Using capillary electrophoresis to study the chemical conditions within cracks in aluminum alloys

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Abstract

The environment-assisted cracking (EAC) susceptibility of some aluminum alloys used for airplane structural components currently limits their use in the peak strength condition. Understanding the mechanism of EAC will facilitate the development of crack-resistant alloys with optimum mechanical properties. One component towards understanding the fundamental processes responsible for EAC is a comprehensive knowledge of the chemical conditions within cracks. The present work uses capillary electrophoresis (CE) to quantify the crack chemistry in order to provide insight into the nature of the mechanism controlling cracking. The highly restricted geometry of cracks in metals means that a crack typically contains less than 10 µl of solution. The high mass sensitivity combined with the inherently robust nature of CE makes it an ideal analytical technique for this application. Complicating factors in the accurate determination of the crack environment include high levels of sodium present from the test solution. Low sample volume and analyte matrix complexity necessitated the development of specific sampling, extraction and analysis methods. Analysis of the crack solutions in EAC-susceptible material revealed high levels of Al^{3+}, Mg^{2+}, Zn^{2+}, and Cl^- near the crack tip. Cations arise from the anodic dissolution of the alloy, whereas chloride ingress from the external environment occurs to maintain solution electroneutrality within the crack. In contrast, EAC-resistant material exhibited significantly lower concentrations of dissolution products. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The high strength, low density, and good corrosion resistance of Al–Zn–Mg–(Cu) alloys make these metals one of the prime materials for aircraft structures. However, these alloys are also suffer from environment-assisted cracking (EAC) when a susceptible material is subjected to the combined effects of stress and an aggressive environment. When these alloys are thermally treated to achieve maximum strength, they exhibit high susceptibility to EAC. These alloys can be made EAC-resistant but at 15 to 20% decrease in strength. This work seeks to help elucidate the cracking mechanism(s) in order to facilitate the optimization of Al–Zn–Mg–(Cu) alloy strength and crack resistance.

A complete mechanistic understanding of the EAC phenomenon in these aluminum alloys still eludes researchers [1,2]. One of the reasons the controlling processes are unknown is the lack of knowledge of the chemical conditions within cracks, which may differ significantly from the external environment [3]. Dissolution of metal within the crack introduces cations into solution and anions (e.g. Cl^-) from the external environment migrate into the crack to maintain electroneutrality. In addition, the hydrolysis

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of cations produces H^+ ions. Thus, an aggressive, low pH, high Cl^- solution is formed within the crack and restricted mass transport helps to maintain that environment.

Whereas it is known that the composition of the solution within cracks may differ from that of the external or bulk environment, little has been done to characterize this environment [3,4]. Difficulties inherent in quantification of the chemistry within cracks include access to the environment and the very small solution volume, on the order of 1 μl/mm of crack length. Until recently, few analytical techniques had the sensitivity to detect the low levels of species in sub-microliter volumes.

Kelly et al. [5] demonstrated the feasibility of using capillary electrophoresis to analyze the chemistry within localized corrosion sites. In the analysis of crack solutions CE offers many advantages over other analytical chemistry techniques. First, the extremely high mass sensitivity allows comprehensive characterization of the complex, yet small, amount of solution contained within cracks. Second, CE allows many species to be detected in a single analysis, including those unexpected a priori. Unambiguous identification of species oxidation state is another advantage of CE.

2. Experimental

Cracks were grown in aluminum alloy specimens using standard fracture mechanics techniques [6]. The composition of the alloy was Al–6.1% (w/w), Zn–2.14% (w/w), Mg–2.19% (w/w) Cu. Fracture specimens were 10.2 cm long×5.1 cm high×1.27 cm thick (4 in.×2 in.×$\frac{1}{2}$ in.). The crack geometry was such that the total crack volume was typically 10 to 40 μl; the crack tip volume, defined in this work as the volume of solution within the first 1.4 mm from the crack tip, was ~0.1 μl. The bulk (external) environment was 0.5 M Na_2CrO_4+0.05 M NaCl, natural pH 9.3. At the end of the crack growth test, the fracture specimen was frozen in liquid nitrogen and then rapidly broken in half along the crack plane.

