Characterisation of stress corrosion cracking (SCC) of Mg–Al alloys

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Abstract

Stress corrosion cracking (SCC) of the Mg–Al alloys AZ91, AZ31 and AM30 in distilled water has been characterised using constant extension rate tests (CERTs) and linearly increasing stress tests (LISTs). AZ91 consists of an α-matrix with extensive β-particles, whereas AZ31 and AM30 consist only of an α-matrix with an Al-concentration similar to that in AZ91. The presence of β-particles in AZ91 was associated with: (i) a lower threshold stress, $\sigma_{SCC}$, for AZ91 (55–75 MPa) relative to AZ31 (105–170 MPa) and AM30 (130–140 MPa); and (ii) a different SCC initiation mechanism for AZ91 relative to AZ31 and AM30. The SCC velocity, $V_c$, for AM30 ($3.6 \times 10^{-10}$ to $9.3 \times 10^{-10}$ m/s) was lower than that for AZ91 ($1.6 \times 10^{-9}$ to $1.2 \times 10^{-8}$ m/s) and AZ31 ($1.2 \times 10^{-9}$ to $6.7 \times 10^{-9}$ m/s). This was attributed to the influence of Zn and second phase particles, which are more concentrated in AZ31, on the diffusivity of H in the α-matrix.

Keywords: Stress corrosion cracking; Hydrogen embrittlement; Magnesium alloys; Constant extension rate test; Linearly increasing stress test

1. Introduction

Our recent publications [1–5] have shown that there exists a considerable body of research outlining the phenomenology of transgranular stress corrosion cracking (TGSCC) of Mg alloys. It is generally accepted that the mechanism for TGSCC of Mg alloys is a form of hydrogen embrittlement (HE) with the hydrogen coming from the cathodic partial reaction (hydrogen generation) of the Mg corrosion reaction [6–9]; however, the specific nature of the HE mechanism remains uncertain. The HE models that may be applicable for Mg alloys are: hydrogen enhanced decohesion (HEDE); hydrogen enhanced localised plasticity (HELP); adsorption-induced dislocation emission (AIDE); and delayed hydride cracking (DHC). AIDE [10] and DHC [11–15] have been proposed for TGSCC of Mg alloys; however, the evidence for both mechanisms is limited. HEDE and HELP also remain possible mechanisms. Detailed reviews of these mechanisms are provided in Birnbaum [16], Lynch [17] and Gangloff [18]. A brief review of factors relevant to this investigation is given below.

1.1. Hydrogen embrittlement mechanisms

HEDE has been proposed as the dominant mechanism for high-strength alloys that do not form hydrides [18]. It involves reduction of the electron charge density between metal atoms in the region ahead of the crack tip, where H accumulates by stress-assisted diffusion. This causes weakening of the bonds between and eventually tensile separation of adjacent metal atoms.

DHC involves repeated stages of: (i) stress-assisted diffusion of H to the region ahead of the crack tip; (ii) hydride precipitation as the local H concentration exceeds the local solvus; and (iii) brittle fracture through the hydride. DHC has been proposed as the mechanism for TGSCC of Mg alloys, although evidence for this is limited [11–14]. Our numerical model for DHC in Mg predicted crack propagation velocities in the lower range of those reported by previous workers; however, the results were based on speculative values for the H diffusion coefficient and solvus concentration [15].

HELP is attributed to enhanced dislocation mobility due to the interactions between H atmospheres at dislocations and obstacles to dislocation motion, resulting in microvoid coalescence more localised than that which occurs in inert environments. This necessitates a sufficiently high H diffusivity such that H atmospheres may move with their respective dislocations.
and reconfigure as they interact with stress fields and other H atmospheres [16,17]. Kuramoto et al. [19] provided some evidence for HELP in the Mg alloy AZ31 by observing H evolution along slip lines during SCC. However, it should be noted that H transport by mobile dislocations might play a secondary role to other HE mechanisms. For example, dislocations emitted at the crack tip by adsorbed H atoms (as per AIDE) may also accumulate H atmospheres [17], which may explain the observations by Kuramoto et al.

Lynch [17,20] proposed that H adsorbed at the crack tip and trapped within the first few atomic layers of metal may weaken metal–metal bonds causing dislocation emission. This would promote crack growth by alternating slip on specific planes, resulting in enhanced localised microvoid coalescence. Lynch and Trevena [10] proposed that TGSCC of pure Mg in NaCl + K₂CrO₄ solution occurred by AIDE based on the similarity of the fracture surface morphology with that produced by liquid metal embrittlement, which involves adsorption of metal atoms at the crack tip.

1.2. Hydrogen trapping and diffusion

The influence of microstructural features on SCC characteristics is indicative of the predominant HE mechanism. Microstructural influences may be rationalised in terms of the rate of H transport within the matrix, which is partly dependent on the strength and distribution of traps and short-circuit diffusion paths. Short-circuit diffusion paths (e.g. grain and phase boundaries) may accelerate diffusion by two to four times the rate in the bulk matrix [21,22]. The influence of traps (e.g. solute atoms, second phase particles, grain and phase boundaries, dislocations and twin boundaries) on H transport depends on their binding energy and whether they are reversible (acting as sinks or sources, depending on conditions) or irreversible (always acting as sinks). There is no data currently available for the binding energies of traps in Mg alloys.

