The Embrittlement of Al-Zn-Mg and Al-Mg Alloys by Water Vapor

C. D. S. TUCK

Al4.5Zn1.5Mg and Al5Mg were reacted in water-vapor saturated air (WVSA) at 120 °C and tensile tested. After an initial loss of ductility with exposure time, probably caused by hydrogen embrittlement of the grain boundaries, between 15 hours and 25 hours exposure the mechanical properties of Al4.5Zn1.5Mg improved, this effect being due both to a reduced corrosion activity of the grain boundaries in producing embrittling hydrogen at the external surface and to grain boundary $MgZn_2$ precipitates acting as hydrogen traps. After 25 hours exposure water was shown to penetrate the grain boundaries, and a layered corrosion product identified as the aluminum hydroxides boehmite and diaspore was formed. This resulted in a marked fall of ductility. Re-solution heat treatment and reaging partially recovered the mechanical properties of Al4.5Zn1.5Mg if the exposure time was less than 50 hours, and would not recover properties for longer exposure times. Small additions (0.1 pct) of iron and nickel to Al4.5Zn1.5Mg lessened the grain boundaries' sensitivity to corrosive attack whereas the addition of 0.1 pct copper did not. Also, the former two additions did not cause the relative ductility increase during 15 to 25 hours exposure in WVSA at 120 °C shown by Al4.5Zn1.5Mg. It is proposed that these elements alter the magnesium segregation levels at the grain boundaries which in turn affects their electrochemical attack.

I. INTRODUCTION

THROUGHOUT the numerous investigations carried out on the stress corrosion[1] and hydrogen embrittlement[2] of Al-Zn-Mg and Al-Mg alloys attention has been centered on grain boundary regions, as the predominant fracture mode is intergranular. Anodic dissolution of material at the grain boundary was thought to be the mechanism controlling stress-corrosion cracking[3] until the relatively recent discovery that intergranular decohesion occurred[4] and that specimens could be embrittled by exposing them to hydrogen-producing environments in the absence of stress, a phenomenon which could be reversed by heat treatment after exposure,[5] testing in vacuum, or natural recovery effects with time.[6] These observations suggested that hydrogen embrittlement was the operative mechanism in stress-corrosion cracking and preexposure embrittlement and led to several investigations into the way in which hydrogen affects the mechanical properties of the boundaries[7,8,9] and to the possibility of utilizing grain boundary precipitates as trap sites to control the ingress of hydrogen.[10]

Fairly recent work by Christodoulou[11] has added to the growing evidence that hydrogen embrittlement occurs when Al-Zn-Mg alloys are exposed to water vapor. This work shows that $MgZn_2$ precipitates on the grain boundaries of these alloys act as traps for the embrittling hydrogen atoms and proposes that they act in this way by causing hydrogen molecules to form around them, producing less debilitating bubbles of hydrogen gas. Hydrogen bubbles on the grain boundaries of Al-Zn-Mg and Al-Mg alloys which have been exposed to water vapor have also been observed by other workers using transmission electron microscopy[12,13] (TEM), but the bubbles have not always been seen to be associated with $MgZn_2$ grain boundary precipitates, and it has been proposed that they result from the decomposition of hydrides (particularly magnesium hydride[9,14]) by the electron beam. Thus, the trapping of hydrogen by the grain boundary $MgZn_2$ precipitates in Al-Zn-Mg could be *via* hydride formation rather than by a discharge mechanism. It was decided to repeat the experiments of Christodoulou using thicker specimens (3 mm as opposed to 0.5 mm) and an alloy more akin to commercial material (7004-type) to try to clarify the mechanisms by which grain boundary chemistry affects the embrittlement and recovery processes. The effect of iron, nickel, and copper additions to pure Al-Zn-Mg was also studied as these are known to promote stress corrosion resistance in Al-Zn-Mg.[1]

II. EXPERIMENTS

A medium strength super-pure base Al4.5Zn1.5Mg alloy was used with and without small additions of iron, nickel, and copper. Al5Mg was also included. The alloy compositions are given in Table I. They were D.C. cast, scalped, homogenized for 16 hours at 465 °C, hot-rolled to 5 mm, and cold-rolled to 3 mm thickness yielding an equiaxed grain structure with grain sizes as given in Table I. Transverse Baty tensile specimens 60 mm long with 25 mm gauge length and 3 mm gauge width were machined from the rolled material and given a solution heat treatment at 465 °C for 30 minutes followed by cold water quench. The exposure of the specimens (in triplicate) to WVSA at 120 °C was carried out in a stainless steel autoclave containing distilled water, above which they were suspended. In addition, Al4.5Zn1.5Mg was exposed to WVSA at 180 °C in a similar way, the temperatures 120 °C and 180 °C being used as these are the conventional commercial aging temperatures. In order to investigate any reversibility of embrittlement by heat treatment after exposure some specimens which had been reacted were re-solution heat treated at 465 °C for 30 minutes. They were then either left in that condition or reaged at 120 °C in dry air for a time equivalent to the autoclave exposure.

Embrittlement of the specimens was measured with the aid of an Optomax image analyzer by observing the percentage reduction in the cross-sectional area (pct RA) of the specimens after fracture by tensile testing. Most of the

---

C. D. S. TUCK is Research Scientist with Alcan International Ltd., Banbury Research Laboratories, Banbury, Oxon, United Kingdom.

Manuscript submitted June 11, 1984.

Table I. Composition of Alloys (in Mass Pct)

	Zn	Mg	Addition	Grain Size (mm)
AlZnMg (base alloy)	4.30	1.50	—	0.13
AlZnMg + iron	4.30	1.50	0.11Fe	0.04
AlZnMg + nickel	4.30	1.50	0.05Ni	0.08
AlZnMg + copper	4.30	1.50	0.04Cu	0.10
AlMg	—	5.11	0.11Fe	0.20

specimens were tested at a strain rate of 6.7×10^{-4} s^{-1}, an order of magnitude lower than that used by most workers observing embrittlement of this type,[5] until the advent of slow strain rate testing techniques.[15] In order to investigate any effects of increasing the strain rate, specimens of Al4.5Zn1.5Mg exposed to WVSA at 120 °C for 65 hours were tested at strain rates of 10^{-3}, 10^{-1}, and 0.4 s^{-1}.

Thin electropolished foils were prepared of all the alloys and, in the case of AlZnMg, thin foils were prepared of material exposed to WVSA at 120 °C for various times and similarly aged in dry air at 120 °C. A TEM study was then carried out to determine the size and distribution of the $MgZn_2$ grain boundary precipitate during aging at 120 °C. The specimens were also exposed to WVSA at 70 °C and observed in a scanning electron microscope (SEM) to investigate the initial corrosion reaction between the alloy and water vapor, a technique used by Scamans and Rehal.[16]

Experiments were also conducted to determine whether hydrogen was evolved from the alloys exposed to WVSA at 120 °C for 50 hours during their tensile testing under normal conditions. After reaction, each specimen was abraded to remove surface hydrous film, the gauge length was encased in a polythene tube containing magnesium perchlorate, and this was sealed at both ends with silicone sealant. After a 24-hour delay to ensure adequate curing of the sealant, the specimens were tensile tested. Immediately following the elastic, plastic, and final fracture stages of the testing process a syringe was inserted through the polythene tube and its contents were then injected into a gas chromatograph which was able to detect hydrogen down to a level of 5 ppm. Syringe samples of the atmospheres in the sealed coupons were taken from some specimens before testing to ensure that there was a negligibly low level of hydrogen initially.

