

AD-A158 944 THE DELAYED FRACTURE OF ALUMINUM ALLOYS(U) MARTIN  
MARIETTA LABS BALTIMORE MD J R PICKENS ET AL. JUN 85  
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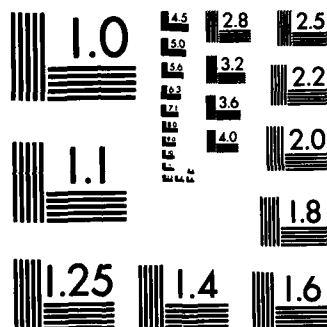
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THE DELAYED FRACTURE OF ALUMINUM ALLOYS

End of Year Report

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MECHANISMS OF STRESS-CORROSION CRACKING  
IN Al-Zn-Mg AND Al-Mg ALLOYS

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## FOREWORD

This document is our yearly report to the Office of Naval Research on Contract No. N00014-84-C-0380. It will also be published as an invited paper in the Proceedings of the Conference entitled: "Office of Naval Research Workshop on Environment-Sensitive Fracture of Metals and Alloys," held at the U.S. Naval Research Laboratory, Washington, DC, June 3-4, 1985.



### ABSTRACT

The major developments in understanding the mechanisms of stress-corrosion cracking (SCC) in Al-Zn-Mg and Al-Mg alloys will be briefly reviewed. In particular, evidence for the involvement of hydrogen embrittlement in the SCC mechanisms will be addressed.

The research at Martin Marietta Laboratories that contributed to the understanding will be emphasized. Specifically, the effect of the loading mode on SCC, the role of grain boundary segregation in cracking, and our overall view of the mechanisms of SCC will be discussed.

## I. INTRODUCTION

Stress-corrosion cracking (SCC) is an embrittlement phenomenon occurring in alloys under the combined influence of tensile stress and environment. The stress may either be applied or residual stress, and for aluminum alloys, the environment is most often aqueous, i.e., containing liquid or gaseous water.

Many service failures of high-strength, structural aluminum alloys have been attributed to SCC.<sup>(1)</sup> In fact, the highest strength aluminum alloys are generally the most susceptible to SCC, and Speidel<sup>(1)</sup> estimated that there were over 450 SCC failures in high-strength aluminum alloys in aerospace products during 1968. The highest strength aluminum alloy system, the Al-Zn-Mg (7xxx) alloys, is often extremely susceptible in the peak-strength tempers.<sup>(2-4)</sup> Furthermore, SCC most often occurs in thick sections, which are often subjected to short transverse (ST) stresses. Susceptibility is generally highest in the ST orientation because the pancake-shaped grain morphology that often results from hot working is particularly amenable to cracking. Such SCC failures have the potential to be catastrophic, in the event that routine inspections fail to detect stress-corrosion (SC) cracks.

The usefulness of both Al-Zn-Mg alloys and a medium-to-high strength system, the Al-Mg (5xxx) alloys, is often limited by SCC susceptibility. High-strength 7xxx alloys are often used in the overaged (OA) condition to reduce susceptibility, but at the expense of about a 15% loss in strength. In addition, weldable 7xxx<sup>(5)</sup> and 5xxx<sup>(6)</sup> alloys are often extremely susceptible in the heat-affected-zone (HAZ) of weldments, which thereby limits their usefulness.

Many alloy development efforts have been undertaken to reduce the SCC susceptibility of Al-Zn-Mg alloys in the peak-aged temper and thus avoid the strength penalty accompanying overaging. A greater understanding of the SCC

mechanism(s) would be extremely helpful in attaining this goal and, consequently, this area has been extensively studied.<sup>(2-4)</sup> In addition, SCC of Al-Zn-Mg alloys is an intriguing phenomenon because it is usually intergranular, is affected by grain boundary (GB) segregation, and involves both anodic dissolution and hydrogen embrittlement (HE). Thus, mechanistic SCC studies of Al-Zn-Mg alloys have been performed for their overall implications to embrittlement phenomena in general.

In the present work, key developments in understanding the SCC mechanisms in Al-Zn-Mg and Al-Mg alloys are briefly reviewed. Contributions made by Martin Marietta Laboratories' investigators are emphasized, and significant findings by others are also discussed.

## II. MECHANISMS OF SCC

A widely accepted theory of SCC, proposed by Dix<sup>(7)</sup> and Mears, Brown, and Dix<sup>(8)</sup> in the 1940's, attributed it to a synergism between tensile stress and corrosion; most often anodic dissolution. That is, corrosion occurred along localized paths, producing fissures that served as stress-concentrators for an applied tensile stress. SCC was generally found to be intergranular, and the anodic  $\text{MgZn}_2$  GB precipitates were assumed to preferentially dissolve. Dissolution of the  $\text{MgZn}_2$  was subsequently observed by Jacobs.<sup>(9)</sup>

Numerous studies were performed to elucidate the dissolution mechanism of SCC. For example, Sedriks et al.<sup>(10)</sup> explained the decrease in SCC susceptibility in the OA temper as compared with the peak-aged (PA) temper by there being a greater mean-free-path between the anodic GB  $\text{MgZn}_2$  precipitates in the OA temper. Subsequent SCC simulation studies were performed to establish the corrosion behavior of the individual microstructural components of the GB region of a Al-Zn-Mg ternary alloy.<sup>(11)</sup> In this work, comparisons were made of the relative corrosion rates of 1) a relatively massive  $\text{MgZn}_2$  crystal; 2) pure aluminum, which simulates the solute-depleted region adjacent to the GB, and 3) the as-quenched ternary alloy, which simulates the vacancy-depleted zone somewhat removed from the boundary. The results indicated that the dissolution rate of  $\text{MgZn}_2$  under comparable electrochemical conditions was far greater than that of the other GB components. Furthermore, the results indicated that the crack-tip environment was governed by solubility product considerations.<sup>(11-12)</sup>

In 1963, Gruhl<sup>(13)</sup> observed that Al-Zn-Mg specimens that were pre-exposed to a saline solution had shorter time-to-failure (ttf) during subsequent SCC testing than non-exposed specimens. Furthermore, he found that this "pre-exposure embrittlement" (PEE) could be eliminated by repeating the entire heat-treatment on the specimens. This reversible PEE led Gruhl to propose that hydrogen, resulting from the corrosion reaction, permeates into the alloy and

promotes embrittlement under the influence of the subsequently applied tensile stress. Thus, Gruhl proposed that HE is involved in the SCC mechanism.

Gruhl's observations and proposed mechanism were initially viewed with skepticism. However, PEE was also noted in subsequent work by Swann and co-workers. For example, Montgrain and Swann<sup>(14)</sup> observed fracture of pre-exposed specimens at lower stress levels than non-pre-exposed specimens; furthermore, fracture occurred without apparent dissolution of the GB precipitates. Moreover, pre-exposed specimens that were subsequently fractured in a vacuum chamber released hydrogen, as measured in a mass spectrometer. In addition, Scamans, Alani, and Swann<sup>(15)</sup> observed reversible PEE in specimens exposed to moist air.

Additional evidence for the role of HE in the SCC of Al-Zn-Mg alloys was provided by Speidel<sup>(3)</sup> who observed SC crack growth in moist air at a humidity level believed to be too low to effect significant dissolution. Speidel also compiled the existing evidence for the role of HE in the SCC mechanisms in a stimulating review.<sup>(16)</sup>

Gest and Troiano<sup>(17)</sup> cathodically charged hydrogen into 7075 T651 specimens, and tested both them and uncharged specimens in tension at various strain rates. The two groups of specimens displayed similar ductilities at high strain rates, but the ductility was lower for the charged specimens at lower strain rates. In addition, the embrittlement was reversible by degassing the charged specimens at elevated temperatures. Furthermore, charged specimens demonstrated increased SCC susceptibility compared with uncharged specimens. Each of these results indicates a role for hydrogen in the fracture process.