Pressouyre [23] proposed that a uniform distribution of irreversible traps would increase resistance to HE by reducing the quantity of H arriving at crack initiation sites, provided that the primary mode of H transport is dislocation sweep or interstitial diffusion (not diffusion along short-circuit paths). Traps may themselves become crack initiation sites if their H concentration exceeds some critical level. The susceptibility of metals to HE is particularly dependent on the role of reversible traps (e.g. low angle grain boundaries and dislocations). The role of reversible traps depends on: (i) the source of H (internal or external); and (ii) the mode of H transport (dislocation sweep or interstitial diffusion) [23]. In the case of H transported with dislocations, reversible traps may act as sinks or as sources of H for mobile dislocations such that H may penetrate further into the specimen than in the absence of traps [23].

1.3. Phenomenology of TGSCC of Mg alloys

A comprehensive review of the phenomenology of SCC in Mg alloys is given in Winzer et al. [1]. Some important considerations, in the context of the present investigation, are given below.

It is difficult to isolate the specific role that alloying elements play in promoting or retarding SCC, since they may have competing influences on H activity, film integrity and dislocation mobility. Moreover, these influences may be specific to combinations of alloy, environment and mechanical loading. Mg alloys used in service typically contain Al and Zn as primary alloying elements. Mg alloys containing Al and Zn are particularly susceptible to SCC [24–28]. The SCC susceptibility of Mg alloys increases with increasing Al concentration [29] despite an increase in the repassivation rate [14]. Mg alloys with >2% Al concentration typically contain Mg₁₇Al₁₂ (β-phase) particles, which are highly cathodic relative to the α-phase. Consequently, the relationship between Al concentration and SCC susceptibility has previously been associated with the propensity for microgalvanic corrosion of the α-phase adjacent to Mg₁₇Al₁₂ precipitates [6,7,14,27,28,30].

Many factors related to mechanical processing influence the SCC susceptibility of Mg alloys [1]. Extruded Mg–Al–Zn alloys may be more susceptible to SCC than cast alloys with similar overall composition due to the influences of microstructural defects and residual stresses [31]. For specimens loaded in tension, residual tensile stresses are detrimental to SCC resistance whereas compressive residual stresses are beneficial [32,33]. The influence of grain size has been studied only with respect to the propensity for intergranular or transgranular SCC [11,28,34,35]. Grain orientation is likely to have strong influence on TGSCC fracture morphology if the propagation mechanism is crystallographic [11,36–37,12].

The influence of strain rate varies between stages of SCC (i.e. initiation and propagation). The influence of strain rate on SCC initiation is associated with the propensity for mechanical film rupture at the surface, which causes localised corrosion and H ingress. The influence of strain rate on SCC propagation is associated with: (i) the propensity for repassivation at the crack tip; (ii) the transition to the inert fracture mode (at high strain rates); and (iii) the time required for embrittlement and fracture of the region ahead of the crack tip [14,16–18,38–41]. It should also be noted that the propensity for surface film breakdown and repassivation at the crack tip is also dependent on the interaction between the alloy and environment.

1.4. Scope of present research

Our review [1] identified a need for a mechanistic understanding of the influences of environment, microstructure and mechanical loading on SCC of Mg–Al alloys to support the growing use of Mg alloys for stressed components in service such as for automotive applications. The principal issues in developing this understanding are: (i) the environmental and mechanical conditions causing film breakdown and H ingress; and (ii) the microstructural and mechanical conditions that promote accumulation of H in such concentrations as to cause HE. These issues may be resolved by comparing alloys under SCC conditions with respect to: (i) fracture surface morphology; (ii) crack propagation velocity; (iii) the sensitivity to...
microstructural modification; and (iv) the sensitivity to various environments. Thus, the present investigation focuses on evaluating, with respect to the possible HE mechanisms, the influence of microstructure on the SCC susceptibility of Mg–Al alloys by comparing the SCC characteristics of AZ91 (consisting of an α-matrix with extensive β-particles), AZ31 (consisting of an α-matrix with Al-concentration similar to that in AZ91) and AM30 (consisting of an α-matrix with similar concentration to AZ31, but with lower Zn-concentration).

2. Experimental method

The Mg alloys AZ91, AZ31 and AM30 were machined into cylindrical tensile specimens with a 5 mm diameter waisted gauge section. AZ91 specimens were machined from as-cast ingots, whereas AZ31 and AM30 specimens were machined from large extrusions such that their tensile axis was parallel with the extrusion direction. The gauge surfaces were polished with 1200-grade emery paper and cleaned using ethanol immediately before testing.

The compositions of the alloys are given in Table 1. The grain sizes were 1–2 mm for AZ91 and 50–100 μm for AZ31 and AM30 (equiaxed in all cases). The compositions of the principal phases were analysed using energy dispersive X-ray spectroscopy (EDS). AZ91 featured an extensive interdendritic phase (approximately 58 wt%Mg, 37 wt%Al, 5 wt%Zn), fine plate-like crystals within the interdentritic phase (approximately 30 wt%Mg, 47 wt%Al, 23 wt%Mn) and small intragranular precipitates (approximately 45 wt%Al, 55 wt%Mn). The composition of the interdendritic phase is consistent with the β-phase Mg17Al12 identified by previous workers [6,7,14,27,28,30]. AZ31 and AM30 featured relatively homogeneous microstructures with large quadrilateral plate-like crystals (approximately 21 wt%Al, 79 wt%Mn), small interdendritic particles (>20 wt%Si), and elongated plate-like crystals that were aligned collinearly in the extrusion direction (>30 wt%Al, >40 wt%Mn). The quadrilateral plate-like crystals were larger and more numerous for AZ31 than for AM30. Key microstructural features of the alloys are shown in Fig. 1.

