breakdown potentials, intergranular attack is the primary driver of corrosion damage.

The presence of the first breakdown potential is consistent with intergranular attack along the grain boundaries that produces an extremely narrow crack-like fissure following the grain boundaries in the AA7075-T6 material examined by Maitra and English. The local grain boundary attack is attributed to precipitate formation at the grain boundaries that depletes the matrix of alloying elements otherwise preventing corrosion.

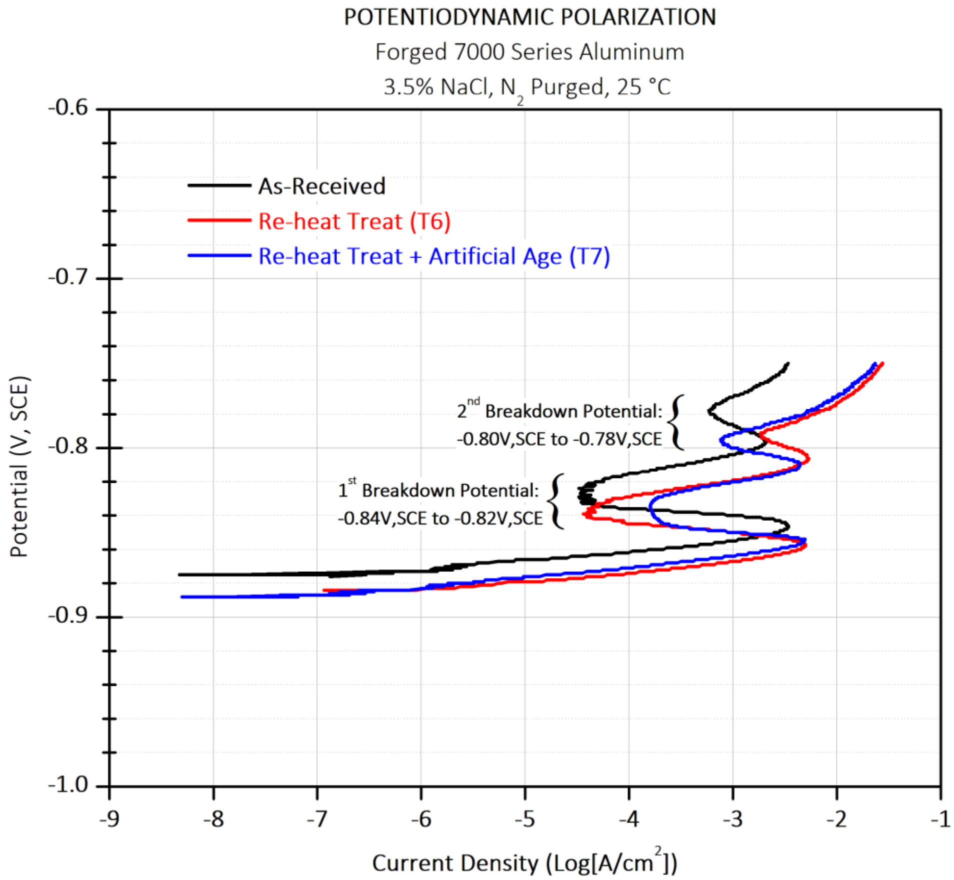

Figure 2: Potentiodynamic polarization results of a proprietary 7000 series aluminum alloy in three different heat treat conditions

In order to investigate the corrosion susceptibility of the anodically polarized 7000 series alloy in the naturally aged T7 (as-received) and T6 (re-heat treat) conditions, samples of each were prepared and tested in the same manner described in the polarization technique section except, instead of a dynamic potential scan, the samples were held at a fixed potential of -0.75 V (SCE) for 24 hours. SEM images in Figure 3 show that the intergranular attack of the re-heat treat T6 condition is significantly more severe than that of the as-received naturally aged T7 condition.

