# THE EFFECT OF H<sub>2</sub>SO<sub>4</sub> SURFACE PRE-TREATMENT ON THE STRESS CORROSION CRACKING OF MAGNESIUM ALLOY AZ31B

# THE EFFECT OF $H_2SO_4$ SURFACE PRE-TREATMENT ON THE STRESS CORROSION CRACKING OF MAGNESIUM ALLOY AZ31B

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### Abstract

The stress corrosion cracking (SCC) behaviour of Mg alloy AZ31B was investigated with respect to surface condition. Salt fog U-bend testing was used to identify changes in SCC as a result of surface conditioning pretreatments. Six surface conditions were investigated: as-received, mechanically-polished, sulphuric acid ( $H_2SO_4$ )-cleaned, mechanicallypolished then  $H_2SO_4$ -cleaned, aged  $H_2SO_4$ -cleaned, and acetic acid ( $C_2H_4O_2$ )-cleaned. Results showed that the rate of SCC was accelerated and the SCC mode was intergranular for all surface conditioning treatments involving  $H_2SO_4$ -cleaning.

It was found that the accelerated intergranular SCC was a result of three contributing factors: a low pH, the presence of aggressive ions, and a porous film which allowed direct contact between the metal surface and the electrolyte. Characterization of the surfaces using potentiodynamic polarization and cross-sectional images of sample surfaces showed that in the absence of one of these three contributing factors intergranular SCC would not occur.

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# Abbreviations and Symbols

### List of Abbreviations

A-AC	Aged Acid-Cleaned (H <sub>2</sub> SO <sub>4</sub> -Cleaned)
AC	Acid-Cleaned (H <sub>2</sub> SO <sub>4</sub> -cleaned)
AES	Auger Electron Spectroscopy
AR	As-Received
EDS	Electron Dispersive X-Ray Spectroscopy
FIB	Focused Ion Beam
HCP	Hexagonal Close Packed
HE	Hydrogen Embrittlement
HER	Hydrogen Evolution Reaction
ICP-OES	Inductively Coupled Plasma –Optical Emission Spectroscopy
IGSCC	Intergranular Stress Corrosion Cracking
LOM	Light Optical Microscopy
MFERD	Magnesium Front End Research and Development
MP	Mechanically-Polished
MP-AC	Mechanically-Polished then Acid-Cleaned ( $H_2SO_4$ -Cleaned)
NDE	Negative Difference Effect
OCP	Open Circuit Potential
O-AC	Organic Acid-Cleaned (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )
SEM	Scanning Electron Microscopy
SCC	Stress Corrosion Crack/Cracking/Cracks

- SSRT Slow Strain Rate Testing
- TGSCC Transgranular Stress Corrosion Cracks

# List of Symbols

A	Ampere
cm	Centimetre
°C	Degrees Celsius
E <sub>b</sub>	Breakdown Potential
E <sub>corr</sub>	Corrosion Potential
E <sub>OCP</sub>	Open Circuit Potential
eV	Electron Volt
g	Gram
h	Hour
I	Current, A
i	Current Density, mA/cm <sup>2</sup>
i <sub>corr</sub>	Corrosion Current Density
kJ	Kilojoule
М	Moles per Litre
m	Metre
min	Minutes
mL	Millilitre
mm	Millimetre
mV/s	Millivolt per second
mV	Millivolt
nm	Nanometre
S	Seconds

Kı	Stress Intensity
KISCC	Stress Intensity required for SCC
V	Volt
wt %	Weight Percent
μm	Micrometre

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Chapter 1: Introduction

## **Chapter 1: Introduction**

The present social and economic climates have triggered a global interest in reducing the impact of greenhouse gas emissions. This increased public awareness has led governments around the world to impose target emission reduction levels for various industries. The transportation sector has been identified as one of the largest contributors to greenhouse gas emissions accounting for 24% of the Canada's total emissions and 26% of the North American emissions [1]. For this reason the automotive industry has been required to increase vehicle fuel efficiencies, which can be partially achieved by the implementation of lightweight automotive materials.

Magnesium alloys are amongst the lowest density metallic engineering materials. They possess a highly favourable strength to weight ratio making them strong candidates for use in the automotive industry. The Magnesium Front End Research and Development project (MFERD), an international joint venture between Canada, the United States, and China was established to develop a magnesium intensive automotive structure that would reduce the overall weight of consumer vehicles [2]. Although it was demonstrated that replacing the traditional carbon steel front end assembly with a magnesium intensive Chapter 1: Introduction

assembly resulted in increased fuel efficiency, further investigation in formability, joining and corrosion resistance was required for implementation as a market ready enabling technology [2].

Investigation into the corrosion resistance of Mg alloys used in the structure was a key initiative of the MFERD project. It is well known that Mg alloys are amongst the most active of metals and are susceptible to many forms of corrosion damage [3]. Corrosion is often times accelerated by aggressive environments such as the chloride (e.g. NaCl) intensive exposures often observed in the automotive industry.

This thesis is focused on a particular aspect of the corrosion resistance of Mg alloy AZ31B, i.e. the resistance to stress corrosion cracking (SCC), and how this resistance is affected by the use of industrially relevant pre-treatment exposures.

## **Chapter 2: Literature Review and Background**

#### 2.1 Stress Corrosion Cracking

Stress corrosion cracking, SCC, is defined as the initiation and propagation of cracks due to the combined influence of a constant noncyclical load and a corrosive environment. SCC occurs as a synergistic effect of three main criteria (shown in Figure 2-1): material susceptibility, exposure conditions and applied tensile stress [4].



Figure 2-1: Stress corrosion cracking (SCC) criteria

SCC susceptibility has been observed in many engineering materials, first noted in brass alloys followed by carbon steels and stainless steels, as well as many nonferrous alloys such as aluminum and magnesium [4]. A unique set of exposure conditions are required to

produce SCC in each metal or alloy and are dependent on a number of material properties such corrosion behaviour [5]. Failures due to SCC typically occur as a brittle fracture, often times at tensile stresses well below the yield stress of the material. In service, these stresses can be induced simply by bolting or fastening components in addition to residual stresses from welding [4].

In theory, there are three stages to SCC: crack initiation, crack propagation and failure. However, these stages are not easily distinguishable during study due to the continuous nature of SCC progression [5]. Throughout these three stages there are a number of intermediary steps that can occur, all having varying effects on the overall SCC [6] [7]. Figure 2-2 generally identifies the nine intermediary steps that occur from initiation (and just prior) through to failure [6].



<sup>9.</sup> Stage III, Rapid propagation

The first step is a precursor step to initiation (stage 1) as electrochemical potential changes occur to create initiation conditions including the formation of various passive oxide films on the surface. Initiation occurs throughout steps 2 to 7, steps 2 and 3 involve the local breakdown of the passive film allowing the exposure of bare metal to

Figure 2-2: Summary of intermediary steps to SCC initiation and propagation [6].

the electrolyte. This is an integral step as the anodic dissolution strongly controls the rate of SCC [8]. Depending on the corrosion mode this penetration can occur via cleavage cracking, pitting, hydrogen embrittlement, dealloying or intergranular corrosion [5]. After penetration has occurred minor cracks begin to form and coalesce (Steps 4 & 5) in the metal until they have reached a critical crack radius such that the stress intensity  $K_{I} >> K_{ISCC}$  at which cracks will propagate (Steps 6 & 7). Crack propagation (Steps 8 & 9) has been attributed to factors such as anodic current density, anodic charge density passed and crack tip strain rate [9]. However, due to the dependence on exposure conditions, experimental data makes it very difficult to develop a predictive approach to determining crack velocities [9]. The mechanistic understanding of SCC propagation and growth kinetics for most metals, suggests a strong dependence of crack coalescence on anodic dissolution rates [8].

In susceptible materials, SCC may be either transgranular or intergranular, where cracks will follow a macroscopic path normal to the tensile direction. The mode of the cracks also depends on a number of factors: material, applied load, anodic dissolution, film growth, susceptibility to hydrogen embrittlement, internal stresses, local corrosion behaviour, etc. Furthermore, depending on the material, the SCC mode can accelerate propagation and failure rates [5] [10].

Transgranular SCC (TGSCC) fracture surfaces have a more brittle, cleavage-like appearance. Cracks propagate straight through grains and have been observed as a more discontinuous process than intergranular cracking [11]. The discontinuity of TGSCC can sometimes give the appearance of "beach" markings commonly seen in corrosion fatigue cracking. "Beach" markings appear as patterned striations on the fracture surface perpendicular to the direction of crack growth. It is argued that cleavage is necessary to facilitate the discontinuous nature of TGSCC because the anodic dissolution and mechanical damage decreases the stress intensity factor (K<sub>1</sub>) below the threshold for crack propagation [12].

Intergranular SCC (IGSCC) is dependent more on the microstructure. Generally, finer grain structures will be more likely to crack along grain boundaries due to the build-up of dislocation energy. Early studies of SCC set the foundation that a particular path may be preferential for SCC due to a localised attack or areas of decreased corrosion resistance; as a result the localised path becomes anodic to the surrounding (cathodic) area [13]. Following this, studies have shown that IGSCC can also be attributed to chemical heterogeneity within grains such as impurity segregation or precipitation leading to more chemically active grain boundaries. These factors reduce the

dependence of IGSCC on the stress intensity factor, therefore giving it a more continuous progression than TGSCC.

