

Hydrogen-environment Embrittlement in High-purity Al-Zn-Mg(-Cu) Alloys

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Abstract: From the viewpoint of a both practical and basic understanding on hydrogen-environment embrittlement (HEE) of high-strength aluminum alloys, high-purity Al-Zn-Mg(-Cu) alloys having contents of primary alloying elements comparable to 7075 alloy are subjected to slow strain rate tensile (SSRT) tests in a high-pressure hydrogen gas and atmospheric air with a controlled relative humidity. The characteristics of HEE have been studied as a function of aging stage, strain rate and test temperature. From the test results on the Al-Zn-Mg ternary alloy in the underaged (UA) with a high sensitivity to HEE, it is confirmed that humid air is so severer than high-pressure gaseous hydrogen to cause embrittlement in aluminum alloys. An increase in each of humidity and temperature of atmospheric air increases the susceptibility to HEE, leading to a remarkable intergranular cracking. The copper-bearing alloy having a higher tensile strength in the peak-aging (PA) state than the ternary alloy exhibits a superiority in the HEE resistance too. For the over-aged (OA) copper-bearing alloy, the higher humidity of air produces the higher elongation and a transgranular dimple fracture, which suggest that the void formation becomes easier by hydrogen trapping at coarsened precipitate particles within grains.

Key words: Al-Zn-Mg(-Cu) alloy; Hydrogen embrittlement; Hydrogen gas; Humid air; SSRT test

1 Introduction

In a recent research and development on hydrogen-fuel cell vehicles, high-strength aluminum alloys are regarded as promising materials to be applied to a high-pressure gaseous hydrogen container liner and its periphery members. The high-strength Al-Zn-Mg system alloys are however known to have usually an increased sensitivity to either stress corrosion cracking or hydrogen embrittlement with progress in age-hardening^[1], so that it must be necessary to ensure a safety to these. “The hydrogen-environment embrittlement (HEE)”, defined as a hydrogen-relating damage induced by external environments such as high-pressure gaseous hydrogen and humid air without any contribution of anodic dissolution, are still under a limited understanding on its process, because of a lot of relating factor and complicated effects.

In the present study, from the viewpoint of a both practical and basic understanding on HEE process, high-purity Al-Zn-Mg (-Cu) alloys having contents of primary alloying elements comparable to 7075 alloy are subjected to slow strain rate tensile (SSRT) tests in high-pressure hydrogen gas and humid air of atmospheric pressure as a function of aging stage, strain rate and test temperature. The characteristics of HEE have been studied to discuss about effects of hydrogen.

2 Experiment

2.1 Material

The tested materials are rolled sheets with 1 mm thickness of high purity Al-Zn-Mg alloy (designated as B) and Al-Zn-Mg-Cu alloy (designated as C). The chemical composition is listed in Table 1. Each alloy was solution-treated, quenched in cold water and subsequently aged to three tempers of underaging (UA), peak-aging (PA) and overaging (OA) given in Table 2. The SSRT test specimen is a compact smooth tensile specimen machined out in the transverse (T) direction of the sheet, having 12mm length and 5mm width in a gage part and 60mm total length.

Table 1 Chemical Composition of the Alloys (Mass%)

Alloy	Zn	Mg	Cu	Fe	Si	Ti
Al-Zn-Mg (B)	5.6	2.5	-	0.06	0.02	0.01
Al-Zn-Mg-Cu (C)	5.6	2.5	2.0	0.06	0.02	0.01

