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ALLOYS: THE CORROSION BEHAVIOR OF GRAIN
BOUNDARY CONSTITUENTS

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CONSTITUENTS

by A. J. Sedriks, J. A. S. Green and
D. L. Novak

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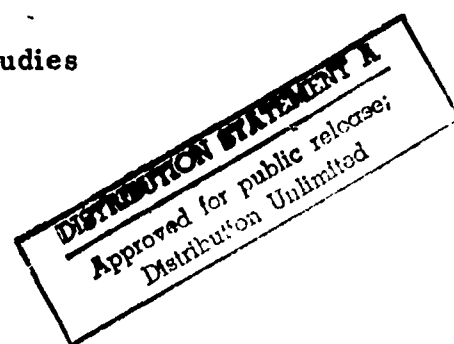
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ABSTRACT

Earlier studies by the authors have supported the view that the propagation of intergranular stress-corrosion cracks in age-hardened Al-Zn-Mg alloys in aqueous chloride solutions occurs by localized anodic dissolution of the material in the grain boundary region. This region is characterized, after age-hardening, by relatively coarse $MgZn_2$ precipitates in the boundary plane and adjacent precipitate-free zones. Hence, if crack propagation does occur by dissolution, then it would be expected that it would be governed by the corrosion behavior of the grain boundary constituents in solutions of compositions approximating those existing at the crack tip (i. e. solutions containing aluminum ions and having a pH = ~3.5). Since the grain-boundary constituents in Al-Zn-Mg alloys are generally too fine for their corrosion behavior to be studied in situ, an experimental approach involving simulation was adopted. This involved the examination of the

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corrosion behavior of a small ingot of $MgZn_2$, the Al-Zn-Mg alloy in the as-quenched state, and pure aluminum. The pure aluminum and the as-quenched alloy were considered to represent the two limiting cases of the material comprising the precipitate-free zone; pure aluminum representing the limiting case of the solute-depleted region and the as-quenched alloy the vacancy depleted region. Potentiostatic polarization and weight-loss studies showed that the $MgZn_2$ was in all cases more active than both the pure aluminum and the as-quenched alloy. These and other observations are examined in terms of a mechanism of stress-corrosion cracking involving the spontaneous dissolution of $MgZn_2$ intermetallic, and the deformation-induced destruction of the bridges of solid solution separating the intermetallic particles.

INTRODUCTION

It is now well-established that stress-corrosion cracks in age-hardened Al-Zn-Mg alloys follow grain boundaries (1), and recent studies by Sedriks et. al. (2-4) have supported the view that the propagation of these cracks in aqueous chloride solutions occurs by localized anodic dissolution of the material in the grain boundary region. Furthermore, work by Brown et. al. (5) has shown that the solution at the tips of propagating stress-corrosion cracks in aluminum alloys contains aluminum ions and exhibits a "steady" pH = ~3.5.

As shown schematically in Fig. 1, the grain boundary in age-hardened (susceptible) Al-Zn-Mg alloys contains coarse $MgZn_2$ intermetallic particles and is delineated on both sides by a precipitate-free zone (PFZ). Hence, if the propagation of intergranular stress-corrosion cracks occurs by a dissolution mechanism, then it would be expected that the stress-corrosion processes would be governed by the corrosion behavior of the grain boundary constituents (i. e., the $MgZn_2$ intermetallic and the PFZ) in solutions of composition observed to exist at the crack tip (i. e. in solutions containing aluminum ions and having a $pH \sim 3.5$). Previous studies of the corrosion behavior of $MgZn_2$ have been carried out in either neutral solutions⁽⁶⁾ or solutions buffered to a $pH = 4.7$ ⁽⁷⁾.

For Al-Zn-Mg alloys which have been quenched and aged at temperatures below the G.P. zone solvus, the solid solution in the PFZ is considered to be "solute depleted"⁽⁸⁾, and in the limiting case approximates to pure aluminum. For alloys aged above the G.P. zone solvus the solid solution within the PFZ varies in composition. Near the $MgZn_2$ particles on the boundary plane the solid solution is "solute depleted". However, further away from these $MgZn_2$ particles the PFZ contains some solute which was prevented from precipitating by vacancy depletion⁽⁸⁾. In the limiting case this would correspond to the as-quenched alloy. Hence, the corrosion behavior of the solid solution within the PFZ would be expected to lie somewhere between the limits defined by the corrosion behavior of pure aluminum and the

as-quenched alloy. Accordingly, in attempting to determine the corrosion behavior of the grain boundary region a comparison was carried out of the polarization behavior and weight-loss data of pure aluminum, the as-quenched alloy, and the intermetallic $MgZn_2$.

