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STRESS-CORROSION CRACKING OF HIGH-STRENGTH ALUMINUM ALLOYS (U)
SEP 80 E N PUGH, R A YESKE AFOSR-77-3175

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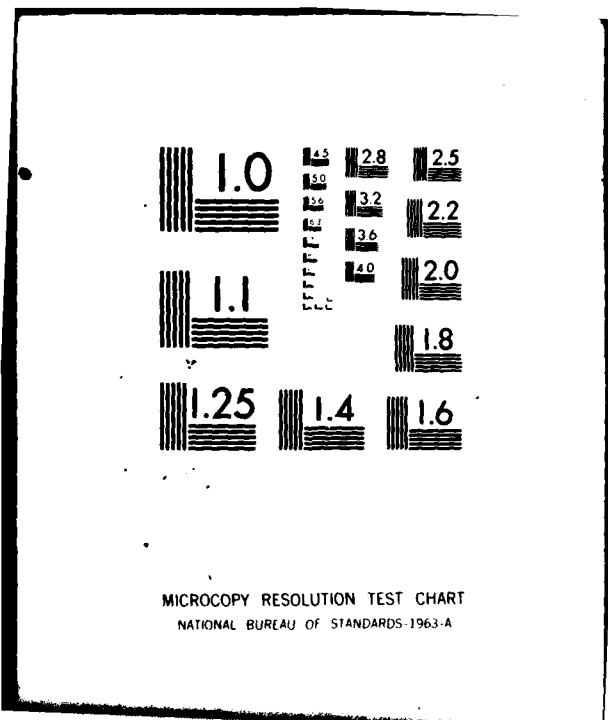
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number): **A study has been made of the mechanism of hydrogen embrittlement (HE) in Al-Zn-Mg alloys, and of the role of hydrogen in the intergranular stress-corrosion cracking (I-SCC) of these alloys. Up to 300 ppm (1 at pct) hydrogen was introduced into a high-purity Al-5.6Zn-2.6Mg alloy, either by room temperature polishing with aqueous slurries of alumina particles or by exposure to water-vapor-saturated air (WVSA) at 70°C, and subsequent tensile tests (stress rate $\sim 10^{-4} s^{-1}$) in inert environments caused brittle intergranular**

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fracture. Embrittlement was found to be reversible, the tensile properties being completely restored when the hydrogen was outgassed. At low hydrogen contents, embrittlement was suppressed by the use of high strain rates ($\sim 10^{-2} s^{-1}$), but could not be suppressed by impact testing at large hydrogen concentrations. The intergranular fracture surfaces were observed to be associated with a fragmented layer, and electron-diffraction experiments indicated that it corresponded to a hexagonal aluminum hydride, AlH_3 , with $a = 2.90 \text{ \AA}$ and $c = 4.55 \text{ \AA}$. This hydride, considered to be stress-induced, was unstable in laboratory air, slowly decomposing to FCC Al . It is concluded that internal HE in this alloy occurs by repeated cycles of the formation and rupture of this brittle hydride. Limited tests were also carried out on high-purity copper-containing Al-Zn-Mg alloys and on 7075-T6. HE was observed in both high-purity alloys, after exposure to 70°C WWSA, although the fragmented layer was observed only in one case. The commercial alloy was not embrittled by exposure to 70°C WWSA, but it was not established that this treatment introduced significant hydrogen concentrations.

Exposure of stressed specimens of Al-5.6Zn-2.6Mg to 70°C WWSA resulted in slow crack growth by the hydride-rupture mechanism. However, fracture surfaces produced by I-SCC in this alloy were not associated with the fragmented, raising the question of whether this process involves hydrogen.

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A. Introduction

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The broad objective of this program was to investigate the role of hydrogen in the intergranular stress-corrosion cracking (I-SCC) of Al-Zn-Mg alloys. Previous work¹⁻⁶ had established that these alloys undergo brittle intergranular fracture when they are stressed after being charged with hydrogen, and this had led naturally to the speculation that I-SCC may also be a form of hydrogen embrittlement (HE), hydrogen being generated at the crack tip by reaction of aluminum with the aqueous solution. However, there was no direct evidence for a casual relationship between hydrogen and I-SCC in these alloys. Moreover, the mechanism of HE itself was not established. Thus the specific objectives of the program were (i) to investigate the mechanism of HE in Al-Zn-Mg alloys, and (ii) to study the possibility that I-SCC is a form of HE.