H pre-charging was carried out in gaseous H2 at 3 MPa for 14 h at 300°C, after which the sample was cooled to room temperature while maintaining the H2 pressure at 3 MPa. A control sample was exposed to pure Ar at 3 MPa for 15 h at 300°C, after which the sample was cooled to room temperature while maintaining the Ar pressure at 3 MPa. These samples were tested in air at a strain rate of 10−4 s−1 as soon as practical after removal from the furnace.

The SCC test environment was double-distilled H2O. Control tests were carried out in laboratory air. The gauge surface of the

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Table 1

<table>
<thead>
<tr>
<th>Mg %</th>
<th>Al %</th>
<th>Zn %</th>
<th>Mn %</th>
<th>Fe %</th>
<th>Sn %</th>
<th>Pb %</th>
<th>Ni %</th>
<th>Be %</th>
<th>Cr %</th>
<th>Cu %</th>
<th>Zr %</th>
<th>Sr %</th>
</tr>
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<tbody>
<tr>
<td>AZ91 &gt;90.11</td>
<td>8.89</td>
<td>0.78</td>
<td>0.21</td>
<td>0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>AZ31 &gt;96.86</td>
<td>2.64</td>
<td>0.84</td>
<td>0.64</td>
<td>&lt;0.001</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>AM30 &gt;96.70</td>
<td>2.88</td>
<td>0.005</td>
<td>0.40</td>
<td>&lt;0.001</td>
<td>&lt;0.002</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

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Fig. 1. SEM images of AZ91 (showing (i) bulk matrix, (ii) interdentritic phase, (iii) plate-like crystals and (iv) intragranular precipitates), AZ31 (showing (v) quadrilateral Al–Mn plate-like crystals), and AM30 (showing (vi) elongated Al–Mn collinearly aligned in the extrusion direction) microstructures.
specimen was completely immersed in distilled water at room temperature and at open circuit conditions in the environment cell, while the distilled water was circulated slowly between the environment cell and a reservoir.

The mechanical load on the specimen was steadily increased under linearly increasing stress test (LIST) or constant extension rate test (CERT) conditions. The total elongation of the specimen was measured using pair of linear variable displacement transducers (LVDTs) connected to the load-train and in parallel with the specimen. For CERTs, the LVDTs were also used to control the crosshead speed of the test machine via a feedback circuit. The LVDT measurements were not representative of the actual strain in the specimen gauge length, due to: (i) deformation in parts of the specimen other than the gauge and in the LVDT fixtures; (ii) the reduction in cross-section by necking (for tests in laboratory air) and SCC (for tests in distilled water); and (iii) misalignment of the LVDTs. Consequently, the strain measured using the LVDTs was considerably greater than that which would be measured at the gauge section. Thus, the measurements have been designated “apparent strain” in Figs. 2–5 and 10–11. The elongation-to-failure was not quantified in most CERTs because complete fracture was sometimes not realised due to time constraints.

SCC initiation was detected using the DC potential drop (DCPD) method as per Dietzel and Schwalbe [42] and Atrens et al. [43–47]. The DCPD method involves applying a constant current (∼5 A) to the specimen and measuring the increase in specimen resistance, ΔR, as the cross-section is reduced, primarily by crack propagation, according to the relationship

\[ \Delta R = \frac{rl}{\Delta A} \]

where \( \Delta A \) is the change in cross-sectional area, \( r \) is the resistivity and \( l \) is the length of the specimen. The voltage probes were attached to the specimen close to the gauge section using brass dowel pins. The current leads were attached further away from the gauge section using brass clamps. A pulsed and reversing current was applied to the specimen to minimise thermoelectric offset voltages due to the coupling of dissimilar metals in a variable-temperature environment. Fluctuations in specimen resistivity due to temperature variations were compensated for by measuring the resistivity of a reference specimen connected in series with the principal specimen for each current pulse. \( \Delta R \) could not be correlated with \( \Delta A \) (and therefore the crack velocity, \( V_c \)) due to the irregularity of the crack front and the difficulty of separating primary and secondary cracking on parallel planes. It is also possible that \( \Delta R \) measurements are
affected by the change in conductivity of the environment at the crack tip due to dissolution of metal atoms.

3. Results

3.1. AZ91 pre-charged in gaseous H₂

Measurements using a LECO H-Analyser showed that AZ91 charged in gaseous H₂ at 3 MPa for 15 h at 300 °C exhibited a large increase in net H concentration; however, the quantity of H existing in the bulk matrix could not be quantified due to the coupling of H existing in Mg(OH)₂ at the surface. Nevertheless, this indicated that breakdown of the protective surface film and H ingress occurred under the charging conditions. The H-affected fracture surface morphology was uniformly distributed across the entire section, suggesting that the H distribution reached equilibrium under the charging conditions [2]. Fig. 2 shows the influence of H₂ pre-charging on the mechanical response of AZ91. The specimen fractured just above the yield stress, σ₉, and without the apparent plastic strain or reduction in load that typically characterises SCC of AZ91 in aqueous solutions under CERT conditions (see Fig. 3) [3]. The control sample, which was exposed to gaseous Ar at 3 MPa for 15 h at 300 °C, had a UTS and ductility comparable to that of the sample tested in air. It follows that HE was responsible for the large reductions in UTS and elongation-to-failure for the specimen pre-charged in gaseous H₂.