2.1. Crack solution sampling

To sample the crack solution, Supor-800 (0.8 μm)

filter paper (Fisher Scientific, Raleigh, NC, USA) was placed between the fracture surfaces of the frozen metal samples. Elastic bands held the sample together. To minimize the amount of condensation and thus dilution of the crack solution, the Al alloy fracture specimen/filter paper assembly was allowed to thaw in a water-free, N_2 environment. Upon thawing, the crack solution was absorbed by the paper. The paper was then sliced into 1.4 mm wide strips to allow profiling of the crack solution down the length of the crack. To extract the components from the paper, the strips were placed into vials containing 100 μl of 1 mM HNO_3 and allowed to sit for 24 hours before preparing samples for analysis using CE.

2.2. Conditions

Analyses were performed using a Quanta 4000 (Waters, Milford, MA, USA) capillary electrophoresis system. For all samples, analyte loading was via 30 s–10 cm hydrostatic injection, the time constant was 0.3 s, and the sample rate was 20 point/second. Capillaries were 60 cm×75 μm I.D. (Polymicro Technologies, Phoenix, AZ, USA) with indirect UV detection at 185 nm. All solutions were prepared using 18.2 MΩ water and analytical grade chemicals.

Chloride and chromate were assessed using a carrier electrolyte of 25 mM phosphate+1 mM tetradecyltrimethylammonium bromide (TTAB) (Sigma, St. Louis, MO, USA) converted to OH^--form, natural pH 8. Separation was achieved using a constant current of 60 μA (~−17 kV).

A modified version of Waters UV-CAT 1 (Waters) electrolyte was used for the cation analysis (excluding Al^{3+}). The electrolyte composition was 5 mM UV-CAT 1, 6.5 mM hydroxyisobutyric acid (Sigma), 15 vol. % methanol, natural pH 4.4. The addition of up to 20% (v/v) methanol to the electrolyte can be advantageous when co-elution of ions occurs and/or when there is a high concentration of one component relative to the others [7]. A constant voltage of +20 kV (~4 μA) was used.

The aluminum ion analysis was performed using a modified 1 mM UV-CAT 2 (Waters) electrolyte, pH 3.1 to 3.2. The modification was to omit the complexant tropolone. The pH was adjusted via 0.05 M H_2SO_4 or 0.1 M HNO_3 and, as noted below, the ability to detect Al^{3+} in the presence of high
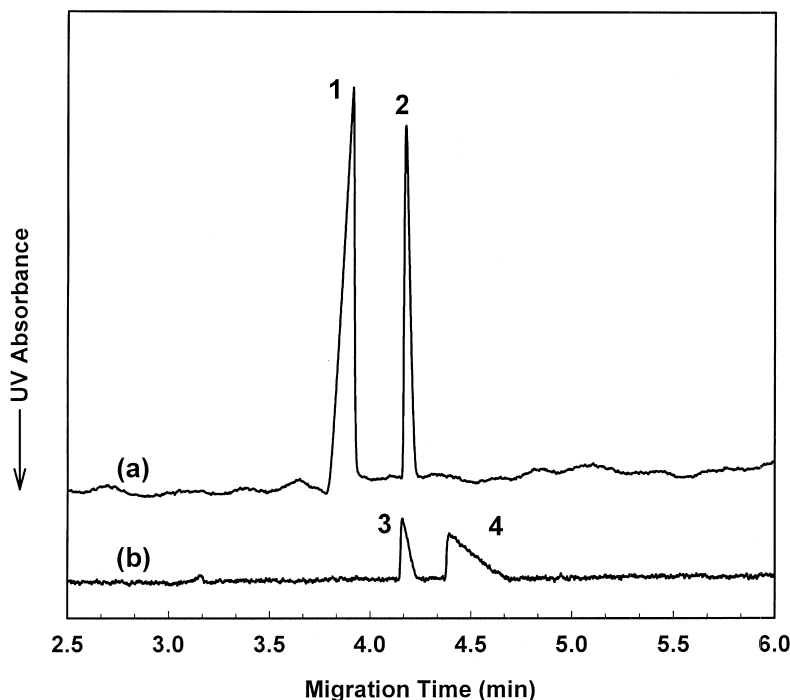
Fig. 1. Electropherograms showing effect of acid used to pH adjust modified Waters 1 mM UV-CAT 2, pH 3.1, carrier electrolyte on the migration of Al^{3+}. Conditions: 60 cm×75 μm I.D. fused silica capillary, 10 cm–30 s hydrostatic injection, voltage +20 kV, indirect detection at 185 nm. (a) pH adjusted with 0.1 M HNO_3 (1 ppm standard of 1=Al^{3+}, 2=Na^+); (b) pH adjusted with 0.05 M H_2SO_4 (5 ppm standard of 3=Na^+, 4=Al^{3+}).