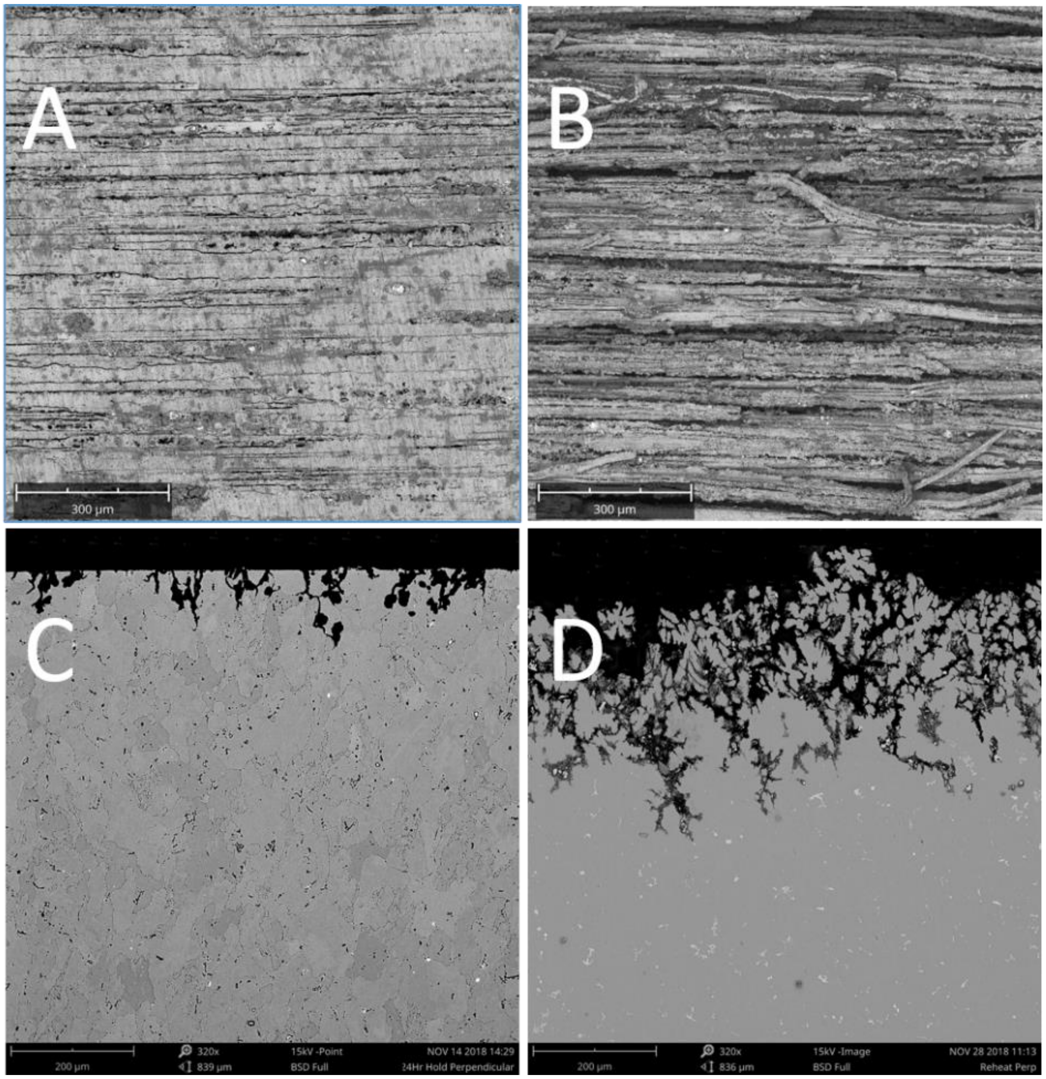

Figure 3: SEM images of 24 hour potentiostatic hold at -0.75V, SCE;
A: as-received (T7) surface, B: re-heat treat (T6) surface, C: as-received (T7) cross section, D: re-heat treat (T6) cross section

