LOCALIZED CHEMICAL ENVIRONMENTS AND THE IMPLICATIONS ON FATIGUE IN AIRCRAFT STRUCTURES

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ABSTRACT

It has been long known that the environmental composition can have a controlling influence on the rate of fatigue crack propagation, but only recently have the effects of physically occluded geometries been considered. The importance of the degree of physical separation of the anodic and cathodic reactions is highlighted as the determining factor in whether the pH within occluded regions becomes acidic or alkaline. Isolated occluded regions, such as those found in wetted aircraft lap joints or other aerospace structures, will contain mildly alkaline solutions, independent of the bulk solution to which they are exposed. This alkaline solution will, in turn, lead to an increase in the open circuit potential of the surface as the passive film thickens and the passive current density decreases. Experimental verification of these effects in both 2XXX and 7XXX series aluminum alloys is presented and the possible effects on damage evolution due to the combined effects of corrosion and fatigue discussed.

1. INTRODUCTION

The environment at the surface controls the nature and the rate of the corrosion processes on metallic materials. For aerospace applications, the environment can range from fully gaseous to one in which the material is fully immersed in an aqueous solution at temperatures ranging from well below 0 ˚C to above 100 ˚C. Although characterization of the nominal environmental conditions to which a structure is exposed can be achieved, spatially localized environments can be far more damaging and are far more difficult to probe. In practice, such local environments develop at physically occluded regions such as joints, within fastener holes, or under delaminated coatings. Their composition can be vastly different from the environment that the boldly exposed surfaces experience. Due to capillary forces and restricted mass transport, such local regions can remain wet for days after the outer surfaces are dry [1]. Understanding the nature of these environments, the parameters that control their composition and corrosivity, and the effects such environments have on fatigue crack propagation (FCP) has been far less studied. Nonetheless, the relevant FCP kinetics for life prediction can only be generated if the tests are performed in environments that mimic those found in service.

Aerospace structures are exposed to a wide range of nominal environments, from low temperature, low pressure water vapor during flight to elevated temperature, high humidity air during ground time. The latter can lead to the development of thin (1 to 50 microns) solution layers on surfaces as well as fully wetted occluded regions. It is from the occluded regions that many, if not most, corrosion-related fatigue cracks develop.

Figure 1 shows a schematic of two different types of occluded regions. Briefly, a physical separation of anodic (dissolution) and supporting cathodic reactions occurs in which the region within the crevice is a net anode, and the region outside the crevice (but exposed to the bulk solution) is the net cathode. Hydrolysis of the metal cations created within the crevice (and retained to some extent due to limited mass transport out of the crevice) leads to a decrease in pH which exacerbates the dissolution. In aerospace aluminum alloys, a typical occluded pH is 3.5, which is aggressive towards Al, particularly in the presence of high chloride concentrations [5].

Recently, the practical importance of isolated occluded regions (Figure 1b) has been demonstrated. Isolated occluded regions develop when the portion of the structure outside the crevice becomes dry while the region inside remains wet. One example of such a situation is an aircraft lap joint, which may be wet internally although the external surface has been dry for several days. Under these conditions, the physical separation of anodic and cathodic reactions cannot occur. This situation leads to alkaline conditions within the occluded region, which pH values of 8 to 8.5 being common for aerospace aluminum alloys.

Although the vast majority of occluded region research has focused on crevices, the same considerations apply for any restricted geometry, including cracks, delaminated coatings, and thin solution layers formed during exposure of surfaces to humid air. Because of the importance of solution chemistry to corrosion-fatigue (*i.e.*, simultaneous corrosion and fatigue) as well as corrosion/fatigue (*i.e.*, corrosion followed by fatigue), the understanding of the local environments is critical to any rational modeling of aerospace structure performance that includes material degradation.

2. EXPERIMENTAL METHODS

Details on the experimental work can be found elsewhere [2-4].

3. RESULTS

Figure 2 shows the results typical of an occluded region for which the anodic and cathodic reactions are physically separated. In Figure 2a, the crack tip of a stress-corrosion crack in AA7050-T6 exhibits a very low pH (ca. 3) relative to the bulk pH outside the crack (pH 9). The dissolution of the aluminum at the tip, combined with the hydrolysis of the aluminum cations produces this low pH [5]. In this case, the external surface of the sample was held potentiostatically, therefore the cathodic reaction supporting the aluminum dissolution occurred outside the crack at the counter electrode of the electrochemical cell.

The situation changes dramatically when the cathodic reaction is forced to occur in close proximity to the anodic reaction. Lewis showed that the pH within a crevice (simulating an aircraft lap joint) after exposure to different solutions for 12 weeks became approximately pH 8, independent of the initial pH. Figure 3 shows the time course of the pH when a small volume of HCl is placed on an AA2024-T3 surface. As corrosion occurs, the pH rises from 0.5 to 8 due to the close proximity of the anodic and cathodic reactions in the limited solution volume.

