Hydrogen Assisted Intergranular Crack Propagation during Environmental Embrittlement in an Al–Zn–Mg–Cu Alloy

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Hydrogen absorbed from the test environment was detected experimentally from an Al–4.9%Zn–2.2%Mg–1.3%Cu alloy deformed in laboratory air, which is a direct evidence of hydrogen embrittlement. The alloy exhibited grain boundary embrittlement when deformed at a strain rate of $10^{-3}$ s$^{-1}$ in laboratory air and hydrogen behavior was studied using deuterium as a tracer of hydrogen. The direct detection of hydrogen supports the idea that gradual propagation of intergranular crack at sufficiently low strain rate may enable continuous absorption and accumulation of hydrogen in the stress field near the crack tip and eventually embrittle the material.

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1. Introduction

The stress-corrosion cracking (SCC) of aluminum alloys is a well-documented phenomenon and SCC of high strength Al–Zn–Mg–(Cu) alloys has been studied most extensively of all the aluminum alloy systems. A number of studies have shown that SCC in high strength Al–Zn–Mg–(Cu) alloys is hydrogen-induced cracking. Solute hydrogen is believed to accumulate in the stress field near the crack tip and to cause embrittlement, though the detailed mechanism of the cracking is still unknown. One of the complicating factors in understanding such mechanism is that lattice transport of hydrogen is extremely slow and the amount of solute hydrogen is very small in aluminum at room temperature. Hence, there have been few reports that show direct evidence of hydrogen embrittlement. Montgrain and Swann studied the embrittlement of a high purity Al–Zn–Mg alloy pre-exposed to the air saturated with water vapor, and detected hydrogen emitted from the embrittled specimen during deformation and fracture in a vacuum chamber. Besides the pre-exposed embrittlement, Al–Zn–Mg–(Cu) alloys show embrittlement in laboratory air when deformed at sufficiently low strain rates. In this case, the embrittlement is thought to be due to breakdown of the surface oxide and absorption of the hydrogen evolved by a reaction between the fresh metal surface and water vapor in air. In the present study, tensile tests were performed at a strain rate ranging $10^{-4}$ to $10^{-7}$ s$^{-1}$ in laboratory air and hydrogen behavior was studied using deuterium as a tracer of hydrogen to provide information about when hydrogen was introduced from the environment into the specimen and participated in the embrittling process.

2. Experimental

An ingot of Al–4.9%Zn–2.2%Mg–1.3%Cu (mass%) was prepared from aluminum of 99.999% purity and zinc, magnesium and copper of 99.99% purity and hot-rolled to a plate of 10 mm thick. Round tensile test pieces with a gauge of 10 mm and 4 mm in diameter were machined from the plate, and subjected to solution heat treatment for 1 hour at 470°C and final aging for 24 hours at 100°C. After the heat treatment, the specimen had an equiaxed grain structure, and average grain size was about 200 μm.

Tensile tests were performed at an initial strain rate ranging from $1.67 \times 10^{-4}$ to $1.67 \times 10^{-7}$ s$^{-1}$ in laboratory air (relative humidity: 40–60%) at ambient temperature. Some specimens were tested in an atmosphere saturated with heavy water vapor to study whether environmental hydrogen had been introduced into the specimen. These specimens were strained to a certain extent at an initial strain rate of $1.67 \times 10^{-7}$ s$^{-1}$, unloaded, and set on another tensile testing machine equipped with a quadrupole mass spectrometer being capable of detecting any gas species that evolved from the surface of the specimen during subsequent deformation and fracture.