III. RESULTS

Figures 1 to 5 show the reduction of area of fracture surfaces against exposure time in WVSA at 120 °C for the various alloys used, both with and without re-solution heat treatment after exposure. Within the first 20 hours there was an initial decrease in ductility followed by an increase which was most marked in the case of Al4.5Zn1.5Mg. Fractography of specimens in this region of the exposure/ductility curves showed intergranular fracture with microdimpling on most of the grain boundary facets around the edges of the fracture and ductile transgranular fracture over the bulk of the fracture surface. In all cases except

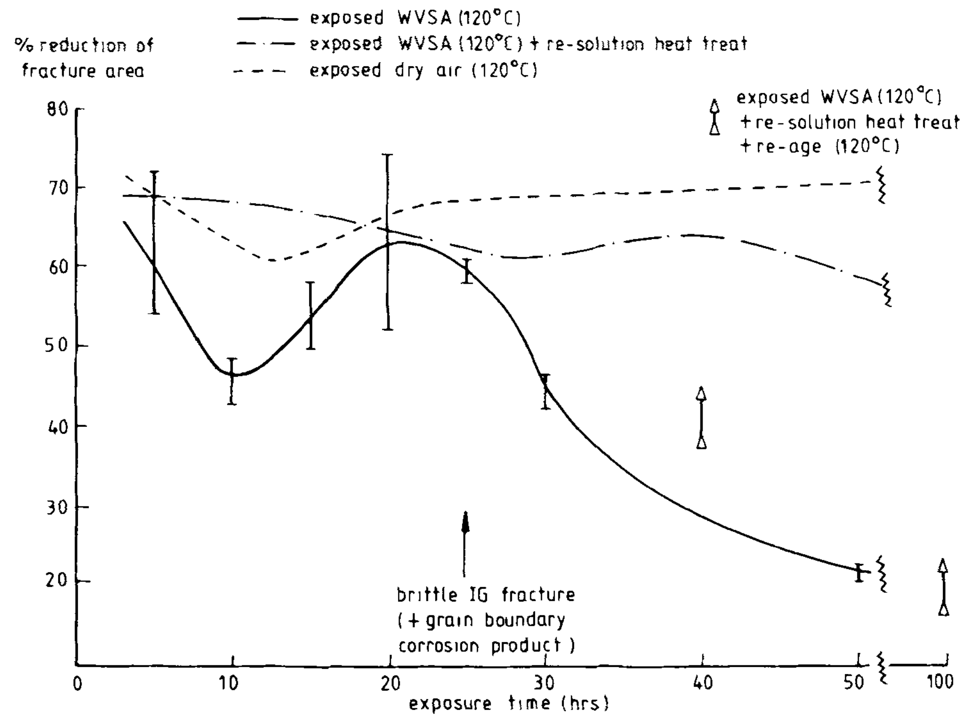

Fig. 1—Graph showing the percent reduction in fracture area for Al4.5 Zn1.5Mg exposed to water vapor saturated air at 120 °C (with and without subsequent solution heat treatment and reaging) and exposed to dry air at 120 °C.

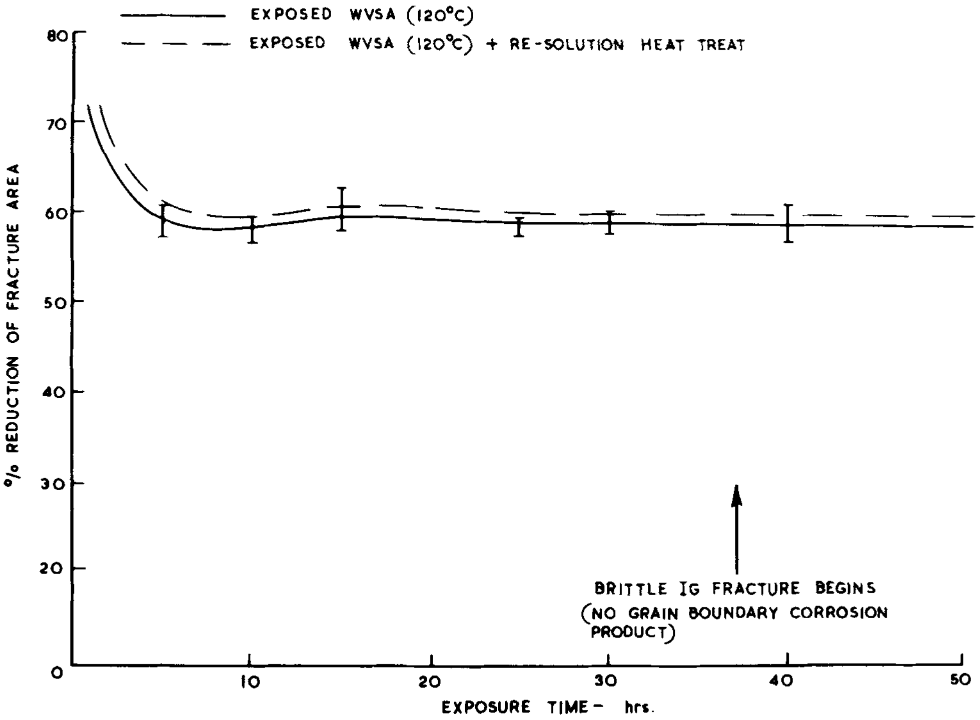

Fig. 2—Graph showing the percent reduction in fracture area for Al4.5Zn1.5Mg0.05Ni exposed to water vapor saturated air at 120 °C with and without subsequent solution heat treatment.

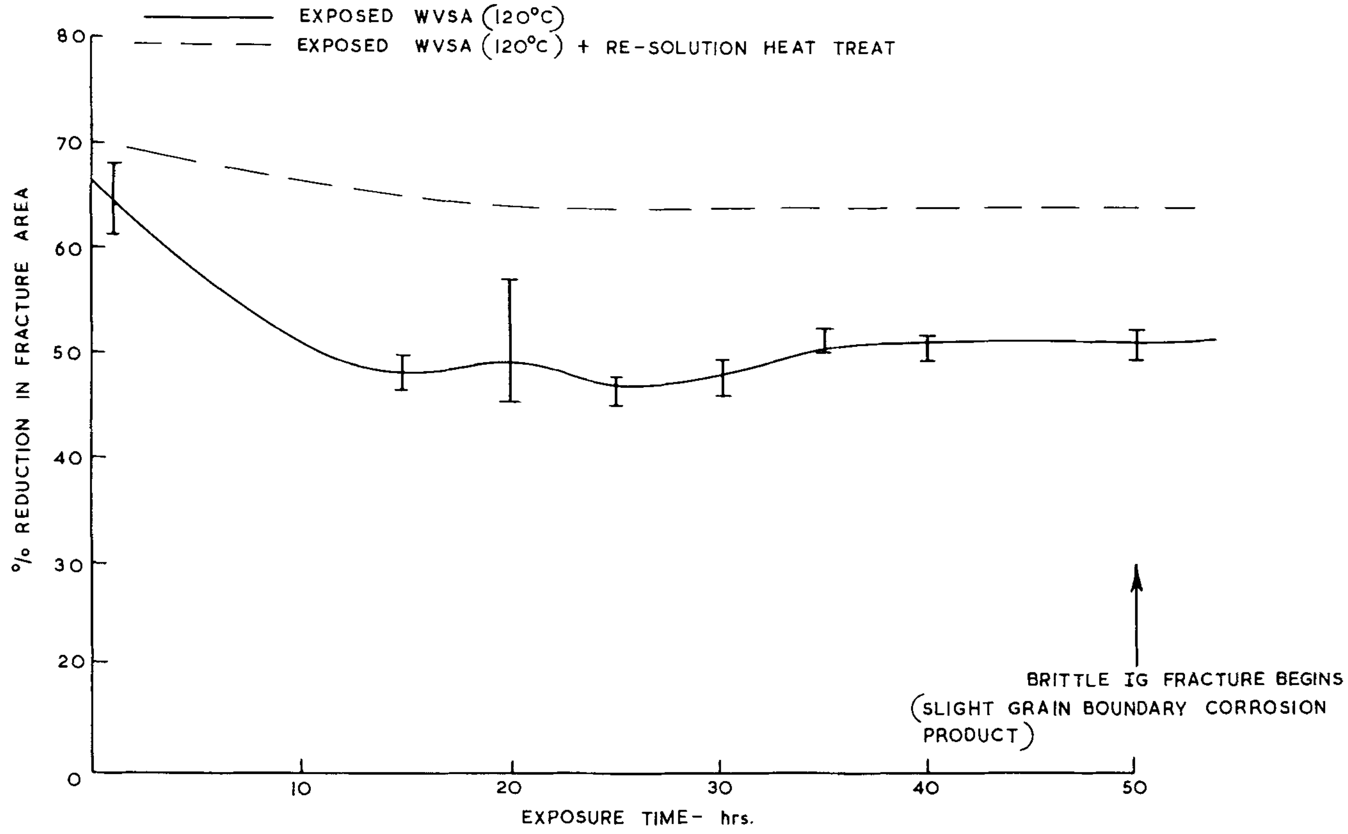

Fig. 3—Graph showing the percent reduction in fracture area for Al4.5Zn1.5Mg0.11Fe exposed to water vapor saturated air at 120 °C with and without subsequent solution heat treatment.