The work was carried out primarily on a high-purity ternary alloy containing 5.6 (wt pct) zinc and 2.6 magnesium, although some work was conducted on commercial 7075 Al and on several other high-purity alloys. The studies of the mechanism of HE focussed on the possibility that the failure involves the formation of a brittle hydride layer. This stemmed from our earlier observation that a fragmented layer existed on the intergranular fracture surfaces of tensile specimens of the Al-5.6Zn-2.6Mg which were charged with hydrogen and stressed to failure in dry argon.^{6,7} Electron-diffraction patterns obtained from this layer at that time corresponded to FCC aluminum, but it was speculated that this was a decomposition product of an aluminum hydride, which is known to be unstable, particularly in moist environments.⁸ Experiments were undertaken to investigate this possibility and to determine the role, if any, played by the layer in the embrittlement process.

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The studies of the possible role of hydrogen in I-SCC involved the construction of V-K curves for Al-Zn-Mg alloys in aqueous sodium chloride solutions, and an attempt to identify the rate limiting process(es) in the plateau regions. Specifically, our objective was to examine whether hydrogen diffusion can be the rate limiting step under certain conditions. It will be seen below that this phase of the program was not completed.

B. Summary of Results

i) Studies of the Mechanism of Hydrogen Embrittlement

The fragmented layer on the intergranular fracture surfaces of the Al-5.6Zn-2.6Mg alloy referred to above, was first observed in specimens embrittled by exposure to room-temperature laboratory air.^{6,7} While this form of pre-exposure embrittlement is now well established,⁴⁻⁷ this method of introducing hydrogen requires exposure times of ~2 months to produce significant embrittlement, and then the layer is observed on only 5-10 pct of the fracture surface. This method presented several difficulties for the electron-diffraction experiments, and therefore initial effort was directed to developing an alternative means for introducing hydrogen into the samples. Cathodic charging was unacceptable in the high-purity alloy because of severe intergranular corrosion,⁶ and high-temperature gas charging was considered unsuitable because of conflicts with heat treatments necessary to produce hardening.

Two methods were found to be suitable. In the first, the gauge lengths of specimens were polished mechanically with a deionized-water slurry of 0.05 μm aluminum particles, using a vibratory polisher or a specially designed polishing apparatus.⁹ Analysis indicated that up to 100 ppm hydrogen was introduced, and the specimens exhibited significant embrittlement in subsequent tensile tests in dry argon, the fragmented layer being observed on many facets

of the intergranular fractures. The second method, developed by Scamans and Tuck,¹⁰ consisted of exposure to water-vapor-saturated air (WVSA) at 70°C for periods up to 7 d. This method introduced up to 300 ppm hydrogen (~1 at pct), and was subsequently adopted as the main method of hydrogenation.

Figure 1 illustrates the effects of exposure to 70°C WVSA on the mechanical properties of the Al-5.6Zn-2.6 Mg alloy tested in dry argon at a strain rate of $1.3 \times 10^{-4} \text{ s}^{-1}$. Both the plastic strain to fracture and the fracture stress can be seen to decrease progressively with increasing exposure time. The data suggested that two stages exist. For exposure times up to ~4 d, there are large reductions in plastic strain but little decrease in fracture stress, whereas there were also large reductions in these stresses for longer exposure times. Those two regions are subsequently referred to as Stage I and Stage II. Increasing exposure times were associated with increasing amounts of brittle intergranular fracture and the associated fragmented layer.

Studies were made of the effects of strain rate and thermal treatments designed to outgas the hydrogen.⁹ These indicated that Stage I embrittlement was completely suppressed by testing at a strain rate of $1.3 \times 10^{-2} \text{ s}^{-1}$. Moreover, testing at slower rates ($1.5 \times 10^{-5} \text{ s}^{-1}$) was observed to increase the degree of embrittlement and the amounts of the fragmented layer. In contrast, there was no significant effect of strain rate in Stage II. Indeed, it was found that Stage II embrittlement was not suppressed under impact loading. Outgassing hydrogen by a complete re-heat treatment (ST at 470°C in argon, NQ, and aged for 24 h at 130°C) completely recovered the mechanical properties of both Stage I and II specimens, demonstrating the reversibility of the phenomenon. TEM studies of samples produced by thinning unstressed specimens which had been exposed for 7 d to 70°C WVSA revealed no evidence for the presence of the layer or other unusual structures at grain boundaries, suggesting that the fragmented layer is not formed prior to stressing.