#### 2.1.1 Effect of Surface Films on SCC Mode

It was evident throughout this work that the SCC mode was dependent on the surface condition prior to salt fog exposure. More specifically, that there was a strong relationship between the SCC mode and the initial state of the surface film. The following section outlines the current understanding of how surface films affect both the kinetics and mode of SCC.

Works by Sieradzki and Newman [8] identified that film-induced cleavage cracks promote TGSCC. Their proposed model suggested that thin films can induce macroscopically brittle behaviour for regularly ductile materials. This behaviour was dependent on interfacial parameters between the film and substrate such as: lattice misfit, elastic modulus misfit, interfacial bonding, film geometry, and film ductility. It was found that the presence of cracks in the film modified the local deformation in such a way to initiate cleavage cracks in the substrate. In general, these thin and brittle films created high interfacial energy through low coherency with the substrates. Their work identified that when cleavage cracks are induced by the substrate-film interaction TGSCC was enhanced.

Further work by Sieradzki et al. [12] defined the relationship between the film, dealloying and SCC. It was found that porous films increased the exposure of bare metal, accelerating anodic dissolution rates. Dealloying is a form of selective dissolution, it occurs when there is a large difference in reactivity between alloying elements. It was found that if dealloying took place the films formed were inherently more porous and allowed the exposure of bare metal. In systems where the matrix was more active, the parting limit (the minimum concentration of an element in an alloy for de-alloying to take place) was approximately 70%; however, for systems with a more noble matrix the parting limit was approximately 10% [8]. This promoted anodic dissolution, which demonstrated a strong relationship with the enhancement of IGSCC [12]. Work by Hancock and Cowling [14] also identified that porous layers, under an applied load, can undergo ductile tearing, which initiated micro-cracks in the substrate and increased anodic dissolution of the newly exposed crack tip.

The initiation of SCC as a result of local corrosion behaviour has been studied extensively. The exposure of susceptible materials to corrosion environments promotes the formation of pits after breakdown of the passive film [4]. It has also been observed that pitting can contribute to the overall acceleration of SCC [15] [16] [17] [18]. The exact cause of this contribution is controversial; some studies show that

the stress concentration from pits increased the number of minor cracks that initiated [15], [16]. However, it has been shown that the added stress concentration from pitting does not aid in crack initiation, instead it accelerates crack propagation [17]. Parkins [18] showed that for varying cases, either of these factors can explain SCC, but in all cases the most important factor to consider was that pitting affected the local environment which impeded or prevented the formation of passive films. Thus, pitting influenced SCC much like a porous film by inhibiting the formation of passive films that retard anodic dissolution. Corrosion pits act as occluded cells, wherein the local environment can undergo significant changes such as increased chloride concentration or change in pH. Parkins [18] showed with slow strain rate testing (SSRT) that the rate of cracking was accelerated when materials were exposed free of passive films. It was also observed that SCC initiation was impeded by the growth of passive films on the exposed surface [19]. As mentioned previously, this research aligns well with the work of Hancock and Cowling [14], who reported that bare surfaces behaved similar to ones with porous films resulting in an increase in anodic dissolution and acceleration of SCC.

### 2.2 Corrosion and SCC of Magnesium

This section focuses on the corrosion behaviour of Mg and its alloys as it pertains to the kinetics and mode of SCC. It is well known that Mg is one of the most active engineering metals, as seen in the galvanic series shown in Figure 2-3. This makes SCC of Mg alloys very environmentally-dependent. Parkins et al. [18] showed that the aggressiveness of the environment could either enhance or inhibit SCC. Environments that were too reactive did not promote SCC and instead enhanced local corrosion and pitting. It was concluded that propagation of SCC required a sharp crack tip and high stress intensity; more reactive environments accelerated anodic dissolution which decreased the stress intensity at the crack tip preventing propagation [18]. Therefore, alloying elements can be used to improve corrosion resistance. Alloying elements such as AI, Zn, Cd, and Sn are used for their active corrosion potentials and high hydrogen evolution overpotentials. Hydrogen evolution overpotential is important to take into account because it is the dominant cathodic reaction in the aqueous corrosion of Mg [20].



Volts vs Saturated Calomel Reference Electrode

Figure 2-3:Galvanic series of metals [21]

Typically Mg alloys are categorized into two classes, Zr-containing alloys and Zr-free alloys. Zr is added along with other rare earth elements for their reactions with Fe, Ni, Co and Cu [3]. These elements are known to create a local galvanic effect and accelerate the corrosion of Mg alloys [22].

The most common alloying element used in Mg-based alloys is Al. Studies have shown that the alloy Al content has a profound influence on corrosion rates [23]. It has been observed in alloys with Al contents above the solubility limit that  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>, is formed, which is cathodic to the  $\alpha$ -Mg matrix [24]. Because the  $\beta$  phase has a higher cathodic activity than the  $\alpha$  phase, it has been argued to either increase the overall corrosion resistance of the alloy or act as a local cathode. Thus, its influence on the corrosion behaviour of the alloy is dependent on its volume fraction and distribution [20]. At small volume fractions, the  $\beta$ phase precipitates out (generally on grain boundaries) which can enhance local corrosion of the  $\alpha$  matrix whereas at higher volume fractions the  $\beta$  phase forms an interconnected grain boundary network and acts as an anodic barrier, increasing the overall corrosion resistance of the alloy [20].

For Mg-Al alloys, minor additions of Mn are used to mitigate the effects of noble metal impurities such as Fe due to the formation of a Al-Mn phase [25] [26]. However, higher Mn contents have also been

attributed to detrimental effects on corrosion resistance due to the increase in AIMn(Fe) intermetallic particles and their associated microgalvanic effects [25].

In both aerated and deaerated aqueous corrosion of Mg alloys, the governing cathodic reaction is the hydrogen evolution reaction, HER, as opposed to the oxygen reduction reaction, ORR, due to its low corrosion potential [27]. The half cell reactions for HER and the anodic dissolution of Mg can be seen in equation (2-1) and equation (2-2) respectively. Additionally the reaction that occurs during the aqueous corrosion of Mg alloys can be seen in equation (2-3).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (2-1)

$$Mg \rightarrow Mg^{2+} + 2e^{-} \tag{2-2}$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$
 (2-3)

The production of  $H_2$  during the HER is of particular concern when regarding the SCC of Mg. This is because during the anodic dissolution of Mg surfaces a unique behaviour has been observed, known as the negative difference effect (NDE).

The NDE is observed during anodic polarization of Mg surfaces during which the rate of hydrogen evolution increases as the potential becomes more noble. This is in contrast to what is expected from mixed potential theory defined by the equations above and what is observed

during the corrosion of most other metals. A number of unverified explanations for the NDE have been proposed. A prominently proposed theory was based on the creation and subsequent recation of intermediate univalent Mg<sup>+</sup> ions [24]. More recent literature suggested that this mechanism is not valid and can be rejected [28] [29]. Other studies have related the NDE to the effects of impurity elements, accelerated film breakdown, localized corrosion undermining leading to spalling of the metal surface, dissolution of MgH<sub>2</sub> and more recently to increased cathodic activity during anodic polarization [27] [28] [30].

It is well established that the introduction of small amounts of hydrogen to many metals and alloys can result in a drastic reduction of mechanical properties of many metals [4]. Atomic hydrogen can be introduced to the lattice (causing hydrogen embrittlement) by the reduction of water, dissociation of acids or the dissociation of hydrogen gas, H<sub>2</sub>. Cracking induced from hydrogen embrittlement can be either transgranular or intergranular with sharp-tips, minor branching and cleavage-like morphologies [4]. Mg, has been noted to be very susceptible to hydrogen embrittlement. T. Watanabe et al. [31] demonstrated that, at standard temperatures and pressures, commercially pure Mg has a hydrogen concentration of approximately 20 ppm by mass. The solid solubility limit of hydrogen in Mg is approximately 0.08 ppm by mass, resulting in a significant excess of

supersaturated hydrogen and increasing the risk of hydrogen embrittlement [31]. Work by Y. Chino et al. [32] found the deleterious effects of hydrogen embrittlement could occur at hydrogen concentrations as low as 16 ppm by mass. Hydrogen mapping, via secondary ion mass spectrometry, identified that hydrogen was segregated to triple junctions and grain boundaries; this directly relates hydrogen embrittlement to the enhancement of IGSCC fracture of Mg alloys [32].

#### 2.1.2 Effects of Mode on SCC of Mg-Al Alloys

Both TGSCC and IGSCC have been observed in Mg alloys. Many studies have concluded that, similar to other metals such as copper/brass alloys and stainless steels, IGSCC failure is more highly influenced by electrochemical attack resulting in more continuous crack progression whereas TGSCC occurs in a discontinuous cleavage-like fashion [13] [33] [34] [35]. Early studies by Mears et al. [13] identified that the SCC mode of Mg-based alloys could undergo a shift from TGSCC to IGSCC by decreasing the pH from a slightly basic pH to an acidic one (8 to 5); This was attributed to the increased anodic activity from the acidic exposure. Fairman et al. [35] furthered this understanding by demonstrating the importance of anodic activity on the mode of cracking using cathodic protection to arrest intergranular crack propagation.