3.2. CERT of Mg–Al Alloys in distilled water

Figs. 3–8 show the mechanical response and DCPD measurements for AZ91, AZ31 and AM30 under CERT conditions in distilled water and laboratory air. A comparison of the stress versus apparent strain curves for the alloys in laboratory air (see Figs. 3–5) shows that AZ91 had a lower σ₉, higher strain hardening rate and lower ductility relative to AZ31 and AM30. The lower σ₉ is attributed to the larger grain size for AZ91, particularly since AZ91, AZ31 and AM30 have similar α-phase compositions. The lower ductility of AZ91 is largely attributed to the presence of β-particles [48]. The higher strain-hardening rate may be attributable to both the larger grain size and the presence of β-particles. The strain hardening rates were not quantified due to the difficulty of evaluating the true stress for specimens containing stress corrosion cracks.

Previous work [3] showed that distilled water causes SCC in AZ91 without localised corrosion. It follows that distilled water is a suitable environment for investigating the influence of strain rate on the integrity of the surface film. For AZ91, AZ31 and AM30 exposed to distilled water there was a considerable reduction in UTS and apparent ductility relative to tests in laboratory air, with the UTS and apparent ductility decreasing with decreasing strain rate (see Figs. 3–5). The apparent ductility of AZ31 was considerably more sensitive to changes in strain rate than that of AZ91 and AM30. The apparent plastic deformation is largely attributed to stress corrosion crack propagation, with some contribution by the inert fracture mode, particularly at higher strain rates. Crack propagation eventually resulted in a reduction in the engineering stress. In most cases the tests were interrupted after some stress reduction in order to prevent corrosion damage of the fracture surface.

The elastic deformation of the materials is characterised by a small, constant and positive gradient at the initial part of the DCPD curve (see Figs. 6–8). In some cases there was an ini-
Fig. 9. DCPD vs. stress curves for AZ31 in distilled water and air under CERT conditions showing threshold stresses.

Fig. 10. Stress vs. apparent strain and DCPD vs. stress curves for AZ91 in distilled water at $3 \times 10^{-8}$ s$^{-1}$.

Fig. 11–14 show the mechanical response and DCPD measurements for AZ31 and AM30 under LIST and CERT conditions in distilled water and laboratory air. The extension rate required to maintain LIST conditions increases rapidly during SCC, approaching infinity at the UTS (i.e. as $\delta \varepsilon / \delta \sigma$ approaches zero). Consequently, there was a decrease in stress after the UTS, when the extension rate required to maintain a constant stress rate exceeded the maximum speed of the test machine (i.e. during the final stages of fracture).

3.3. LIST of AM30 and AZ31

Table 2 shows the increase in the measured stress corrosion crack velocity, $V_c$, with increasing strain rate for AZ91. In contrast, $V_c$ appeared independent of strain rate for AZ31 and AM30, whilst $V_c$ for AZ31 was slightly lower than for AZ91. $V_c$ was calculated from $\Delta a / \Delta t_{SCC}$, where $\Delta a$ is the maximum size of the stress corrosion crack on the fracture surface (see Winzer et al. [2]) and $\Delta t_{SCC}$ is the time between crack initiation (furnished by the DCPD results) and end of the test.

If the stress corrosion crack front advances steadily, this calculation would yield a reasonable value for $V_c$; however, it should be noted that Pugh et al. [49] measured $V_c$ to be proportional to $K_{II}^2$ for TGSCC of Mg-7.5Al alloy, implying that $V_c$ would increase with increasing crack length.

### Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta \varepsilon / \delta t$ ($\times 10^{-8}$ s$^{-1}$)</th>
<th>$\sigma_{SCC}$ (MPa)</th>
<th>$\sigma_{SCC}/\sigma_Y$</th>
<th>$\sigma_{SCC}/UTS$</th>
<th>$\Delta a$ (µm)</th>
<th>$\Delta t_{SCC}$ (h)</th>
<th>$V_c$ ($\times 10^{-9}$ m/s)</th>
</tr>
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<tbody>
<tr>
<td>AZ91 ($\sigma_Y = 70$ MPa, $UTS = 165$ MPa)</td>
<td>3</td>
<td>55</td>
<td>0.79</td>
<td>0.33</td>
<td>265</td>
<td>1500</td>
<td>1.6</td>
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<tr>
<td></td>
<td>10</td>
<td>60</td>
<td>0.86</td>
<td>0.36</td>
<td>83</td>
<td>1120</td>
<td>3.7</td>
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<tr>
<td></td>
<td>30</td>
<td>75</td>
<td>1.1</td>
<td>0.45</td>
<td>30</td>
<td>1140</td>
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<tr>
<td></td>
<td>50</td>
<td>70</td>
<td>1.0</td>
<td>0.42</td>
<td>30</td>
<td>1300</td>
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<td></td>
<td>5</td>
<td>105</td>
<td>0.58</td>
<td>0.42</td>
<td>92</td>
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<td></td>
<td>10</td>
<td>145</td>
<td>0.81</td>
<td>0.58</td>
<td>101</td>
<td>710</td>
<td>2.0</td>
</tr>
<tr>
<td>AZ31 ($\sigma_Y = 180$ MPa, $UTS = 250$ MPa)</td>
<td>20</td>
<td>165</td>
<td>0.92</td>
<td>0.66</td>
<td>34</td>
<td>817</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>160</td>
<td>0.89</td>
<td>0.64</td>
<td>66</td>
<td>296</td>
<td>1.2</td>
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<td></td>
<td>80</td>
<td>170</td>
<td>0.94</td>
<td>0.68</td>
<td>86</td>
<td>1708</td>
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<td></td>
<td>10</td>
<td>140</td>
<td>0.80</td>
<td>0.61</td>
<td>262</td>
<td>340</td>
<td>0.36</td>
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<td></td>
<td>30</td>
<td>130</td>
<td>0.74</td>
<td>0.57</td>
<td>81</td>
<td>270</td>
<td>0.93</td>
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<tr>
<td></td>
<td>50</td>
<td>140</td>
<td>0.80</td>
<td>0.61</td>
<td>136</td>
<td>271</td>
<td>0.55</td>
</tr>
</tbody>
</table>