concentrations of sodium was dependent on which acid was used. A constant voltage of +20 kV (~8 μA) was used.

Components were identified by matching their migration time with the migration time of known species and/or sample spiking. Quantification was performed by comparison of peak areas to calibration curves generated from standards of known concentrations.

3. Results and discussion

3.1. Aluminum analysis

Accurate analysis of the crack solution Al ion content is essential. The use of UV-CAT 2 electrolyte without the addition of a complexant was found to give acceptable results. However, the acid used to adjust the electrolyte pH influenced whether the Al^{3+} migrated faster or slower than Na^+. Be-

cause of the high concentration of Na^+ in the bulk environment, it was desirable to use an electrolyte in which aluminum migrated faster than sodium.

Fig. 1 shows electropherograms of Al^{3+} and Na^+ standards analyzed using the modified UV-CAT 2 electrolyte, pH adjusted using H_2SO_4 or HNO_3. Aluminum selectivity was improved when nitric acid was used for pH adjustment in comparison to when sulfuric acid was used to fix the electrolyte pH. In addition to Al^{3+} migrating faster than Na^+, the minimum detection limit (MDL)[1] was much lower when the electrolyte was pH adjusted with nitric acid. For example, the Al^{3+} MDL was 1.43 and 0.15 ppm when the electrolyte was pH adjusted using H_2SO_4 and HNO_3, respectively. Aluminum analyses reported in this work used the UV-CAT 2 electrolyte pH adjusted with nitric acid.

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[1]The minimum detection limit was defined as MDL=3 (h_b/h_i) × C_i, where h_b=background (noise) height, h_i=peak height of species i, and C_i=concentration of species i in parts per million.

3.2. Crack solution analysis

The crack solution consists of ions from the bulk electrolyte (Na^+, Cl^-, CrO_4^{2-}), cations dissolved from the alloy (Al^{3+}, Mg^{2+}, Zn^{2+}, Cu^{2+}) and Cr^{3+} from the electrochemical reduction of chromate which occurred within the crack. Electropherograms comparing the crack-tip cation levels for EAC-susceptible and -resistant materials are shown in Fig. 2. The cation analysis using UV-CAT 1+methanol electrolyte, Fig. 4a, shows Na^+, present from the bulk environment, as well Mg^{2+}, Zn^{2+} and Cu^{2+} dissolved from an EAC-susceptible aluminum alloy. Copper ions were rarely detected and only at concentrations near the MDL of 0.25 ppm.

Note in Fig. 2a the significant difference in the amount of alloying elements, Mg and Zn, in the crack-tip sample for the EAC-susceptible material as compared to the EAC-resistant material. Indeed, for the crack-resistant material, the Mg and Zn peaks are barely visible, and are less than the MDL.