#### 2.1.3 Mg Corrosion in Salt Fog Exposure

Investigations into the corrosion resistance and SCC resistance of Mg and Mg alloys is typically done under two types of exposures: immersion and salt fog. Standardized testing procedures have been developed for both, ASTM G31 and ASTM B117, respectively. Many variations of these testing procedures have been used to improve their correlation to corrosion performance in aerospace and automotive industrial practices [36] [37]. It should be noted that comparison of the two environments has revealed very unique corrosion behaviour under each exposure. Work by Martin et al. [38], compared cyclic salt fog exposure to immersion testing; it was revealed that the general corrosion rates and pitting density were higher for immersion surfaces, but overall pit surface area and depth was higher for salt fog exposures. Further studies showed that for immersion testing, in comparison to salt fog testing, accelerated pit nucleation as a result of continuous exposure and the faster dissolution of protective oxides [39]. Figure 2-4, as presented in a review by Winzer et al. [20], illustrates the comparison of corrosion performance for various alloys under both exposures, clearly identifying salt fog exposures to be less aggressive for Mg alloys. It was also noted that the pit coalescence rate was increased for immersion testing likely due to the increased nucleation rate and resultant pitting density [39]. This confirms the findings of both

Parkins [18] and Lindley et al. [15], in that solutions that are too aggressive promote pitting and localized corrosion while inhibiting SCC propagation. It has been identified that this effect is likely due to a decrease in the stress intensity factor (K<sub>1</sub>) by reducing the sharpness of the crack tip. As seen in Figure 2-2 when  $K_1 << K_{ISCC}$  crack propagation is inhibited. This shows that a cyclic salt fog environment is more effective for the study of SCC [37].



Figure 2-4: Comparison of corrosion rates of High Purity alloys (HP) and commercially pure Mg (CP) in both Salt Immersion Testing (SIT) and Salt Spray Testing (SST) [20].

Chapter 3: Research Objective

### **Chapter 3: Research Objective**

Recent work has indicated that the as-received (AR) surface of Mg alloy AZ31B can contain contaminants that are detrimental to the corrosion resistance of the material [40]. It was also seen in solution screening testing that the AR surfaces were more susceptible to pitting corrosion than in the treated surface conditions. It has also been shown that aggressive environments which enhance pitting and local corrosion can inhibit stress corrosion crack propagation [9] [18]. For this reason, and aligned with common industrial practice, knowledge of surface conditions is necessary for the study of SCC; both acid-cleaning (AC) and mechanical-polishing (MP) are commonly encountered surface conditions for the study of Mg alloys and were therefore used in this investigation [41] [42] [43] [44].

it is likely that the previously observed surface contamination was due to machining and milling processes and for this reason it is common for research purposes to mechanically-polish sample surfaces to remove such contaminants. The use of Mg alloys in industrial practice however, often uses bulk surface treatments such as acid cleaning for surface preparation. This research evaluates the relative effects of these surface conditions on the corrosion behaviour of AZ31B sheet materials.

Chapter 3: Research Objective

In particular, the present investigation focused on the SCC of Mg alloy AZ31B after various surface conditioning treatments. Samples were stressed and exposed to a salt fog environment until SCC occurred. Post exposure characterization of the fracture surfaces using SEM and LOM was used to identify differences in SCC. Further characterization of the surface conditions was conducted using polarization techniques and SEM cross-sectional imaging.
# **Chapter 4: Experimental Methods**

# 4.1 Pre-Exposure Characterization

#### 4.1.1 As-Received Material

This work used U-bend samples to investigate the effect of the surface condition of AZ31B-H24 sheet material on the kinetics and mode of SCC when exposed in a salt fog environment. All U-bend samples were machined from commercial 2 mm thick rolled sheet material. The H24 designation refers to a strain hardened then partially annealed temper as per ASTM standard B90 [45]. The bulk composition was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The sample was measured three times for each element, and the average composition results of this analysis are shown in Table 4-1 along with the ICP standard calibration errors for the analyzed elements. The composition is consistent with the ASTM B90 specification for Mg alloy AZ31B [45].

AZ31B	AI	Zn	Mn	Ni	Cu	Fe	Mg
wt %	2.88±0.02	1.08±0.01	0.29±0.01	<0.01	<0.01	<0.01	Balance
ASTM B90 [45]	2.5-3.5	0.6-1.4	0.2-1.0	0.005	0.05	0.005	Balance

Table 4-1:Mg Alloy Composition

The unexposed, as-received (AR) material was mounted in crosssection for microstructural observation. Samples were ground with abrasive papers to 4000 grit and then polished to a mirror finish using an OPS water-free silica colloidal suspension. Samples were then etched and observed using light optical microscopy (LOM). Typical microstructures are shown in Figure 4-1. The etchant used for all metallography was a picric acid solution (2.1 g C<sub>6</sub>H<sub>3</sub>N<sub>3</sub>O<sub>7</sub> [picric acid], 25 mL C<sub>2</sub>H<sub>6</sub>O [ethanol] and 5 mL C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> [acetic acid]). The average grain size was evaluated using the linear intercept method according to ASTM E122-09 [46]. The average grain size for the material in both the rolling and transverse directions was approximately 8.6 ± 1.3 µm.



Figure 4-1: Images of the AZ31B-H24 microstructure cut in cross-section of the: (A) transverse direction and (B) rolling direction

# 4.2 Salt Fog U-Bend Testing

## 4.2.1 U-Bend Samples

The U-bend samples were rolled using the two stage approach described in ASTM G30 [45]. The two stage approach, as shown in Figure 4-3, involves an initial bending operation with sufficient plastic

deformation to maintain a "U" shape after unloading (Figure 4-2 A and B) followed by a final bending operation to induce a static applied load on the bend just prior to exposure (Figure 4-2 C and D).



Figure 4-2: ASTM G30 U-bend two-stage process [45].

U-bend samples were selected for this study because the two stage process for U-bend samples applies both plastic and elastic loads, this ensures that the applied stress is greater than the yield stress and sufficient to initiate and propagate SCC.

Preparation of the U-bend samples was done by first cutting flat coupons, 2.54 cm x 17.78 cm. The flat coupons were then cold rolled followed by surface conditioning (which will be explained in more detail below) and finally loaded to make the "U" shape shown in Figure 4-2. Immersion in an ultrasonic bath of acetone ( $C_3H_6O$ ) for 300 s was used as a cleaning step between first stage loading, surface conditioning and second stage loading.

The flat coupons were cut with the long axis perpendicular to the rolling direction so that they could be loaded in the transverse direction.

The transverse direction was selected for all U-bend samples for consistency. Preliminary salt fog exposures showed no significant differences in corrosion performance between the rolling direction and transverse direction. The corrosion performance of preliminary samples was based on exposure times and was evaluated by visual inspection and LOM.

The first stage loading was done with a manual rolling press. At this stage the ends were approximately 9 cm apart, as shown in Figure 4-3 A. All samples were then cleaned by immersion in an ultrasonic bath of acetone for 300 s. Each sample was then treated with one of six surface conditions: as-received [AR], mechanically-polished [MP], sulphuric acid [H<sub>2</sub>SO<sub>4</sub>]-cleaned [AC], H<sub>2</sub>SO<sub>4</sub>-cleaned and aged for 300 h [A-AC], mechanically-polished and then H<sub>2</sub>SO<sub>4</sub>-cleaned [MP-AC], C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>-cleaned [O-AC]. Sulphuric acid has been used in studies to simulate surface conditions used in the automotive industry [37] [47]. These surface conditions using automotive industrial practice were selected to comparatively study the effect of H<sub>2</sub>SO<sub>4</sub> treatments on the resultant SCC resistance. Detailed descriptions of these surface conditions will be discussed in section 4.2.4.1.

Following surface conditioning, U-bend samples were once again cleaned by immersion in an ultrasonic bath of acetone for 300 s. The ends of all U-bend samples were then coated with a galvanic primer

paint. Polymer washers were also added as spacers to prevent galvanic coupling between the U-bends and stainless steel load bolts. The edges of the U-bend samples were coated with silicone to mitigate edge effects during exposure.

Figure 4-3 shows an as-received U-bend sample after completion of these preparation steps, just before exposure. The second stage loading (shown in Figure 4-2 C and D) was done by tightening the stainless steel load bolt until the ends were 3 cm apart, as shown in Figure 4-3 B. The geometry of the U-bends and load bolt prevented tightening to gaps smaller than 3 cm.



Figure 4-3: Two stage U-bend loading process as per ASTM G30 prior to exposure: (A)Stage 1 unloaded sample with 9 cm distance (B) Stage 2 loaded sample to 3 cm distance

All salt fog exposures were conducted in an Ascott 450cc salt fog chamber. The salt fog was generated by means of an atomizing spray nozzle using pressurized air and salt solution. At the base of the salt fog chamber there was a heating coil to assist in maintaining the fog

through humidity and temperature control. The chamber was calibrated by measuring the volumetric flow rate at various points within the chamber maintaining a uniform volumetric flow rate. Volumetric flow rates were also measured throughout the full duration of testing. Exposure conditions in the chamber were controlled by temperature, humidity, volumetric flow rate, acidity and salinity. The appropriate exposure conditions were determined by only varying the salinity of the neutral pH neutral NaCl salt solution. All salt fog testing was conducted at 35°C, a relative humidity of 95-98%, and a volumetric flow rate of 1.5-1.8 mm/h.

#### 4.2.2 Summary of Salt Fog Testing

There were two experimental objectives studied through salt fog testing. The first objective was to identify an appropriate NaCl concentration to study the SCC resistance through solution screening testing. The second objective was to study the effect of surface condition on the SCC as a comparative test. A summary of exposures to identify which surface conditions were exposed during both of the salt fog tests is provided in Table 4-2. In this table, when a sample of a given surface condition was exposed it is denoted by a ✓ if they were not exposed it is denoted with an ×.