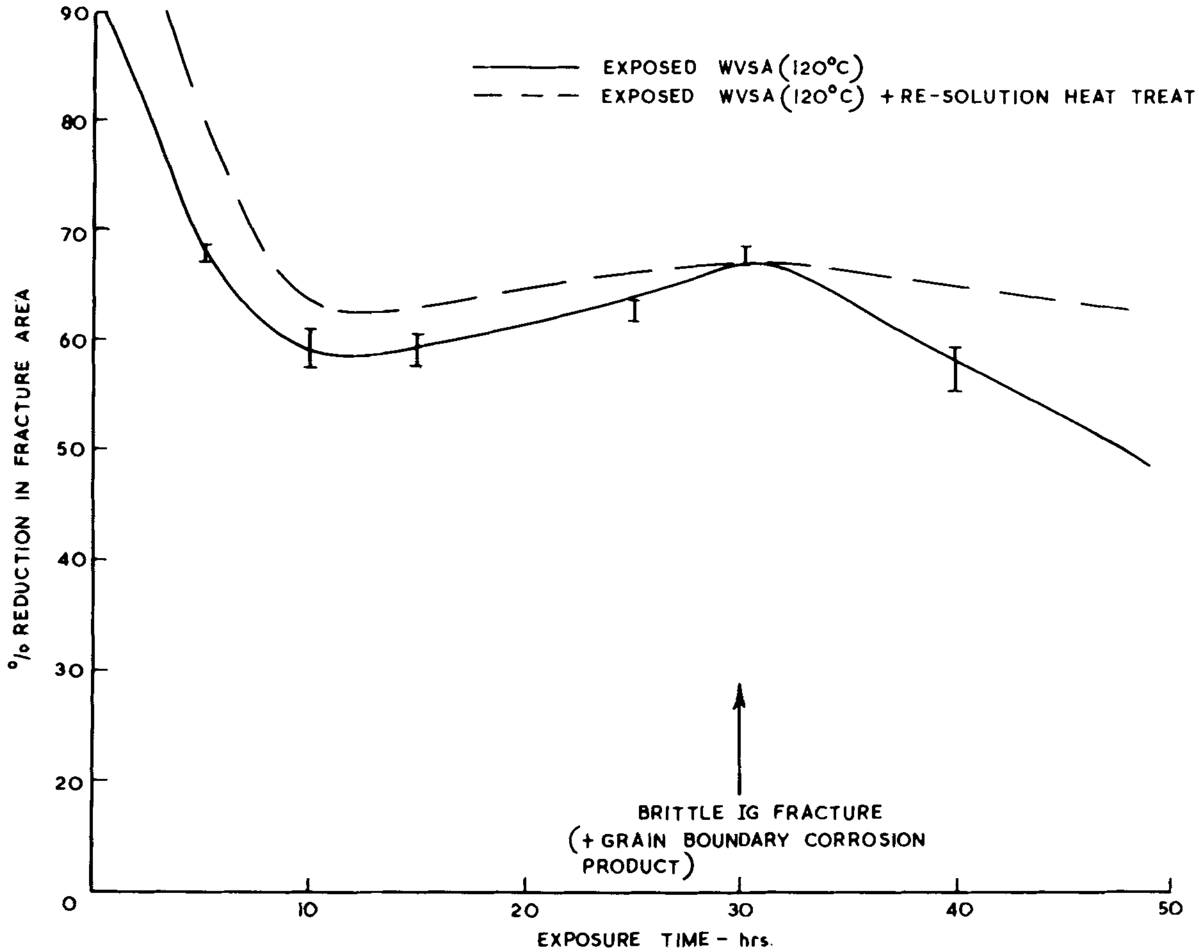

Fig. 4—Graph showing the percent reduction in fracture area for Al4.5Znl.5Mg0.04Cu exposed to water vapor saturated air at 120 °C with and without subsequent solution heat treatment.

AlZnMg + Fe and AlMg some grain facets at the specimen edge exhibited totally brittle failure with no evidence of dimpling. After 25 to 30 hours exposure the ductility of Al4.5Zn1.5Mg, Al5Mg and Al4.5Zn1.5Mg + Cu again decreased. Similar behavior was evident in Al4.5Zn1.5Mg exposed to WVSA at 180 °C (Figure 6), although in this case the ductility increase took place after about 5 hours and the subsequent fall-off was more rapid. For the other alloys at 120 °C there was initially a slight fall in ductility followed by a period in which area reduction on fracture was fairly independent of exposure time. Fractography of the failed specimens in this region of the exposure/ductility curve showed brittle intergranular fracture in all cases except Al5Mg, which exhibited ductile intergranular fracture. High magnification micrographs of the fracture (Figure 7) revealed the surfaces of the grains to be covered with thin layers of a corrosion product. Blisters below this layered structure could also be seen which were probably pressurized with hydrogen gas. The corrosion product was in the form of a multi-layered structure of one, two, or three layers depending on the distance of the grain on which it was formed from the center of the specimen. The layers were often of a total thickness over 1 μm, but the film nearer the center was composed of just a single layer varying from a few hundred mm in thickness to one only just visible by using secondary electrons of 5 keV. Fracture matching was carried out (Figure 8) and this showed that, during fracture, parts of the corrosion product would adhere to one grain face and other parts would remain with the other facet.

Using a brush, some of the corrosion product was removed from the surface of a freshly fractured Al4.5Zn 1.5Mg specimen which had been exposed to WVSA at 120 °C for 50 hours, the surface of which had been abraded to remove hydrous film. Electron diffraction of the material was carried out in a TEM and d-spacings were calculated. Two types of material were identified as Table II shows. D-spacings labeled (a) were very much more commonly observed than those labeled (b), and both are compared in the table with likely compounds which could be present. The d-spacings of material (a) most closely resembled those of boehmite, whereas diaspore gave the best fit of material (b).

The presence of this grain boundary corrosion product was first observed after about 25 hours in the case of Al4.5 Zn1.5Mg and 30 hours in the case of Al4.5Zn1.5Mg + Cu, but after much longer times in the case of Al4.5Zn1.5Mg with iron and nickel. It was apparently absent in the case of Al5Mg. Re-solution heat treatment of Al4.5Zn1.5Mg exposed for 40 hours in WVSA at 120 °C produced an increase in ductility, a change in the fractography to ductile transgranular, and the apparent disappearance of the layered corrosion product. However, reaging the same specimen in

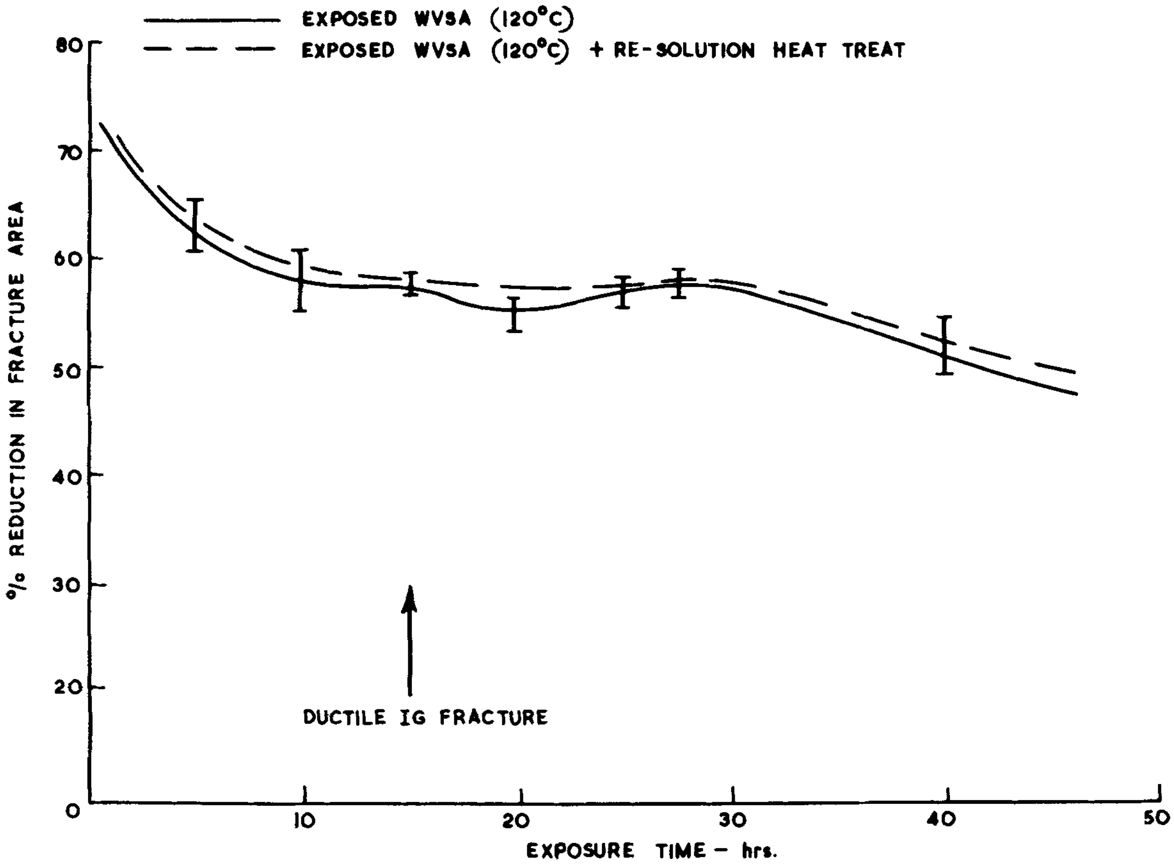

Fig. 5 — Graph showing the percent reduction in fracture area for Al5Mg exposed to water vapor saturated air at 120 °C with and without subsequent solution heat treatment.