3. Results and Discussion

The effect of strain rate on the true fracture strain of the Al–Zn–Mg–Cu samples tested in laboratory air is presented in Fig. 1. True fracture strain obviously decreases with decreasing strain rate, which is in good agreement with the results of Welpmann et al. and Holroyd and Hardie. Fracture appearances are presented in Fig. 2. Intergranular fracture was barely visible on the fracture surface of the specimen tested at an initial strain rate of $1.67 \times 10^{-4}$ s$^{-1}$, while it is obvious that the fracture mode changes completely to an intergranular one when tested at the lowest rate of $1.67 \times 10^{-7}$ s$^{-1}$. As shown in Fig. 2(c), detailed observation revealed that there were numerous slip steps, ledges, which are believed to arise from the intersection of intense matrix slips and grain boundaries. Fracture morphology of the specimen tested at an intermediate rate of $1.67 \times 10^{-6}$ s$^{-1}$ was a mixture of intergranular and transgranular. The intergranular fracture at the lowest strain rate can be attributed to hydrogen absorbed from the testing environment as has been reported. However, it is not clear when hydrogen is absorbed and how it affects the crack initiation and propagation. Therefore, additional tests were performed to obtain such information. Applied test conditions and results are summarized in Table 1. When a specimen was

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deformed in tension at the lowest strain rate of $1.67 \times 10^{-7}$ s$^{-1}$ to the maximum load and subsequently deformed at the highest rate of $1.67 \times 10^{-4}$ s$^{-1}$, it showed almost as high ductility as that tested at the highest strain rate in Fig. 1. On the other hand, the specimen deformed at the lowest strain rate after maximum load exhibit lower ductility, although the degree of embrittlement was not as severe as that at the lowest strain rate shown in Fig. 1. At any rate, the deformation process before maximum load does not cause the embrittlement, and hydrogen may be absorbed which induces embrittlement in the specimen after the maximum load.

Figure 3 shows examples of load vs. displacement curves of the specimens. Strain localization began at a lower strain when tested at a lower strain rate, which indicates that hydrogen accelerated crack initiation along grain boundaries. However, further experimental information should be needed about the crack initiation and propagation for detailed discussion on the effect of hydrogen. It is noted at the lowest strain rate that the load decreased from maximum to zero gradually (Fig. 3(a)). The time needed for such deformation can be calculated from displacement that corresponds to local deformation after maximum load and is roughly estimated at 12 hours. This implies that the crack initiates at the surface and propagates gradually along grain boundaries at the lowest strain rate, and finally forms the intergranular fracture surface shown in Figs. 2(b), (c). This deformation behavior is apparently different from that in the specimens tested at the higher strain rates, in which the load decreased suddenly after certain amount of local deformation shown in Figs. 3(b), (c).

Since the lattice diffusion rate of hydrogen in aluminum is extremely slow at room temperature, about $10^{-11}$ m$^2$/s,$^8$ it is difficult to rationalize how hydrogen can keep up with a moving crack only by lattice diffusion. Thus there must be a more rapid mode of hydrogen transport, namely, as solute atmospheres associated with mobile dislocations.$^9,10$ One of the present authors has reported such rapid hydrogen transport by visualizing hydrogen emission along slip bands on the surface of pure aluminum.$^{11}$ Hence, it is likely that continuous absorption and rapid transport of hydrogen occurs during crack propagation along grain boundaries after maximum load. To evaluate the amount of hydrogen absorbed from a test environment, further experiments were performed using deuterium as a tracer of hydrogen. Some of the test pieces were pre-deformed at the lowest strain rate in air saturated with heavy water vapor. The specimens were deformed via maximum load until the load started to decrease, and were unloaded before they broke. Then the pre-deformed specimens were removed from the tensile testing machine, and set in the vacuum tensile testing machine equipped with a quadrupole mass spectrometer, in which hydrogen emission was detectable during subsequent deformation and fracture. Amount of pre-deformation was changed by varying the timing for unloading.

An example of the analyses is shown in Fig. 4(a). Variations of ion currents that represent the amounts of emitted H$_2$ and HD are plotted as a function of displacement, and the load-displacement curves are also shown in the same figure. It is obvious that hydrogen and deuterium evolved from the surface of the specimen during deformation and fracture. Two
Table 1 Test conditions and results of additional tensile tests. Strain rates were alternated at maximum load.

