The Role of Chemical and Electrochemical Conditions in the Environment Assisted Cracking of an Al-Zn-Mg-Cu Alloy

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High strength Al-Zn-Mg-(Cu) alloys are susceptible to environment-assisted cracking (EAC) in some temper conditions 1. Overaged material exhibits enhanced EAC resistance in comparison to peak-aged material but at a ~15% loss in strength. Attempts to develop peak-strength EAC-resistant material are currently hampered by an incomplete understanding of the cracking mechanism of these alloys. The intergranular cracking process has been proposed to be controlled by hydrogen embrittlement and anodic dissolution 2, 3. Independent of the controlling process, however, there exists a need to understand the crack environment. The goal of this work is to understand the role of the local environment during cracking in order to help elucidate the relative roles of hydrogen embrittlement and anodic dissolution.

A significant limitation to understanding the role of crack tip electrochemistry in Al alloys has been a lack of knowledge of the crack tip chemistry. Cracks are inherently tight and therefore contain very small solution volumes (~1 mL/mm crack length/cm crack width).

Small crack solution volumes have inhibited quantitative analysis of the crack chemistry.

Both in-situ and ex-situ methods were used to analyze the crack environment. Real time, in-situ measurements of the crack pH, chloride concentration and electrochemical potential were obtained using microelectrodes placed within fracture specimens undergoing Stage II crack growth in chromate-inhibited chloride solutions (Fig. 1). Specimens were under potential control. Quantitative determination of the complete crack chemistry was determined via post-test sampling and analysis using capillary electrophoresis, an analytical chemistry technique with very high mass sensitivity ideally suited for the analysis of inorganic ions associated with corrosion processes 4, 5.

The pH of the crack solution was a function of the crack growth behavior of the material tested. For EAC-resistant material, no pH change from the bulk solution was observed. In contrast, the solution within cracks of EAC-susceptible material attained a pH of ~3 that extended 3-5 mm from the crack tip followed by a sharp transition to alkaline conditions near to the bulk (pH 8-9).

The crack solution consisted of ions derived from the bulk electrolyte (Na+, Cl-, CrO42-), cations dissolved from the alloy (Al3+, Mg2+, Zn2+, Cu2+) and Cr3+ from the electrochemical reduction of chromate which occurred within the crack. Fig 2 shows the crack tip cation levels for EAC-susceptible and resistant materials. Copper ions were rarely detected and only at concentrations near the minimum detection limits (~200 parts per billion). The fact that the concentration of alloy components in the crack solution is a strong function of the materials EAC behavior indicates that the crack chemistry is dominated by metal dissolution during cracking advance and not passive dissolution of the crack walls.

Measurement of the crack potential distribution provides additional information on the role of the crack environment (Fig. 3). A potential drop (IR) of ~ 0.35 V was observed at the crack tip when the applied potential was -0.495 VSCE. Generally, most of the IR was limited to very close to the crack tip: almost complete polarization of the crack flanks to the applied potential occurs within ~3 mm from the tip. The large potential gradient near the crack tip (~1 V/cm) supports steep chemical concentration gradients within the crack solution.

Characterization of the electrochemical behavior of phases relevant to the intergranular EAC of Al-Zn-Mg-Cu alloys in an electrolyte representative of the crack tip solution indicates that h (MgZn2) was active relative to the Al matrix (Fig. 4). Al-based phases such as the matrix and precipitate free zone are passive in the low pH, high chromate crack tip simulant. Incorporation of Cu and Al into the h-phase, which occurs during aging, increases the nobility of this phase relative to MgZn2. As such the driving force for intergranular corrosion and hydrogen production is significantly reduced and may account in part for the increased EAC-resistance of overaged Al-Zn-Mg-Cu alloys. The enhanced intergranular corrosion resistance of overaged material in comparison to the peak-aged temper was supported by the observation of severe intergranular corrosion of the latter material (Fig. 5) but not the former in the crack tip solution analog.

Additional work is being done to elucidate the relative contributions of hydrogen embrittlement and anodic dissolution to the EAC of these alloys.

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REFERENCES