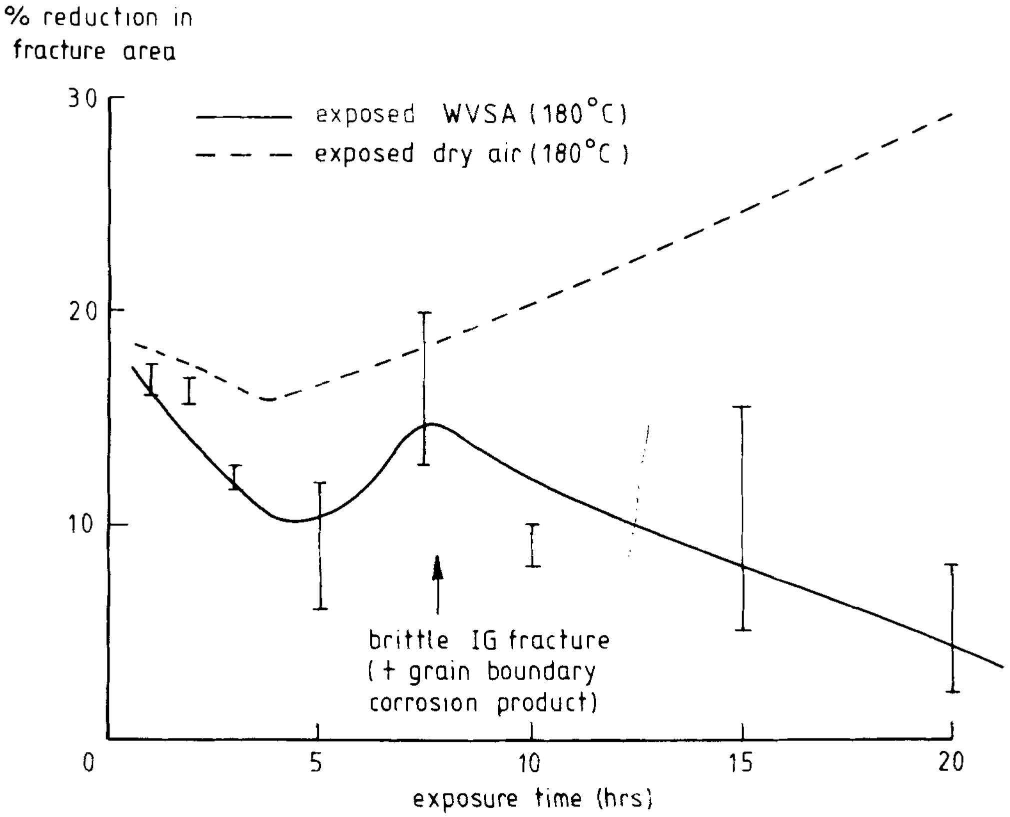

Fig. 6 — Graph showing the percent reduction in fracture area for Al4.5Zn1.5Mg exposed to water vapor saturated air at 180 °C.

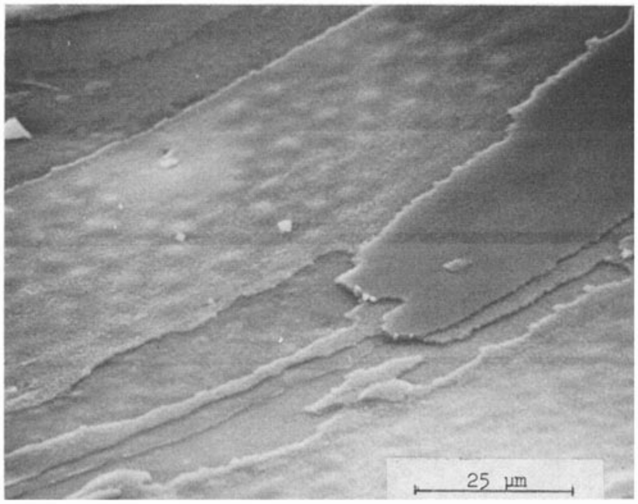

Fig. 7—A scanning electron micrograph of the fracture surface of Al4.5Zn1.5Mg exposed to water vapor saturated air at 180 °C for 15 h showing the multi-layered nature of the grain boundary corrosion product and its blistered appearance. The same morphology is seen on Al4.5Zn 1.5Mg exposed longer than 35 h in WVSA at 120 °C. Magnification 814 times.

dry air for 40 hours after re-solution heat treatment caused the fracture to revert partially to an intergranular mode although the fracture surface displayed ductility (although on a micro scale) and there was again little evidence of the layered corrosion product (Figure 9). The mechanical properties could also be recovered to some extent, the reduction of specimen area on fracture being 40 to 45 pct as compared to less than 30 pct for specimens exposed as normal (see Figure 1). However, a specimen of AlZnMg which had been exposed to WVSA at 120 °C for 100 hours showed no recovery on being re-solution heat treated and reaged. In this case the grain boundary corrosion product became noticeably more brittle. These observations implied that the layered corrosion product did not decompose during the re-solution heat treatment but remained in the material, its presence being masked by a change in fracture mode.

The effect of increased strain rate on the fracture of Al4.5Zn1.5Mg exposed to WVSA for 65 hours was to reduce the brittleness of the intergranular fracture, although the reduction in specimen area at fracture remained similar at the different strain rates. At a strain rate of 0.4 s^{-1} most of the grains fractured in a ductile manner, although the

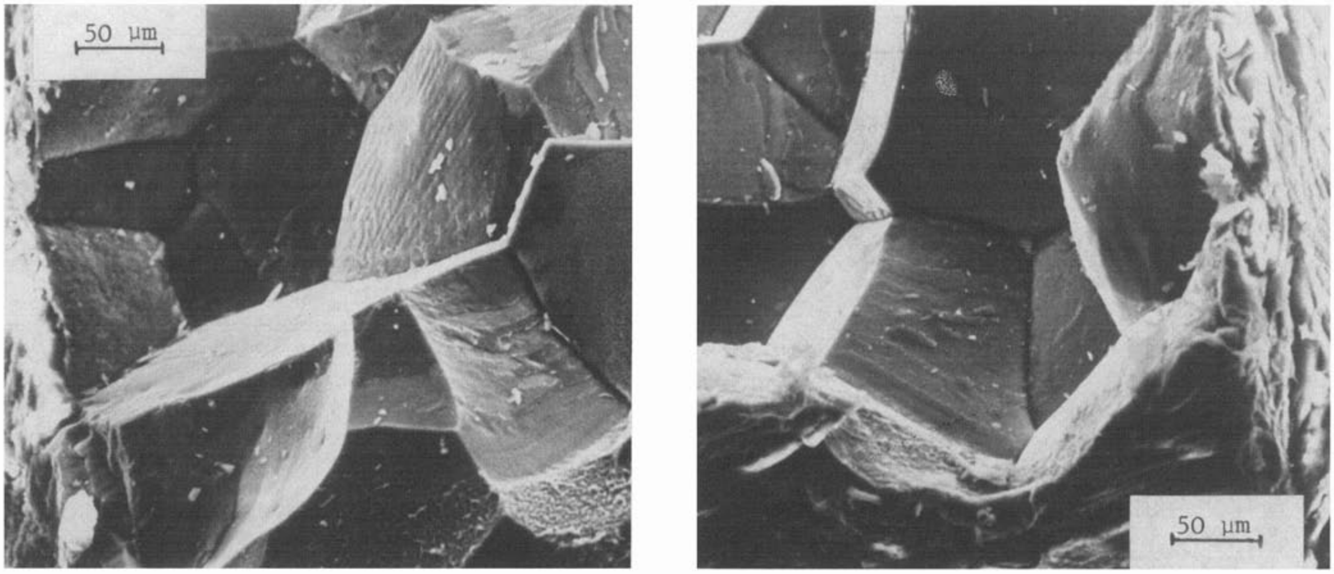

Fig. 8—Scanning electron micrography showing opposite fracture faces of Al4.5Zn1.5Mg exposed to water vapor saturated air at 180 °C for 15 h.