Surface Condition		Experimental Objective			ctive	Description and Purpose		
		Solution Screening			Surface			
		(NaCl concentration)			Condition			
		5 wt%	0.5 wt%	0.05 wt%	0.05 wt%			
		for 3	for 5	for 11	NaCl			
		days	days	days				
A)	As-Received <b>AR</b>	1	~	\$	×	Determine exposure conditions to study SCC resistance.		
						<ul> <li>Determine baseline corrosion SCC resistance without surface conditioning.</li> </ul>		
	Mechanically-Polished <b>MP</b>	1	~	<i>√</i>	\$	<ul> <li>Determine exposure conditions to study SCC resistance</li> </ul>		
B)						<ul> <li>Investigate effect of surface condition</li> </ul>		
						without use of $H_2SO_4$ .		
						<ul> <li>Determine exposure conditions to study SCC resistance.</li> </ul>		
C)	l₂SO₄.Cleaned \ <b>C</b>	\$	\$	1	<i>✓</i>	<ul> <li>It was necessary to study the effect of H<sub>2</sub>SO<sub>4</sub> cleaning on SCC resistance as it is an industrially practiced surface treatment for AZ31B.</li> </ul>		
D)	Aged H <sub>2</sub> SO <sub>4</sub> -Cleaned <b>A-AC</b>	×	×	×	<i>✓</i>	<ul> <li>Qualitatively assess possible influence of hydrogen embrittlement on SCC resistance.</li> </ul>		
E)	Mechanically-Polished then H <sub>2</sub> SO <sub>4</sub> Cleaned <b>MP-AC</b>	×	×	×	1	<ul> <li>Validate whether or not acid-cleaning result is intrinsic to H<sub>2</sub>SO<sub>4</sub> exposure or is linked to</li> </ul>		
F)	Organic acid ( $C_2H_4O_2$ )-Cleaned <b>O-AC</b>	×	×	×	1	exposure to acidic media.		

# Table 4-2: Summary of Salt Fog Experimentation

#### 4.2.3 Salt Fog Solution Screening Experiments

This set of tests was used to find a suitable NaCl concentration to study the effect of the surface condition on the SCC resistance of AZ31B-H24 sheet material. The ASTM B117 [48] standard was used as a baseline NaCl salt concentration, which was then diluted to find an appropriate concentration to permit the study of SCC and identify an exposure time in order to induce SCC. Three environments were evaluated: 5 wt% NaCl, 0.5 wt% NaCl, and 0.05 wt% NaCl. Solutions were prepared by dissolving NaCl in deionized water and naturally aerated. All solutions were neutral pH. The exposure times were increased as the salt fog was made more dilute to account for the associated decrease in corrosivity. Exposure times were as follows: 3 days for the 5 wt% salt fog, 5 days for the 0.5 wt% salt fog, and 11 days for the 0.05 wt% salt fog. However, U-bends were removed if failure occurred before the total time had elapsed. The 0.05 wt% NaCl solution was the only concentration able to initiate SCC on all surfaces exposed. Thus, it was determined to be the most appropriate solution and as such was used for all further studies.

#### 4.2.4 U-bend Surface Condition Experiments

Photographs of four U-bends with four of the six surface conditions are shown in Figure 4-4. Although not shown, the A-AC and the MP-AC

surfaces showed no visible differences when compared to the AC surface condition.



Figure 4-4: As-prepared U-bend of each surface condition: (A) AR (B) MP (C) AC\*, MP-AC, A-AC (D) O-AC

\* Note: No visible differences were seen for all H2SO4-cleaned samples; thus, the AC surface shown is representative of the AC, MP-AC and A-AC surfaces.

#### 4.2.4.1 Surface Conditions

All six surface conditions were applied after the first stage of loading (Figure 4-2 B), prior to second stage loading (Figure 4-2.D). This was to ensure that the time between second stage loading and exposure was consistent for all samples and surface conditions.

#### A) As-Received, AR

No surface preparation was applied to the U-bend samples after rolling save for acetone cleaning. As shown in Figure 4-4 A, the surface was smooth, but darkened by a scale that likely formed during rolling.

The scale was very adherent to the sample surfaces and was indicated in previous work to have Cu and Fe contaminants [40].

#### B) Mechanically-Polished, MP

U-bends were subjected to mechanical polishing using SiC paper sequentially from 400 grit to 4000 grit. Water was used as the lubricant during all steps of polishing. After the final polishing step, the U-bends were rinsed with acetone and dried to prevent corrosion from the lubricant water. As it was polished to a matte finish, the samples were reflective with a smooth surface seen in Figure 4-4 B. This surface condition was used as a baseline for corrosion and SCC. These samples were used to identify characteristics of SCC after the removal of impurities in the AR condition and without the influence from the acidic exposures.

#### C) $H_2SO_4$ -Cleaned, AC

The AC surface was prepared by immersing the U-bends in an aqueous solution of 10%  $H_2SO_4$  for 10 s. This solution had a pH of one. This was immediately followed by an acetone rinse and immersion for 60 s in the acetone ultrasonic bath. The AC U-bend samples were acid cleaned 8 h prior to exposure. This surface condition was intended to identify if SCC was influenced by the high concentrations of H<sup>+</sup> ions and aggressive ions from this acidic exposure. A typical AC surface can be found in Figure 4-4 C. It should be recalled that this surface was also

typical of the A-AC and MP-AC surfaces, to be discussed below. From Figure 4-4 C it can be seen that the  $H_2SO_4$ -cleaned surfaces had a relatively rough surface due to the corrosion products formed during the  $H_2SO_4$  exposure.

#### D) Mechanically Polished then Acid Cleaned, MP-AC

U-bend samples were first mechanically-polished according to the procedure described above. The MP surface was then acid-cleaned by immersion in an aqueous 10% H<sub>2</sub>SO<sub>4</sub> solution of pH one for 10 s. The purpose of testing this surface condition was to determine if the observed SCC resistance of the AC surface condition was a direct consequence of the H<sub>2</sub>SO<sub>4</sub>-cleaning and, thus, independent of the AR surface condition.

#### E) Aged $H_2SO_4$ -Cleaned, A-AC

U-bends for the A-AC samples were allowed to age at room temperature for an additional 300 h after being acid-cleaned and before second stage loading and exposure. Because Mg is sensitive to the effects of hydrogen embrittlement the additional aging time for the A-AC samples was intended to allow any H trapped in the samples from the acid cleaning to diffuse out of the samples. The 300 h aging time was selected to allow sufficient time for the H to diffuse out of samples at room temperature [49]. It should be noted that this only accounts for HE

from surface conditioning treatment and does not account for HE that could occur during exposure to the salt fog.

#### F) Organic Acid Cleaned, O-AC

The U-bends were exposed to an aqueous 10% acetic acid solution of pH three for 10 s, 30 s and 60 s followed by immediate rinsing with acetone before being immersed in the ultrasonic acetone bath. This rinsing was done to prevent contamination of the acetone. This surface conditioning procedure was modified from the Magnesium Elektron standard operating procedure for acid pickling of Mg mill products [50]. As  $C_2H_4O_2$  is a much weaker acid than  $H_2SO_4$  longer exposure times were tested to observe the effects of more prolonged acid exposure. However, there were no visible differences between the 10, 30 and 60 s acetic acid exposure times and no significant differences were observed in either the SCC kinetics or mode of cracking. For this reason only one exposure time is shown in the experimental summary in Table 4-2. Previous studies identified changes in corrosion behaviour from the exposure of inorganic acid surface conditions [41]. The  $H_2SO_4$ cleaning was observed to have induced IGSCC in U-bends. The purpose of this organic acid-cleaned surface condition was to identify any sensitivity to the type of inorganic ions present in the acid (ie. sulphates,  $SO_4^{2-}$ ) and determine if changes in pH had an effect on SCC kinetics or mode.

#### 4.2.4.2 Observation during surface condition salt fog experiments

U-bends were periodically examined during exposure by stopping the salt fog chamber and removing the samples for macroscopic observation. For each surface condition tested, samples were examined at a minimum every hour until visible SCC could be observed on the surface. However, the AC U-bends demonstrated accelerated cracking initiation and, therefore, were examined every 20 min. After initiation, U-bends were visually inspected to identify propagation of SCC to failure.

A set of three U-bends for a given surface condition were removed after indications of SCC were visible for subsequent metallographic examination (defined here as the "initiation stage") using LOM. A second set of seven U-bends of a given surface condition were exposed further to permit a study of the propagation stage.

# 4.3 Post Exposure Characterization

#### 4.3.1 U-Bend Post Exposure Treatment

After removal from the salt fog chamber, U-bends were immediately rinsed with de-ionized water to remove salt crystallized on the surface. The load bolt was then unloaded followed by a cleaning step to remove the corrosion products formed on the surface. The aqueous cleaning solution used was 200 g/L  $CrO_3$  and 10 g/L  $AgNO_3$ . Using an ultrasonic

bath, U-bends were submerged in this solution for 120 s followed by a second immersion for 300 s in acetone.