UA	120°C x 4h
PA	120°C x 48h
OA	120°C x 4h → 180°C x 10h

2.2 SSRT test

The SSRT test under a range of strain rate from 1.39×10^{-4} to 1.39×10^{-6} [1/s] was carried out in hydrogen environments; high-pressure gaseous hydrogen of about 14MPa and atmospheric air with a constant relative humidity RH=65%. The reference environments of these are high-pressure nitrogen gas of about 14MPa and dry nitrogen gas (DNG) of an atmospheric pressure, respectively. The SSRT test to know an effect of test temperature on HEE was also performed in RH65% humid air at 20°C to 80°C under strain rate 1.39×10^{-6} [1/s]. The index $I(\delta)$ of susceptibility to embrittlement is given as equation (1), indicating a reduction ratio of elongation (δ) in hydrogen environments to that (δ_0) in an inert reference environment

$$I(\delta) = 1 - \frac{\delta}{\delta_0} \tag{1}$$

3 Results

Figure 1 shows the stress-strain diagrams of alloy B-UA subjected to the SSRT test under strain rate 1.39×10^{-6} [1/s] at 30°C. The maximum stress and elongation in RH65% air of atmospheric pressure are lower than those in high-pressure hydrogen gas and the decrease in elongation is remarkable compared to that in the inert nitrogen gas environment. The values of $I(\delta)$ defining susceptibility to HEE are 0.62 in RH65% air of atmospheric pressure and 0.19 in high-pressure hydrogen gas. Thus it is found that the former environment is much severer than the latter.

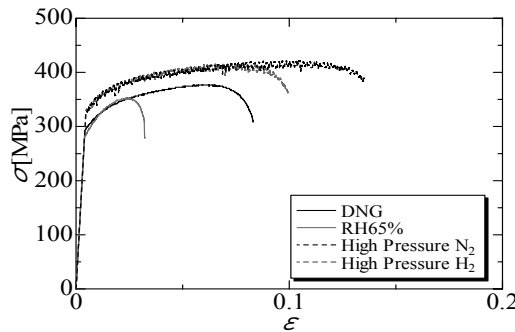


Figure 1 Stress-strain Diagrams of Alloy B Underaged (UA) in SSRT Testing at Strain Rate: 1.39×10^{-6} [1/s]

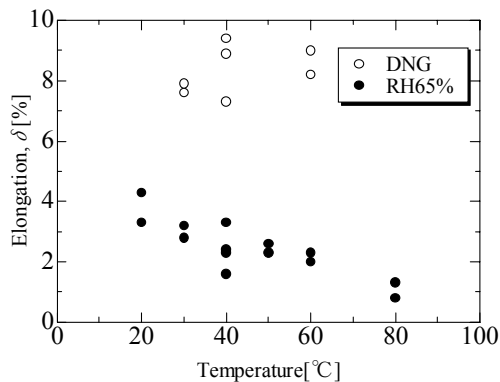


Figure 2 Elongation δ vs. Temperature plot for Alloy B-UA. Strain Rate: 1.39×10^{-6} [1/s]

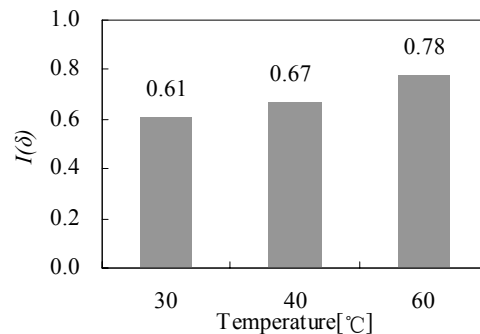


Figure 3 HE Susceptibility Index for Alloy B UA. Strain Rate: 1.39×10^{-6} [1/s]

Figure 2 presents the effect of test temperature in RH65% air on elongation δ . With increasing temperature, δ shows a trend to increase slightly in DNG, while decreases remarkably in RH65% air. At the higher temperature, the higher $I(\delta)$ is revealed in Fig.3, and on the fracture surface of these ruptured specimens an extension of intergranular cracking is markedly observed.