This effect can be seen on a larger scale in Figure 4 in which a simulated AA7075-T6 aircraft lap joint had its mouth constantly exposed to a highly acidic, oxidizing, concentrated chloride solution (EXCO [6]). This configuration represents an isolated. Although the bulk pH was approximately 0.5, after 10 days, the pH within lap joint became neutral to mildly alkaline for all regions that were more than 1” from the mouth. Similar results have been found for isolated occluded regions of AA2024-T3 [2,3,7].

Typically, acidic conditions cause the potential of an actively corroding Al surface to become more negative, whereas alkaline conditions lead to passivity and a more noble potential. Thus, localized corrosion often leads to a decrease in the open circuit potential as the active pit polarizes the passive surface external to the pit to low potentials [8]. In isolated occluded regions, localized corrosion is stifled by the alkaline conditions and the inability to spatially separate the anodic and cathodic reactions sufficiently. These conditions lead to elevated potentials within the isolated occluded region relative to the same material in the bulk solution. This elevation in potential can be several hundred millivolts [7].

4. DISCUSSION

The vast majority of corrosion-fatigue studies have been performed in water vapor or in full immersion in solution [9]. The environmental conditions to which many occluded regions on aerospace structures are exposed are poorly described by either of these extremes. While water vapor may be appropriate for freely exposed surfaces, the condensed solutions within occluded regions typically contain a variety of dissolved species [7]. However, full immersion studies of corrosion-fatigue have generally used fairly concentrated chloride solutions the compositions of which approximate seawater. Again, most aircraft are not exposed to full immersion in seawater. While the occluded regions can stay wet for extended periods of time [1], the limited volume and the inability of the anodic and cathodic reactions to be physically separated combine to produce two important effects: (a) an alkaline occluded solution, and (b) an elevated open circuit potential.

For occluded regions undergoing corrosion, it is generally thought that the pH becomes acidic due to hydrolysis of metal cations. This lowering of the occluded pH has been observed experimentally in crevices and cracks [5]. However, in all of these cases, the occluded region was in electrical and ionic contact with a surface that was exposed to a bulk electrolyte and could therefore act as a site for cathodic reactions. This arrangement allows the anodic and cathodic reactions to be separated spatially. A primary result of this separation is moving any production of alkalinity (e.g., by reduction of water) away from the occluded region. Under such an arrangement, the pH of the occluded region approaches that of a concentrated solution of the salts based on the main metallic components of the alloy and the dominant anion in the solution (typically chloride).

In the case of many atmospheric conditions, however, the separation of the anodic and cathodic reactions cannot occur. For example, when an occluded region remains wet while the free surface dries, all of the cathodic reaction necessary to balance the anodic (dissolution) reactions must occur within the isolated occluded region. Under these conditions, not only can the pH of the occluded region not become acid, but also it cannot maintain acidity even if that acidity can be replenished by bulk solution as shown in Figure 3. Instead the pH of the isolated occluded region is controlled by the equilibrium between the metal ions and the hydroxyl ions created by the cathodic reaction (Table 1). Typically, the values for such equilibrium pH are between 7 and 10.

The alkaline pH leads to higher open circuit potentials for most materials due to the increased passivity exhibited under these conditions. The passive film spontaneously formed is generally more protective under mildly alkaline conditions as manifested by a lower passive current density. Combined with unchanging cathodic reaction kinetics, mixed potential theory predicts what is observed in practice: an interfacial potential that is more electropositive.

The implications of these two effects on crack propagation can be important. Although not well documented for corrosion-fatigue, stress-corrosion crack growth rates increase with increasing potential. For 7XXX aluminum alloys, the increase is approximately an order of magnitude for every 100 mV increase in potential [2,7]. Under these conditions, the mildly alkaline conditions do not inhibit the cracking; in fact, due to the decrease in the likelihood of localized corrosion on the surfaces outside the crack, the elevated pH actually supports the high crack growth rates. The situation may be different in the case of corrosion-fatigue where any corrosion products that precipitate in the crack could increase closure, thereby reducing the crack propagation rate.

When such considerations are applied to a flight cycle, the situation becomes substantially more complex and poorly characterized. The conditions inside occluded regions can be approximated based on laboratory and field data while the aircraft is on the ground. However, fatigue stresses are low to non-existent during this phase. At cruising altitude, it may be assumed that any solutions within occluded regions and cracks are either frozen or dehydrated, fatigue under this portion of the flight cycle can probably be well modeled by low pressure water vapor. The challenges lie in how to model the ascent and descent portions of the flight cycle, where not only are the fatigue stresses high (and spectrum loading effects can be important), but also where the solution chemistry within crevices and cracks is evolving. During these phases, true corrosion-fatigue can occur, but likely under conditions far from steady state.