Table II. Electron Diffraction d-Spacings of Experimental Material Together with Those of Possible Compounds Present

Observed Diffraction Patterns, d-Spacings		d-Spacings							
(a)	(b)	Magnesium Hydride	Aluminum Hydride	Boehmite	Bayerite	Diaspore	Gibbsite	Zinc Hydroxide	Magnesium Hydroxide
6.2	—	—	—	6.11	—	—	—	—	—
—	4.8	—	—	—	4.72	4.71	4.82	—	4.77
—	—	—	4.55	—	4.36	—	4.34	4.41	—
—	3.9	—	—	—	—	3.99	4.30	—	—
3.2	3.2	3.19	—	3.16	3.19	3.20	3.35	3.28	—
—	2.6	2.51	2.51	—	2.69	2.56	2.44	2.71	—
2.4	—	2.26	2.28	2.35	2.21	—	2.37	2.28	2.36
1.9	—	1.68	1.69	1.85	—	—	1.98	1.85	1.79

Fig. 9—Scanning electron micrograph of the fracture surface of Al4.5Zn 1.5Mg which had been exposed to water vapor saturated air at 120 °C for 40 h followed by heat treatment at 465 °C for 30 min then aging for 40 h at 120 °C in dry air. Magnification 777 times.

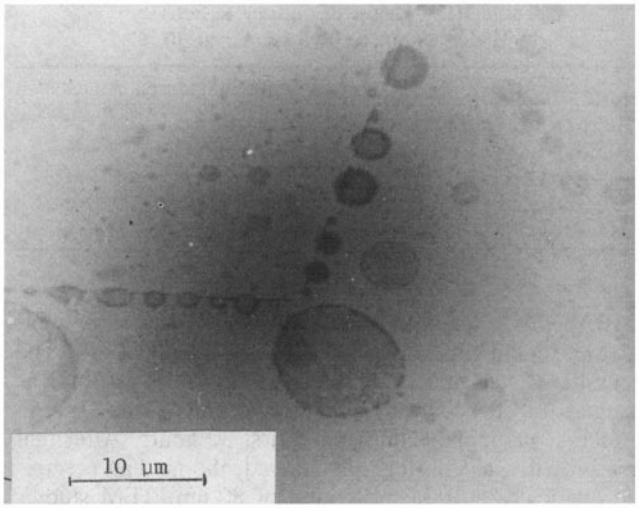

Fig. 11—A scanning electron micrograph of an electropolished surface of Al4.5Zn1.5Mg exposed to water vapor saturated air at 70 °C for 10 min.

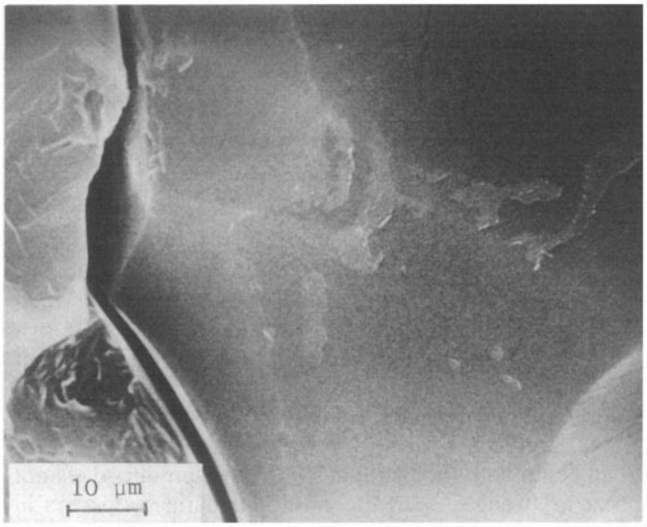

Fig. 10—A scanning electron micrograph of part of the fracture surface of Al4.5Zn1.5Mg exposed to water vapor saturated air at 70 °C for 40 days under slight tensile stress. Magnification 890 times.

presence of the layered corrosion product was still observed on the remaining brittle-fractured facets.

A comparison of the fractography observed in the present work was made with previous work which had been carried out on Al4.5Zn1.5Mg under slight tensile stress while being exposed to WVSA at 70 °C for 40 days.[2] Figure 10 shows a previously obtained micrograph depicting the zone of fracture between the brittle outer region and ductile inner region produced by fracturing the specimen by an overload after exposure. A layered corrosion product could be seen on the boundary surfaces, indicating that the grain boundary corrosion product observed at 120 °C could also be produced at lower temperatures.

Scanning electron microscopy of electropolished foils which had been exposed to WVSA at 70 °C for 10 minutes revealed that the grain boundaries were generally seen to be attacked to a much greater extent than the matrix material. This is demonstrated by Figure 11 which shows the three boundaries of Al4.5Zn1.5Mg which have blisters or the remains of blisters along their lengths. The matrix material is attacked but to a much lower degree, and some boundaries also exhibit lower levels of attack. Fifteen to 20 boundaries were observed from each alloy and their reactivities tabulated as a percentage of the number of boundaries of each sample. These are shown in Table III, and it is evident that the boundaries of pure AlZnMg and AlMg are most reactive, showing almost total coverage by blisters. The least reactive are the boundaries of AlZnMg + Fe. Figure 12 shows a graph depicting grain boundary reactivity of WVSA-exposed Al4.5Zn1.5Mg. There were seen to be differences between the reactivities measured after the various times of exposure, with lowest being after 20 to 30 hours. The results after longer exposure times than 30 hours were undoubtedly affected by the presence, on some boundaries, of the layered corrosion product; thus, the only significant observation from these experiments was that grain boundary reactivity fell significantly during the first few hours of exposure. The extent of reactivity of the matrix with WVSA at 70 °C was similar for all the alloys except AlZnMg + Cu which reacted at more sites per unit area than the others.

Hydrogen was found to be evolved from all the specimens tensile tested although different total levels of hydrogen were found for the complete tests, the maximum being shown by Al4.5Zn1.5Mg (0.01 pct in 1 ml total volume around the gauge length) and minimum by both Al4.5Zn 1.5Mg + Cu and Al4.5Zn1.5Mg + Fe (0.003 pct). The results for approximately six tests in each case are shown in Figure 13, and it is evident that the hydrogen evolution from Al4.5Zn1.5Mg exhibited different behavior from the others in that most of the hydrogen was evolved during the elastic portion of the load-time curve. With all the other alloys, the maximum quantity of hydrogen was evolved during the plastic region, although it should be noted that during that time numerous cracks initiating at grain boundary/surface intersections opened up.

TEM studies on the grain boundary $MgZn_2$ precipitation during aging of Al4.5Zn1.5Mg were quantified by the use

Table III. Grain Boundary Reactivity in Water Vapor Saturated Air at 70 °C

Alloy	Pct of Grain Boundaries Attacked
Al4.5Zn1.5Mg	95 pct
Al5Mg	95 pct
Al4.5Zn1.5Mg + Fe	20 pct
Al4.5Zn1.5Mg + Ni	50 pct
Al4.5Zn1.5Mg + Cu	70 pct

of IBAS image analysis, and the resulting median precipitate size/aging time response is shown in Figure 14. The precipitates were quite small at the start of aging, but, as aging at 120 °C occurred, some grew in size at the expense of others, particularly during the first 30 hours. After that time growth was considerably slowed, the median precipitate diameter being in the region of 80 nm. TEM studies through foils prepared from the central region of WVSA-exposed Al4.5Zn1.5Mg showed the occurrence of hydrogen bubbles on the grain boundaries of specimens given an exposure of more than 5 hours, particularly nucleating at grain boundary precipitates. However, there was no evidence that the bubbles existed in the material before exposure to the electron beam, and bubble growth was rapid once nucleation had occurred.