Anodic polarization of a metal can occur as a result of galvanic coupling. In a galvanic couple, current flow drives a reduction reaction and an oxidation reaction at the cathode and anode, respectively. Potentials of the electrodes shift toward a shared mixed potential somewhere between their respective uncoupled corrosion potentials. By overlaying the polarization curves of two metals measured individually, this mixed potential (and galvanic corrosion current) can be approximated by the intersection of the anodic curve of the active metal with the cathodic curve of the more noble metal.[10]

Figure 4 depicts an example of mixed potential theory applied to the 7000 series and Al-bronze materials (with a shift representing a hypothetical surface area ratio as discussed later). By overlaying the individual polarization response curves measured on each material, the mixed potential can be determined by the intersection of the cathodic portion of the Al-bronze curve with the anodic portion of the aluminum curve.

Galvanic corrosion, and the magnitude of its effect, is dependent on the surface area ratio of the cathode and anode in contact with the corrosive electrolyte. Because of this, a general mixed potential analysis intended to indicate the nature of the potential shift must involve polarization curves plotted with total current as opposed to current density. A change in anode to cathode surface area ratio will shift the relative positions of the polarization curves and change the intersection point, and thus provides an indication of the magnitude of the galvanic effect. In situations in which galvanic corrosion is a concern, mitigation is often attempted through the use of electrical isolation coatings or anodization layers. If this barrier layer is damaged in any way, the anode to cathode area ratio will likely be very small, which would greatly amplify the local galvanic effect and accelerate attack of the anodic regions on the less-noble material surface. Figure 4 illustrates this with a hypothetical surface area ratio of 1 to 90.

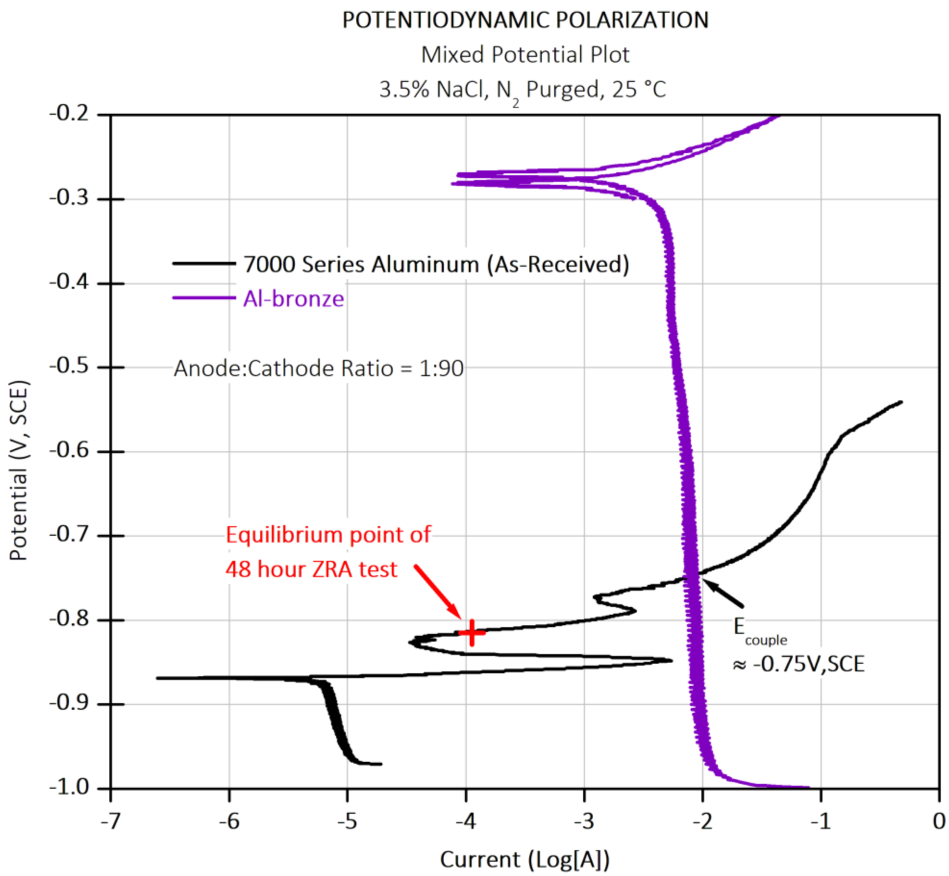

Figure 4: Mixed potential theory applied to polarization curves of a 7000 series alloy and Al-bronze

Mixed Potential Theory shows that, when electrically connected in a galvanic couple, the 7000 series material will be anodically polarized to a potential E_{couple} while the Al-bronze material will also be polarized to E_{couple} but in the cathodic direction. This shift will cathodically protect the Al-bronze from corrosion while accelerating the corrosion response of the aluminum.