Electron-diffraction studies were carried out directly from the fragmented layers on intergranular fractures produced in specimens exposed for 7 d to 70°C WWSA, and subsequently fractured in dry argon and transferred quickly (within 5 min) to the TEM without exposure to laboratory air. Under these conditions, the patterns were quite different from those obtained in the early experiments.^{6,7} in which the fractured specimens were stored in laboratory air for long periods (greater than 3 d) before the diffraction experiments were conducted. The patterns were now characterized by continuous rings, indicating an extremely fine grain size, and the plane spacings were found to be consistent with those for a hexagonal aluminum hydride, AlH₃, with $a = 2.90 \text{ \AA}$ and $c = 4.55 \text{ \AA}$.¹¹ The spacings were also compared to those of various forms of alumina and aluminum hydroxide, but no correspondence was found.

Several fractured specimens for which the AlH₃ structure had been observed were subsequently to laboratory air for ~ 150 h, and further electron diffraction patterns were obtained. In no cases were the AlH₃ patterns observed, all the patterns being indexed as polycrystalline aluminum, as in the earlier studies.^{6,7} The polycrystalline nature was interesting, since patterns taken from the fracture surfaces of non-embrittled specimens corresponded to single-crystal aluminum, as would be expected in view of the large grain size of the alloy (~ 300 μm) and the small diameter of the electron beam (200-300 Å). Possible reasons for the fine grain size of the AlH₃ and the polycrystalline nature of the aluminum decomposition product are discussed elsewhere.⁹

It was concluded from these results that the hydride is stress-induced, and that its formation is responsible for internal hydrogen embrittlement in this alloy, by the hydride-rupture model proposed for zirconium¹² and

niobium.¹³ The occurrence of two stages of embrittlement for specimens hydro-generated by exposure to 70°C WWSA, Fig. 1, was rationalized in terms of the several different roles of stress in such an embrittlement process. When the hydrogen content was low, Stage I, it is considered that the large stresses are necessary to concentrate sufficient hydrogen (by the Troiano-Oriani mechanism) to form AlH_3 . The fact the hydrogen diffusion is thus required is consistent with the observed strain-rate dependence in this stage. In Stage II, it is thought that sufficient hydrogen is already present at the grain boundaries to form AlH_3 , so that diffusion over long distances is not required during straining -- hence the absence of a strain-rate dependence. This view requires that all the hydrogen in the alloy is at the boundaries for a layer of stoichiometric AlH_3 , $\sim 1 \mu\text{m}$ thick, to be formed. Under these conditions, the formation of AlH_3 requires only the stress necessary to induce the phase transformation, considered displacive. The third stress to be considered is that required to fracture the hydride. Thus the low fracture stresses in Stage II correspond to either the transformation stress or the fracture stress, whichever is larger.

Limited studies were carried out on other alloys, namely two high-purity alloys (kindly provided by the E. A. Starke, Georgia Institute of Technology) containing 6 (wt pct) Zn; 2.2 Mg and either 1.5 or 2.5 Cu; and commercial 7075-T6.⁹ These were exposed for various times to 70°C WWSA and then tested in dry argon at $1.3 \times 10^4 \text{ S}^{-1}$. Both high-purity alloys showed considerable embrittlement, the fracture mode changing from ductile transgranular to brittle intergranular. However, the fragmented layer was detected only in the alloy containing the lower copper content. No embrittlement was detected only in commercial alloy, but it should be noted that no analysis was carried out to determine whether it contained significant hydrogen concentrations after exposure.

ii) Studies of Intergranular Stress-Corrosion Cracking

It was seen in Section A that this part of the program involved the generation of V-K curves for I-SCC. The double-torsion (DT) method was used in this work because it promised a number of advantages. For example, it offered the possibility that plane-strain conditions could be maintained at the crack tip in relatively thin sheet. The use of thin sheet is also advantageous for studies of high-purity alloys which are not available in the large quantities necessary for other test configurations, and for aluminum alloys in general, since it permits uniform microstructures to be obtained during heat treatments, often not possible in thick sections.