#### 4.3.2 Post Exposure Analysis

A set of fractured samples were cross-sectioned and observed using LOM to investigate the mode and extent of SCC. Cross-sections were etched, as described previously, to reveal the microstructure. In addition some of the U-bends were forcibly broken to expose the crack propogation surface and observed with LOM. It was found that the AC U-bends underwent IGSCC at much faster rates than the TGSCC found in the MP U-bend samples. For this reason select fracture surfaces of the MP and AC surface conditions were observed by scanning electron microscopy (SEM) along with the O-AC surface condition for comparison purposes.

## 4.4 Surface Condition Characterization

The following experiments were done to compliment the U-bend SCC testing with the intent of characterizing the surface conditions prior to and after salt fog exposure. The U-bend exposures identified that the AC surface conditions greatly exacerbated SCC damage and as a result the following tests were focused on investigating effects of the  $H_2SO_4$  cleaning on the surface.

#### 4.4.1 Profilometry Testing

These measurements were taken to characterize dimensional changes as a result of the pre-treatment surface condition for both the MP and AC samples. A Zygo NewView 5000 white light interferometer was used for this characterization. This instrument detects the light reflected off of the sample surface to quantify the surface roughness. The interferometer scan area was approximately 0.7 mm x 0.5 mm. The roughness measurements of this system had an approximate resolution of  $\pm 0.01 \mu$ m. Ten areas of each surface were scanned to establish repeatability and obtain measurement statistics.

#### 4.4.2 Electron Microscopy

Samples were observed using a SEM with focused ion beam (FIB) capabilities. Using the ion milling capability of the FIB, samples could be lifted out and mounted for Auger Electron Spectroscopy (AES) measures. All SEM and AES microscopy was conducted on unexposed samples after surface conditioning.

The effects noted from  $H_2SO_4$ -cleaning, accelerated IGSCC, required investigation into the initial state of the pre-treatment surface for AC samples. For comparison, the unexposed surfaces of the MP, and O-AC samples were also investigated using SEM-FIB. Focused ion

beam (FIB) cross-sections were made to observe the films formed from each pre-treatment.

Auger electron microscopy was also attempted for AC crosssections. However, due to the rapid oxidation of sulphates at the metal/oxide interface, these samples could not be properly examined. This effect will be discussed further in the following chapter.

#### 4.4.3 Potentiodynamic Polarization Scans

Potentiodynamic polarization measurements were made on the MP, AC, MP-AC and O-AC surfaces. This was done to identify differences in electrochemical behaviour to with respect to the observed SCC test results.

To observe the electrochemical behaviour, exposure conditions of the salt fog testing were mirrored using a naturally aerated 0.05 wt% NaCl aqueous environment at 35°C. A flat cell was used for these measurements along with a Gamry Reference 600 instrument. A saturated calomel reference electrode (SCE) was used for all measurements. Flat coupon samples 3 cm x 3 cm were used with a graphite counter electrode. All working surfaces were prepared as described in section 4.2.4.1.

Anodic and cathodic polarization were conducted separately for each sample and results were repeated five times to assess reproducibility.

Samples were held at open circuit potential ( $E_{OCP}$ ) for 2 h for each sample prior to polarization to allow the potential to stabilize. Potentiodynamic scans were conducted using a scan rate of 0.02 mV/s and carried out to a minimum of +/- 1000 mV  $E_{ocp}$  or +/- 2000 mV if no breakdown potential was observed. The post exposure surfaces were photographed and observed using LOM.

Additional potentiodynamic polarization measurements were taken to identify the corrosion behaviour of MP samples in two acidic NaCl salt solutions. As will be discussed in greater detail in subsequent chapters, the H<sub>2</sub>SO<sub>4</sub>-cleaned exposures resulted in accelerated IGSCC due to a combination low pH, aggressive ions and a more porous, less adherent surface film which allowed the rapid mass transfer of these ions and the electrolyte (NaCl salt solution) to the metal surface. These potentiodynamic polarization tests in acidic salt solutions we designed to measure the isolated corrosion behaviour at the metal/film interface to simulate the interaction for a porous film exposure. Two acidic 0.05 wt% NaCl aqueous solutions were used: 0.5% H<sub>2</sub>SO<sub>4</sub> and 0.5% C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> with pH 1 and 3, respectively. These exposures were consistent with the above acidic surface condition pre-treatments. However, the acid concentrations were reduced to be less aggressive to account for the longer exposure times during potentiodynamic polarization.

# **Chapter 5: Results**

The following presents the results of salt fog solution screening and surface condition testing as well as unexposed surface condition characterization.

# 5.1 Solution Screening Results

The set of solution screening experiments tested three NaCl concentrations each for the three surface conditions under study with the intent of identifying a salt fog exposure suitable to study the effect of the surface condition on the SCC resistance of AZ31B-H24 sheet material. The matrix in Table 5-1 summarizes the results of these experiments.

Surface Condition	NaCl Salt Fog Exposure Conditions (at 35°C)				
	5 wt% up to 3 days	0.5 wt% up to 5 days	0.05 wt% up to 11 days		
As-Received <b>AR</b>	Pitting to failure	Pitting damage	SCC initiated at the base of pits		
Mechanically- Polished <b>MP</b>	Pitting damage	SCC and pitting	SCC to failure		
H <sub>2</sub> SO <sub>4</sub> -Cleaned <b>AC</b>	Pitting damage	SCC and pitting	SCC to failure		

Table 5-1: Summary of solution screening experimental results.

#### 5.1.1 5 wt % NaCl Salt Fog Exposure

The results showed that the 5 wt% NaCl solution was far too aggressive to produce SCC. The only mode of corrosion observed on all three surfaces for this exposure was pitting. The pitting damage was most extensive for the AR surface. All but two exposed U-bends had undergone localised pitting corrosion which perforated through the sample. A photograph documenting the typical corrosion mode on the as-received (AR), mechanically-polished (MP) and H<sub>2</sub>SO<sub>4</sub>-cleaned (AC) U-bend surface is shown in Figure 5-1. Aggressive pitting covered most of the exposed surface in each case. The severity of pitting was highlighted by the residual yellowish green deposit left behind in the base of pits from the post exposure cleaning step (i.e. 200 g/L CrO<sub>3</sub>, 10 g/L AgNO<sub>3</sub>). Deeper pits trapped some of the cleaning solution despite the ultrasonic cleaning in acetone, which precipitated the green solid product observed upon evaporation.



Figure 5-1: 5 wt% NaCl post exposure surfaces: (a) AR, (b) MP and (c) AC.

Exposed U-bends were cross-sectioned and observed using LOM. Cross-sectional images can be seen in Figure 5-2. The average pit depth on the AR surface was  $1.52 \pm 0.32$  mm. There was a notable decrease in the depth and severity of pitting for the MP and AC surface conditions. There was no significant differences between MP and AC surface surfaces. The average pit depth for the MP and AC samples was  $1.0 \pm 0.32$  mm.



Figure 5-2: 5 wt% NaCl exposure – pitting damage observed on the (A) AR (B) MP (C) AC surfaces as observed in cross-section.

#### 5.1.2 0.5 wt% NaCl Salt Fog Exposure

The reduction of salt concentration to 0.5 wt% NaCl resulted in a significant decrease in the depth of pitting on the AR surface as seen Figure 5-3. In this case, the average pit depth was reduced to  $0.76 \pm 0.13$  mm. However, the only mode of damage seen was pitting corrosion.

For both of the surface conditioned U-bends (MP and AC), a change in the corrosion mode was observed. Local corrosion (pitting) was still visible on the surface of these U-bends, but due to the shallow depth of the pits and local corrosion the more predominant corrosion mode was determined to be SCC.

Ten U-bend samples for both the MP and AC surfaces were exposed for 5 days. During this time all samples had developed SCC, which propagated to failure. The post-exposure surface appearance of both the MP and AC U-bends is shown in Figure 5-3.



Figure 5-3: Plan-view and cross-sectional view of the corrosion damage observed on the (A) AR (B) MP (C) AC U-Bend surfaces after exposure for 5 days in 0.5 wt% salt fog at  $35^{\circ}$ C

#### 5.1.3 0.05 wt% NaCl Salt Fog Exposure

The 0.05 wt% NaCl salt fog exposure for 11 days was the only exposure condition capable of producing SCC in all three surface conditions (AR, MP and AC). Pitting corrosion of the two surface conditioned U-bend exposures (MP and AC) was eliminated altogether whereas, the AR U-bends still underwent localized corrosion. In this case, the damage was minimized to superficial depths (0.24  $\pm$  0.08 mm).

A image documenting the typical post exposure appearance of each set of surface conditioned U-bends is shown in Figure 5-4. Cracks were clearly visible on the MP and AC U-bend surfaces. However, cracking within the AR U-bends was not evident until the U-bends were cut in cross-section and observed using LOM. A cross-sectional image showing typical features of the cracking found within each set of conditioned U-bends is also shown in Figure 5-4.

The AR samples showed that SCC had initiated from the base of the shallow pits. It is also noted that only the AR surface condition was exposed for the full 11 day exposure time. From the cross-sections, it was evident that SCC propagation was not as advanced for this surface condition. All twenty MP and AC U-bends (ten each) were tested,

fractured and had been removed prior to reaching the 11 day maximum exposure time.

Due to the SCC observed in both the MP and AC U-bends, the 0.05 wt% salt fog environment proved to be the most appropriate for further study of the effect of surface condition on the SCC resistance of AZ31B-H24 sheet material. Due to the pitting corrosion observed, the AR surface condition exhibited higher SCC resistance despite being more significantly damaged overall; Parkins [18] showed that aggressive environments that enhance local corrosion and pitting tend to decrease the stress intensity factor and sharpness of the crack tip to inhibit SCC propagation. It is also noted that the AR condition is not an industrially relevant surface condition. Industrial practice for the use of AZ31B-H24 incorporates surface conditioning pre-treatments prior to the application of coatings. As a result, no subsequent testing was conducted using U-bends with the AR surface condition due to the aggressive local corrosion observed to better focus on the studies of SCC resistance.



