HYDROGEN EMBRITTLEMENT IN GRAIN BOUNDARIES STUDIED BY FATIGUE CRACK PROPAGATION IN Al-Zn-Mg BICRYSTALS
A. Niegel, H.-J. Gudladt, V. Gerold

To cite this version:
A. Niegel, H.-J. Gudladt, V. Gerold. HYDROGEN EMBRITTLEMENT IN GRAIN BOUNDARIES STUDIED BY FATIGUE CRACK PROPAGATION IN Al-Zn-Mg BICRYSTALS. Journal de Physique Colloques, 1988, 49 (C5), pp.C5-659-C5-664. <10.1051/jphyscol:1988585>. <jpa-00228082>

HAL Id: jpa-00228082
https://hal.archives-ouvertes.fr/jpa-00228082
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
HYDROGEN EMBRITTLEMENT IN GRAIN BOUNDARIES STUDIED BY FATIGUE CRACK PROPAGATION IN Al-Zn-Mg BICRYSTALS

A. NIEGEL, H.-J. GUDLADT and V. GEROLD

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, and Institut für Metallkunde der Universität Stuttgart, Seestrasse 92, D-7000 Stuttgart 1, F.R.G.

ABSTRACT

High cycle fatigue crack propagation in grain boundaries was studied in precipitation hardened Al-Zn-Mg specimens containing a single grain boundary (gb) perpendicular to the load axis. In peak-aged bicrystals tested in wet nitrogen atmospheres, cracks propagated in an intercrystalline manner. Under cyclic loading conditions two different mechanisms contribute to crack propagation which are termed stress corrosion cracking (SCC) and intergranular corrosion fatigue (CF). In both cases, it is well established that intercrystalline crack propagation is influenced by hydrogen penetrating into the gb during each load cycle. For SCC it is the hydrogen dissolved into the gb, resp. areas close to the boundary whereas for CF it is the trapped hydrogen which initiates the intergranular cracking. Both terms will be discussed under microstructural aspects.

1. INTRODUCTION

The role of microstructure in stress corrosion cracking (SCC) of Al-Zn-Mg alloys in gaseous surroundings has been discussed by various authors (1,2). In most cases the experiments were performed under monotonic loading conditions in different atmospheres. More recently, attention has been paid to the transition from cracking under monotonic loading to the phenomenon of corrosion under cyclic loading conditions (3,4). It is well known that grain boundary (gb) embrittlement, influenced by hydrogen atoms penetrating into the gb, depends on its microstructure. In order to study this influence on the crack growth behavior, investigations of the gb region were undertaken using TEM, SEM and EDS.
2. EXPERIMENTAL DETAILS

The material used for this study was a high purity Al-4.5wt%Zn - 1.25wt%Mg alloy. Bicrystals with a single gb in the middle of the specimen were prepared by a modified strain annealing technique. The cylindrical bicrystals were machined by spark erosion into flat specimens, having a rectangular cross-section of 1.5 x 6 mm². Usually, the specimen axes were oriented for single slip in one of the two grains with the broad surface parallel to the Burgers vector of the primary slip system. In most cases, the gb plane was normal to the loading axis. The misorientation of the two grains typically was below 10° as revealed by Laue pattern and by etching techniques. The gb did not show any special symmetry.

All samples were homogenized at 480°C for 30 min, quenched into water and electrolytically polished. To initiate cracks into the gb, notches having a depth of 500 µm were spark machined into one of the small faces of the specimens. Thereafter, the final heat treatment at 135°C was made either for 100 h leading to the peak-aged state (PA) or for 1000 h leading to an overaged condition (OA). The crack propagation tests under cyclic loading conditions (100 Hz) were carried out using an electrodynamic system. The experimental results of inter- and transgranular crack growth as a function of the water vapor pressure p and the aging condition have been described and discussed in a previous paper (5).

For TEM investigations, undeformed PA and OA bicrystals with a thickness of about 100 µm were spark cut from thick specimens. Thin foils were prepared from these flat samples using a jet polishing method in order to investigate the microstructure of the gb region, i.e., precipitate free zones (PFZ) and the morphology of gb precipitates. TEM investigations were also carried out on fatigued specimens and it was possible to observe gb crack tips in bicrystals fatigued in wet nitrogen and crystallographic stage I crack tips in single crystals.