EXPERIMENTAL

Studies were performed on a ternary Al-Zn-Mg alloy (5.35 Zn, 2.52 Mg, 0.01 Cu, 0.02 Fe, 0.025 Si, 0.02 Mn, 0.01 Cr and 0.003 Ti, weight percent), a high purity (99.999 pct) aluminum, and the intermetallic $MgZn_2$. The intermetallic, which was prepared from high purity materials, was kindly supplied by Dr. F.H. Cocks of the Tyco Corporate Technology Center.

On the basis of the arguments presented in a previous publication⁽⁹⁾, the solution at the tip of a propagating stress corrosion crack should have a pH of ~ 3.5 and contain $\sim 10.6\%$ $AlCl_3$. This solution represents the composition at which $Al(OH)_3$ begins to precipitate. In practice, however, it was found impossible to investigate the corrosion behavior in such a border-line solution because of the ease with which $Al(OH)_3$ could be precipitated on weight-loss specimens, electrodes and container walls. Consequently, the studies were carried out in two more "stable" solutions, i. e. a pH = 2.75, 10.6% $AlCl_3$ solution and a pH = 3.5, 2.05% $AlCl_3$ solution.

To determine weight-loss, the procedures outlined by Fontana and Greene⁽¹⁰⁾ were followed, and the results were expressed as "mils

per year" (mpy). In the polarization studies the cell and electrode arrangements adopted were similar to those described by Greene⁽¹¹⁾, although the use of sheet specimens made it necessary to modify the electrode holder and to use masking materials. In all cases polarization was commenced at the open circuit potential and the potential was increased at a stepping rate of 20 mV per min using a Wenking potentiostat in conjunction with a saturated calomel electrode (SCE). During all polarization studies the solution was stirred at a fixed rate.

Some straining electrode studies, also, were carried out which were aimed at establishing the re-passivation characteristics of the alloy. In these studies the specimens were mounted in polyethylene containers and gripped in a constant-load tensile test rig. The test solution was added and the open-circuit potential recorded prior to stressing. The potential was set at the open circuit value (zero net current) by means of the Wenking potentiostat. The specimen was then rapidly stressed in tension to a value above its yield stress, and the current required to maintain the set potential was obtained using a Clevite Brush Mark 250 recorder operating at a chart speed of 5 in/sec.

RESULTS

The weight-loss studies, carried out using the above solutions, showed that the $MgZn_2$ was in all cases more active than both pure aluminum and the as-quenched alloy. The open circuit potentials,

E_{CORR} , and the weight-loss data for these materials in the pH = 3.5, 2.05% AlCl_3 solution are shown in Table I. Typical anodic and cathodic polarization curves of the materials are shown in Figs. 2 and 3. These results clearly demonstrate that the MgZn_2 particles at the grain boundary will actively dissolve in "crack-tip solutions" while the solid within the PFZ will act as a cathode.

The straining electrode studies were aimed at establishing whether the solid within the PFZ would continue to dissolve actively or would re-passivate in the "crack-tip solution". To date, all the results indicate that the solid within the PFZ will rapidly passivate after the MgZn_2 particles have been dissolved. For example, Fig. 4 shows a typical trace of the build-up and decay of current after plastically deforming the Al-Zn-Mg alloy in the pH = 3.5, 2.05% AlCl_3 solution. While some of the current may be consumed by dissolution, it is evident from the trace that the surface becomes passivated within less than one second of the time the protective film is ruptured by plastic deformation.

DISCUSSION AND CONCLUSIONS

The present studies show that the solid within the PFZ is significantly noble (cathodic) in relation to the intermetallic MgZn_2 . Also, it is found that when the film on the solid solution is ruptured (e. g. by plastic deformation) it will rapidly reform to passivate the surface.