Fig. 2b shows electropherograms from the same samples shown in Fig. 4a, but analyzed using the modified UV-CAT 2 electrolyte. Because a complexant was not added, the divalent cations co-migrate, however, Al^{3+} and Na^+ are evident as distinct peaks. Again note the significantly greater levels of aluminum for the EAC-susceptible material in comparison to a material which exhibits high cracking resistance.

Chromium(III) was detected in the cracks of EAC-susceptible material. Because the alloy used in this study was Cr-free, the presence of Cr^{3+} was not expected. Chromate reduction is the source of the Cr^{3+} ions. The detection of Cr^{3+} illustrates two advantages of CE over some analytical techniques. First, CE allows determination of species valence. Specifically, both Cr(III) and Cr(VI) were detected in this work. Second, CE allows detection of species without knowledge of their presence beforehand. In this instance, Cr(III) ions were observed without specifically attempting to analyze for this species and in the presence of large concentrations of Cr(VI).

Chromate solutions are buffers at pH ~7.5. Electrochemical reduction of chromate may aid acidification of the crack environment by decreasing the concentration of buffering agent thus diminishing the buffering capacity of the solution.

3.3. Crack tip vs. crack wake samples and concentration profiles

Although quantitation of the crack tip solution is of greatest interest, reactions occurring a few millimeters far from the crack tip (i.e., the crack wake) may also be important to the cracking process. Thus, profiling of the crack solution composition as a function of distance from the crack tip was performed.

Fig. 3 demonstrates the difference in crack solution composition of samples taken at the crack tip and wake of an EAC-susceptible material. Near the crack tip, the solution contains high levels of cations dissolved from the alloy relative to the bulk Na^+ concentration. In contrast, within the crack wake very low levels of metal ions were present in solution. This result indicates that the source for the metal ions was localized to the crack tip. That is, dissolution of the crack walls was small relative to the metal oxidation rate at the crack tip.

Raw data of the sort shown above are useful for qualitatively comparing the concentration of species within cracks as, for example, a function of position within the crack and two materials of different cracking susceptibility. However, knowing the true species concentration allows further assessment of the processes important to the cracking phenomenon. Estimation of the true solution composition was based on the following assumptions: (a) known crack solution volume based on an experimentally determined trapezoidal crack geometry, (b) all of the crack solution is absorbed up by the filter paper, (c) concentration profiles are maintained within the filter paper, (d) extraction of solution components from the filter paper is 100%.