The galvanic effect of the two alloy couple was directly measured using the Gamry potentiostat configured as a zero resistance ammeter (ZRA) to monitor the mixed potential and current when exposed to the 3.5 wt% NaCl electrolyte for 48 hours. The test samples were configured for a relatively small anode to cathode surface area ratio. The average equilibrium point is plotted in Figure 4 in relation to the polarization curve of the aluminum. As can be seen, the measured open circuit mixed potential and corrosion current point falls along the polarization curve in the active region between the first and second breakdown potentials. This provides empirical evidence that a galvanic couple of the 7000 series aluminum and Al-bronze in a 3.5 wt% NaCl environment can anodically polarize the aluminum alloy to a state favorable for intergranular corrosion attack.

A cross sectional SEM evaluation of this ZRA galvanic couple sample pictured in Figure 5 shows significant corrosion damage and crack-like fissures along grain boundaries.

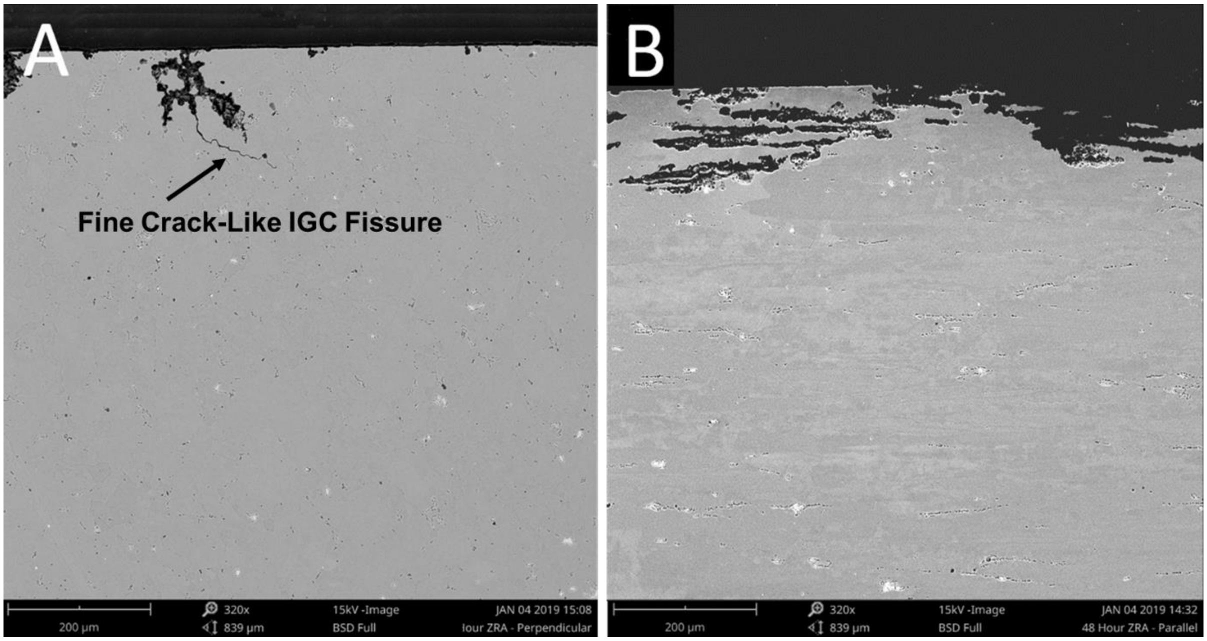

**Figure 5: SEM images of 48 hour ZRA-monitored galvanic exposure sample;
A: perpendicular to grain orientation, evidence of crack-like fissures,
B: parallel to grain orientation**

Galvanic Exposure

As described earlier, galvanic exposure test samples were removed from the exposure and evaluated at 20, 40, 80, and 100 days.