Figure 5-4: Photograph showing the typical appearance of plan-view and cross-section views of (a) AR, (b) MP, and (c) AC surface condition after exposure in 0.05 wt% NaCl salt fog at 35 °C

# 5.2 Surface Condition Salt Fog Exposure Results

A summary of the 0.05 wt.% NaCl salt fog SCC data for the U-bends prepared with the five surface condition pre-treatments of interest is provided in Table 5-2. The SCC resistance was semi-quantitatively described by both the time required to initiate SCC and the time to failure by SCC. The SCC mode was then investigated for each surface condition. It is noted that a minimum of ten samples were exposed for all surface conditions, with consistently reproducible results The results from surface condition salt fog testing showed no significant differences between the three  $H_2SO_4$ -cleaned surface conditions (AC, MP-AC, A-AC) with respect to both SCC kinetics (initiation and failure) and SCC mode. Thus, the results for these surface conditions are presented together in Table 5-2.

Surface Condition		Average Time to Visible Cracking (h)	Propagation Time* (h)	Average Time to Failure (h)
A)	Mechanically- Polished <b>MP</b>	48.4 ± 2.2	24.1	72.5 ± 4.3
B)	H <sub>2</sub> SO <sub>4</sub> - Cleaned AC			
C)	Mechanically- Polished then H <sub>2</sub> SO <sub>4</sub> -Cleaned <b>MP-AC</b>	2.0 ± 0.6	1.2	$3.2 \pm 0.6$
D)	Aged H <sub>2</sub> SO <sub>4</sub> - Cleaned <b>A-AC</b>			
E)	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> -Cleaned	32.3 ± 2.3	24.0	56.3 ± 2.2

Table 5-2: Summary	of SCC Data	for all Surface	Conditions	Tested.
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Note: Propagation time was not recorded independently, it was calculated as the difference between time to visible cracking and the time to failure.

# 5.2.1 MP and AC Surface Conditions

MP U-bends showed visible evidence of SCC after 48 h of exposure. An additional 24 h was required for the cracks to propagate through the sample thickness to failure. SCC of the AC U-bends was significantly accelerated versus the MP surface condition, as visible cracks were observed after 2 h of exposure and fracture was observed after an additional 1 h of exposure.

Randomly selected SCC indications on the MP and AC U-bends were cut in cross-section and observed using LOM. Numerous cracks

were observed. The images shown in Figure 5-5 are representative of cracks found in the U-bends. The MP U-bends showed characteristics of TGSCC: i.e. cracks linearly propagating through bulk grains. However, the AC U-bends showed characteristics of IGSCC: i.e. jagged, multi-directional cracks propagating along grain boundaries.



Figure 5-5: Etched cross-section images of the SCC found within the Ubends that were (a) MP and (b) AC after exposure in 0.05 wt.% NaCl salt fog at 35°C until fracture.

An examination of a fracture surface from each surface condition was conducted using SEM. Secondary electron images of the fracture surface of a MP and AC U-bend are shown in Figure 5-6. Both fracture surfaces show evidence of brittle fracture associated with SCC. This is characterized by the cleavage and beach markings across the fracture surface seen as the bright contrasting lateral striations across the fracture surfaces. The notable difference between the two was the contrast and faceted fracturing seen on the IGSCC (AC) fractured surface. The IGSCC was characterized by this faceted structure because of the cracking propagated down grain boundaries, leaving sharp interfaces. The TGSCC (MP) fracture surface, on the other hand, was much smoother due to the linear propagation of cracks through grains along crystallographic planes.



Figure 5-6: SEM images of the post-exposure SCC fracture surface of a (A) MP and (B) AC U-bend after exposure to 0.05 wt.% NaCl salt fog at 35°C.

### 5.2.2 MP-AC U-bend Samples

The salt fog testing results of the MP-AC U-bend samples closely followed the results of the AC U-bend samples. Per Table 5-2, the MP-AC U-bend samples had visible cracks after just 2 h of exposure and

propagated to fracture after an additional 1 h of exposure. Images of the fractured U-bend sample showing the SCC in plan-view and in cross-section are shown in Figure 5-7.



Figure 5-7: Image of the fractured U-bend showing the SCC within a MP-AC U-bend (A) plan-view and (B) cross-section after exposure in 0.05 wt.% NaCl salt fog at 35°C

The images shown in Figure 5-7 are representative of the results seen for all MP-AC samples. The crack tip shown in the cross-section image [Figure 5-7 (B)] can be compared to those in Figure 5-5, where it can be seen that the mode of cracking was similar to that of the AC U-bend samples. This shows that the effect of  $H_2SO_4$ -cleaning on SCC

was independent of the AZ31B-H24 AR surface condition prior to  $H_2SO_4$  exposure. Furthermore, this suggests that the shift from TGSCC to IGSCC was a direct result of  $H_2SO_4$  exposure during cleaning.

#### 5.2.3 A-AC U-bend Samples

A-AC U-bend samples were exposed and observed to investigate the possible effect of hydrogen embrittlement (HE) on the acid cleaned samples SCC. Samples were H<sub>2</sub>SO<sub>4</sub>-cleaned and aged at room temperature for 300 h to allow hydrogen from the H<sub>2</sub>SO<sub>4</sub> exposure to diffuse out of the samples. However, there were no significant differences found between SCC of the A-AC and AC samples as noted in Table 5-2. This indicates that the shift from TGSCC to IGSCC was not an effect of HE during the surface condition procedure. This was expected due to the short acid exposure times of only 10 s. This does not however, give an indication as to whether HE occurred during the salt fog exposure to influence SCC propagation behaviour.

#### 5.2.4 O-AC U-Bend Samples

U-bends that were cleaned using  $C_2H_4O_2$  (acetic acid – i.e. an organic acid) in place of  $H_2SO_4$  (an inorganic acid) were tested. This test was to confirm that the accelerated IGSCC induced by  $H_2SO_4$ -cleaning in consequence of the aggressive inorganic ions (sulphates) in combination with a low pH.

The exposure results from all three  $C_2H_4O_2$ -cleaning times were insignificantly different. SCC cracks were observed for all three sets of O-AC U-bend samples; however there were no notable differences in SCC resistance from visual inspection or LOM examination. The time to visible cracking and fracture was, however, significantly longer than that recorded for the set of AC U-bends as seen in Table 5-2.

Of the thirty U-bends tested (ten for each cleaning time) the exposure time required to produce visible cracking was about 32 h (Table 5-2). Six of the cracked U-bends (two for each cleaning time) were removed for characterization at that time. The remaining 24 U-bends fractured after an additional 24 h of exposure.

When compared to the AC samples it is evident that the SCC initiation times were longer and kinetics were slower for O-AC samples. The time to visible cracking on the O-AC U-bends was found to be only slightly faster than that observed for the MP U-bends. In addition, the time for cracks to propagate to fracture was the same for the O-AC U-bends as it was for the MP U-bends (about 24 h).

Cross-sectional imaging was also conducted for the O-AC U-bends. These images along with the plan-view images of the exposed surface can be seen in Figure 5-8. The exposed surface and fracture area in plan-view looked very similar to those of the AC U-bends. However, the

mode of cracking, as imaged in cross-section, showed characteristics of TGSCC similar to those observed for the MP U-bends.



Figure 5-8: Image of the fractured O-AC U-bend showing the SCC within in (A) plan-view (B) lower magnification cross-section and (C) higher magnification cross-section after exposure in 0.05 wt.% NaCl salt fog at 35°C.
#### 5.3 Surface Condition Characterization Results

#### 5.3.2 Profilometry

An examination of the unexposed MP and AC surfaces was conducted using an interferometer to investigate the geometric differences between the two surface conditions prior to salt fog exposure. These results can be seen in Figure 5-9.



Figure 5-9: Interferometer results of pre exposed (a) MP and (b) AC surfaces. The differences in scale between the two datasets should be noted.

It is evident from Figure 5-9 that the AC surface was significantly rougher. The average roughness ( $R_a$ ) measured across the ten areas sampled was 1.367 ± 0.11 µm. This same measurement for the MP surface was only 0.165 ± 0.03 µm. Although there is a considerable difference between these  $R_a$  values it is an average value across the

scanned area and does not represent the extreme peaks and valleys of the surfaces. The images in Figure 5-9 clearly show how the roughness distribution across the surface films for both surface conditions, identifying the AC surface to have much larger variations in its profile.

# 5.3.3 Focused Ion Beam and Auger Electron Microscopy Imaging of the Surface Films

FIB-SEM imaging to characterize the film was done on a comparative basis between a MP, AC and O-AC samples. Samples were cross-sectioned using Ga ion milling in the FIB-SEM to avoid oxidation of the cross-sectional surface. A protective tungsten layer approximately 200 nm thick was sputtered onto the surface via ion beam deposition prior to milling to mitigate damage of the surface films from the Ga ions.

The difference between the films formed on the MP, AC and O-AC surfaces was quite significant. Both the thickness and morphology of the films are drastically affected by the pre-treatment, it is evident that these differences were likely an important contributing factor in the observed SCC. To highlight this relationship, a summary of the film characteristics along with the corresponding exposure data for each surface condition can be seen in Table 5-3.