5. CONCLUSIONS

1. Experimental measurements of fatigue crack propagation must account for the actual surface solution composition which can be substantially different within occluded regions relative to bulk solution.
2. Isolated occluded regions on aluminum alloys develop solutions with mildly alkaline pH values independent of the bulk solution pH.
3. The elevated pH leads to elevated open circuit potentials due to the improved passivity. The effects of these elevated potentials on fatigue crack growth rates need characterization for high-fidelity damage evolution.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1 – Gui, F. K. R. Cooper, L. B. Simon, R. G. Kelly, "Laboratory Evaluations of Corrosion Prevention Compounds" Aging Aircraft 2001, DoD, Orlando (2001).

2 – Ferrer, K. S., Ph.D. Dissertation, University of Virginia (2003).

3 – Lewis, K. S. Master's Thesis, University of Virginia (1999).

4 – Ciccone, M. R. P. Gangloff, R. G. Kelly, "Test Environment Selection for Corrosion Fatigue Testing of AA7075-T6," R. G. Buchheit, et al., eds., *Corrosion and Protection of Light Metal Alloys*, PV 2003-23, The Electrochemical Society, Inc., Pennington, NJ (2003), pp. 82-93.

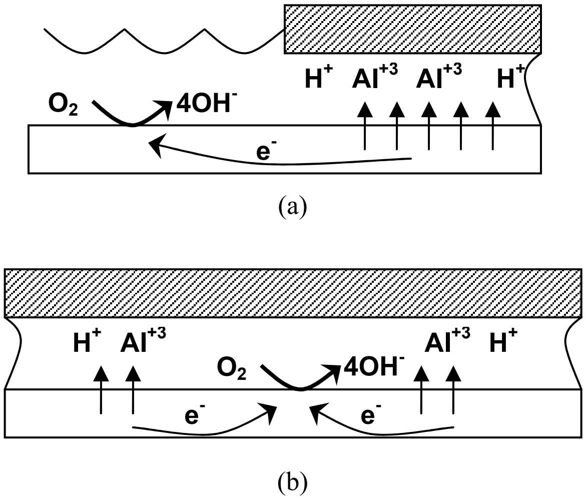
5 – Turnbull, A., "Chemistry Within Localized Corrosion Cavities," in Advances in Localized Corrosion, H. Isaacs, U. Bertocci, J. Kruger, S. Smialowska, NACE, Houston, pp.359-374 (1990).

6 – ASTM G34, "Method for Exfoliation Corrosion Susceptibility in 2XXX and 7XXX Series Aluminum Alloys (EXCO Test)", Amer. Soc. Testing Materials, Philadelphia (2002).

7 - K.S. Ferrer, R.G. Kelly, "Development of an Aircraft Lap Joint Simulant Environment." *Corrosion*, **58**(5): 452-459, 2002.

8 – Kelly, R. G. "Ch. 18: Pitting Corrosion," in Manual on Corrosion Tests and Standards : Applications and Interpretations, R. Baboian, ed., ASTM, Philadelphia, pp. 166-75 (1995).

9 - Gangloff, R. P., "Corrosion Fatigue Crack Propagation in Metals," in Environment-Induced Cracking of Metals, R. P. Gangloff, M. B. Ives, eds., NACE, Houston, pp. 55-110 (1990).



(a)

(b)

Figure 1: Schematics of (a) conventional crevice with increased dissolution (and hydrolysis creating H^+) within crevice, and cathodic reaction (creating OH^- outside the crevice). This separation leads to acidic conditions within the crevice; (b) isolated crevice with both dissolution and entire cathodic reaction within crevice, leading to mildly alkaline conditions.