Figures 6 and 7 are SEM images of cross sections of the 20 and 40 day galvanic exposure samples. The images show significant intergranular corrosion starting from the first 20 day examination, with increasing prevalence of fine crack-like fissures at the 40 day duration. Additional samples tested for extended durations of 80 and 100 days and evaluated in the same manner showed significantly more gross corrosion with minimal advancement of the crack-like fissures deeper below the surface. Those images are not reported.

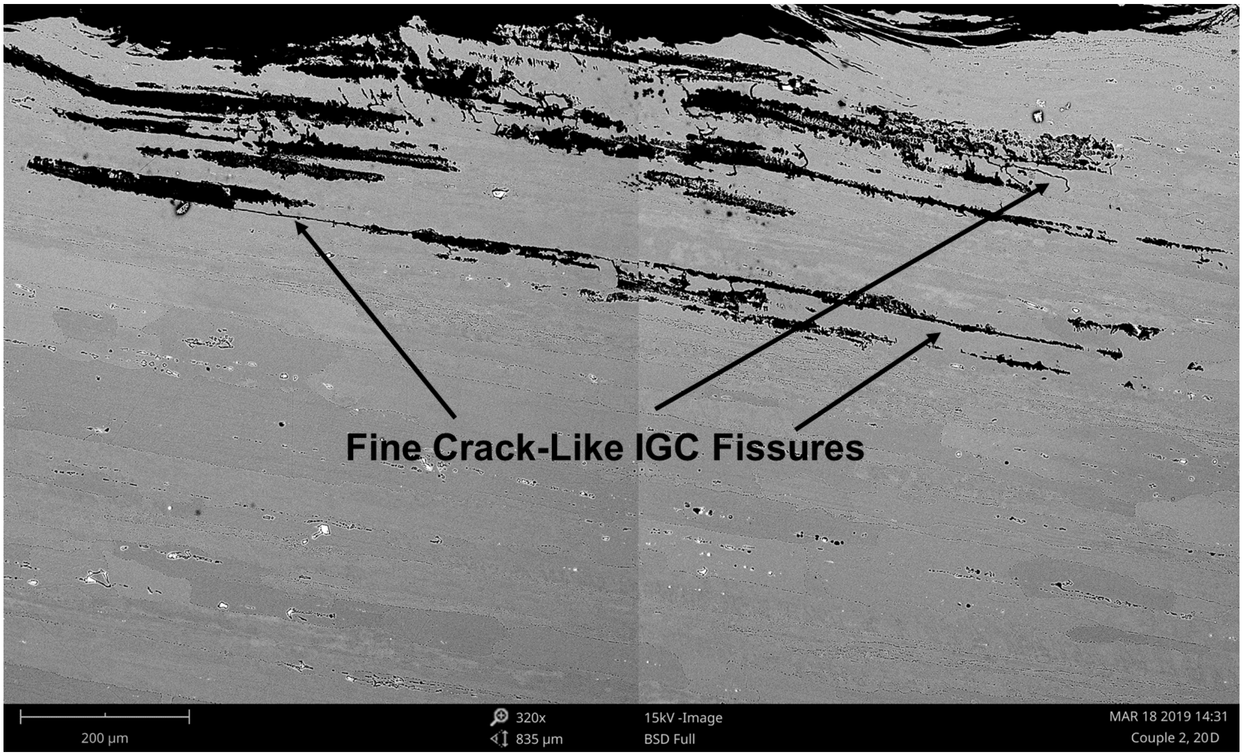

Figure 6: 20 day galvanic exposure showing significant intergranular fissures from corrosion damage