Since the MgZn_2 particles will rapidly dissolve in "crack-tip solutions", Table I, the mechanism of crack propagation then can be equated with the mechanism by which the crack progresses through the "bridges" of solid solution separating the MgZn_2 particles at the grain boundary. If it is argued that the crack propagates through these "bridges" by dissolution, not only is it necessary that the solid comprising these "bridges" be rendered active by plastic deformation, but also that this active state be maintained until the next MgZn_2 particle is reached by the crack front. Alternatively, it could be argued that the dissolution of the "bridges" is not necessary and that the sharp crevices left by the dissolved MgZn_2 particles will link by ductile rupture (i. e. plastic flow) enabling the crack front to reach MgZn_2 particles further along the boundary. However, a mechanism which does not involve the dissolution of aluminum is inconsistent with the observed composition of the solution at the crack tip. If dissolution was confined to MgZn_2 particles only, then a steady pH region of $\text{pH} = \sim 6.5$ would be expected⁽¹²⁾, as characterized by the solubility product of zinc hydroxide. Yet Brown et. al.⁽⁵⁾ have reported a $\text{pH} = \sim 3.5$ and the presence of aluminum ions in solutions in the steady pH region. Clearly, then, some dissolution of aluminum is occurring at the crack tip, with the pH being determined by the solubility product of aluminum hydroxide. However, it could be argued that while dissolution of aluminum does occur - for example at the fresh surfaces exposed by the ductile rupture process prior to

repassivation - the crack advances primarily by ductile rupture and not by dissolution. Thus, the unresolved mechanistic question at this stage is whether the crack advances through the "bridges" of solid solution separating the MgZn_2 particles by dissolution, ductile rupture, or by a combination of both processes, and further work should address itself to this question.

In terms of promising approaches to mitigate susceptibility to stress-corrosion cracking, the present work suggests that factors which influence the size and distribution of the MgZn_2 particles at the grain boundary plane may also influence susceptibility. For example, provided that other factors are kept constant, it would be expected that heat treatments or minor alloying additions which would yield increased MgZn_2 interparticle spacing along the boundary also would yield improved resistance to stress-corrosion cracking.

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TABLE I

Open-circuit potentials. E_{CORR} , and weight loss of various materials in a solution of pH = 3.5 containing 2.05% AlCl_3 .

<u>Material</u>	<u>E_{CORR}</u> (mV vs. SCE)	<u>Weight-Loss</u> (mpy)
Pure aluminum	- 720	3.1
As-quenched Al-Zn-Mg	- 900	5.5
MgZn_2	- 1035	52.8

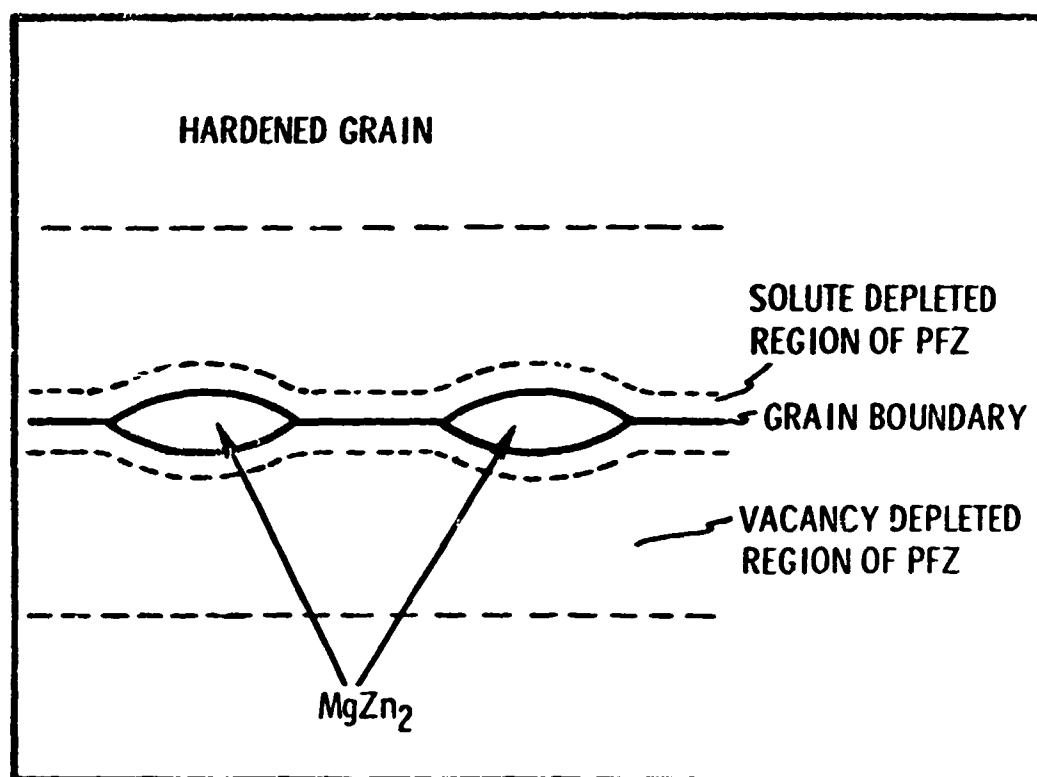


Fig. 1. A schematic representation of the grain boundary region in an Al-Zn-Mg alloy aged above the G.P. zone solvus.