The aforementioned studies, as well as others not discussed, indicate that Al-Zn-Mg alloys can be susceptible to HE, and that HE plays a role in the SCC mechanism of these alloys. Research at Martin Marietta Laboratories over the past decade has provided additional evidence for the involvement of HE in SCC and has also elucidated the overall mechanism by which SCC occurs. Some of these major contributions are discussed in the following sections.

### III. MECHANISTIC STUDIES OF SCC AT MARTIN MARIETTA LABORATORIES

#### A. LOADING MODE EXPERIMENT

Investigators at Martin Marietta Laboratories<sup>(18-19)</sup> and elsewhere<sup>(20-22)</sup> developed the loading mode test to determine whether HE is involved in the SCC mechanism of a particular alloy system in a specific environment. In Mode I (tension), a triaxial tensile stress field exists ahead of the crack-tip. This stress field provides a driving force for hydrogen concentration, which can lead to embrittlement. In Mode III (antiplane shear, i.e., torsion), little or no triaxiality exists, thereby reducing or eliminating this driving force for hydrogen concentration and subsequent embrittlement, even in alloys susceptible to HE. Thus, the response of an alloy to this difference in triaxiality may be used as a diagnostic tool to determine if cracking under load in a corrosive environment involves HE, or is primarily attributable to dissolution.

Green and Hayden<sup>(18)</sup> and Green et al.<sup>(19)</sup> used the loading mode technique on a Ti-8wt%Al-1wt%Mo-1wt%V alloy in a saline environment, where HE has been clearly established to play a role in SCC, and on alpha-brass in an aqueous ammonia environment, where HE is believed to play no role in the cracking process. The ttf in Modes I and III was measured for each alloy-environment experiment, and differences in ttf at a given normalized stress intensity --  $K_I/K_{IC}$  and  $K_{III}/K_{IIIC}$  -- were taken as evidence that HE was operating. For the titanium-base alloy in the saline environment, the plot of normalized stress intensity vs ttf for Mode I revealed much greater susceptibility (shorter ttf) than that for Mode III (Fig. 1a). This is strong evidence of HE involvement in the SCC mechanism. For the alpha-brass in the aqueous ammonia environment, the normalized stress intensities vs ttf curves in Modes I and III were virtually coincident, indicating that HE was not operating (Fig. 1b).

With the validity of the test method demonstrated, Green et al.<sup>(19)</sup> then applied it to 7075 T6 aluminum alloy and found results similar to those for the

change the substructure of the alloy. Along with these subtle changes, it must also be noted that none of these SHT studies was carried out on alloys with exactly the same composition. For example, the alloys had various Zn/Mg ratios, different total solute contents (wt%Zn + wt%Mg), and some alloys contained copper. Consequently, it would be easy to speculate on why different investigators have observed different trends in susceptibility with SHT. We can only emphasize that in the present work, we were as careful as possible in isolating SHT and its effect on segregation as an independent variable.

A correlation between SCC susceptibility and free Mg was not found,<sup>(48)</sup> as would be expected from the proposed Mg-H interaction mechanism. Perhaps the boundaries were so saturated with free Mg that enough was present to contribute to the SCC mechanism, and the excess had no effect. Nevertheless, although the existence of free Mg on the GB of Al-Zn-Mg alloys has been unequivocally shown, the Mg-H interaction mechanism of SCC remains unproven.

As the evidence for the role of HE in the SCC mechanism of Al-Zn-Mg alloys became more extensive, Pickens et al.<sup>(55)</sup> endeavored to determine whether HE plays a role in the SCC of Al-Mg (i.e., 5xxx) alloys. In this alloy system, SCC was almost universally believed<sup>(2,56-59)</sup> to proceed by dissolution of the anodic  $Mg_2Al_3$  ( $\beta$ ) phase on the grain boundaries. The loading mode experiment advanced by Green et al.<sup>(19)</sup> was used with the following two improvements: specimens were precracked and crack velocity was measured in each mode.

Results of the experiments showed<sup>(55)</sup> that ttf was significantly greater in Mode III than Mode I, and that the addition of As, a hydrogen recombination inhibitor, decreased ttf in Mode I (Fig. 8). These findings show that HE is indeed involved in the SCC mechanism of 5xxx alloys, as shown earlier for 7xxx alloys. Furthermore, SC crack velocity in Mode III was an order of magnitude slower than that in Mode I -- in which there is no triaxial stress to concentrate hydrogen. Pickens et al. concluded that most of the crack advance during SCC is by HE, not dissolution. Thus, this research demonstrated that