AZ31 was interpreted as the stress corresponding to the subsequent sharp increase in $\delta V / \delta \sigma$ (see Fig. 9) and to the onset of apparent plastic deformation (see Fig. 10). The correlation between $\sigma_{SCC}$ and the increase in $\delta V / \delta \sigma$ has been validated by marking SCC fracture surfaces with dye penetrant for AZ91 specimens fractured in distilled water under constant stress slightly above $\sigma_{SCC}$, which was measured separately under CERT conditions [3]. In the case of fracture in air, the onset of plastic deformation was also characterised by an increase in $\delta V / \delta \sigma$, although this occurred at stresses $\gg \sigma_{SCC}$.

The SCC parameters ($\sigma_{SCC}$, $\sigma_{SCC}/\sigma_Y$, $\sigma_{SCC}/UTS$ and $V_c$) for each material and strain rate ($\delta \varepsilon / \delta t$) are summarised in Table 2. $\sigma_{SCC}$ for AZ91 was significantly lower than for AZ31 and AM30. There was also a decrease in $\sigma_{SCC}$ with decreasing strain rate for AZ91 and AZ31 (see also Fig. 9 for AZ31); however, this trend was not identified for AM30 due to the narrow range of strain rates used. The ratio $\sigma_{SCC}/\sigma_Y$ was lower for AZ31 than for AZ91 at low strain rates, whereas the ratio $\sigma_{SCC}/UTS$ was generally lower for AZ91 than for AZ31 and AM30.

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3.3. LIST of AM30 and AZ31

Figs. 11–14 show the mechanical response and DCPD measurements for AZ31 and AM30 under LIST and CERT conditions in distilled water and laboratory air. The extension rate required to maintain LIST conditions increases rapidly during SCC, approaching infinity at the UTS (i.e. as $\delta \varepsilon / \delta \sigma$ approaches zero). Consequently, there was a decrease in stress after the UTS, when the extension rate required to maintain a constant stress rate exceeded the maximum speed of the test machine (i.e. during the final stages of fracture).
The stress rate used in these LISTs \(7 \times 10^{-4} \text{ MPa/s}\) is equivalent to the strain rate \(10^{-7} \text{ s}^{-1}\) assuming linear-elastic conditions and a Young’s Modulus of 44 GPa [50]. Consequently, the conditions affecting film breakdown and H ingress at stresses below \(\sigma_{\text{SCC}}\) are similar. The results are consistent with those for AZ91 [3] in that under LIST conditions rapid and complete fracture ensued soon after \(\sigma_{\text{SCC}}\) was attained, with limited stress corrosion crack propagation, whereas under CERT conditions significant stress corrosion crack propagation occurred. \(\sigma_{\text{SCC}}\) was 155 MPa and 140 MPa for AZ31 and AM30, respectively. In the case of AZ31, \(\sigma_{\text{SCC}}\) was slightly higher under LIST conditions than under CERT conditions at the equivalent strain rate. In the case of AM30, \(\sigma_{\text{SCC}}\) was the same under LIST and CERT conditions; however, the increase in engineering stress during SCC (or apparent strain hardening rate) was greater under LIST conditions, and similar to that in laboratory air. This may be associated with the lower \(V_c\) for AM30 relative to AZ31. Under LIST conditions, a lower \(V_c\) would result in a smaller \(\Delta \Delta \alpha\), such that the mechanical behaviour of the specimen above \(\sigma_{\text{SCC}}\) is defined by the remaining cross-section, which is unaffected by H.

3.4. Pitting and secondary cracking

Secondary cracks were apparent on the gauge surfaces of AZ91, AZ31 and AM30 specimens fractured in distilled water (Fig. 15). The density of secondary cracks in AZ91 specimens was considerably less than in AZ31 and AM30 specimens. In all cases the secondary cracks were normal to the loading direction. Secondary cracks in AZ91 specimens were macroscopically sharp, with cracks nucleating within β-particles ahead of the principle crack tip and propagating transgranularly in a relatively constant direction (Fig. 16, detail B–C). Cracks within β-particles were generally normal to the loading direction, indicating that β-particles fracture in favour of the surrounding matrix in response to mechanical loading. This is consistent with the brittle nature of the β-particles, and the relatively low ductility of AZ91 in air. Perpendicular cliffs were formed between converging consecutive cracks, which undercut the cliffs by \(\sim 10 \mu\text{m}\) (Fig. 16, detail A).

Secondary cracks in AZ31 and AM30 specimens were typically 100–200 μm deep and often diverged into several roughly parallel tunnels (Figs. 17 and 18). They appeared to be due to highly localised dissolution; however, in contrast with the known mechanism for intergranular SCC in Mg alloys [1], the dissolution did not occur adjacent to second phase particles.
Fig. 15. Secondary cracking for (A) AZ31 at $2 \times 10^{-7}$ s$^{-1}$, (B) AM30 at $3 \times 10^{-7}$ s$^{-1}$ and (C) AZ91 at $3 \times 10^{-7}$ s$^{-1}$.