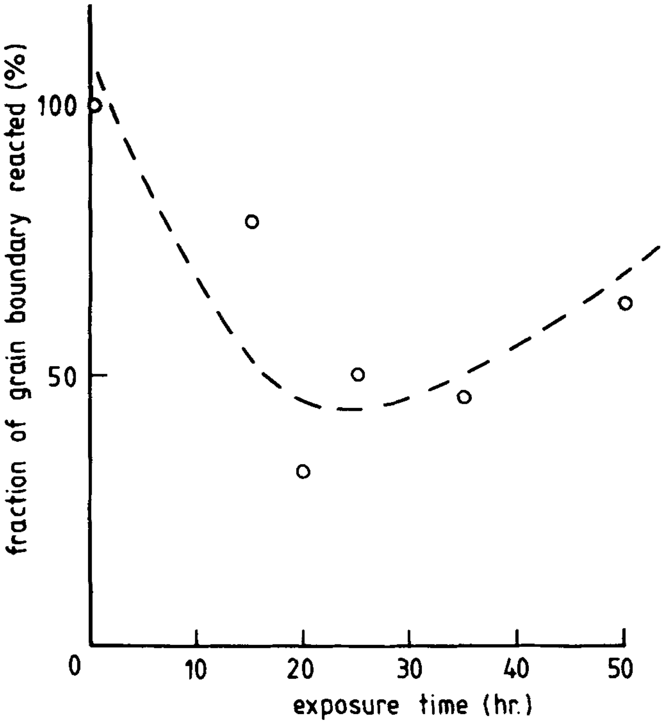

Fig. 12—A graph showing the reactivity of grain boundaries of Al4.5Zn 1.5Mg (exposed as pct of total) with time of exposure to water vapor saturated air at 120 °C. The boundaries were viewed on electropolished samples and exposed to water vapor saturated air at 70 °C for 10 min.

IV. DISCUSSION

Discussion of these results is made in the light of previous work carried out by Christodoulou and Flower[11] and Pugh *et al.*,[8] and centers on the presence and nature of the layered corrosion product. Observation of this product on the fracture surfaces of Al6Zn3Mg which had been exposed to WVSA at 120 °C was not mentioned by Christodoulou but was seen by Pugh on Al5.6Zn2.6Mg which had been exposed to WVSA at 70 °C for seven days. The latter film was very similar in appearance and thickness to the product seen in the present work, and fracture matching was similarly carried out. However, electron diffraction work suggested that the layer initially consisted aluminum hydride and that this decomposed with time to aluminum. The evidence is convincing, although it is unfortunate that the 0.455 nm (4.55 Å) spacing of AlH_3 was not used in the identification as this would have added a conclusive factor to their case, spacings of less than 0.30 nm (3 Å) being shared by a number of different materials. In the present work the layered corrosion product is identified as being largely composed of the aluminum hydroxide boehmite although there is some evidence for the existence of another aluminum hydroxide, diaspore. Diaspore forms only under high pressures of water, 1.3 k bar being used by Roy and Osborn,[17] but it is possible that its formation along the boundaries of AlZnMg alloys results from the pressurization caused by hydrogen in the intergrain boundary region. Boehmite is the hydroxide usually associated with hydrothermal reaction of aluminum in the temperature range 100 °C to 374 °C.[18]

Another question of prime importance is at what stage does the corrosion product form? The fracture-matching evidence indicates that it is unlikely to have formed after fracture, and Pugh *et al.*[8] suggest that it is formed during stressing as a stress-induced phase. The present work strongly suggests that the layered product is formed prior to tensile testing as (i) boehmite and diaspore are unlikely to form at ambient temperature, (ii) the corrosion product appears in the dry mechanical testing conditions under which the hydrogen evolution was monitored, and (iii) the corrosion product appears to different extents in the different alloys investigated and its thickness and morphology argues against its rapid formation during or after tensile testing. Counter-arguments for its formation during tensile testing would begin with the fact that the layered product does not appear to "wedge" apart the grain boundaries as occurs in similar types of grain boundary corrosion, *e.g.*, exfoliation[19] (although in this case the corrosion products are pseudo-boehmite and bayerite). Also, it apparently disappears when samples of Al4.5Zn1.5Mg exposed for less than 50 hours are re-solution heat treated (with a corresponding partial recovery of mechanical properties). It is also less evident when exposed specimens of Al4.5Zn1.5Mg are pulled at fast strain rates, this argument being used by Pugh to support its stress induced origin. It is felt that these counter-arguments are not convincing, although it is difficult to explain why the presence of these compounds along the grain boundaries do not produce a wedging action as their volumes should be about 2.5 times that of the aluminum from which they were formed. The degree of cohesion between the product and boundaries must be extremely good to allow the boundaries to remain together in spite of its presence, and internal compressive stresses must exist in the material. If the exposure is only for about 40 hours, then enough grain boundaries free of corrosion product must exist to allow the specimen to remain intact. In this case, when the material is solution heat treated, the matrix strength of the matrix material is weakened sufficiently

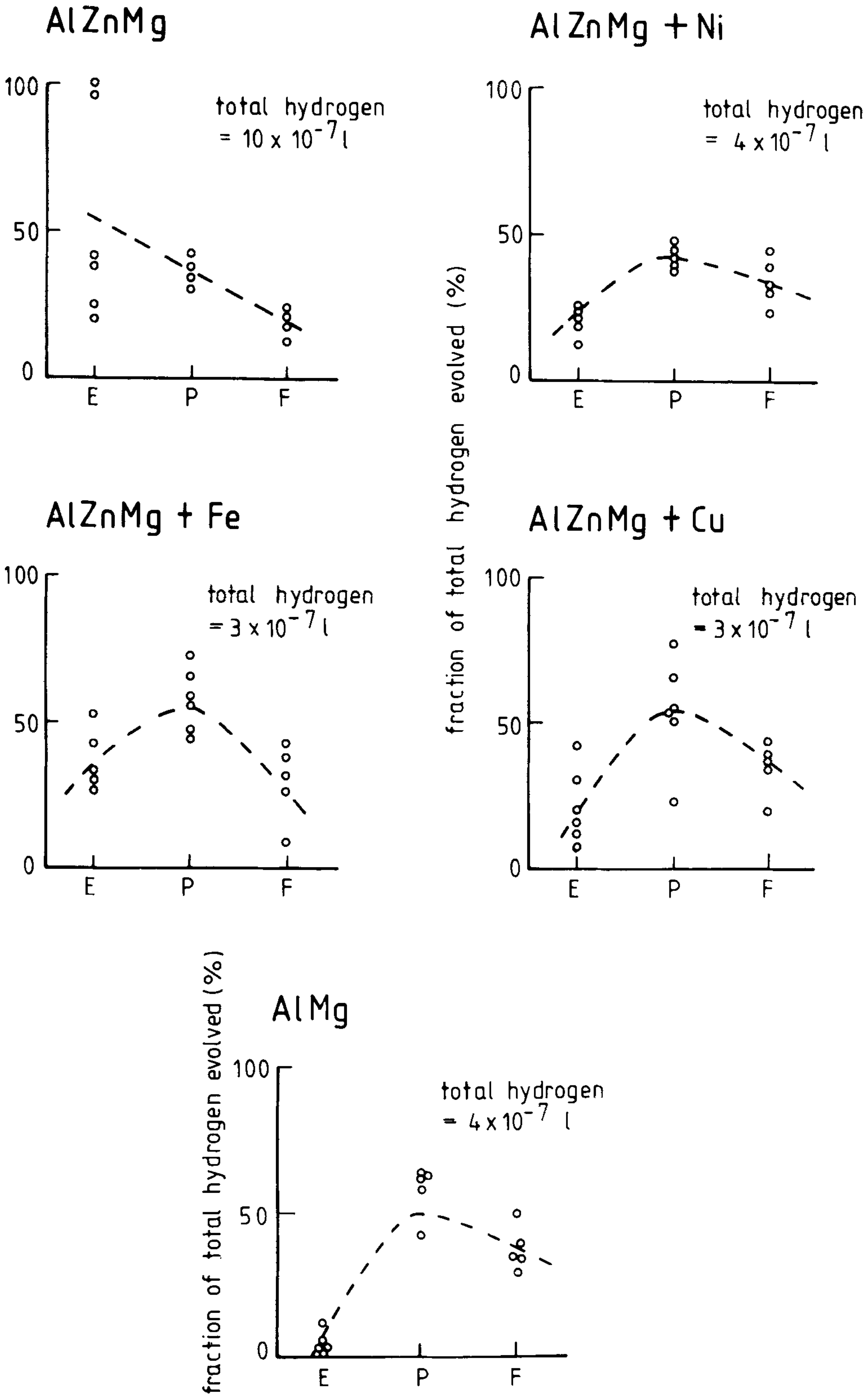

Fig. 13—Graphs showing the evolution of hydrogen (expressed as pct of total) after the elastic (E), plastic (P), and failure (F) regions of the load time curve of specimens exposed for 50 h in water vapor saturated air at 120 °C.