Calculated 'true' crack concentration profiles are shown in Fig. 4. For comparison, results for a material susceptible to and a material resistant to environment-assisted cracking are shown. Note that estimated chloride, sodium and chromate concentrations at positions within the wake are approximately half that of the bulk solution suggesting that perhaps a factor of two should be applied to the reported results. There are a number of potential sources for the discrepancy between calculated wake and bulk concentrations: (1) incomplete extraction of species absorbed by the filter paper, (2) over estima-
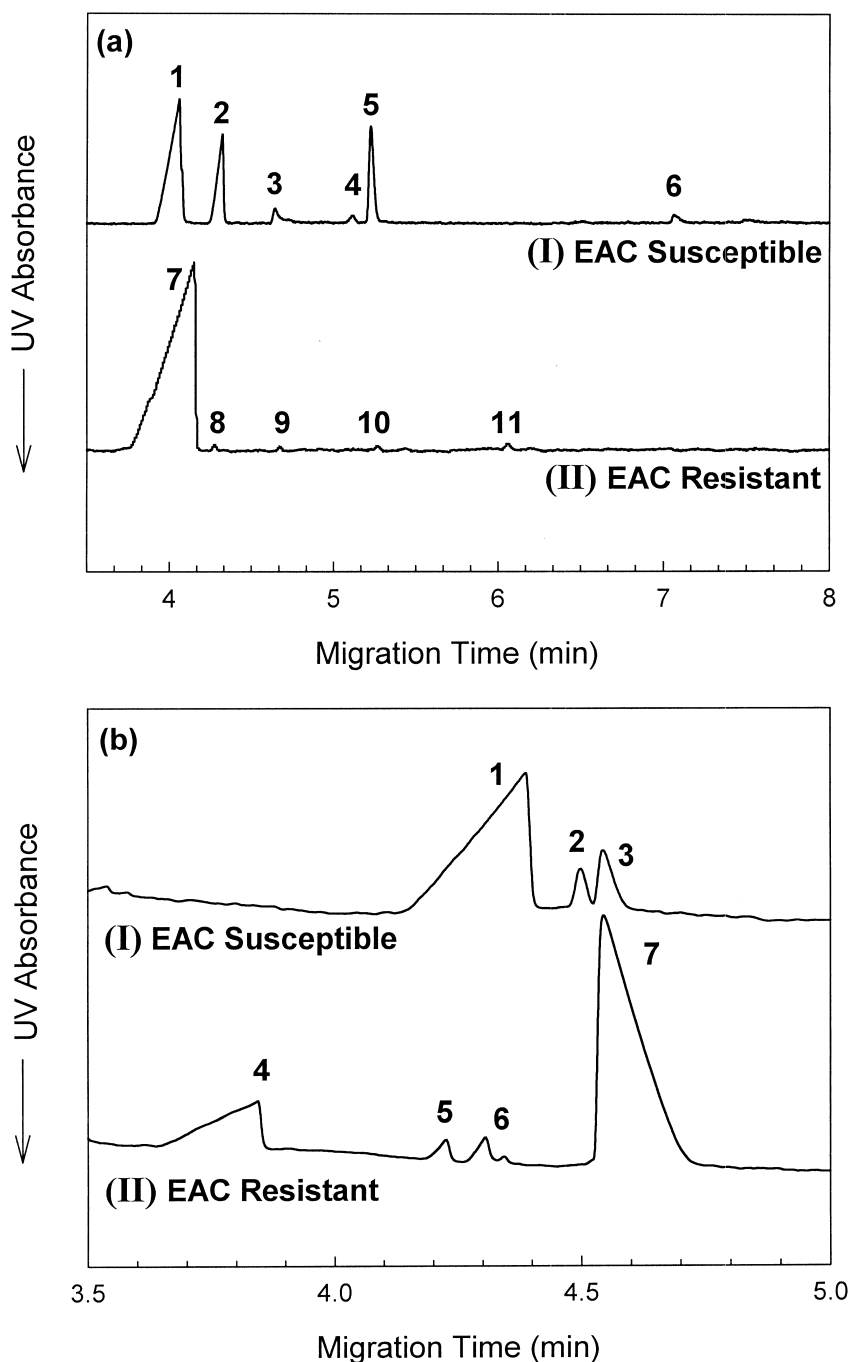
Fig. 2. Electropherograms showing difference between crack tip chemistry for (I) EAC-susceptible and (II) EAC-resistant