The concentration profile of Zn was measured across the gb with an analytical TEM (JEOL 200 CX) using energy dispersive X-ray spectroscopy (EDS). For the analytical EDS as well as for TEM examination the gb planes were always parallel to the electron beam. The calculation of the Zn concentration was based on the method of Cliff and Lorimer (6), applying their correction function for absorption.

3. EXPERIMENTAL RESULTS

Fig. 1 shows a TEM micrograph which is typical for PA bicrystals. Besides the bulk which contains coherent n°-precipitates a PFZ was observed. Its total width depended on the aging condition and was measured on the average to be 70 nm for the PA specimens (Table 1). The examination of the gb reveals the existence of oblated gb precipitates with visible dimensions of 110 and 25 nm parallel and normal to the gb.
In contrast to the gb microstructure of the PA specimen the microstructure of the OA sample was quite different, as seen in Fig. 2. This microstructure indicates that the precipitates in the bulk are much coarser and not as finely distributed as those of the PA specimens. The average width of the PFZ in OA bicrystals was measured to be 175 nm. In addition, Fig. 2 shows the strong coarsening of the stable gb precipitates. These large incoherent particles have an average diameter of 226 nm and an average thickness of 85 nm, and show a marked globular character comparable to the oblate PA gb precipitates.

In PA bicrystals tested in wet nitrogen the crack always propagates intergranularly. Fig. 3 shows a micrograph of a typical gb crack surface obtained from a PA specimen fatigued in wet nitrogen at crack propagation rates greater than $10^{-7}$ m/cycle. The crack surface is covered with incoherent gb precipitates (white dots), similar to those seen in TEM observation. For small crack rates close to the threshold region no such contrast could be observed.

For OA bicrystals it was impossible to initiate an intergranular crack in wet atmospheres. Therefore, Fig. 4 shows the intergranular crack surface from a coarse polycrystalline specimen, which was in the same OA condition as the bicrystals (135°C for 1000 h). In polycrystalline specimens the intergranular crack represents less than 30 percent of the total crack surfaces. The size, shape and distribution of the stable precipitates are visible in Fig. 4. Furthermore, their volume fraction is nearly 2.5 times greater than that of the PA specimens. Hence, it follows that the distance between the centers of gb precipitates in the OA specimens is three times greater than the distance between the centers in the PA specimens.
The Zn concentration profiles was measured across the gb in PA and OA bicrystals using the microanalytical technique of EDS. Fig. 5 shows the Zn concentration normalized to the mean Zn concentration in the bulk for PA (open circles) and OA (open squares) conditions plotted against the distance from the gb. The Zn concentration is always defined as the local average of the Zn content of both precipitates and depleted matrix. For the PA specimens the first deviation from the mean value occurs at a distance d of 350 nm where with decreasing d an increase of the Zn content occurs which reaches its maximum value of 1.3 at d = 60 nm which is close to the border of the PFZ (35 nm). For shorter distances the Zn content drops down to 0.4 and shows a small peak immediately at the gb (the Zn content of the gb precipitate is not included.

The further aging at the same temperature to the OA state leads to a broadening of the concentration profile and a reduction of the maximum value which is now located at d = 250 nm which is far outside the PFZ (d = 90 nm). The minimum Zn content within the PFZ is much smaller compared to that of the PA condition (Table I). These concentration profiles result from diffusion of the Zn atoms to the gb precipitates and out of the PFZ into the bulk.

![Fig. 5 Zn concentration measurements across a grain boundary in PA and OA specimens](image)

4. DISCUSSION

The crack propagation experiments during cycling of Al-Zn-Mg bicrystals in wet atmospheres have been described elsewhere (5) and for the PA specimens the following results were obtained:

(i) Only for partial water vapor pressures p above 0.8 kPa intercrystalline crack propagation was obtained.

(ii) Close to the threshold range (da/dN < 10^-8 m/cycle) the necessary stress intensity range ΔK depends on p roughly as 1/√p.
(iii) For large propagation rates \(3 \times 10^{-7} < \frac{da}{dN} < 10^{-6} \text{ m/cycle}\) there exists no dependency on \(p\). Compared to intercrystalline stage II cracks the rate is larger by one order of magnitude.

(iv) For still larger propagation rates only transcrystalline cracks are possible.

From these facts (i-iv) it is concluded that under cyclic loading conditions two mechanisms are necessary in order for moisture to affect intergranular cracking.