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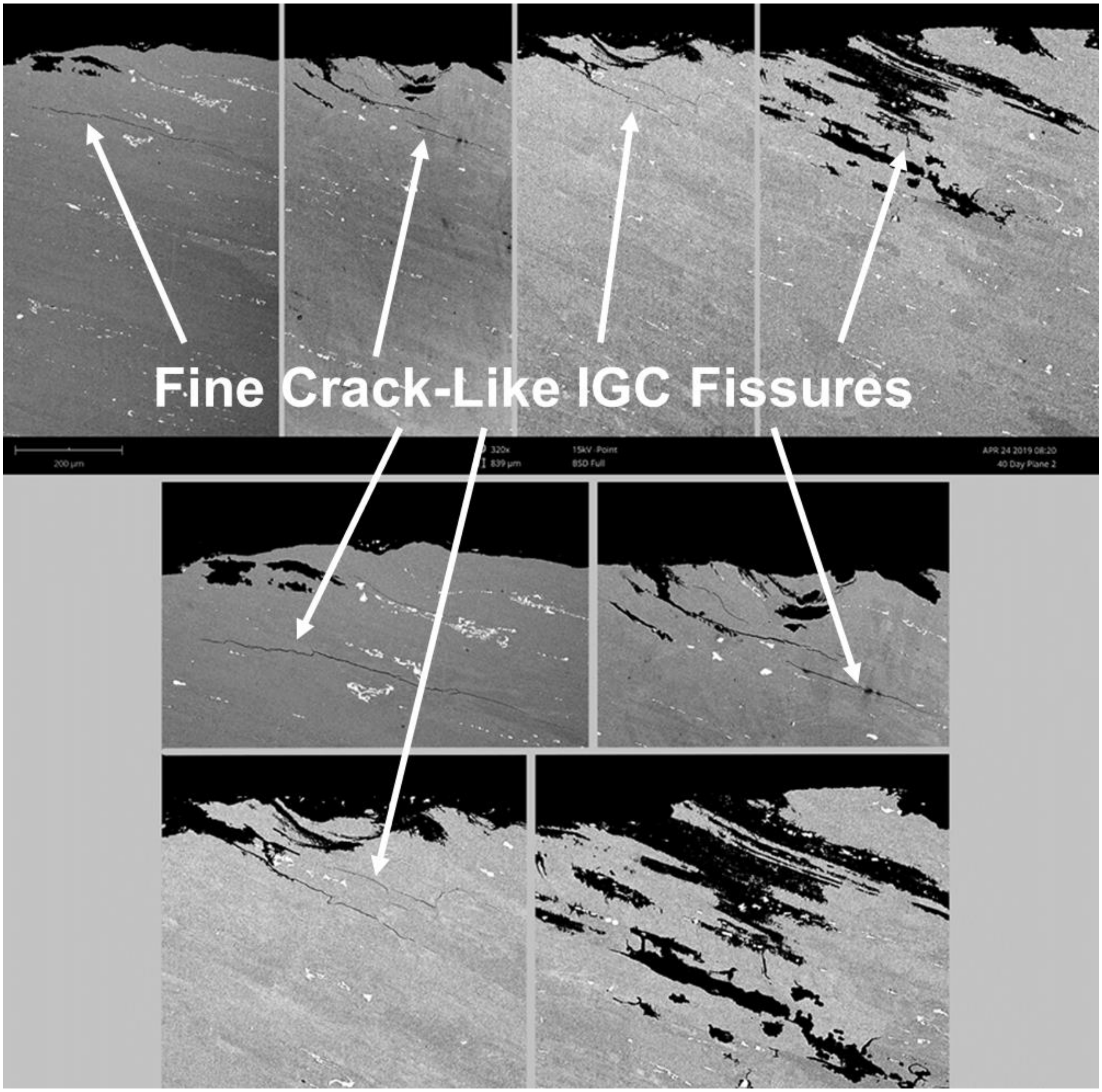

Figure 7: 40 day galvanic exposure showing intergranular corrosion damage and crack-like fissures (top), enlarged detail of each image (bottom)

SEM composite images are shown in Figure 8 comparing the 20 day exposure sample with an as-received (no galvanic corrosion exposure) section. This figure confirms the absence of corrosion damage on the surface prior to the galvanic exposure testing.