aluminum alloy. Conditions: 60 cm×75 μm I.D. fused silica capillary, 10 cm–30 s hydrostatic injection, voltage +20 kV, indirect detection at 185 nm. (a) Cation analysis using UV-CAT 1+15% (v/v) methanol carrier electrolyte (I: dilution=2x, 1=16.33 ppm Na^+, 2=3.07 ppm Mg^{2+}, 3=1.42 ppm Cr^{3+}, 4=unknown, 5=5.57 ppm Zn^{2+}, 6=0.80 ppm Cu^{2+}; II: dilution=1×, 7=68.3 ppm Na^+, 8=Mg^{2+}, 9=Cr^{3+}, 10=Zn^{2+}, 11=unknown). (b) Cation analysis using modified UV-CAT 2 carrier electrolyte (I: dilution=5×, 1=50.1 ppm Al^{3+}, 2=divalents, 3=14.69 ppm Na^+; II: dilution=1.2×, 4=unknown, 5=0.75 ppm Al^{3+}, 6=divalents, 7=31.43 ppm Na^+).
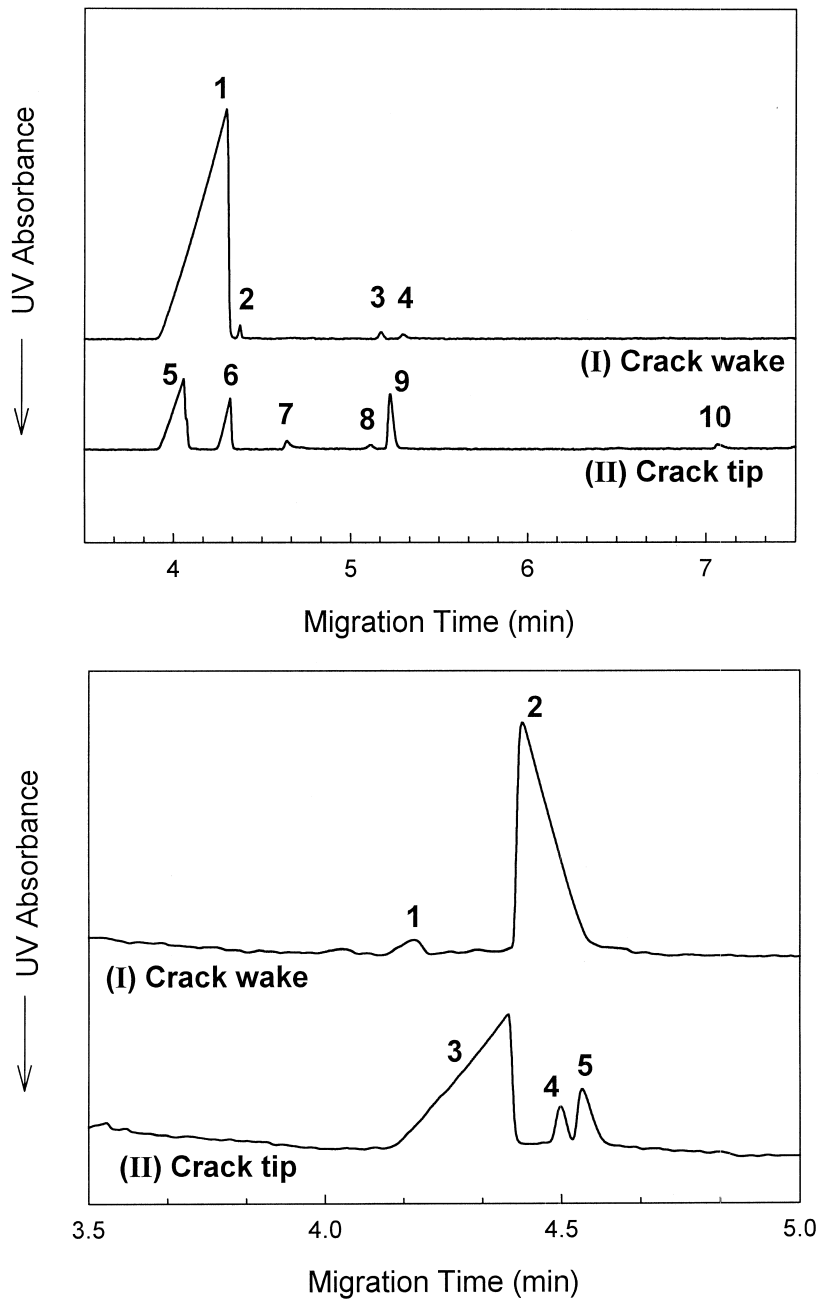