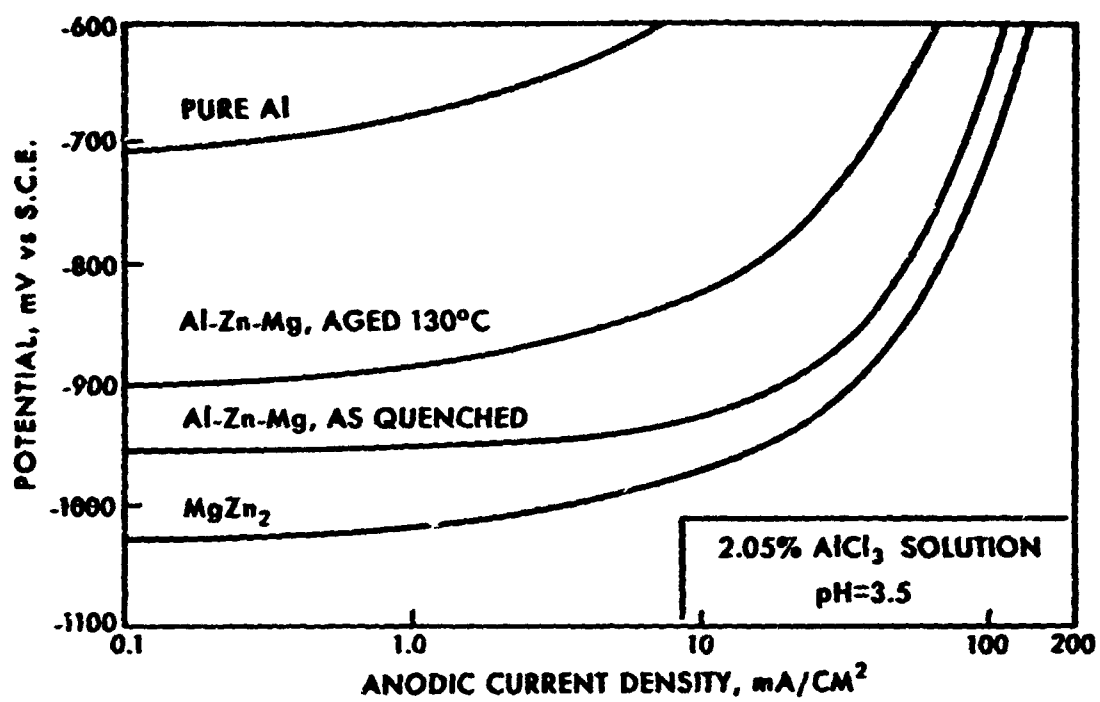


Fig. 2. Potential-anodic current density variation.