Fig. 16. Optical microscopy of secondary crack for AZ91 in double distilled water at $3 \times 10^{-7}$ s$^{-1}$. 
There was no evidence of irregular pitting (as occurs for AZ91 in 5 g/L NaCl [3]) on the gauge surface for any alloy fractured in distilled water; however, AZ31 and AM30 specimens exhibited coarse markings along the length of the exposed surface and parallel to the axis of the specimen (Figs. 15 and 19). These markings were not apparent on specimens tested in air. Given that the AZ31 and AM30 specimens were machined with their axes parallel to the extrusion direction, and that no such markings were observed for the cast AZ91 specimens, they may be attributed to localised corrosion at the axially aligned Al–Mn particles (see Fig. 1).

4. Discussion

4.1. The role of the β-phase in SCC of Mg–Al alloys

The comparison between AZ91 and AZ31 provides new mechanistic insights into the influence of microstructure on the SCC susceptibility of Mg–Al alloys. Table 2 shows that $\sigma_{SCC}$ and $\sigma_{SCC}/UTS$ were generally lower for AZ91 than for AZ31. This is contrary to the negative influence of residual stresses (which were expected in the extruded AZ31) on the SCC resistance of specimens loaded in tension [31]. AZ91 and AZ31 had similar α-phase compositions, so they also had similar repassivation rates, surface film compositions and α-phase H diffusivities. Thus, the conditions affecting SCC initiation in AZ91 and AZ31 are similar, suggesting that the comparison of $\sigma_{SCC}$ values is valid. However, it should be noted that grain size, which is considerably greater for the cast AZ91 than for the extruded AZ31 and AM30, might also have an influence if the SCC initiation mechanism involves mechanical film rupture at emerging slip steps (as proposed for AZ31 and AM30 in Section 4.3).

The morphology of the secondary cracking (Section 3.4) indicated that the mechanism for SCC initiation in AZ31 and AZ91 is different (see Figs. 16 and 17). Secondary cracks in AZ91 were macroscopically sharp, with cracks nucleating within β-particles ahead of the principle crack tip. In contrast, secondary cracks in AZ31 were caused by localised dissolution. The fractography for ongoing stress corrosion crack propagation in AZ91 also indicated a mechanism involving crack nucleation within β-particles [2,3]. Thus, the low $\sigma_{SCC}$ for AZ91 may be attributed to: (i) the tendency for the β-particles to fracture in favour of the surrounding matrix; and (ii) their behaviour as reversible H traps, which enhance H transport within the matrix (see Section 4.4). This implies that the increasing susceptibility of Mg alloys to SCC with increasing Al concentration [29] is related to the presence of, and propensity for crack nucleation within, β-particles.
4.2. SCC initiation stress

The $\sigma_{SCC}$ values for AZ91 in distilled water given in Table 2 are comparable to those measured by Miller [51]. Miller measured $\sigma_{SCC}/\sigma_Y \approx 0.4–0.5$ for AZ91 specimens under constant load in distilled water, with the tests taking up to 500 days. This implies a very low effective strain rate relative to those used in the present research. In the present research, $\sigma_{SCC}/\sigma_Y \approx 1.0$ at the strain rate $5 \times 10^{-7}$ s$^{-1}$, with $\sigma_{SCC}/\sigma_Y$ decreasing with decreasing strain rate. Thus, it is conceivable that $\sigma_{SCC}/\sigma_Y$ would continue to decrease to 0.4–0.5 at very slow strain rates.

4.3. SCC initiation

The contrast in secondary crack morphology for AZ91 with that for AZ31 and AM30 is indicative of different mechanisms for SCC initiation. Winzer et al. [3] investigated the fracture surface morphology corresponding to early stage crack propagation in AZ91 by removing specimens from the environment at various stresses slightly above $\sigma_{SCC}$. The fracture surfaces featured small (<100 $\mu$m across) macroscopically smooth regions adjacent to the gauge surface, which were observed under high magnification to be comprised of fine parallel markings or micro-dimples. Considering the tendency for $\beta$-particles to fracture at relative low stresses in the presence of H, it seems likely that fracture of the macroscopically smooth regions occurs subsequent to crack nucleation in $\beta$-particles close to the gauge surface. That no localised corrosion is apparent on the gauge surface of AZ91 specimens after testing, and that $\sigma_{SCC}$ corresponds with the onset of apparent plastic deformation (Fig. 10), suggests that H ingress is facilitated by mechanical rupture of the surface film. Thus, the $\beta$-particles involved in SCC initiation must be sufficiently close to the surface to be affected by concentration-driven diffusion of H into the matrix.

Figs. 17 and 18 indicate that the mechanism for SCC initiation in AZ31 and AM30 involves highly localised dissolution. That the secondary cracks occur independently of microstructural features suggests that this mechanism is facilitated by mechanical rupture of the surface film (as per the mechanism for SCC initiation in AZ91). Previous workers [25,52–54] have attributed features as shown in Figs. 17 and 18 to mechanical film rupture at emerging slip steps, resulting in rapid localised dissolution of the exposed substrate due to the difference in electrochemical potentials for the substrate and adjacent protected areas. The tunnel propagates due to continued film rupture at its base, until the stress concentration is sufficient for some HE mechanism to overwhelm the rate of dissolution [25].