Al-3.0 at. % Zn-3.3 at. % Mg-0.03 at. % Zr  
Peak-Aged

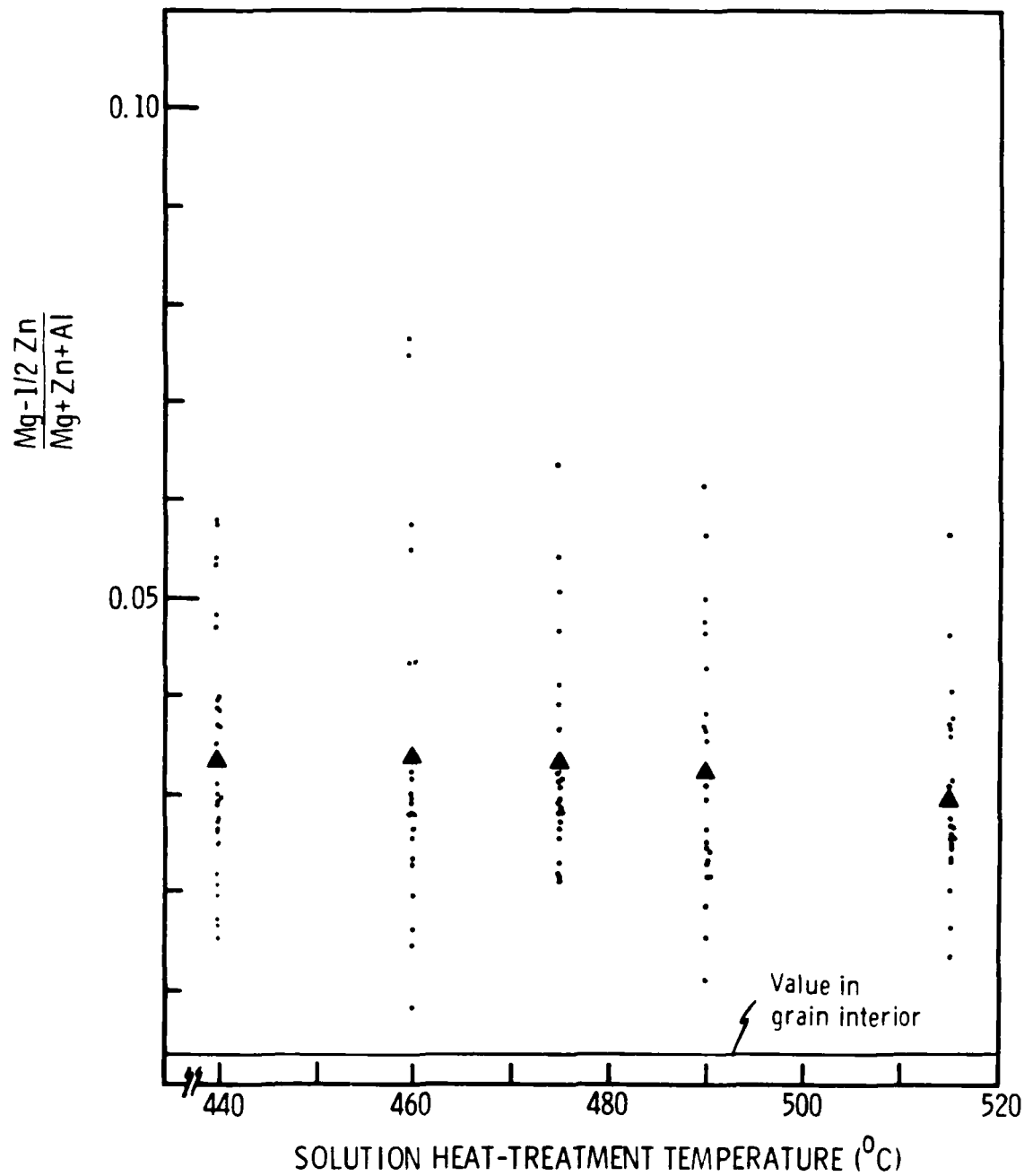


Figure 7. Free magnesium parameter vs. solution heat-treatment temperature for Al-6.9Zn-2.9Mg-0.12Zr (wt%) alloy (from Ref. 48).



Al-3.0 at. % Zn-3.3 at. % Mg-0.03 at. % Zr  
Peak-Aged

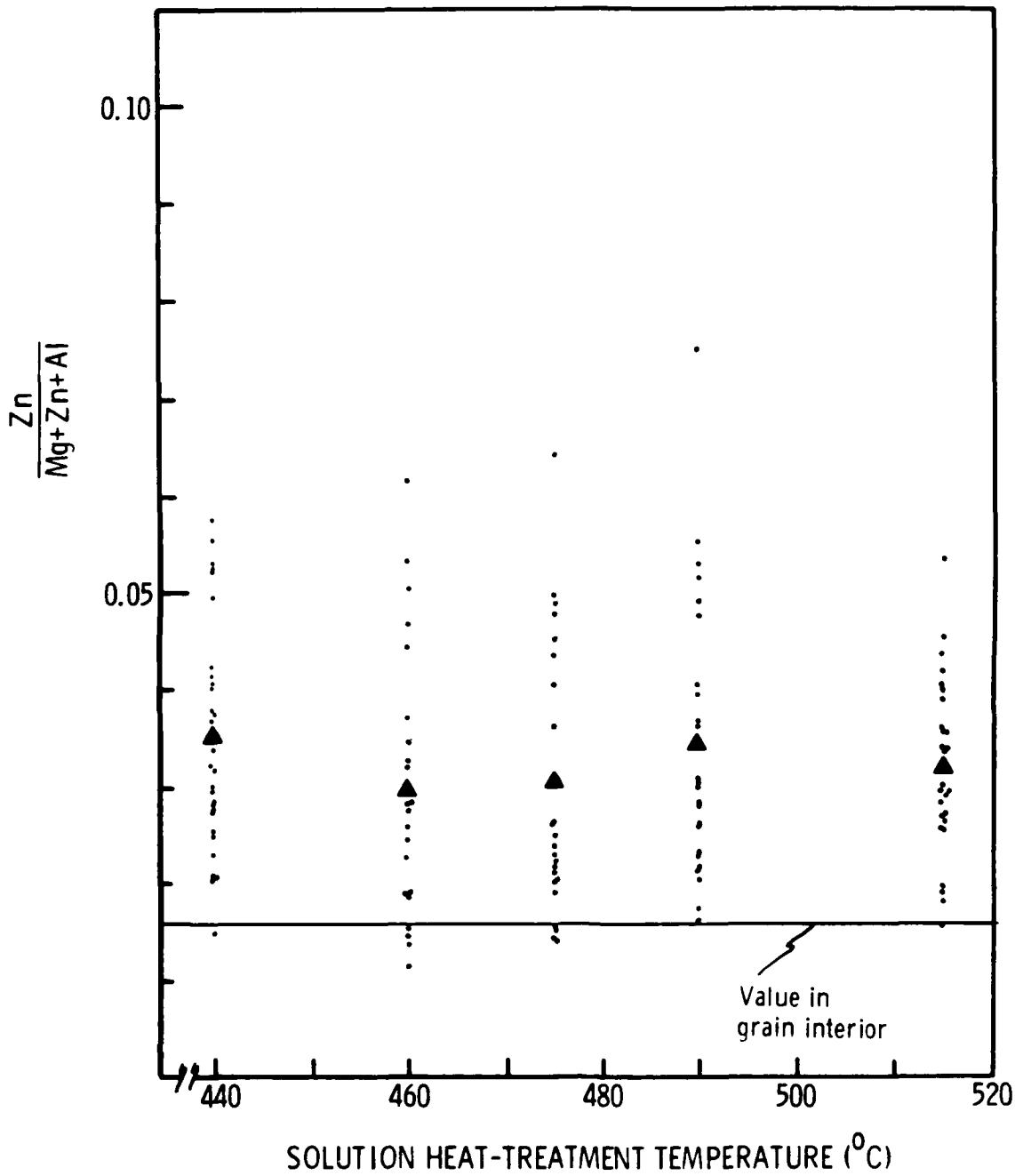


Figure 6. Zinc GB concentration vs. solution heat-treatment temperature for Al-6.9Zn-2.9Mg-0.12Zr (wt%) alloy (from Ref. 48).