For low crack growth rates (ii) near the threshold a mechanism should dominate which depends on the partial water vapor pressure and which leads to a crack propagating close to the grain boundary but not within it. The latter follows from the fact that no gb precipitates could be found in SEM micrographs of the corresponding crack surfaces. It is suggested that this cracking is controlled by dissolved hydrogen which has diffused into the gb and spread into areas close to it. The embrittling phenomenon leading to intergranular cracking is referred to cyclic SCC. Under monotonic loading conditions SCC is a well established mechanism and is discussed by different authors. After Gruhl (7) the sensitivity to SCC increases with increasing Zn content. Since the zinc atoms are important for SCC it is believed that this concentration is highest in areas of high zinc concentration, i.e., at the rim of the PFZ (Fig.5). This should result in a crack at this rim between PFZ and matrix as observed by SEM.

For high crack propagation rates (iii) the second mechanism governs intergranular cracking, but in this case the crack propagation rate is independent from the partial water vapor pressure \(p\). This mechanism is believed to be due to hydrogen which may have been trapped at the gb precipitates. This effect will be called intergranular CF in contrast to SCC.

After Wei (3), three mechanisms are necessary in order for moisture to affect cracking. These are transportation of water vapor to the intergranular crack tip, adsorption of water vapor on the newly created crack surface during each half load-cycle and its dissociation. The latter step generate hydrogen atoms penetrating the gb via mobile dislocations during cycling until they were trapped by gb precipitates. Two arguments can support this idea. The first argument is given by Tuck (8) who claimed a possible formation of hydrides at the gb precipitates. An alternative possibility is given by Christodoulou and Flower (9) who suppose an immediate trapping of hydrogen by the precipitates which can be detected by TEM as bubbles. Preliminary investigations showed this type of contrast in the corresponding bicrystals.

Secondly, it has been found experimentally that a fast crack propagating in wet nitrogen continues to propagate in an intercrystalline manner if the atmosphere has been changed to a dry one (8). Even an annealing at 135°C does not change the intergranular crack extension. Usually, only transcrystalline cracks do occur under this condition if the crack was initiated in dry atmospheres. Only a full solution heat treatment followed by quenching and re-aging led to transcrystalline crack propagation. From these facts it must be concluded that a corrosive agent must have been trapped in the gb during cycling.

For OA bicrystals neither SCC nor CF has been observed during cycling. Even in wet atmospheres \((p > 3.1 \text{ kPa})\) the crack propagates in an transgranular manner. In this case, both the concentration of Zn in the PFZ and the Zn enrichment at the rim of the PFZ decreases with increasing annealing time (Fig.5) and the dissolved hydrogen penetrates further into the bulk. Therefore, the gb loses its sensitivity to SCC and the crack initiation becomes transgranular. A further discussion of all effects will be given in a subsequent paper.
Table 1 Comparison of Characteristic Values for PA and OA Specimens

<table>
<thead>
<tr>
<th>Characterization</th>
<th>PA-condition</th>
<th>OA-condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>gb-precipitate characterization</td>
<td>\eta ,(MgZn_2)</td>
<td>large \eta ,(MgZn_2)</td>
</tr>
<tr>
<td>width, nm</td>
<td>110 \pm 40</td>
<td>226 \pm 50</td>
</tr>
<tr>
<td>height, nm</td>
<td>25 \pm 4</td>
<td>85 \pm 18</td>
</tr>
<tr>
<td>mean gb particle spacing, nm</td>
<td>300 \pm 100</td>
<td>700 \pm 250</td>
</tr>
<tr>
<td>total width of PFZ, nm</td>
<td>70 \pm 10</td>
<td>175 \pm 20</td>
</tr>
<tr>
<td>peak Zn-conc. c/\text{c}_{\text{matrix}}</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>distance from gb, nm</td>
<td>60</td>
<td>270</td>
</tr>
<tr>
<td>minimum Zn conc. c/\text{c}_{\text{matrix}} in PFZ</td>
<td>0.42</td>
<td>0.27</td>
</tr>
<tr>
<td>crack propagation behavior</td>
<td>intergranular SCC and CF</td>
<td>transgranular strong resistance to SCC</td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft. The authors are obliged to Dr. W. Mader and Mr. E. Feuerstein for their assistance in performing the EDS measurements.

REFERENCES

(2) Speidel, M.O., "The Theory of Stress Corrosion Cracking in Alloys". Published by NATO Scientific Affairs Division Brussels 1971, 289.