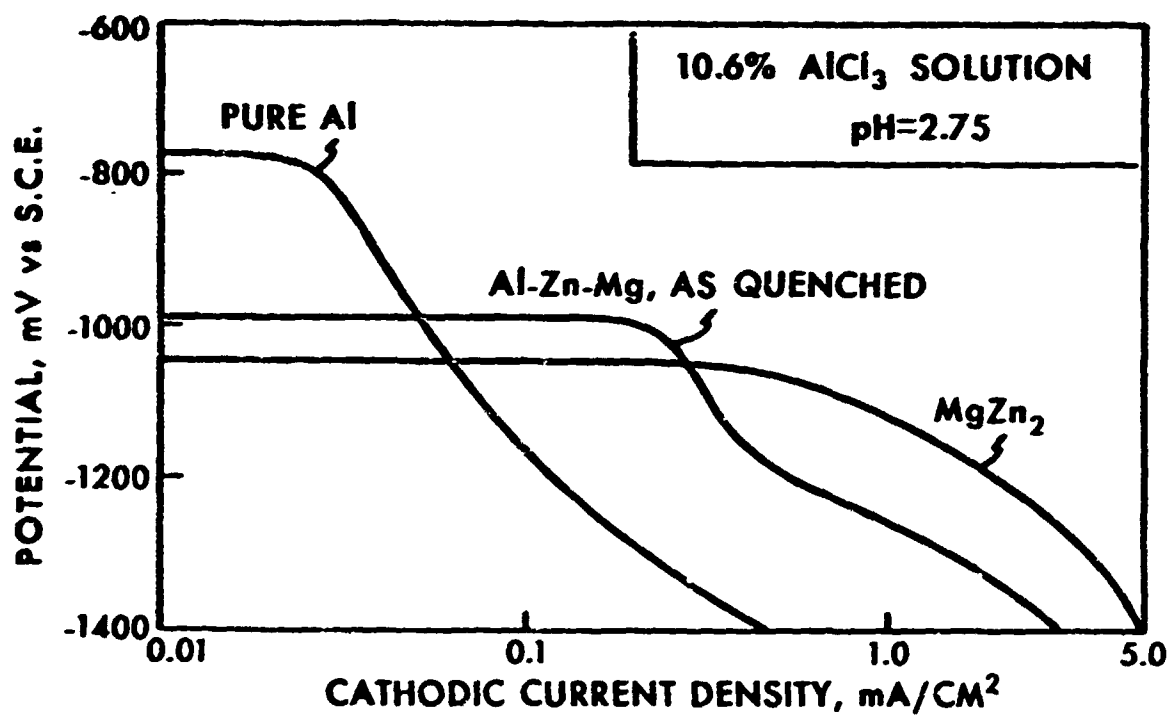


Fig. 3. Potential-cathodic current density variation.

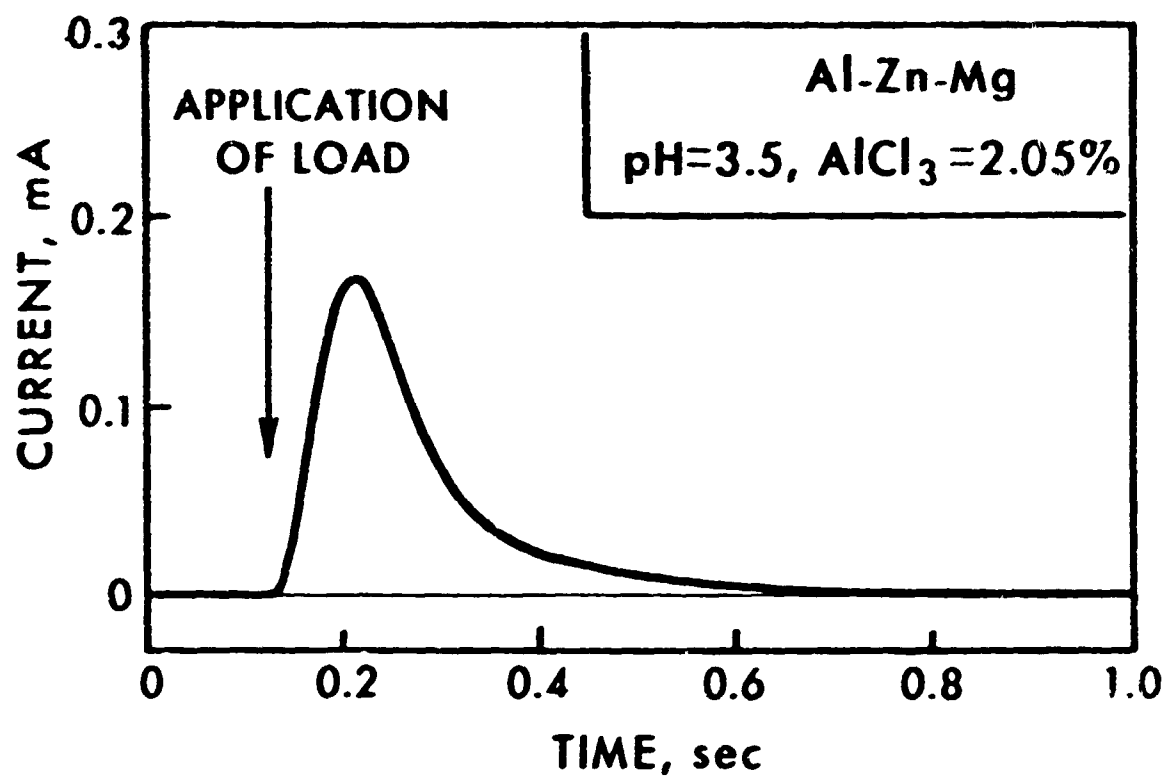


Fig. 4. Potentiostatic current flow, as a function of time, resulting from the disruption of the surface film by plastic deformation.