Fig. 3. Electropherograms showing difference between (I) crack wake and (II) crack tip chemistry for EAC-susceptible aluminum alloy. Conditions: 60 cm×75 μm I.D. fused silica capillary, 10 cm–30 s hydrostatic injection, voltage= +20 kV, indirect detection at 185 nm. (a) Cation analysis using UV-CAT 1+15% (v/v) methanol electrolyte (I: dilution=2×, 1=124 ppm Na^+, 2=0.61 ppm Mg^{2+}, 3=unknown, 4=0.64 ppm Zn^{2+}; II: dilution=2×, 5=16.33 ppm Na^+, 6=3.07 ppm Mg^{2+}, 7=1.42 ppm Cr^{3+}, 8=unknown, 9=5.57 ppm Zn^{2+}, 10=0.80 ppm Cu^{2+}). (b) Cation analysis using UV-CAT 2 electrolyte without complexant (I: dilution=2×, 1=0.88 ppm Al^{3+}, 2=54.8 ppm Na^+; II: dilution=5×, 3=50.1 ppm Al^{3+}, 4=divalents, 5=14.69 ppm Na^+).
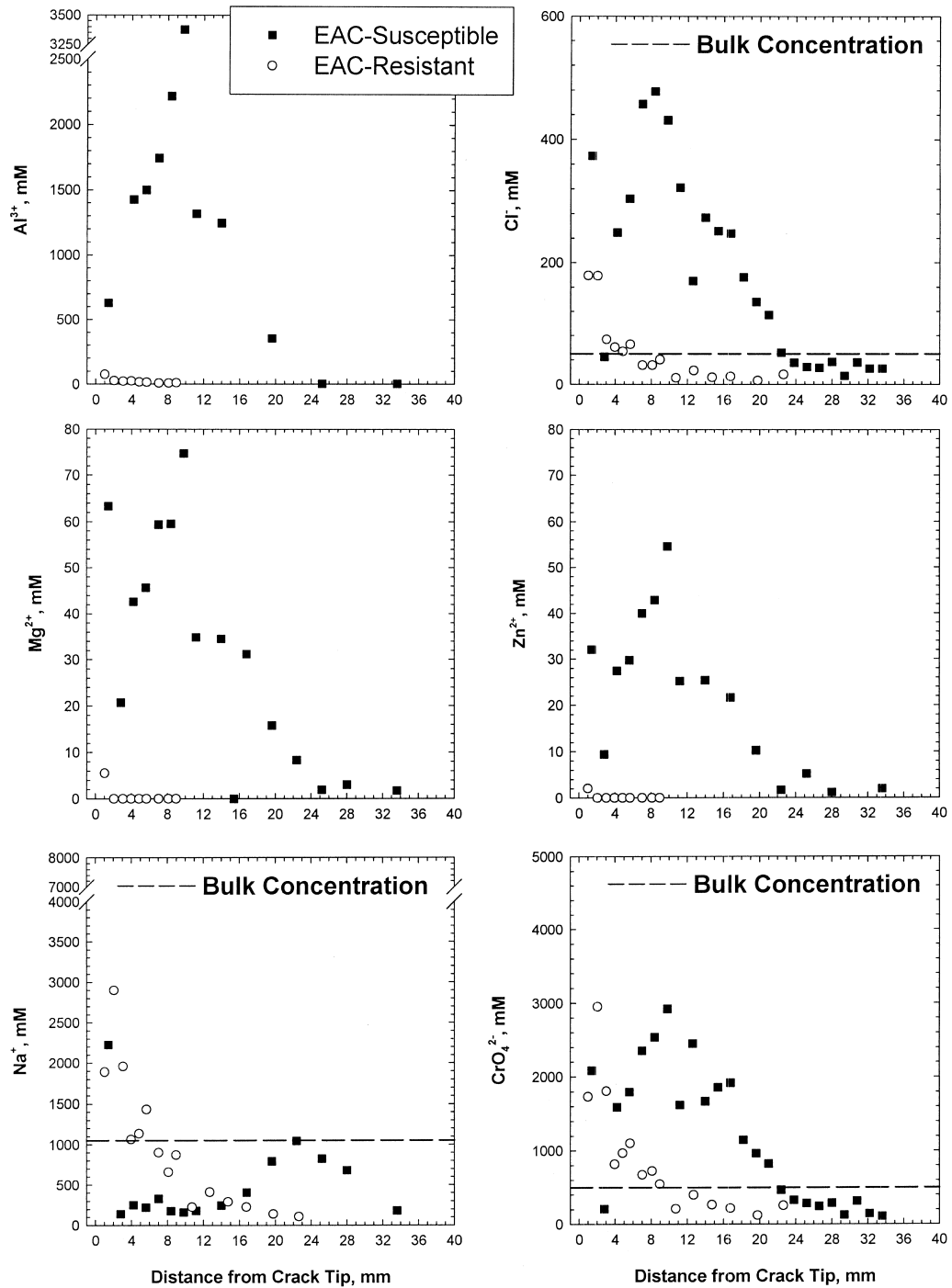
Fig. 4. Crack chemistry profiles for an EAC-susceptible and -resistant aluminum alloy.