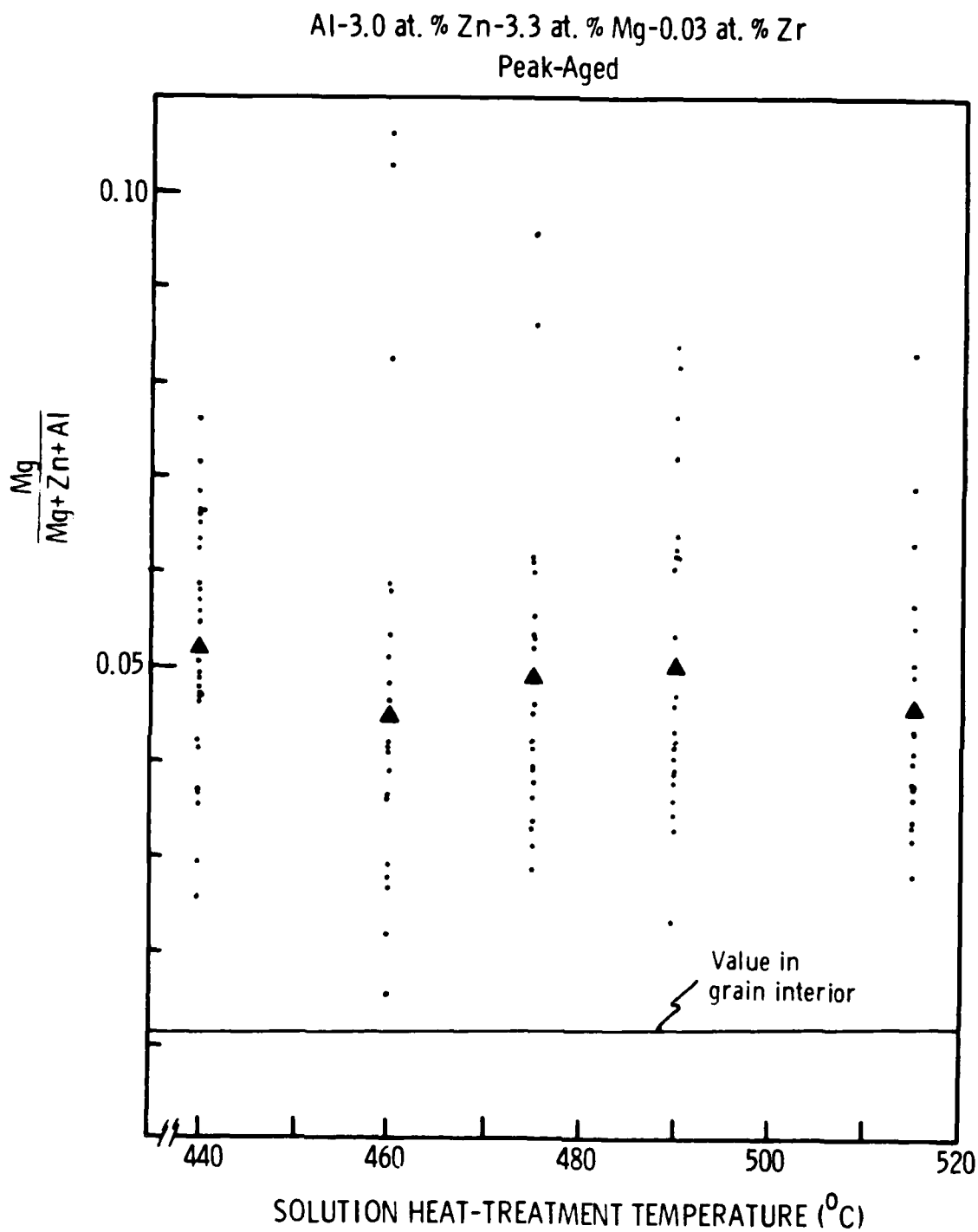


Figure 5. Magnesium GB concentration vs solution heat-treatment temperature for Al-6.9Zn-2.9Mg-0.12Zr (wt%) alloy (from Ref. 48).

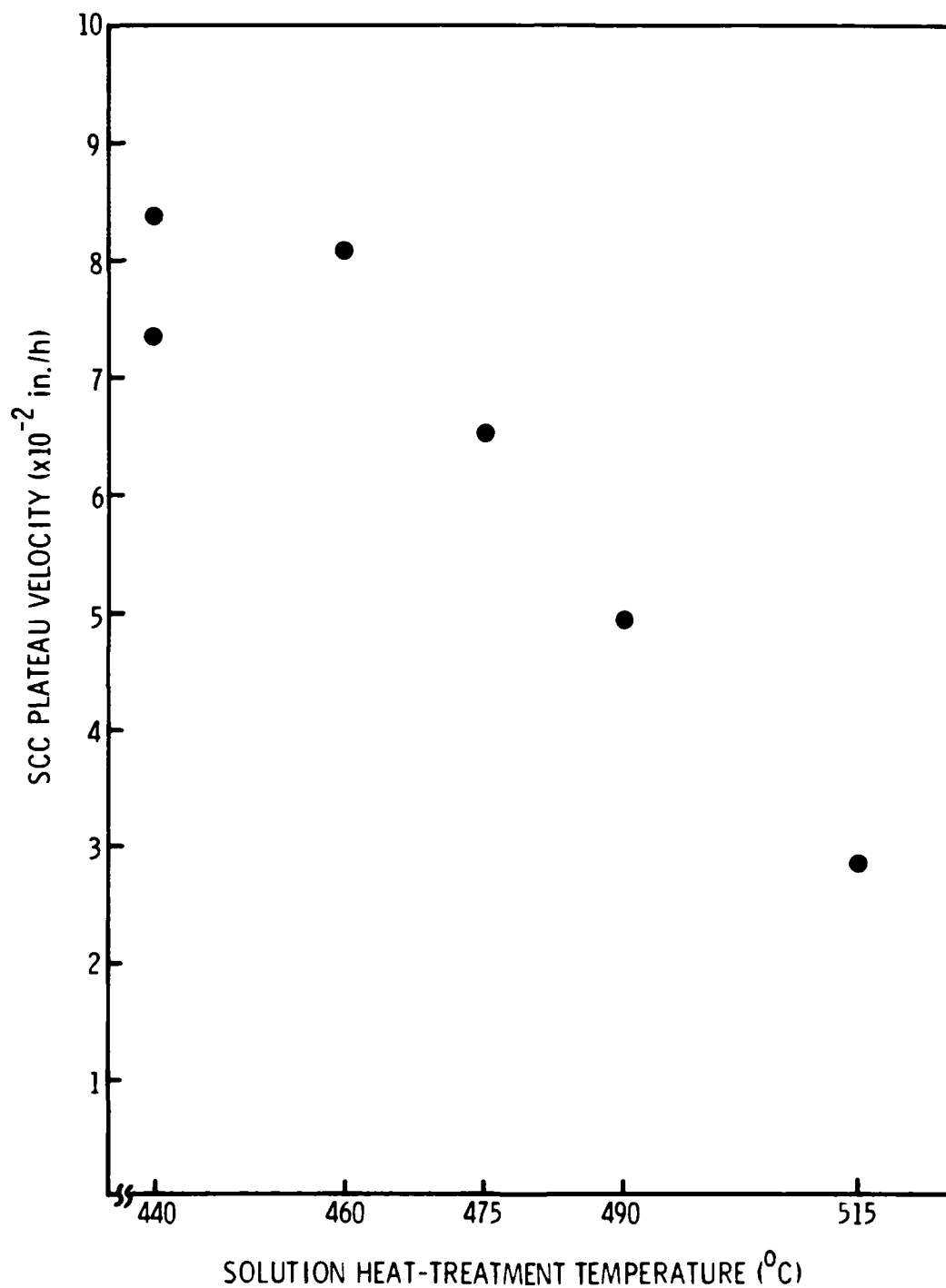


Figure 4. SCC plateau velocity vs solution heat-treatment temperature for Al-6.9Zn-2.9Mg-0.12Zr(wt%) alloy (from Ref. 48).

treatment to isolate SHT, and its effect on GB segregation, as a variable. SCC susceptibility was assessed using precracked bolt-loaded double cantilever beam specimens in a chromate-inhibited brine solution.<sup>(49)</sup> SCC plateau velocity decreased with increasing SHT (Fig. 4). The 1000 Å probe of the scanning Auger microprobe (SAM) was placed on dimple-free intergranular facets, and Mg and Zn scans were obtained. The peak-to-peak heights were measured for Mg, Al, and Zn from the differentiated spectra, corrected using published sensitivity factors,<sup>(50)</sup> and the following ratios were computed:  $Mg/(Mg+Zn+Al)$ ,  $Zn/(Mg+Zn+Al)$ , and  $Al/(Mg+Zn+Al)$ , where each symbol in these ratios signifies the corrected peak-to-peak height for the element.