The D-T method had previously been used only for very high-strength materials such as glass, alumina, and high-strength steels, and thus preliminary experiments were necessary to establish its applicability to the relatively low-strength Al-Zn-Mg alloys. In a first series of tests,¹⁴ the stress intensity for "pop-in" of fatigue pre-cracked D-T specimens of 7075-T6 was measured and these values of K_q were compared with the value of K_{IC} determined using compact-tension specimens of the same material. The D-T specimens were taken from sheets of various thicknesses down to 0.125 in., and side grooves of up to 50 pct of the sheet thickness were used. In all cases, the values of K_q were in good agreement with K_{IC} , establishing that valid plane-strain conditions exist in the D-T specimens. Values of K_q were also determined for D-T specimens of the high-purity alloy which had been solution treated at 470°C, water quenched and aged to maximum hardness at 130°C. These specimens were of thickness 0.125 in. and contained side grooves of up to 50 pct of the sheet thickness. The values of K_q were in good agreement for all depths, and therefore subsequent stress-corrosion tests were carried out on D-T specimens 0.125 in. thick containing side grooves 0.03 in. deep. In a second series of tests, compliance calibrations were conducted using saw-cut and pre-fatigued D-T specimens of both 7075-T6 and the high-purity alloy.¹⁴ The relationships

between load, crack length, specimen geometry, compliance and stress intensity derived from linear elastic fracture mechanics was found to be in good agreement with the experimentally determined relationships, thereby justifying the use of load relaxation to monitor crack growth.

Stress-corrosion tests were then carried out using D-T specimens of both the high-purity alloy, aged to peak hardness at 130°C, and 7075-T6; these were conducted at room temperature using 3 pct aqueous NaCl. A series of V-K curves was generated for both cases,¹⁴ and the data were in good agreement with those from the literature obtained using "thick" specimens.¹⁵ A single plateau was observed in Stage II for both alloys. At this point, it had been planned to study the effects of various factors including heat treatment/microstructure, temperature, solution composition, and potential on the V-K curve for the Al-5.6Zn-2.6Mg alloy. However, the departure of the Principal Investigator (ENP) from the University caused this phase to be terminated. The studies are being continued by E. N. Pugh at the National Bureau of Standards (NBS), Washington, D.C.

Despite the incompleteness of this phase of the program, several points can be made. First, the intergranular fracture surfaces produced in the stress-corrosion tests on the high-purity Al-5.6Zn-2.6Mg alloy did not exhibit the fragmented layer prevalent in the HE studies of the same alloy. Moreover, earlier tests had shown that this layer was present when a stress-corrosion crack in this alloy was halted and the specimen then fractured in dry air; the fragmented layer was observed in a narrow (200-300 μm) transition zone between the stress-corrosion facets and ductile-overload fracture.^{6,16} This observation is considered to indicate that hydrogen is absorbed at the tip of the advancing stress-corrosion crack, that it diffuses for significant distances ahead of the crack tips and that it is present in significant concentrations to produce HE in subsequent tensile tests. The absence of the layer

on the stress-corrosion fractures raised the possibility that while hydrogen is generated, it plays no role in the stress-corrosion process, and that an alternative mechanism is operative, e.g., the film-rupture (anodic dissolution) model.¹⁷ It should be noted here that slow crack growth was produced in the high-purity alloy in the present work when it was stressed under constant deflection in 70°C WWSA.^{9,16} Significantly, the resulting intergranular fracture surfaces exhibited the fragmented layer, indicating that the hydride-rupture mechanism can operate when the source of hydrogen is external.

Pursuing the possibility that a second mechanism of slow crack growth can operate in the high-purity alloy in aqueous solutions in addition to hydride rupture, it is interesting to note that double plateaus have been reported in V-K curves for Al-Zn-Mg alloys in some cases.^{15,18,19} It may be speculated that this results from the overlapping of two independent V-K curves, one corresponding to HE and the other to a second mechanism. In the majority of cases, as in our D-T experiments, a single plateau is observed, suggesting that one of the V-K curves becomes completely submerged by the other, so that the corresponding mechanism plays no role in the fracture process. The preceding observations could be interpreted to indicate that HE is the "submerged" mechanism in this specific system. Further work is in progress at NBS to pursue these possibilities.