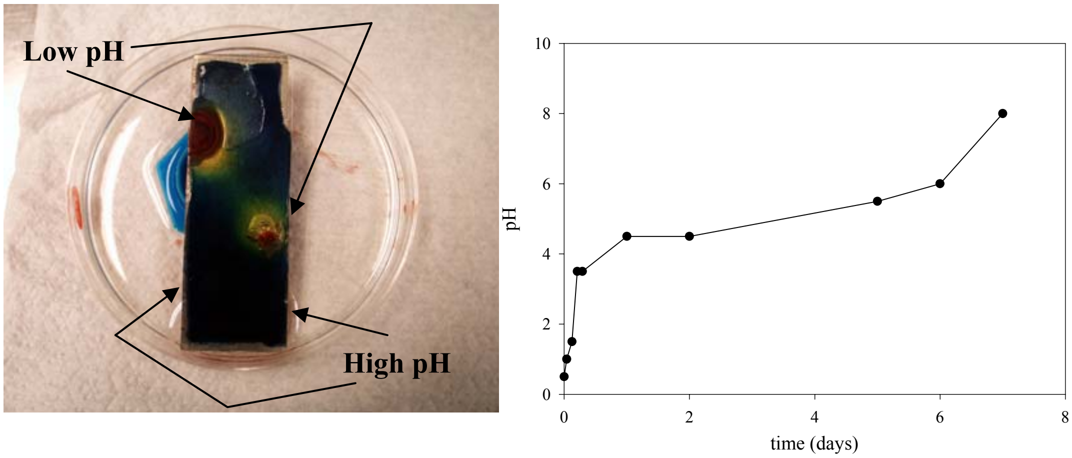
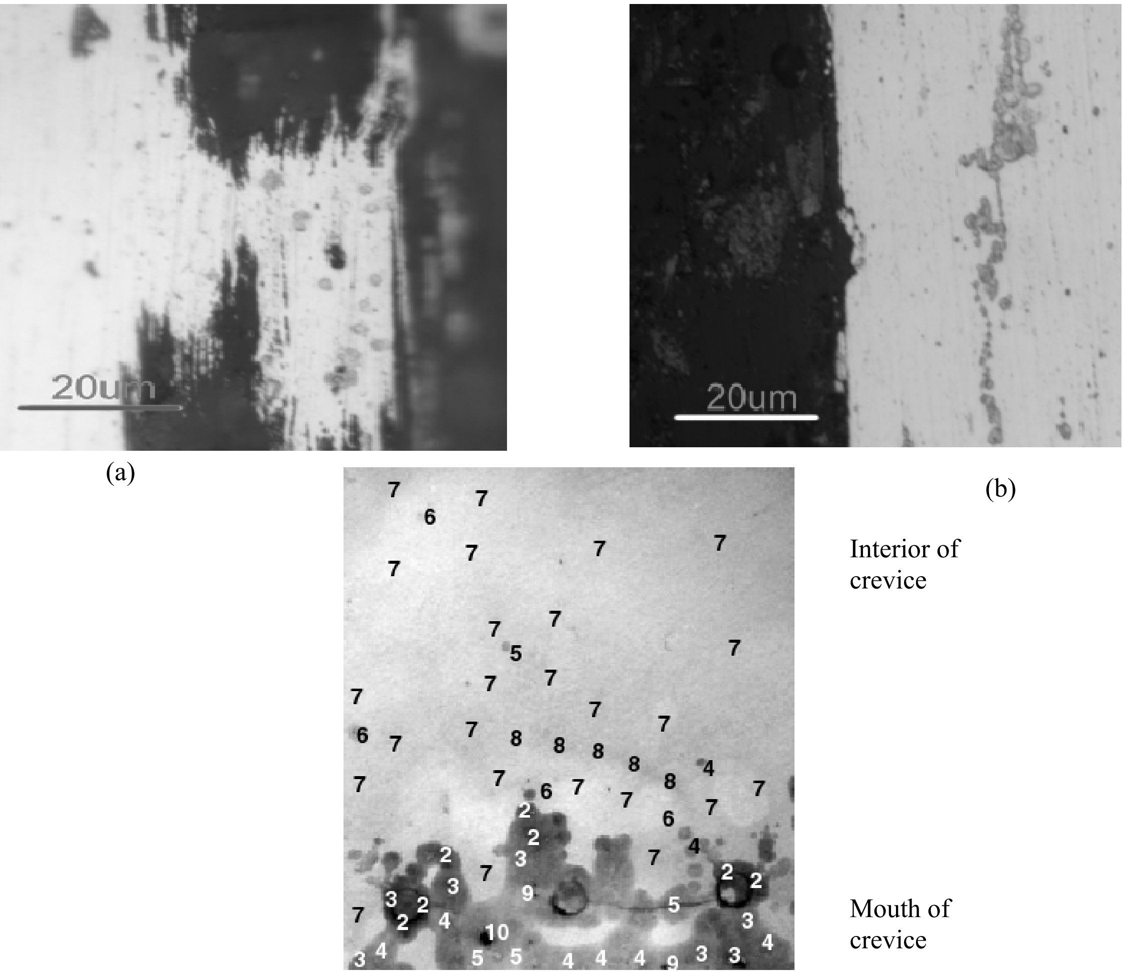


Figure 2: (a) Localized corrosion of AA2024-T3 covered with agar containing 0.5 M NaCl and a pH indicator. Note the regions of low and high pH due to separation of anodic and cathodic reactions. (b) pH evolution for small volume of 0.01 M HCl placed on AA2024-T3 surface



(a)

(b)

(c)

Figure 3: Figure 3. Isolated occluded joint sample exposed to EXCO solution [ref] for 235h. (a) Corrosion morphology for a section in the mouth region (pH 3) shows extensive exfoliation and dissolution, (b) corrosion morphology for a section in an interior region (pH 7) shows more uniform and less extensive attack, and (c) a pH map for the sample. [ref MPC]