Both Mg and Zn segregation were observed on the boundaries, and the segregation was similar for each SHT (Figs. 5 and 6), with  $Mg/(Mg+Zn+Al)$  significantly greater on the boundaries than in the bulk. If it is assumed that all the Zn atoms on the boundaries are bound in the  $MgZn_2$  precipitates, then the parameter  $(Mg - 1/2 Zn)/(Mg+Zn+Al)$  would be a measure of free Mg on the boundaries. Auger survey scans were made on a stoichiometric  $MgZn_2$  crystal and verified that the Zn:Mg peak-to-peak ratio, corrected using published sensitivity factors, is 2:1. From the plot of the free Mg parameter vs SHT in Fig. 7, it is clear that there indeed is free Mg on the boundaries, and its concentration is essentially independent of SHT. We emphasize that we are assuming that free Zn does not exist, as claimed in earlier work.<sup>(30)</sup> Nevertheless, if some Zn atoms were not bound in the  $MgZn_2$  precipitates, then there would be even more free Mg than is shown in Fig. 7.

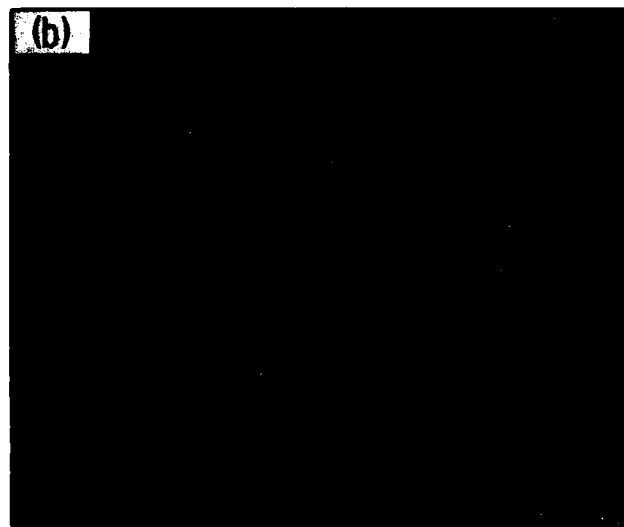
The decrease in SCC susceptibility with increasing SHT is consistent with the work of Taylor and Edgar<sup>(51)</sup> and Scamans,<sup>(33)</sup> but opposite that of Vlasova et al.<sup>(53)</sup> In addition, Joshi et al.<sup>(53)</sup> and Shastry et al.<sup>(54)</sup> found that SCC susceptibility passes through a minimum at a SHT of 438°C for an Al-Zn-Mg-Cu alloy -- results that differ from all of the above. There are many factors besides changes in segregation that can affect SCC susceptibility that could be altered by variations in SHT. For example, grain size can change by grain growth or static recrystallization. In addition, static recovery can

DSC scans on  $\text{MgH}_2$ . The charged specimens showed several exothermic peaks that were very similar to those observed for the  $\text{MgH}_2$ . However, not all the peaks observed for the  $\text{MgH}_2$  were detected for the pre-exposed Al-Zn-Mg and Al-Zn specimens. Tuck interpreted these results as indirect evidence for the existence of the Mg-H complex in Al-Zn-Mg and Al-Mg specimens that were hydrogen charged. Furthermore, based on the great similarities between PEE and SCC,<sup>(14,15)</sup> Tuck proposed that the Mg-H complex plays a role in the SCC mechanism.

To provide more conclusive evidence for the suspected Mg-H complex, Pickens et al.<sup>(37)</sup> cathodically charged Al-4.4wt%Zn-3.7wt%Mg specimens with hydrogen, fractured them under UHV, and performed high-resolution Auger scans to characterize the Mg spectrum. They had hoped to observe satellite peaks from which they could measure the plasmon loss energy (PLE). High-resolution survey scans were also performed on both  $\text{MgH}_2$  and high-purity Mg as a basis for identifying PLE values in the charged specimens. Unfortunately, no  $\text{MgH}_2$  satellite peaks could be discerned. In an attempt to identify a magnesium or an aluminum hydride, they also performed micro-diffraction on thin foil specimens of Al-4.4wt%Zn-3.7wt%Mg that were pre-exposed to distilled water. Unfortunately, no evidence for a hydride phase was found.

Following the failure of the sophisticated surface science techniques to elucidate the role of hydrogen and magnesium in cracking, Pickens and Langan<sup>(42,48)</sup> endeavored to seek unequivocal evidence for free Mg on the GBs of Al-Zn-Mg alloys, and to correlate its concentration with SCC susceptibility. The experiment they chose was to vary solution heat-treatment temperature (SHT) of a Al-Zn-Mg alloy, measure changes in GB segregation from in-situ fractures induced under UHV, measure SCC susceptibility as a function of SHT, and seek correlations between susceptibility and segregation.

For their experiment, they devised an extremely SCC-susceptible alloy composition -- Al-6.9wt%Zn-2.9wt%Mg-0.1wt%Zr (Al-3.0at%Zn-3.3at%Mg-0.03at%Zr) -- and carefully<sup>(42,48)</sup> controlled thermo-mechanical processing and aging



**Figure 3.** Al-Zn-Mg alloys pre-exposed to WVSA at 15 psig, showing (a) induced intergranular fracture, and (b) its facets, which are often featureless at high magnifications (from Ref. 43).

Gallium-induced liquid metal embrittlement (LME) of aluminum alloys is perhaps the most devastating embrittlement phenomenon for such alloys.<sup>(44-46)</sup> In fact, a Ga<sub>L</sub> pre-exposed specimen can crumble intergranularly under its own weight. High-resolution scanning electron microscopy of Ga<sub>L</sub>-embrittled Al-4.4wt%Zn-3.7wt%Mg specimens revealed intergranular fracture surfaces with no evidence of microdimpling up to a resolution limit of 30 Å.<sup>(41-43)</sup> Thus, Ga<sub>L</sub>-embrittled fracture is believed to occur on the actual GB surface.

Unfortunately, Langan and Pickens<sup>(43)</sup> found that Ga interacts with the GB region such that measured Mg segregation increases with time after fracture. Furthermore, this effect is exacerbated at relatively poor vacuum levels (e.g.,  $>10^{-8}$  torr). In addition, the energies of several major Ga peaks in the Auger spectrum are similar to those for Zn, thereby making accurate Zn measurement difficult. Thus, pre-exposure to Ga<sub>L</sub> does induce fracture on the actual GB surface, but also introduces difficulties in interpreting segregation measurements.

Numerous investigators<sup>(3,14-16)</sup> have found that pre-exposing Al-Zn-Mg alloys to liquid or gaseous aqueous environments reduces alloy ductility. Pickens et al.<sup>(41-42)</sup> and Langan and Pickens<sup>(43)</sup> exposed various Al-Zn-Mg alloys to WVSA at 1 atmosphere (gauge) at 100°C. The specimens were severely embrittled, particularly in peak-strength tempers, and fracture was intergranular (Fig. 3a). Most regions appeared featureless (Fig. 3b) on a scanning electron microscope (SEM) with a resolution limit of 30 Å with the exception of the GB precipitates visible on the surface.

Hence, Langan and Pickens<sup>(43)</sup> concluded that hydrogen pre-exposure induces fracture on the actual GB surface and therefore is the most advantageous of the three techniques for exposing Al-Zn-Mg alloy boundaries for examination by AES.

Tuck<sup>(47)</sup> provided indirect evidence for the existence of the suspected Mg-H complex. He pre-exposed Al-Zn-Mg and Al-Mg alloy specimens to aqueous environments, and performed differential scanning calorimeter (DSC) scans on both the hydrogen-charged and uncharged specimens. In addition, he performed

that Mg would be available to form a Mg-H complex. Consequently, the reduced SCC resistance of the thermal film is probably caused primarily by its porosity.