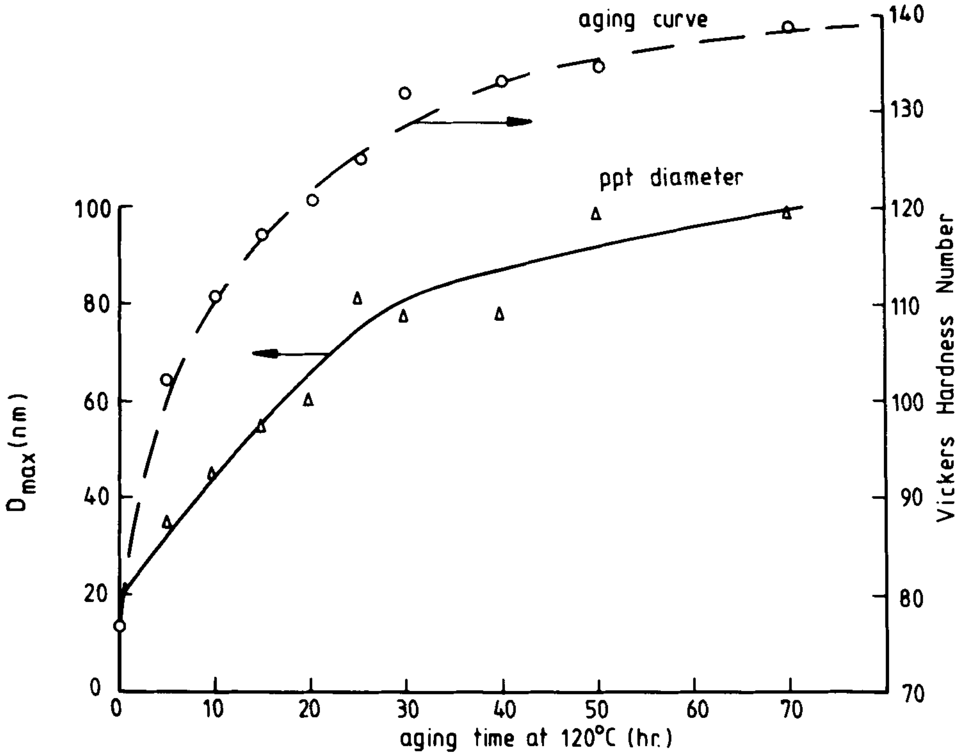

Fig. 14 — A graph showing the aging curve and variation of median grain boundary precipitate size (diameter) during the exposure of Al4.5Zn1.5Mg to water vapor saturated air at 120 °C.

(350 MNm^2 to 245 MNm^2 UTS on 40-hour exposed material) for fracture to occur in a transgranular manner, resulting in the apparent disappearance of the corrosion product. The effect of increased strain rate could also be to induce fracture away from the product-boundary interface so that it appears as a more ductile intergranular fracture. After long exposure times (*e.g.*, 100 hours) almost all the boundaries contain the corrosion product, and re-solution heat treatment is not effective in changing the fracture mode. The inability of Al5Mg to display brittle intergranular fracture even after prolonged exposure to WVSA at 120 °C is also probably due to the relatively low UTS of this material (200 MNm^{-2}), although it may be that the absence of zinc at the grain boundary inhibits the formation of the corrosion product.

The general shape of the exposure/ductility curve for Al4.5Zn1.5Mg is in agreement with the results of Christodoulou and Flower[11] in that there is a ductility increase in the region of exposure between 15 hours and 25 hours. The work of Pugh *et al.*[8] also suggests a slight increase of ductility in his alloys exposed for 4 days at 70 °C in WVSA, although this is not pointed out in their discussion. The fall in ductility in the initial stages of exposure to WVSA at 120 °C can be attributed mostly to aging of the alloys resulting in increased mechanical properties of the matrix, which increases from 246 MNm^{-2} to 340 MNm^{-2} after 20 hours, as this fall is also apparent in the specimens exposed to dry air. There is probably also a contribution from embrittlement of the grain boundaries by hydrogen, as bubbles of hydrogen are produced in the TEM on boundaries of Al4.5Zn1.5Mg exposed to WVSA at 120 °C for 5 hours or more, the grain boundary/surface intersections being extremely reactive. Some grain boundary fracture facets display a brittle fractography indicative of grain boundary decohesion.[2] The subsequent rise in ductility is displayed most markedly by Al4.5Zn1.5Mg, but Al4.5Zn1.5Mg + Cu also exhibits the phenomenon to a lesser extent. The effect has previously been explained by the trapping of embrittling hydrogen species on the grain boundaries by $MgZn_2$ precipitates,[11] and this would be supported by the present work as $MgZn_2$ precipitates are growing rapidly during this period (Figure 14).

As embrittlement of AlZnMg alloys can be effected by the presence of hydrogen at the grain boundaries, initial entry of the hydrogen is a crucial step in the process. Another factor is the form the hydrogen takes in the boundary, as it could either be a debilitating decohesive influence or exist as an innocuous species. It is fairly well established that in AlZnMg and AlMg alloys magnesium segregation at the grain boundaries is a common phenomenon[20,21,22] and this will result in increased magnesium concentration at the boundaries. Magnesium is much more electrochemically active than aluminum, and this would explain the observed corrosion behavior of the grain boundaries. Also, magnesium very readily forms a hydride with gaseous hydrogen;[23] thus the presence of free magnesium at the boundaries would enable the ready accumulation of hydrogen in these regions. The formation and growth of grain boundary $MgZn_2$ precipitates would result in a depletion of the free magnesium, and could also give more stable conditions under which separate hydride phases could form. They do seem to be centers of hydride formation as hydrogen always appears to be associated with them during electron beam irradiation.[12] The present results suggest that during the first 25 hours of exposure at 120 °C the grain boundary precipitates of Al4.5Zn1.5Mg grow considerably, and this corresponds to a decrease of grain boundary reactivity with water vapor (see Figure 12 and Figure 14). Thus it is probable that the increase in ductility observed for Al4.5Zn 1.5Mg in the 15 to 25 hour exposure period is due to both a concentrating of hydrogen at $MgZn_2$ trap sites (probably in the form of a hydride) and decreased hydrogen entry caused by a lower degree of grain boundary reactivity. Copper will combine with magnesium in the boundary precipitates and it is also known that it will catalyze magnesium hydride formation when alloyed with magnesium;[24] thus it is not surprising that this addition to Al4.5Zn1.5Mg allows a similar increase in ductility to that of the pure alloy when exposed to WVSA at 120 °C between 15 and 25 hours. The fall of ductility displayed by Al4.5Zn1.5Mg and Al4.5Zn 1.5Mg + Cu after 30 hours exposure in WVSA at 120 °C is undoubtedly due to the increasing occurrence of grain boundary corrosion product which causes severe debilitation of grain boundary strength as its thickness increases. The formation of this product to such an extent in the grain boundary region contrasts with the degree of reaction displayed by the bulk of the alloy to this environment. It suggests that a rapid path of attack exists at the boundary which is able to carry the reaction deep into the material. A suggested reaction route would be that the free magnesium along the boundaries initially reacts with hydrogen produced by the preferential corrosion reaction of the boundary/surface interface to form magnesium hydride or a similar hydride phase. This hydride would then react with water vapor to yield magnesium hydroxide and hydrogen, magnesium hydroxide then absorbing water to undergo partial hydrolysis and allowing further reaction with aluminum adjacent to the boundary to form aluminum hydroxide. The layer of free magnesium in the unreacted boundary has been calculated to be of the order of 1.0 nm (10 Å) in thickness;[9] thus it is unlikely that magnesium hydroxide will be detected in the much thicker corrosion product layers used in the electron diffraction exercise, but its presence in the boundary would ensure the eventual rapid diffusion of water into the inter-boundary region. The reason for the multi-layered morphology of the corrosion product is not clear, although it could be due to differences in alloy composition adjacent to the boundary caused by the presence of precipitate-free zones or other segregation effects.

From the results of the exposure of Al4.5Zn1.5Mg to WVSA at 70 °C it is likely that the ingress of water into the boundaries to form corrosion product is not limited to exposures at higher temperatures. It appears to follow after the initial diffusion of hydrogen along the boundaries,[2] and in its early stages it could be responsible for the embrittlement which appears in the outer regions of Al4.5Zn1.5Mg exposed to WVSA at 70 °C.[4] In these cases, mechanical recovery by re-solution heat treatment and reaging would undoubtedly be possible even though a thin hydroxide film existed along the boundary, as the present work shows it is possible with much thicker films in existence, particularly if the strain rate of tensile test is fast. Thus it may be more difficult than hitherto thought to categorize hydrogen embrittlement by the existence of a recovery effect by heating. However, the recovery effect produced by vacuum testing[5,6] is difficult to explain in any other way but by hydrogen embrittlement.