Of primary importance, the grain boundary corrosion, similar in appearance as SCC but are not actually cracks, occurred in a surface that was in high residual compression from the previously applied shot peening (see Figure 10 in the following residual stress section), and in the absence of any applied tensile stress. The results confirm a mechanism for a crack-like failure formation in a surface under high residual compression where SCC cannot occur.

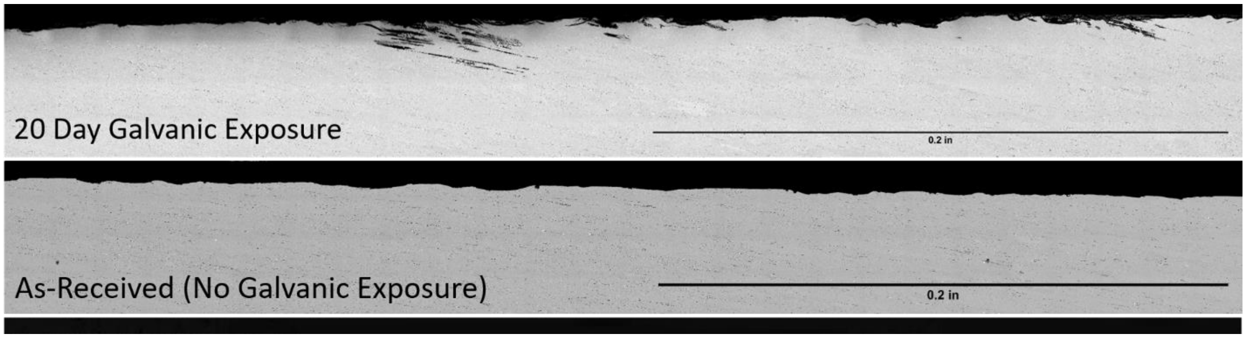

Figure 8: Composite SEM images showing SCC-like damage from galvanic exposure

Further evidence that the observed intergranular attack is galvanically driven is shown in Figure 9; a cross section SEM image of an as-received shot peened 7000 series sample exposed for 20 days to the same test environment as the galvanic couple samples. This aluminum sample taken from the same lot of material used for the galvanic exposure tests, was not galvanically coupled to a corresponding Al-bronze section, and exhibited no signs of subsurface corrosion damage. The galvanic couple to the Al-bronze material was necessary to create the grain boundary attack.

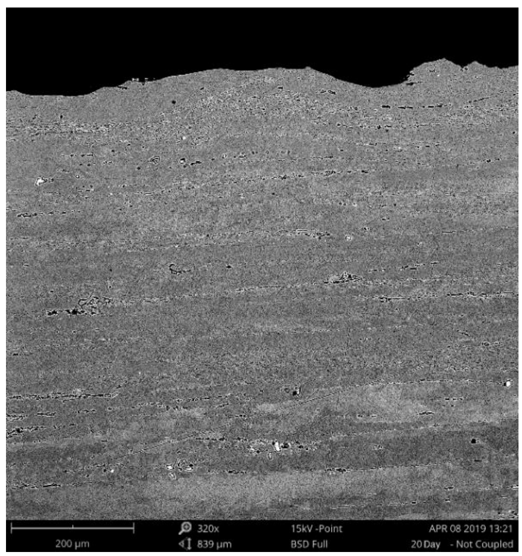

Figure 9: 20 day exposure with no galvanic couple showing no corrosion damage

Residual Stress

The subsurface residual stress distributions measured on the shot peened aluminum surface are shown graphically in Figure 10. Compressive stresses are shown as negative values, tensile as positive, in units of ksi (10^3 psi) and MPa (10^6 N/m^2). The results are typical of a shot peen process with peak compression below the surface. The material is in compression from the surface down to a depth of nominally 0.040 inches. Maximum compression is roughly -65 ksi, which is on the order of the yield strength of the material. The 0 and 90 degree residual stress distributions are comparable through the compressive layer, indicating uniform compression.