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	Film Characteristics		Salt Fog Exposure Results		
Surface Condition	Thickness	Morphology	SCC Mode	Average Time to Visible Cracking	Average time to failure
a) Mechanically -Polished <b>MP</b>	20-35 nm	continuous and compact	TGSCC	48.4 ± 2.2 h	72.5 ± 4.3 h
b) H <sub>2</sub> SO <sub>4</sub> - Cleaned <b>AC</b>	10-15 µm	Porous with exposed bare metal	IGSCC	2.0 ± 0.6 h	3.2 ± 0.6 h
c) C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> - Cleaned <b>O-AC</b>	1.5-4.7 µm	Compact with minor cracking	TGSCC	32.3 ± 2.3 h	56.3 ± 2.2 h

Table 5-3: Summary of Film Characteristics and Corresponding Exposu	re
Results for Each Surface Condition.	

It can be seen from Table 5-3 that as the film thickness increases and becomes more porous SCC is accelerated. The air-formed film on the MP surface can be seen in Figure 5-10. its thickness is ranged from 20-35 nm thick and it appeared to be relatively continuous and compact. However, the film formed on the AC surface, seen in Figure 5-11, was much thicker, approximately 10-15  $\mu$ m and was extremely porous. Many of these pores breach from the film-metal interface to the film surface which would allow exposure of the bare metal to the electrolyte. Comparatively, the O-AC surface film which can be seen in Figure 5-12 although it is not as thick as the ranged from 1.5-4.7  $\mu$ m thick and was reasonably compact but did, however, have cracks through the film to the film-metal interface. The AC surface, as imaged

in cross-section, showed large cavities penetrating through the film to the-AZ31B-H24 interface.



Figure 5-10: SEM-FIB cross-sectional examination of the air formed

surface film formed after MP surface conditioning.



Figure 5-11: SEM-FIB cross-sectional examination of the surface film formed on AZ31B as a result of the AC surface condition.



Figure 5-12: SEM-FIB cross-sectional examination of the surface film formed on AZ31B as a result of the O-AC surface preparation.

A FIB-prepared cross-sectional sample of the AC surface film across the film-metal interface was lifted out and characterized with SAM. The lifted out view of the cross-section was prepared for Auger characterization of the film/metal interface. The sample was transferred from the FIB-SEM to the SAM, during which time it was exposed to air for approximately 5 min. Upon viewing the sample in the SAM, a large oxide growth formed on the cross-sectional surface at the film/metal interface this can be seen in Figure 5-14. Superimposed on Figure 5-13

in red is the outline of the original  $H_2SO_4$  formed film along with the two main cracks that could be seen in Figure 5-11.



Figure 5-13:SAM characterization of an AC cross-sectional lift-out; an oxide growth formed on the surface during transfer from the FIB-SEM.

Auger electron elemental mapping in the SAM was conducted, the results of which are shown in Figure 5-14. It was found that the additional corrosion product that was formed was primarily comprised of magnesium, sulphur and oxygen. Note that the tungsten detected was

from the protective coating applied during the FIB milling process and the contents of zinc, aluminum and carbon were too low to be accurately detected. The additional corrosion product may have formed in one of two ways: either from the transformation of the original MgO film to a sulphur containing product or as a result of a corrosion reaction at the magnesium oxide film interface. Regardless, the sulphur and oxygen is believed to have played a critical role in the formation of the additional corrosion product. Although it was not validated, it was likely that the sulphur was contained within the AC surface pre-treatment film. Both the rate and severity at which this growth formed is indicative of the exposure that occurred during the salt fog experiments. This porous and reactive film engenders the rapid mass transfer of the possible aggressive ions in addition to the aggressive salt fog environment to the metal interface.



Figure 5-14: Auger electron mapping of the AC surface film.

#### 5.3.1 Potentiodynamic Polarization Scans

Potentiodynamic polarization scans of the MP and AC surfaces were conducted to identify any differences in electrochemical behaviour between the two surface conditions. Five samples of each surface condition were tested to ensure a consistent and repeatable behaviour. The results of these tests are shown in Figure 5-15.



Figure 5-15:Potentiodynamic polarization scans of the MP and AC surfaces for 0.05 wt% NaCl exposure.

The cathodic curves of both surfaces did not show any significant differences at high overpotentials but do indicate increased cathodic kinetics at low to intermediate overpotentials for the AC surface condition. The anodic curves also showed a change in behaviour between the two surface conditions. The MP surface had a breakdown potential of approximately  $-1.126 \pm 0.083$  V<sub>SCE</sub> (i.e. -0.35 V above E<sub>OCP</sub>). The AC surface did not exhibit this behaviour, as can be seen by the lack of a breakdown event being present for the anodic polarization curves. It is noted that there was more variation in the MP anodic

polarization data, likely due to its dependence on the native film structure breakdown. This breakdown behaviour is consistent with the surface film morphologies seen in the previous section. The air-formed film on the surface of the MP samples is continuous enough to provide adequate protection until the breakdown event occurs. It can also be said that the porous H<sub>2</sub>SO<sub>4</sub>-formed film on AC surfaces is effectively already broken down during polarization. The porosity of the film allows exposure of the rapid mass transfer of the electrolyte directly to the metal interface, this is why no breakdown event is seen in the anodic polarization behaviour.

The open circuit potential OCP measurements for the MP and AC surfaces can be seen in Figure 5-16. From the anodic behaviour seen in Figure 5-15, the breakdown events for AC surfaces were expected to be clearly visible in the OCP scans. This was indeed the case as the film breakdown is characterized by a large spike followed by a significant increase in 'noise' throughout the rest of the scan [51]. The breakdown points are marked with an arrow in the plot. It is evident from this that the breakdown occurred almost immediately after immersion, one of which showed evidence of breakdown occurring immediately after immersion prior to measurement.

The MP OCP transients are more uniform than those of the AC samples and contained no features indicating breakdown occurred, as

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expected because the films on the MP surfaces (as seen previously) are more uniform, more stable and thinner.



Figure 5-16:  $E_{OCP}$  measurement of MP and AC samples.

The post polarization surfaces were observed and imaged both macroscopically and using an optical stereoscope. Representative images of these results can be seen in Figure 5-17. The post polarization surfaces were consistent with the electrochemical behaviour observed in Figure 5-15. The corrosion observed on the MP

surface was more localized in nature, which is consistent with the breakdown seen during anodic polarization whereas the AC polarization sample was visibly corroded across the entire surface. This was consistent with the observed anodic current densities which were higher for the AC surfaces.



Figure 5-17: Post exposure image of (a) polarized MP surface and (b) polarized AC surface.

Potentiodynamic polarization measurements were taken of MP-AC and OAC surfaces, the results of which can be seen in Figure 5-18 and Figure 5-19. The potentiodynamic scans of the MP-AC surface were superimposed on those of the AC surface which showed that the polarization behaviour of both surfaces were insignificantly different,

this is consistent with the results of the salt fog testing. In addition, there were no visible differences (microscopic or macroscopic) in the corrosion observed between MP-AC and AC surfaces.



Figure 5-18: Potentiodynamic polarization behaviour of the MP-AC surfaces compared to AC surfaces.

The O-AC surface however, did not exhibit the same polarization behaviour as the AC series of surfaces. There is a clear breakdown potential for all the anodic polarization measurements much like the MP surfaces. This again is consistent with the observed behaviour during

U-bend salt fog testing. The results shown in Figure 5-19 have been superimposed on potentiodynamic scans of MP and AC surfaces to show the comparison. This comparison can also be correlated to the data summarized in Table 5-3, it can be noted that the two surface conditions with a compact relatively continuous film exhibited a breakdown during anodic polarisation. It should also be noted that although the O-AC and AC samples had much thicker films than the MP samples, it is only the AC sample that exhibited faster corrosion kinetics. This can also be attributed to the porosity of the film. The thicker film on the AC samples is porous which provides little protection to the metal surface, the thicker film on the O-AC sample however is much more compact and uniform which can provide protection until the film breakdown occurs.



Figure 5-19: Potentiodynamic polarization behaviour of the O-AC surfaces compared to MP and AC surfaces.

Polarization measurements conducted in acidic salt solutions revealed the behaviour at the film-metal interface. It has been established that the porous film was an important contributing factor in accelerated SCC of the AC surface condition. The polarization measurements shown in Figure 5-20 simulate the exposure from a porous film so as to evaluate the effects of pH and aggressive  $ions(SO_4^{2^-})$ . As discussed previously, Mears et al. [13] showed a reduction in pH can induce a shift from TGSCC to IGSCC in Mg alloys. However, the results in Figure 5-20 showed that decreasing the pH from 3 to 1 actually decreased both the cathodic kinetics and corrosion

potential. Additionally the OCP measurements in Figure 5- 21 show that the open circuit potential of O-AC samples was higher.



Figure 5-20: Potentiodynamic polarization measurements of polished samples exposed to acidified salt solutions.



Figure 5- 21:  $E_{OCP}$  Measurements of mechanically-polished surfaces exposed under acidified salt solution conditions.

## **Chapter 6: Discussion**

#### 6.1 Contributing Factors Required for IGSCC

The discussion will focus on the effects of the AC surface condition on SCC. As the results showed, it is evident from both the fracture kinetics and the mode of SCC that the use of  $H_2SO_4$  during surface pretreatment changes how the salt fog exposure environment interacts with the alloy and ultimately changes the behaviour of SCC.