In a follow-up investigation, Pickens et al.<sup>(38)</sup> studied the effect of surface oxide film thickness on SCC resistance, as measured by ttf in acetic acid-brine. Film thickness was varied from 25 to 2000 Å by anodizing in tartaric acid at various voltages. SCC resistance (as measured by ttf) increased with film thickness in the range of 25 to 2000 Å (0.2 μm). This information, coupled with earlier work by Skoulikidis and Karageorgos,<sup>(39-40)</sup> shows that SCC resistance increases with film thickness for smaller thicknesses (up to 0.2 μm, and from 1.7 to 3.4 μm),<sup>(39)</sup> but in general, not for larger thicknesses.

#### D. GRAIN BOUNDARY FRACTURE AND RECENT SEGREGATION STUDIES

Pickens et al.<sup>(41-42)</sup> and Langan and Pickens<sup>(43)</sup> performed detailed investigations of GB segregation to further elucidate the SCC mechanisms in Al-Zn-Mg alloys. They examined the following three embrittlement techniques for exposing the grain boundaries for examination: 1) fracture at near-liquid nitrogen temperatures, 2) fracture after pre-exposure to liquid gallium (Ga<sub>L</sub>) at ~35°C for approximately 1 h, 3) fracture after pre-exposure to water-vapor saturated air (WVSA) at 100°C at 1 atmosphere (gauge). After each embrittlement procedure, specimens were fractured under ultra-high vacuum (UHV) and Auger measurements were then performed.

Fracture at near-liquid nitrogen temperatures was intergranular, but at high magnifications, fine dimples were observed on the grain facets. Thus, the fracture was not entirely on the actual GB surface, but was most likely in the precipitate-free zone. Consequently, information obtained using this technique is, at least partly, not representative of the actual GB surface.



thick, whereas the thermal film is typically 2000 Å thick. They compensated for this disparity by anodizing 2000 Å thick alumina films on several specimen surfaces in tartaric acid. Specimens with comparable film thickness were tested and ttf was measured at various stress levels in the acetic acid-brine solution developed by Pistulka and Lange.<sup>(36)</sup>

At the same thickness, ttf for the Mg-rich thermal film was about 50% shorter than that for the tartaric acid-anodized (TAA) Mg-free (Fig. 2) film.<sup>(35)</sup> In fact, ttf for the 2000 Å thermal film was similar to that for the 25 Å film that forms naturally after polishing. However, the Mg-rich film was subsequently found to be considerably more porous than the TAA film, so that the differences in ttf may not have been caused directly by the magnesium in the film, but possibly by the porosity of the thermal film resulting from Mg sublimation during solutionizing.

In subsequent work using surface science techniques, Pickens et al.<sup>(37)</sup> did not observe elemental Mg atoms in the thermal film; thus, it is unlikely

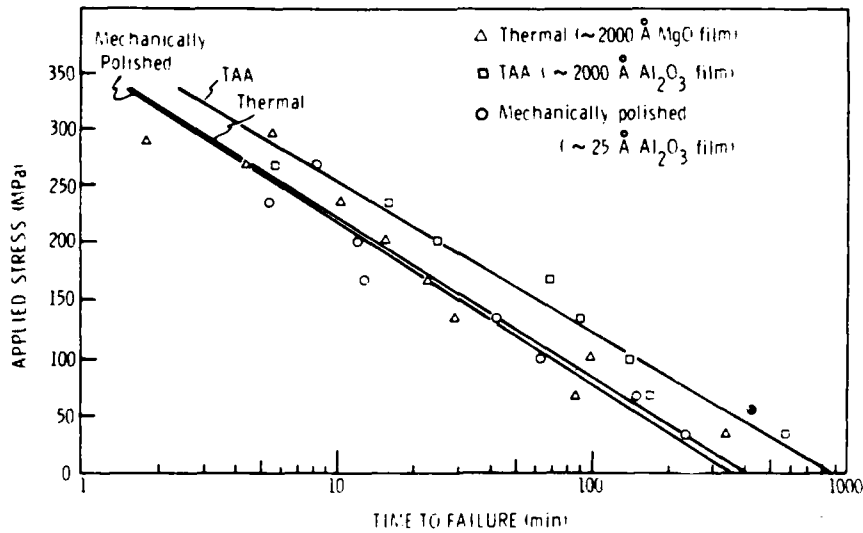


Figure 2. Comparison of susceptibility of Al-4.4Zn-3.7Mg specimens with various surface oxide films (from Ref. 35).

fractures, and segregation was then measured by AES from the fracture surfaces. Information from each fracture was obtained to a depth of 3-6 atomic layers from about 6-8 grains under the electron beam, from which these investigators concluded that both Mg and Zn atoms segregate to the boundaries. The equilibrium GB precipitates in these alloys are  $\text{MgZn}_2$  -- i.e., two Zn atoms for one Mg atom -- however, the atomic concentration measurements revealed more Mg than Zn atoms, suggesting that some of the Mg atoms on the boundaries were not bound in the precipitates. The existence of this "free Mg" was further supported by measurements of the plasmon-loss energies of the Auger spectra, which indicated that in the solutionized, quenched, and aged temper, nearly all the Zn atoms, but only 40% of the Mg atoms, are in the GB  $\text{MgZn}_2$  precipitates, leaving about 60% of the Mg atoms unbound in the interparticle space.<sup>(30)</sup>

Viswanadham et al.<sup>(32)</sup> then extended these segregation studies to the surface oxide films on several Al-Zn-Mg alloys. They found that the film that forms during solutionizing -- i.e., the "thermal film" -- is enriched in Mg and contains mostly  $\text{MgO}$ , as opposed to  $\text{Al}_2\text{O}_3$  as initially had been expected. Thus, Viswanadham et al. observed Mg segregation at the two critical regions of Al-Zn-Mg alloys pertinent to SCC: the GB and the surface oxide film. Coupling this information with the great mutual affinity between Mg and H reported in the literature, they proposed in general terms the following Mg-H interaction mechanism of SCC. Mg and H atoms interact by forming a Mg-H complex which probably facilitates both hydrogen entry through the film and hydrogen accumulation on the boundaries, which then leads to embrittlement. Scamans independently proposed a similar Mg-H interaction mechanism of SCC in Al-Zn-Mg alloys.<sup>(33)</sup>

### C. SURFACE OXIDE FILM STUDIES

Pickens et al.<sup>(34-35)</sup> endeavored to determine whether the Mg-rich thermal film provides less protection than an alumina film. Such a comparison could not easily be made because the natural alumina film is typically 25 Å

titanium alloy, i.e., shorter ttf in Mode I than in Mode III (Fig. 1c). Furthermore, the addition of 10 ppm of As, a well-known hydrogen recombination inhibitor,<sup>(23)</sup> increased embrittlement in Mode I and reduced embrittlement in Mode III. They rationalized that under Mode I loading, where hydrostatic stresses force the concentration of hydrogen to the region of triaxial stress ahead of the crack-tip, the addition of arsenic retards the kinetics of hydrogen evolution, thereby increasing hydrogen concentration within the metal, which enhances the hydrogen embrittlement. Under Mode III loading, however, where there is insufficient hydrostatic stress to cause the localized concentration of hydrogen, the slower dissolution mechanism takes precedence. In this experiment, the arsenic merely served to retard the cathodic reaction ( $2H^+ + 2e^- \rightarrow H_2$ ), which controls the rate of the overall dissolution process. Thus, the SCC mechanism in 7075 was shown to involve HE by a test that does not precharge hydrogen into the specimens.