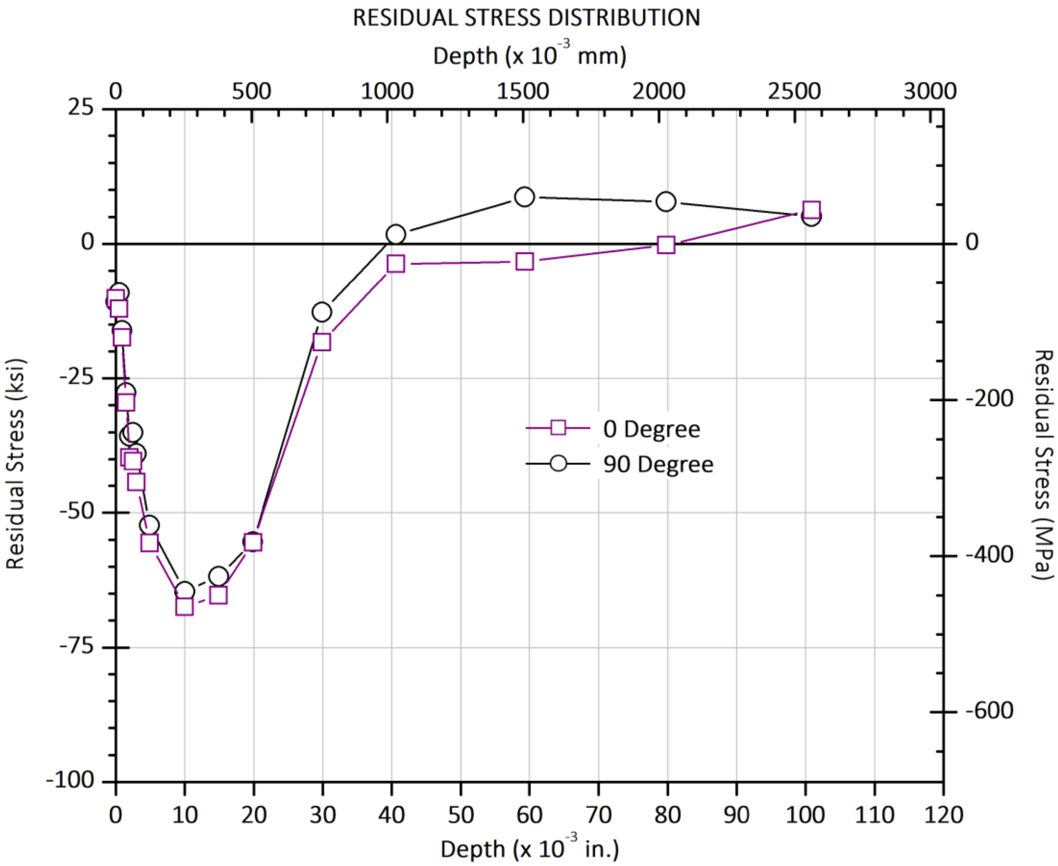

Figure 10: Residual stress depth profile of the shot peened aluminum surface

CONCLUSIONS

Anodic polarization driven intergranular corrosion, as described by Maitra and English in AA7075-T6, was produced in a separate proprietary 7000 series aluminum alloy in laboratory controlled DC electrochemical testing, producing crack-like fissures following grain boundaries. Galvanic coupling between the aluminum alloy and a more noble Al-bronze alloy caused similar damage with only 20 days of exposure to salt water vapor. It was shown that galvanic grain boundary corrosion of this 7000 series aluminum can manifest as crack-like fissures visually similar to SCC but in the presence of a highly compressive surface layer.

This investigation reveals that residual compression does not inhibit the galvanic grain boundary attack mechanism for this aluminum alloy. This investigation demonstrates that proper identification of the failure mechanism is crucial when determining proper mitigation methods.

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