All surface pre-treatments involving the use of  $H_2SO_4$  (AC, MP-AC and A-AC) resulted in IGSCC, the rates of which were much faster than other surface conditions. By comparison, the surface conditions that were found to have slower SCC kinetics ie. MP and O-AC, when exposed to the same salt fog conditions showed TGSCC.

It can be concluded from this work that under favourable conditions to induce SCC, IGSCC is the resultant of the confluence of three primary factors: low pH (high H<sup>+</sup> ion concentration), the presence of aggressive ions, and the porous film that allowed the rapid mass transfer of the electrolyte and aggressive ions to the film-metal interface. The relationship of these three factors is summarized in Figure 6-1. It was observed that when all three of these factors influence SCC, the mode will be intergranular as seen in AC, MP-AC,

and A-AC samples. However, when lacking one of these three, the mode of SCC would be transgranular as seen in the MP and O-AC samples.



Figure 6-1:Contributing factors required for IGSCC to occur

Work by Sieradzki and Newman [8] have identified a strong correlation between IGSCC in Mg alloys and increased anodic dissolution rates. This is supports all three factors identified in Figure 6-1 as will be discussed individually.

#### 6.2 The influence of the Surface Film on SCC

The key factor that influences the mode of SCC is the state of the surface film. This is because it either inhibits or enables mass transfer of the electrolyte to the film-metal interface.

In a study of involving organic pickling of AZ31B sheet using a  $C_2H_4O_2$ -cleaning process by Nwaogu et al. [52], it was established that corrosion resistance in chloride containing aqueous solutions was improved by the formation of a uniform hydroxide film; much like the MP and O-AC surface films seen in Figure 5-10 and Figure 5-12.

.The inverse of this has also been studied, Baril and Pebere [53] demonstrated that the exposure of Mg alloys to sulphate solutions resulted in extremely porous films formed on the metal surface, consisting mainly of MgO and Mg(OH)<sub>2</sub>. More importantly it was observed that Mg surface was not afforded any protection by the sulphate-formed film; as the immersion time increased, the film thickness showed proportional increases while corrosion rates stayed constant [53]. This is also in agreement with the AC sample films observed using SEM Figure 5-11 and SAM Figure 5-13 microscopy.

The porous AC surface film cannot provide the same level of protection as the uniform surface films from the MP and O-AC surface conditions. Thus, it can be concluded that state of the surface film

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accounts for the differences in exposure results for the AC and O-AC surface conditions with respect to mode and kinetics of SCC.

These studies in addition to the SCC results show the correlation between the mode of SCC and the corrosion resistance ie. anodic dissolution. More specifically it indicates that higher anodic dissolution rates such as the AC exposures favour IGSCC. This is because the porous AC film shown to have higher anodic dissolution rates than that of MP and O-AC samples, resulted in IGSCC as opposed to TGSCC.

Furthering this conclusion, the polarization measurements also indicated that the surface film has a strong influence on the mode of SCC. Firstly, it was noted in the OCP measurements shown in Figure 5-16 that the surface film on the AC sample underwent film breakdown almost immediately after immersion. Second, the polarization measurements of surface conditioned samples shown in Figure 5-19, illustrates the higher corrosion current densities for AC samples which are an order of magnitude higher than that of the MP and O-AC samples. Finally, the slightly acidic polarization measurements shown in Figure 5-20, simulated porous films for both acidic exposures; in this measurement, the  $C_2H_4O_2$  corrosion kinetics are actually faster than that of the H<sub>2</sub>SO<sub>4</sub>, highlighting how much protection is provided by the compact O-AC film.

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#### 6.3 The influence of pH on SCC

The shift in mode of SCC from TGSCC to IGSCC as a result of pH change was observed by Mears et al. [13]. This work identified that more acidic environments were conducive to IGSCC furthering the basis that increased anodic dissolution has a strong influence on the mode of SCC.

It was shown in the comparative exposure results of the MP, AC, and O-AC surface conditions that the pH during pre-treatment can affect the mode of SCC. The samples which were exposed to H<sub>2</sub>SO<sub>4</sub>, pH of 1, underwent IGSCC. It should be noted however that this behaviour was not isolated to the effect of pH, as stated previously all three factors need to be present for IGSCC to occur. The AC samples had both sulphates present in the film during exposure as well as the porosity observed in Figure 5-11. It is reasonable to assume however that the formation of the porous film and introduction of aggressive ions into the film.

#### 6.4 The influence of Aggressive Species on SCC

Parkins [18] demonstrated that the introduction of aggressive ions during exposure increased the anodic dissolution and ultimately lead to IGSCC. Comparison of the O-AC and AC surface condition exposures

highlights the effect of an aggressive ion on SCC. Results from the O-AC surface condition were closer to that of the MP samples than the AC samples. This O-AC and MP surface condition pre-treatments did not expose the samples to the  $HSO_4^-$  ions which resulted in exposure to aggressive ions. It can be seen that in the absence of these ions, the mode of SCC is transgranular. thus, the aggressive ions introduced contribute to the intergranular mode of SCC.

The presence of the HSO<sub>4</sub><sup>-</sup> ions was noted in the SAM imaging in Figure 5-13 and Figure 5-14. The chemical mapping showed clear indications that the aggressive ion species was present in the film. Furthermore the sulphur and oxygen growth that was observed in Figure 5-13 demonstrated the reactivity of these ions when exposed to lab air during transport.

The aggressive ions present in the AC exposures can also be directly attributed to the increased anodic dissolution rates through the polarization measurements. As seen in Figure 5-19, the average corrosion current densities of AC samples were an order of magnitude higher than that of the O-AC samples. Again, because the anodic dissolution rates are tied to all three factors, the results discussed are not isolated to effects of the aggressive ions. They are however still indicative of the influence that aggressive ions have on the mode of SCC.

## **Chapter 7: Conclusions**

This work investigated the effects of surface condition on the stress corrosion cracking of Mg alloy AZ31B. Salt fog testing of U-bend samples and pre-exposure characterization techniques were carried out using six surface pre-treatments, including combinations of mechanical polishing, H2SO4 cleaning and cleaning using an organic (acetic) acid.

The key results are summarized below.

- A primary focus of this study was the effects H<sub>2</sub>SO<sub>4</sub>-cleaned surface condition on SCC. It was found that the SCC kinetics were drastically accelerated compared to other surface conditions as a result in a change of the mode of SCC. All surface conditions involving the use of H<sub>2</sub>SO<sub>4</sub> resulted in IGSCC.
- 2. The current understanding of IGSCC is that it is highly dependent on the rate of anodic dissolution [8] [13] [18] [29]. The shift from TGSCC to IGSCC for H<sub>2</sub>SO<sub>4</sub>-cleaned surfaces was therefore attributed to the confluence of three primary factors that influence anodic dissolution:

- A porous film that allows the rapid mass transfer of the electrolyte and aggressive species directly to the film metal interface.
- A low pH, introduced during the H<sub>2</sub>SO4-cleaning (pH of 1) which aids in anodic dissolution of the metal surface.
- c. The presence of an aggressive ion resulting in accelerated anodic dissolution.
- 3. It was shown that all three of these contributing factors needed to be present for IGSCC to occur. Experimentation involving the use of inorganic (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, pH of 3) showed that with by eliminating any one of the three factors (porous film, low pH, aggressive ions) the mode of corrosion would remain TGSCC.
- 4. The cross-sectional SEM images of the unexposed MP, AC and O-AC surfaces (Figure 5-10, Figure 5-11, Figure 5-12) identified that the H<sub>2</sub>SO<sub>4</sub>-cleaning for AC samples formed a thick porous film in contrast to the O-AC and MP samples which, by comparison were relatively thin and continuous. In addition, SAM (Figure 5-13) and Auger electron mapping (Figure 5-14) of the AC surface film suggested that the aggressive ions were dissolved in the film.

- 5. Polarization measurements in acidic solutions of mechanicallypolished surfaces isolate the behaviour of porous films and applied it to the organic acid for comparison (Figure 5-20). This demonstrated the protection provided by the continuous O-AC film inhibited IGSCC because without this protective film during C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> exposure exhibited corrosion kinetics comparable to that of H<sub>2</sub>SO<sub>4</sub>.
- 6. Initial solution screening salt fog exposures determined 0.05 wt% NaCl to be a suitable concentration for the study of SCC of Mg AZ31B in a salt fog environment. In addition, the susceptibility of the AR surface condition to pitting and local corrosion was found to be too high for the adequate study of SCC.
- 7. MP-AC samples exhibited the same accelerated IGSCC as AC samples, indicating the accelerated SCC kinetics manifested in the TGSCC to IGSCC transition were a direct effect of H<sub>2</sub>SO<sub>4</sub> exposure. MP-AC samples (Figure 5-7) shared the same accelerated IGSCC as the AC samples (Figure 5-5). This indicates that the effect was independent of the initial surface and was a direct effect from exposure to H<sub>2</sub>SO<sub>4</sub> during cleaning.

8. the salt fog testing results from A-AC samples were also consistent with that of AC samples, indicating that the H<sub>2</sub>SO<sub>4</sub>-cleaning did not induce hydrogen embrittlement. This result was expected due to the short exposure times from the acid cleaning i.e. room temperature aging would allow any hydrogen ingress from the acid cleaning to diffuse out of samples prior to loading and exposure.

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