The determination of hydrogen evolved during tensile testing of the alloys which had been exposed to WVSA at 120 °C showed that the most embrittled alloy, namely, Al4.5Zn1.5Mg, displayed the highest hydrogen level (0.05 vol pct in the alloy) and also was the only material whose hydrogen mostly evolved during the elastic portion of the load-time curve. This suggests that the hydrogen was evolved during the opening up of grain boundaries at the surface, releasing trapped hydrogen. In the other cases, particularly with Al5Mg, the hydrogen was mostly evolved during the plastic regions of the tensile test. This suggests that internal grain boundary hydrogen was being evolved as ductile intergranular fracture was occurring along the gauge length and might suggest some hydrogen/dislocation association.

Perhaps the most interesting observation in this work is that the addition of iron and nickel to Al4.5Zn1.5Mg hinder the formation of the intergranular corrosion product observed when the pure alloy is exposed to WVSA at 120 °C and that this results in the relative retention of mehanical properties. It is not clear how these additions perform this function, but they must alter the chemical nature of grain boundaries in AlZnMg, as is shown by the decreased reactivity with WVSA at grain boundary/surface intersections (Table III). Grain boundary reactivity in this case is most probably due to magnesium segregation, the resulting differences in electrochemical potential at the boundary/matrix interface allowing local electrochemical cells to become active. Thus the alloy addition either acts to reduce magnesium segregation at boundaries or causes the difference in electrochemical potential between boundary and matrix to be reduced by other methods. Iron and nickel display partition coefficients very much less than unity when alloyed with aluminum and cause constitutional supercooling, acting to reduce the dendrite arm spacing during the casting process.[25] This results in a much more even distribution of segregated zinc and magnesium in the cell boundaries compared with that of cast AlZnMg without these additions, as well as producing a much finer grain size (see Table I). These two factors would explain the marked decrease of grain boundary reactivity exhibited by Al4.5Zn1.5Mg with iron and nickel additions. Copper will combine with magnesium to form intermetallics of more noble electrochemical potential than the matrix,[26] explaining the relatively greater susceptibility of AlZnMg with this addition to attack by water vapor at the grain boundaries.

V. CONCLUSIONS

1. All the alloys showed an initial decrease in ductility with exposure to water vapor saturated air (WVSA) for times up to 15 hours. This was due both to aging effects and hydrogen embrittlement of the grain boundaries.
2. Between 15 to 25 hours exposure to WVSA at 120 °C the relative ductility increased in all alloys, particularly for Al4.5Zn1.5Mg and Al4.5Zn1.5Mg + Cu. This was associated with a decrease in reactivity of the grain boundaries probably caused by a depletion in the level of magnesium segregation at the boundaries. The growth of $MgZn_2$ grain boundary precipitates during this period of exposure accounted for this depletion and, as they could also act as hydrogen traps, grain boundary hydrogen embrittlement was reduced.

3. After 30 hours exposure in WVSA at 120 °C, Al4.5Zn 1.5Mg and Al4.5Zn1.5Mg + Cu underwent a further fall in ductility and the presence of a layered corrosion product (identified as mainly boehmite with some diaspore) was observed on the fracture surfaces. It was most likely that this product formed during exposure in WVSA, and could also occur at lower temperatures than 120 °C (*e.g.*, 70 °C). Its formation was probably due to the ingress of water along the boundaries following an initial diffusion of hydrogen atoms along the grain boundaries to form a precursive hydride layer.
4. Different levels of grain boundary reactivity with water vapor were found for Al4.5Zn1.5Mg with different metal additions, which correlated with the extent of subsequent embrittlement of the alloys by WVSA. The addition of 0.1 pct iron was the most beneficial in this respect, and this was probably due to a decrease in magnesium segregated at boundaries as well as some grain refinement.
5. Re-solution heat treatment and reaging partially recovered the mechanical properties of Al4.5Zn1.5Mg which had been exposed for less than 50 hours to WVSA at 120 °C, and there was an apparent decrease in the observed level of corrosion product on the fracture surface. An increased tensile test strain rate also had this effect. The effect was caused by changes in fracture mode produced by reduction of the matrix strength.

ACKNOWLEDGMENTS

The author would like to thank J. S. Wakeman for assistance in carrying out a large part of the experimental work and his colleagues P. G. Enright, N. J. H. Holroyd, and G. M. Scamans for invaluable discussion regarding interpretation.

REFERENCES

1. M. D. Speidel: "Stress Corrosion and Corrosion Fatigue Crack Growth in Aluminium Alloys", NATO Advanced Study Institute in Stress Corrosion Cracking, Copenhagen, Denmark, 1975.
2. C. D. S. Tuck and G. M. Scamans: Proc. 2nd Int. Congress on Hydrogen in Metals, Paris, 1977, Paper 4A 11.
3. P. K. Poulouse, J. E. Moral, and A. J. McEvily: *Metall. Trans.*, 1974, vol. 5, pp. 1393-400.
4. L. Montgrain, G. M. Scamans, and P. R. Swann: *Proc. 3rd Tewkesbury Symposium on Fracture Processes*, C. J. Osborn and R. C. Gifkins, eds., University at Melbourne, Australia, 1974, pp. 194-200.
5. G. M. Scamans, R. Alani, and P. R. Swann: *Jnl. Corr. Sci.*, 1976, vol. 16, pp. 443-60.
6. D. Hardie, N. J. H. Holroyd, and R. N. Parkins: *Metal Science*, 1979, vol. 13, pp. 603-11.
7. S. P. Lynch: *3rd Int. Conference on the Effects of Hydrogen on Behavior of Materials*, I. M. Bernstein and A. W. Thompson, eds., TMS-AIME, 1980, pp. 863-71.
8. S. W. Ciaraldi, J. L. Nelson, R. A. Yeske, and E. N. Pugh: *ibid.*, pp. 437-47.
9. C. D. S. Tuck: *ibid.*, pp. 503-11.
10. L. Christodoulou and H. M. Flower: *ibid.*, pp. 493-501.
11. L. Christodoulou and H. M. Flower: *Acta Metall.*, 1980, vol. 28, pp. 481-87.
12. G. M. Scamans: *Jnl. Mat. Sci.*, 1978, vol. 13, pp. 27-36.
13. R. Alani and P. R. Swann: *Br. Corros. Jnl.*, 1977, vol. 12, no. 2, pp. 80-85.
14. T. Schober: *Metall. Trans. A*, 1981, vol. 12A, pp. 951-57.
15. N. J. H. Holroyd and G. M. Scamans: *Environment-Sensitive Fracture: Evaluation and Comparison of Test Methods*, S. W. Dean, E. N. Pugh, and G. M. Ugiansky, eds., ASTM, Philadelphia, PA, 1984, pp. 202-41.
16. G. M. Scamans and A. S. Rehal: *Jnl. Mat. Sci.*, 1979, vol. 14, pp. 2459-70.
17. R. Roy and F. F. Osborn: *Amer. Mineral*, 1954, vol. 39, pp. 853-85.
18. R. S. Alwitt: "The Aluminum-Water System", in *Oxide and Oxide Films*, J. W. Diggle, ed., Marcel Dekker, New York, NY, 1976, vol. 4, pp. 169-254.
19. M. J. Robinson: "Mechanics of Exfoliation Corrosion in High Strength Aluminium Alloys" presented at Conference "Control and Exploitation of the Corrosion of Aluminium Alloys," Inst. Corrosion Science and Technology, Cranfield, U.K., 1983.
20. G. M. Scamans, N. J. H. Holroyd, and C. D. S. Tuck: "The Role of Magnesium Segregation in the Intergranular Stress Corrosion Cracking of Aluminium Alloys," paper presented at TMS-AIME Fall Meeting, St. Louis, MO, October 1982.
21. J. M. Chen, T. S. Sun, R. K. Vishwanatham, and J. A. S. Green: *Metall. Trans. A*, 1977, vol. 8A, pp. 1935-40.
22. P. Doig and J. W. Edington: *Metall. Trans. A*, 1975, vol. 6A, pp. 943-45.
23. T. N. Dymova, Z. K. Zterlyadkina, and V. G. Safronov: *Russ. J. Inorg. Chem.*, 1961, vol. 6, pp. 389-92.
24. J. Genossar and P. S. Rudman: *Zeitschrift f. Phys. Chem. Neue Folge*, 1979, vol. 116, pp. 215-24.
25. M. C. Flemmings: *Solidification Processing*, McGraw-Hill, New York, NY, 1974, ch. 3, pp. 58-92, ch. 5, pp. 146-48.
26. C. J. Peel and P. Poole: *International Conference on Mechanisms of Environment Sensitive Fracture of Materials*, P. R. Swann, F. P. Ford, and A. R. C. Westwood, eds., The Metals Society, London, 1977, pp. 147-57.