SCC is most often intergranular in aluminum-base alloys,<sup>(2)</sup> so the role of grain boundary (GB) segregation has been studied extensively to elucidate the cracking mechanism.<sup>(24-31)</sup> Furthermore, with HE clearly contributing to SCC, the issue of how hydrogen interacts with the grain boundary and the local segregation there clearly becomes important.

## B. EARLY SEGREGATION STUDIES

Most of the early work on GB segregation in Al-Zn-Mg alloys was performed using electron energy loss measurements and X-ray microanalysis on GB profiles in thin foils in a transmission electron microscope.<sup>(24-26)</sup> However, these techniques were limited in spatial resolution and consequently offered only limited information on the composition of the actual GB surface. Green and coworkers<sup>(27-31)</sup> endeavored to use the excellent surface sensitivity of Auger electron spectroscopy (AES) to obtain segregation information from the actual grain boundary. Specimens of several Al-Zn-Mg-Cu alloys were fractured under ultra-high vacuum (UHV) at approximately -194°C to produce intergranular

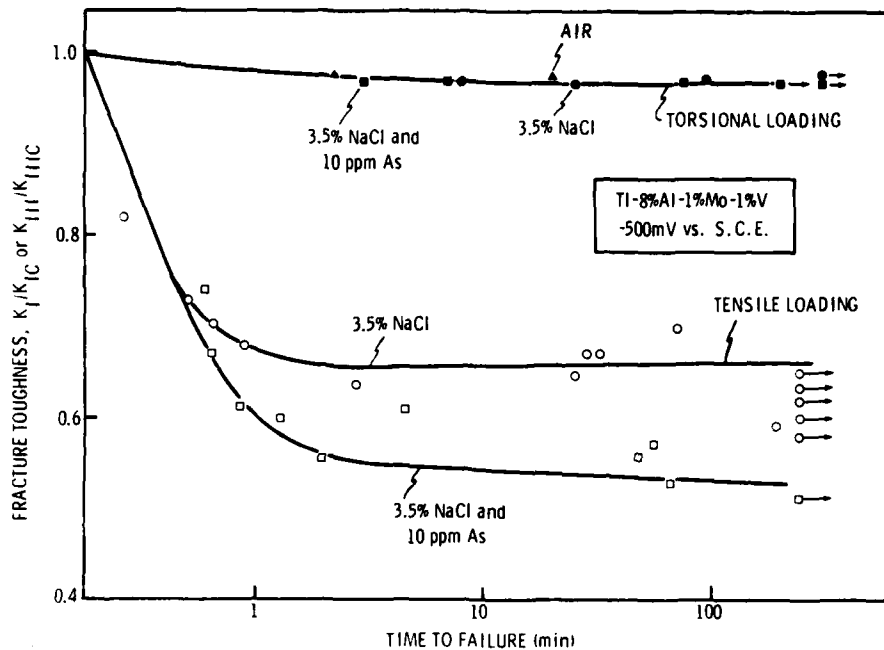


Figure 1a. Influence of loading mode on the susceptibility of Ti-8Al-1Mo-1V to SCC in various salt solutions (from Ref. 19).

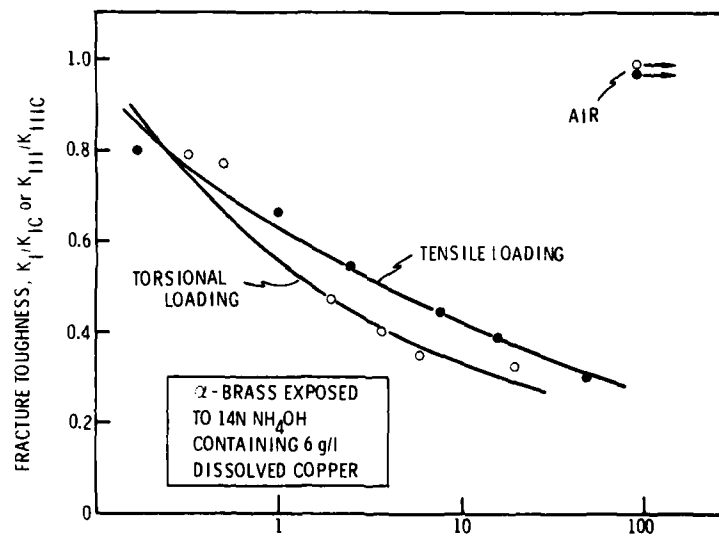


Figure 1b. Influence of loading mode on the susceptibility to SCC of  $\alpha$ -brass exposed to tarnishing ammoniacal environments (from Ref. 19).

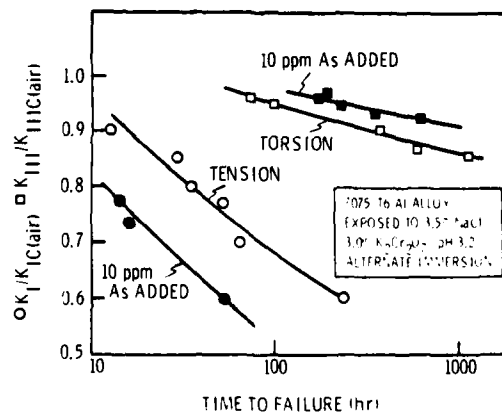


Figure 1c. Influence of loading mode on the susceptibility of 7075-T6 Al alloy to SCC in various saline solutions (from Ref. 19).

the conventional view of the SCC mechanism in 5xxx alloys is incorrect; SCC is not due solely to dissolution, but to a very different process -- cracking dominated by HE.

More recently, Pickens et al.<sup>(60)</sup> and Pickens<sup>(61)</sup> used the loading mode technique on Al-Zn-Mg powder metallurgy (P/M) alloy 7091 and found that SCC in this alloy is also dominated by HE.

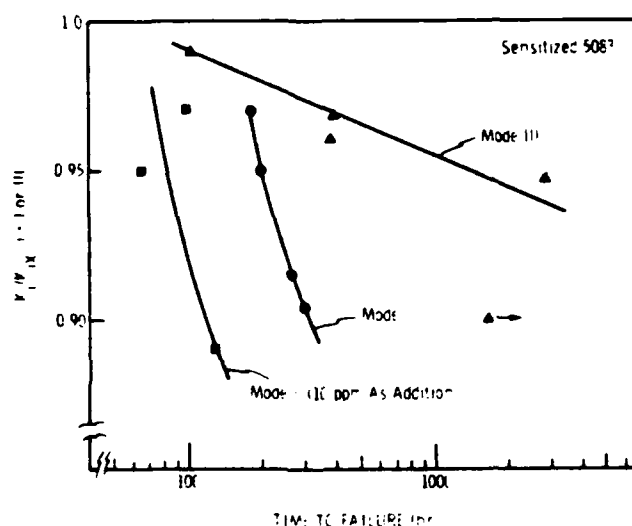


Figure 8. Normalized stress intensity vs ttf in Modes I and III for alloy 5083 (from Ref. 55).

#### IV. PRESENT VIEW OF THE SCC MECHANISM

After many years of studying SCC of Al-Zn-Mg and Al-Mg alloys at Martin Marietta Laboratories, we have developed the view of the SCC mechanism that is summarized in Fig. 9. This mechanism applies primarily to Al-Zn-Mg alloys, but is likely similar for Al-Mg alloys.