Figure 4 shows elongation δ , tensile strength σ_B and each of index $I(\sigma_B)$ and $I(\delta)$ for alloy B and alloy C with each of temper UA, PA and OA SSRT-tested under strain rate 1.39×10^{-6} [1/s] at 30°C. The SEM images of fracture surface in ruptured specimens of alloy B with temper UA and OA are presented in comparison with those of alloy C in Figure 5. For UA and OA of alloy B as shown in Fig.5 (a) and (b), respectively, intergranular cracks each occur, leading to a relatively high susceptibility to HEE, even $I(\delta) = 0.28$ for OA. On the other hand, intergranular cracking occurs too in UA of alloy C as shown in Fig.5 (c), while does not at all in OA shown in Fig. 5(d), but a transgranular dimple fracture takes place. Thereby the resistance to HEE of alloy C is improved by overaging: C-OA exhibits $I(\delta) = -0.09$, indicating rather an increase in elongation than a decrease in RH65% air relative to that in DNG.

Then, the effect of relative humidity RH of air on elongation δ is examined for alloy C. Fig.6 illustrates the obtained relation between δ and RH [%] for each of UA and OA. Here the abscissa is plotted as a function of the square root of RH [%] according to Sieverts' law. With increasing RH, δ of UA is decreased, while OA presents a slight increase in δ . From these results, therefore, the high susceptibility to HEE for UA or PA is caused by intergranular cracks initiated when a hydrogen concentration at grain boundaries reaches a critical level sufficient to be required for intergranular fracture. On the other hand, it is suggested for OA that a hydrogen accumulation at grain boundaries is retarded by trapping at coarsened η (MgZn₂)-phase precipitates within grains^[2] and then intergranular cracking is inhibited. Instead, however, a micro-void formation can become easier, leading to an increase of elongation.

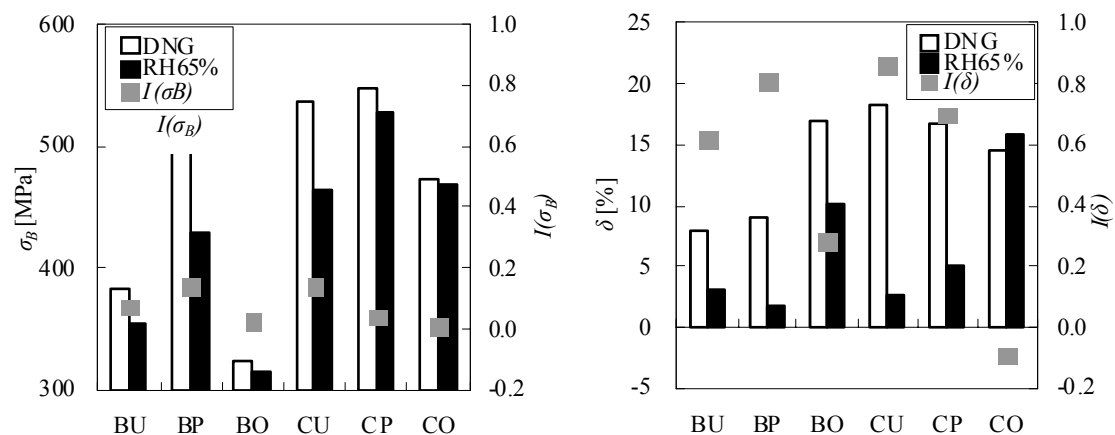


Figure 4 Tensile strength σ_B or elongation δ and HE susceptibility index for alloy B and alloy C. Strain rate: 1.39×10^{-6} [1/s]

4 Summary

The SSRT test for high-purity Al-Zn-Mg alloy (B) and Al-Zn-Mg-Cu alloy was conducted in high-pressure hydrogen gas and humid air of atmospheric pressure as a function of aging temper, strain rate and test temperature. The characteristics of hydrogen-environment embrittlement (HEE) and its fracture were studied. The obtained results are summarized as follows.