The correlation of SCC initiation with the onset of apparent plastic deformation is also a characteristic of ferritic steels [55], $\alpha$-brass [56], Ni–Al bronze [57], pipeline steels [58,59] and high strength steels [60]. Thus, the correlation can be rationalised with many SCC initiation mechanisms. The mechanism for SCC initiation in AZ91 appears to involve HE of $\beta$-particles, whereas the mechanism for SCC initiation in AZ31 and AM30 involves localised dissolution of the $\alpha$-matrix. SCC initiation in AZ31 and AM30 occurs at stresses significantly higher than for AZ91 (although $\sigma_Y$ is also significantly higher for AZ31 and AM30 than for AZ91). Thus, the resistance of Mg–Al alloys to SCC initiation appears to be degraded by the presence of $\beta$-particles. Generalisation of this result implies that two-phase Mg alloys have low SCC resistance if there is a hydrogen influence on the fracture of the second phase.

4.4. The influence of strain rate

The influence of strain rate on the susceptibility of Mg alloys to SCC has previously been ascribed to, at low strain rates, the balance between repassivation and mechanical film rupture at the crack tip and, at high strain rates, the propensity for the inert fracture mechanism to overwhelm the SCC fracture mechanism [14,38,39]. In the present work, decreasing strain rate is associated with a continuous increase in SCC susceptibility (characterised by: (i) an increasing difference between $\sigma_{SCC}$ and the UTS; (ii) a decreasing elongation-to-failure; and (iii)
a decrease in $\sigma_{SCC}$ for AZ91 and AZ31). It follows that, at these strain rates, the influence of repassivation at the crack tip is negligible, and the influence of strain rate is related to the mechanism for crack propagation. In contrast with the present work, previous workers [13,14,36,37,12,38,39,49] used strongly passivating solutions containing K$_2$CrO$_4$. This indicates that the occurrence of maximum SCC susceptibility at intermediate strain rates observed for Mg alloys in strongly passivating solutions is a characteristic of these environments rather than a characteristic of Mg alloys.

For mechanisms involving diffusion of solute H (such as HEDE and DHC), the influence of strain rate may be resolved in terms of: (i) variations in the hydrostatic stress near the crack tip; or (ii) the time required to reach some critical combination of H concentration and stress at the fracture site. If the fracture site is a $\beta$-particle ahead of the principle crack tip (as in the case of AZ91), then the influence of strain rate may be resolved in terms of the amount of H arriving at, and the time required to reach the critical tensile stress within, the particle. Thus, an important variable may be the H diffusivity in the Mg lattice.

For mechanisms involving H-enhanced dislocation mobility (such as HELP and, to some extent, AIDE) the influence of strain rate is related to the ability of H atmospheres to remain bound to mobile dislocations. For a given temperature there exists a maximum strain rate, corresponding to the H diffusivity, above which no amount of H will affect dislocation motion [16,17,23]. In the present work, the decrease in apparent ductility with decreasing strain rate was greater for AZ31 than for AZ91 (see Figs. 3 and 4). Pressouyre [23] proposed that, in the case of H transport with mobile dislocations, the influence of strain rate is mitigated by the presence of H at multiple internal sources. In the case of AZ91, $\beta$-particles initially behave as H sinks. However, if the fracture of $\beta$-phase particles is accompanied by a reduction in internal stress, then those particles may subsequently behave as H sources. The H released by fractured $\beta$-particles may then cause embrittlement of the surrounding matrix. Thus, the sensitivity (in terms of apparent ductility) of AZ31 to changes in strain rate may be attributed to the absence of $\beta$-particles. This is consistent with our previous investigation of SCC of AZ91 in distilled water, which showed that the orientation of fracture surface markings was influenced by the distribution of $\beta$-particles [3].

The reduction in apparent ductility with decreasing strain rate may also be associated with the time available for creep due to the inert fracture mode, which contributes somewhat to the apparent plastic deformation at high strain rates. The mechanical response of a specimen (see Figs. 3–5) containing multiple growing stress corrosion cracks is defined by the properties of the remaining ligament. The size of the remaining ligament is dependent on the applied strain rate and $V_c$, which may have a contribution from the inert fracture mode at high strain rates. Because SCC initiation corresponds with the onset of apparent plastic deformation in the specimen, the apparent ductility may be attributed to the “creep response” of the highly stressed remaining ligament. At high strain rates (e.g. $5 \times 10^{-7} \text{s}^{-1}$) the stress corrosion crack size is relatively small as there is less time available for crack growth. Consequently, the apparent ductility can approach that of the specimen tested in air. At the low strain rates (e.g. $3 \times 10^{-8} \text{s}^{-1}$) the stress corrosion crack size is larger and there is more time for creep of the highly stressed remaining ligament. Consequently, the apparent ductility is lower.

For AZ91, $\sigma_{SCC}$ and $V_c$ decrease with decreasing strain rate (see Table 2), such that more time is available for creep at low strain rates. For AZ31, $\sigma_{SCC}$ and $V_c$ are largely independent of strain rate, such that less time is available for creep at low strain rates, so that AZ31 shows a very large decrease in apparent ductility with decreasing strain rate. In the case of AM30, the relatively low sensitivity of apparent ductility to strain rate may be partly associated with its relatively low $V_c$; the stress corrosion crack sizes are small and the mechanical response approaches that measured in air.