C. Personnel, Advanced Degrees Awarded, and Publications

The program was directed by Professors E. N. Pugh and R. A. Yeske, Co-Principal Investigators. Professor Yeske left the University in January 1978 to join Westinghouse Electric Corporation, Pittsburgh, but continued his participation in the program in an informal capacity. Professor Pugh also left in August 1979 to take a position with the National Bureau of Standards in Washington, D.C., but, as an Adjunct Professor, made frequent visits to

Urbana-Champaign during the remainder of the grant. During the latter period, Professor M. Metzger kindly acted as Co-Principal Investigator, providing assistance in the day-to-day direction of the program.

The grant provided support for two students to obtain advanced degrees:

- (i) T. L. Bond. Received MS degree (August 1978) for a thesis on "Studies of Stress-Corrosion Crack Growth in Al-Zn-Mg Alloys Using the Double-Torsion Method."
- (ii) S. W. Ciaraldi. Received Ph.D. degree (May 1980) for a thesis entitled "Internal Hydrogen Embrittlement in the Al-Zn-Mg System."

Four publications have been prepared on the work carried out under this grant, and have either been submitted or are in the final stages of revision:

1. Determination of V-K Data for Al-Zn-Mg Alloys Using the Double-Torsion Method, T. L. Bond, E. N. Pugh, and R. A. Yeske, J. Testing and Evaluation (ASTM).
2. Hydrogen Embrittlement of an Al-Zn-Mg Alloy Induced by Mechanical Polishing in Aqueous Solutions, S. W. Ciaraldi, R. A. Yeske, and E. N. Pugh, Corrosion.
3. Hydride Formation and Hydrogen Embrittlement in an Al-Zn-Mg Alloy, S. W. Ciaraldi, R. A. Yeske, and E. N. Pugh, Met. Trans A.
4. Studies of Hydrogen Embrittlement and Stress-Corrosion Cracking in an Al-Zn-Mg Alloy, S. W. Ciaraldi, J. L. Nelson, R. A. Yeske, and E. N. Pugh, Proc. Internat. Conf. on the Effect of Hydrogen on Behavior of Materials, Jackson Lake Lodge, August 1980, TMS-AIME. This paper also describes work supported by U.S. Department of Energy.

Reprints of these publications will be circulated as they become available.

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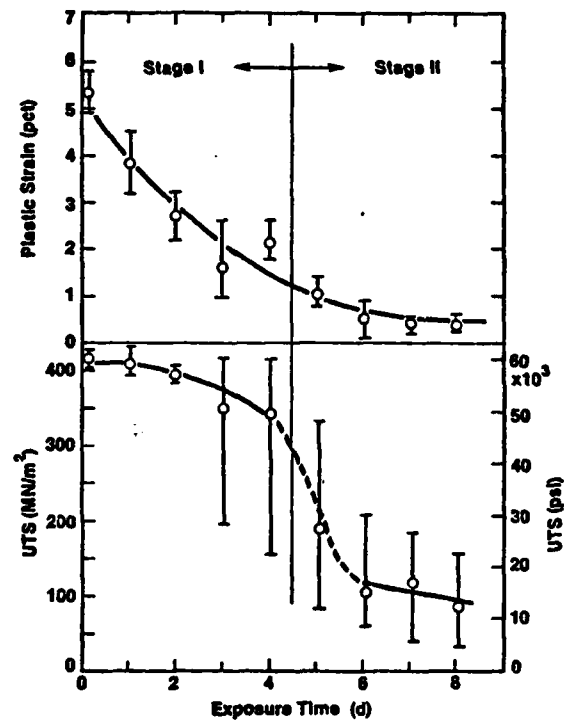


Fig. 1 - Effect of exposure to 70°C WWSA on the mechanical properties of the high-purity Al-5.6Zn-2.5Mg alloy tested in dry argon at a strain rate of $1.3 \times 10^{-4} \text{ S}^{-1}$.

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