- (1) It is confirmed that humid air is severer to cause embrittlement than high-pressure gaseous hydrogen.
- (2) An increase in either humidity or temperature of atmospheric air for the alloy B-UA (underaged) brings about an increase in the susceptibility to HEE, leading to a remarkable intergranular cracking.
- (3) The copper-bearing alloy C with a higher tensile strength in the peak-aging (PA) state is superior in the HEE resistance to the ternary alloy.
- (4) The higher humidity of air for the alloy C-OA (over-aged) produces the higher elongation and a

transgranular dimple fracture, which suggest that the void formation becomes easier by hydrogen trapping at coarsened precipitate particles within grains.

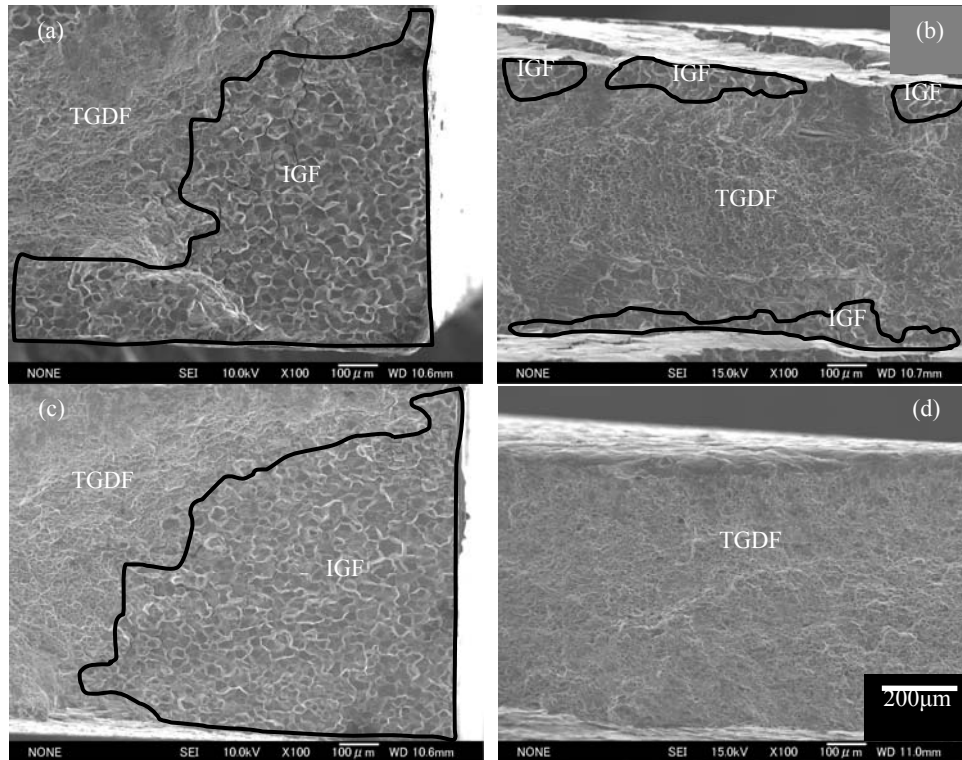


Figure 5 SEM images Showing Fracture Surface of (a) UA and (b) OA in Alloy B and (c) UA and (d) OA in Alloy C

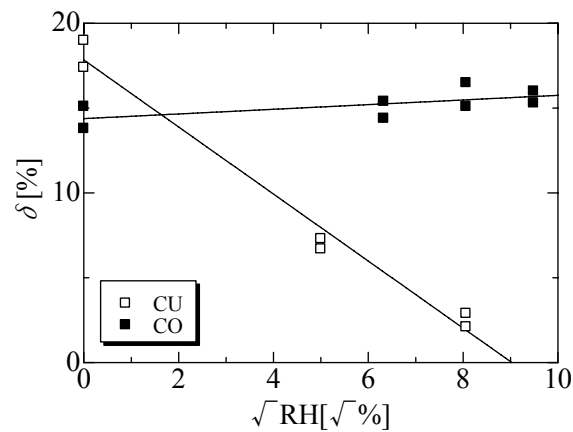


Figure 6 Effect of Relative Humidity on Elongation δ of Alloy C-UA and OA.

References

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