tion of the crack volume, and (3) dilution of the crack solution from the inevitable layer of condensate which forms on the sample prior to insertion into the water-free environment.

EAC-susceptible material showed high levels of ions near the crack tip: 1.5 M Al^{3+}, 60 mM Mg^{2+}, 30 mM Zn^{2+}, 0.5 M Cl^- and 2 M CrO_4^{2-}. In contrast, EAC-resistant material exhibited essentially no metal ions from the alloy at any position within the crack as well as little or no increase in the concentration of anions (over external levels) within the crack. These results further illustrate the significant difference between the chemical environments within cracks for material with and without a propensity to crack in this environment.

The dramatic increase in Al concentration at ~8 mm from the crack tip warrants consideration. The crack solution pH increases from 3 at the crack tip to 9.3 (the bulk solution pH) in the wake. In addition, the minimum solubility of $Al(OH)_3$ occurs at pH 5.3. It is believed that as the pH within the crack moves toward neutral with increasing distance from the crack tip, the solubility of hydrated Al species is exceeded and local precipitation of $Al(OH)_3$ occurs [8–10]. The very narrow crack geometry restricts convection and thus the movement of the precipitate out of the crack. The $Al(OH)_3$ is collected during sampling of the crack solution and dissolved in the acidified (pH 3) extraction solution. As a result, very high Al^{3+} concentrations are observed a few millimeters from the crack tip.

4. Conclusions

1. Capillary electrophoresis can be used to analyze the chemical environment within cracks in aluminum alloys
2. The crack solution can be sampled from the fracture surface using filter paper and then extracted from the filter paper using a dilute acid solution.
3. Al ions can be detected and quantified using a modified UV-CAT 2 electrolyte. Al^{3+} selectivity and sensitivity is enhanced if the electrolyte pH is modified with HNO_3 in comparison to using H_2SO_4.

4. The crack chemistry is a function of the cracking resistance of the alloy. EAC-susceptible material attained a crack chemistry concentrated in dissolution products (Al^{3+}, Mg^{2+}, Zn^{2+}) and anions from the bulk environment (Cl^-, CrO_4^{2-}). In contrast, EAC-resistant material exhibits a crack chemistry similar to the bulk environment with very low concentrations of dissolved metal when exposed to aqueous chromate solutions.
5. For EAC-susceptible material the crack chemistry was a strong function of distance from the crack tip. Far from the tip, the crack chemistry was essentially that of the bulk electrolyte; near the crack tip the solution composition was concentrated in cations dissolved from the aluminum alloy and anions from the bulk electrolyte.
6. The reduction of CrO_4^{2-} chromate within cracks can be detected via the presence of Cr^{3+}.
7. Estimates of the true solution composition within cracks can be made by assuming a crack geometry and therefore solution volume picked up from the fracture surface.

Acknowledgements

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