For SCC to occur, the surface oxide film must first be penetrated which most easily occurs at the coarse constituent particles and is facilitated by the presence of the  $\text{Cl}^-$  ion. Water -- either liquid or gaseous -- then has access to the exposed aluminum alloy. If liquid water contacts a GB-surface intersection, dissolution occurs in the GB region where anodic precipitates ( $\text{MgZn}_2$  in 7xxx,  $\text{Mg}_2\text{Al}_3$  in 5xxx) preferentially dissolve. We must emphasize that dissolution in the usual sense may not be a necessary condition for SCC. Montgrain and Swann<sup>(14)</sup> and Scamans<sup>(62)</sup> observed SCC in Al-Zn-Mg alloys exposed to moist air with no apparent evidence of dissolution on the SC fracture surface. Scamans performed the matching fractography to show that the  $\text{MgZn}_2$  precipitates were still present on the fracture surface after cracking. In addition, Speidel<sup>(3)</sup> observed cracking at humidity levels too low to effect dissolution. Presumably, gaseous water can react with the exposed metal atoms as an adsorbed species, and produce hydrogen. We believe that it is the hydrogen produced as a result of adsorption and/or in dissolution reactions that is primarily responsible for cracking. This hydrogen enters the alloy at GB-surface intersections and proceeds along the GB by interacting with the free Mg there. Although free Mg has not been shown to exist in Al-Mg alloys, we suspect its presence there based on the following observations of Scamans and Holroyd.<sup>(63)</sup> They provided indirect evidence for both the presence of free Mg on the boundaries of Al-Mg alloys and the role of Mg in SCC by showing far greater hydrogen permeation in as-quenched (i.e., minimal precipitation on GBs) Al-Zn-Mg and Al-Mg alloys than in as-quenched Al-Zn alloys and pure aluminum. Thus, only the Mg-containing alloys display rapid hydrogen permeation. The hydrogen collects at regions of triaxial tensile stress ahead of local fissures in the alloy and when the hydrogen concentration reaches a critical concentration, cracking occurs. This hypothesis is substantiated by the discon-

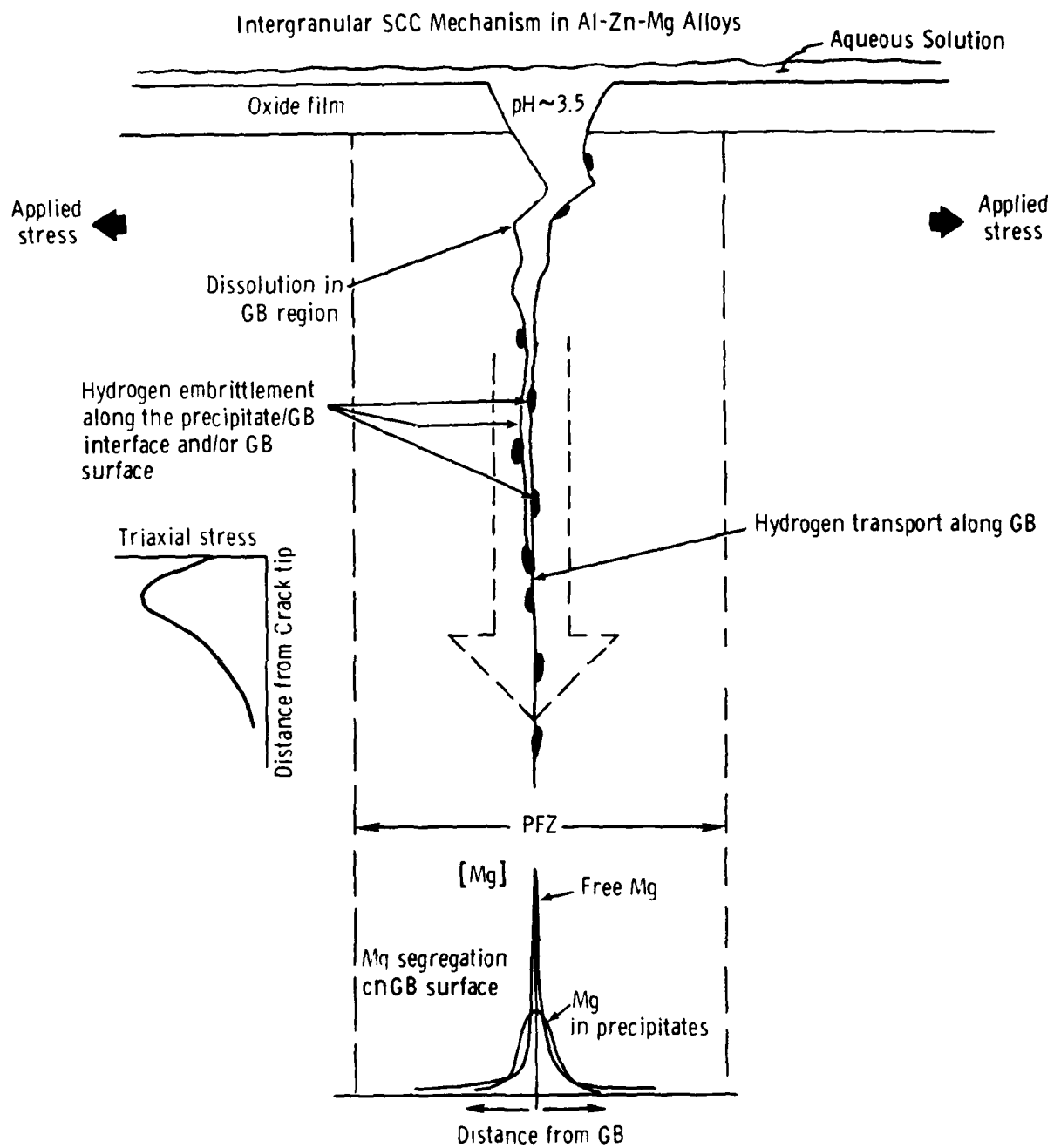


Figure 9. Schematic of SCC mechanism in Al-Zn-Mg alloys.

tinuous crack growth during SCC of Al-Zn-Mg alloys reported by Scamans.<sup>(64)</sup> The mechanism\* by which the hydrogen embrittles the GB is not known, but the following are plausible possibilities:

1. The hydrogen collects at the second-phase particle/GB interface, thereby embrittling the interface and serving to nucleate cracks.
2. A brittle hydride (i.e., Mg-H complex) forms on the GB surface.
3. The hydrogen collects along the entire boundary surface, thereby embrittling it.
4. Some combination of the above.

Number 1 is particularly intriguing because no one has unequivocally observed SCC in an alloy devoid of second-phase particles. Until recently, SCC has never been observed in Al-Zn-Mg or Al-Mg alloys without GB precipitates. Pickens et al.<sup>(65,66)</sup> recently demonstrated SCC in an Al-Mg-O-C P/M alloy that had no GB precipitates, but did have oxide ( $MgO$ ,  $Al_2O_3$ ) and carbide ( $Al_4C_3$ ) particles on the boundaries. Thus, the presence of a second-phase particle/GB interface appears to be a necessary condition for SCC. Could a local triaxial stress state exist around such GB particles to cause high local concentrations of hydrogen and resulting embrittlement?

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\* By mechanism, we refer to the microstructural features on the GBs that crack under the influence of H. It is also not known how H disturbs the atomic bonding of Al-Zn-Mg alloys — e.g., by decohesion or facilitating dislocation nucleation.



In summary, the SCC mechanism in these alloys is not completely understood. However, we do know that crack advance is largely a result of HE, that free Mg exists on the GBs — the region where cracking occurs — and that the presence of second-phase particles on the boundaries is likely a necessary condition for SCC.

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