<table>
<thead>
<tr>
<th>Strain rate, $R_s^{-1}$</th>
<th>True fracture strain</th>
<th>Reduction in area (%)</th>
</tr>
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<tbody>
<tr>
<td>Before maximum load</td>
<td>After maximum load</td>
<td></td>
</tr>
<tr>
<td>$1.67 \times 10^{-7}$ s$^{-1}$</td>
<td>$1.67 \times 10^{-4}$ s$^{-1}$</td>
<td>0.187</td>
</tr>
<tr>
<td>$1.67 \times 10^{-6}$ s$^{-1}$</td>
<td>$1.67 \times 10^{-7}$ s$^{-1}$</td>
<td>0.135</td>
</tr>
</tbody>
</table>

Fig. 3 Load vs. displacement curves of the specimens tested at an initial strain rate of (a) $1.67 \times 10^{-7}$ s$^{-1}$, (b) $1.67 \times 10^{-6}$ s$^{-1}$, and (c) $1.67 \times 10^{-4}$ s$^{-1}$.

Fig. 4 Hydrogen emission during deformation and fracture from specimens that were pre-deformed by about 1% at a strain rate of $1.67 \times 10^{-7}$ s$^{-1}$ (a), and only pre-exposed (b) in air saturated with heavy water vapor.

sources of hydrogen and deuterium can be considered, a) the surface oxide layer, b) the specimen matrix under the surface oxide. Hydrogen and deuterium from the surface oxide layer was found even in specimens which were only pre-exposed to air saturated with heavy water vapor without any deformation, as shown in Fig. 4(b). In that case, emission of hydrogen and deuterium decreased after the onset of plastic deformation.

On the other hand, emission of hydrogen and deuterium started at the onset of plastic deformation, and continued through subsequent plastic deformation in the pre-deformed specimens (Fig. 4(a)). It is noted that the ion current of HD in Fig. 4(a) maintained a higher value during plastic deformation and eventually decreased after fracture of the specimen accompanied by a burst of hydrogen and deuterium. In this case, the source of hydrogen and deuterium is attributed to the specimen matrix under the surface oxide, which were introduced into the specimen during the pre-deformation in air saturated with heavy water vapor.

Observation of the fracture surface made after the above analyses revealed that the ratio of intergranular fracture surface to the entire fracture surface has a certain relation to the amount of pre-deformation at the lowest strain rate. Relation of the ratio of intergranular fracture and the amount of pre-deformation, which is represented by ratio of load decrease to maximum load, is plotted in Fig. 5. Increasing amount of pre-deformation tends to increase the ratio of intergranular fracture. In addition, numerical slip steps, ledges, were observed on the intergranular fracture surfaces as shown in Fig. 2(c). Such microscopic morphology indicates that absorbed hydrogen may be easily accumulated in the stress field near the crack tip by enhanced transport that arises from mobile dislocations. The series of results support the idea that the amount of absorbed hydrogen increased with repetition of the following process during pre-deformation at the lowest strain rate: exposure of fresh metal surface, adsorption and absorption of hydrogen, accumulation of hydrogen in the stress field near the crack tip by dislocation motion, and intergranular crack propagation. Thus, intergranular crack propagation after maximum load was accompanied by continuous absorption of hydrogen, and such hydrogen was experimentally detected in the present study.

4. Summary

Tensile tests of an aged Al–Zn–Mg–Cu alloy were performed at a strain rate ranging $10^{-4}$ to $10^{-7}$ s$^{-1}$ in laboratory air and hydrogen behavior was studied using deuterium as a tracer of hydrogen. Ductility decreased with decreasing strain rate, and the fracture mode changed from transgranular to completely intergranular when tested at the lowest rate of $1.67 \times 10^{-7}$ s$^{-1}$. This degradation was attributed to hydrogen that was absorbed from the environment accompanied by
the crack propagation along grain boundaries, and such hydrogen was experimentally detected. This direct evidence of hydrogen behavior supports the idea that gradual propagation of intergranular crack at the lowest strain rate enables continuous absorption and accumulation of hydrogen in the stress field near the crack tip and eventually embrittles the material.

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REFERENCES