4.5. Stress corrosion crack velocities

Table 2 shows that the stress corrosion crack velocities for AM30 ($V_c = 3.6 \times 10^{-10}$ to $9.3 \times 10^{-10} \text{m/s}$) are much slower than for AZ91 ($V_c = 1.6 \times 10^{-9}$ to $1.2 \times 10^{-9} \text{m/s}$) and AZ31 ($V_c = 1.2 \times 10^{-9}$ to $6.7 \times 10^{-9} \text{m/s}$). These results are consistent with the crack velocity measured by Speidel et al. [61] for the Mg alloy ZK50A-T5 in distilled water, but much slower than those measured for Mg alloys in other aqueous environments [13,14,36,38,39,49,61] and predicted using our numerical model for DHC ($V_c \approx 10^{-7} \text{m/s}$), although this result was based on a speculative diffusion coefficient ($D = 10^{-9} \text{m}^2/\text{s}$) since no data exists for Mg alloys at room temperature [15]. The different crack velocities for AZ91, AZ31 and AM30 may be due to a difference in the predominant mechanism for SCC propagation. H may be transported more rapidly with mobile dislocations than by diffusion [62]. Thus, HELP is associated with higher crack velocities than HEDE and DHC. AIDE is associated with very high crack velocities, which exceed the rate of H transport by stress-assisted diffusion and for which initial velocity of dislocations emitted from the crack tip is too high to attract H atmospheres [10,20]. In the present case, the difference in mechanism might be related to the influence on H transport of second phase particles and Zn in solid solution with the $\alpha$-phase, which are more concentrated in AZ31. The results are consistent with the behaviour of second phase particles as sources of H for mobile dislocations (as per the $\beta$-particles in AZ91), or an increase in H diffusivity with Zn concentration. Alternatively, the SCC mechanism could be the same for all three alloys, with the lower stress corrosion crack velocity for AM30 being due to the influence of Zn on the diffusivity of H in the bulk matrix.

4.6. $H_2$ pre-charging

The comparison between AZ91 specimens pre-charged in $H_2$ gas and fractured in distilled water is discussed principally in Winzer et al. [2] with respect to fracture surface morphology. It is sufficient to note here that the apparent lack of plastic deformation for AZ91 specimens pre-charged in $H_2$ gas is consistent with a mechanism involving the formation and fracture of a brittle hydride phase and is in stark contrast with the apparent ductility of AZ91 in distilled water.
The stress corrosion crack velocities for AM30 A mechanism for crack initiation in AZ91 involving fracture 
• The mechanism for SCC initiation in AZ31 and AM30 spec-
• The mechanism for SCC propagation in AZ91 involves: (i) 
The susceptibility of Mg alloys to SCC with increasing Al concen-
• For all alloys in distilled water under CERT conditions, SCC 
• AZ91, AZ31 and AM30 were susceptible to SCC in dis-

5. Conclusions

- AZ91, AZ31 and AM30 were susceptible to SCC in distilled water. The threshold stresses, $\sigma_{SCC}$, were 55–75 MPa for AZ91, 105–170 MPa for AZ31 and 130–140 MPa for AM30.
- For all alloys in distilled water under CERT conditions, SCC susceptibility increased with decreasing strain rate. This was characterised by: (i) an increasing difference between $\sigma_{SCC}$ and the UTS measured in air; (ii) a decreasing elongation-to-failure; and (iii) a decreasing $\sigma_{SCC}$ (for AZ91 and AZ31).
- The mechanism for SCC propagation in AZ91 involves: (i) H trapping by $\beta$-particles ahead of the primary crack tip; (ii) fracture of $\beta$-particles upon reaching some critical H concentration; (iii) release of H trapped in $\beta$-particles due to the reduction in internal hydrostatic stress; and (iv) embrittlement of the surrounding matrix by the released H.
- The low $\sigma_{SCC}$ of AZ91 is attributed to: (i) the tendency for the $\beta$-particles to fracture in favour of the surrounding matrix; and (ii) their behaviour as reversible H traps, which enhance H transport within the matrix. This implies that the increasing susceptibility of Mg alloys to SCC with increasing Al concentration is related to the presence of, and propensity for crack nucleation within, $\beta$-particles. Generalisation of this result implies low SCC resistance for two-phase Mg alloys if there is a hydrogen influence on the fracture of the second phase.
- The mechanism for SCC initiation in AZ31 and AM30 specimens involves localised dissolution at stresses significantly higher than for AZ91. The specific nature of this mechanism is unknown, although a mechanism involving mechanical film rupture at emerging slip steps seems likely.
- A mechanism for crack initiation in AZ91 involving fracture of $\beta$-particles close to the surface, with H ingress facilitated by mechanical rupture of the surface film, is proposed; however, further examination of the kinetics of H ingress and transport in the absence of stress gradients is required to verify this model.
- The stress corrosion crack velocities for AM30 ($V_c = 3.6 \times 10^{-10}$ to $9.3 \times 10^{-10}$ m/s) are much slower than for AZ91 ($V_c = 1.6 \times 10^{-9}$ to $1.2 \times 10^{-8}$ m/s) and AZ31 ($V_c = 1.2 \times 10^{-9}$ to $6.7 \times 10^{-9}$ m/s), indicating a different SCC mechanism. The results are consistent with a lower H diffusivity in the $\alpha$-phase in the absence of Zn, or the behaviour of Al–Mn plate-like particles as sources of H for mobile dislocations (as per the $\beta$-particles in AZ91).
- AZ91 pre-charged in gaseous H$_2$ at 3 MPa for 14 h at 300 °C fractured just above the yield stress, $\sigma_y$, and without the apparent plastic strain or the reduction in load. This is consistent with a mechanism involving the formation and fracture of a brittle hydride phase.

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