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Assessment of hydrogen embrittlement via image-based techniques in Al-Zn-Mg-Cu aluminum alloys

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Abstract

Hydrogen repartitioning and the related embrittlement behavior were characterized by studying Al-Zn-Mg-Cu aluminum alloys with different intermetallic particle contents. Using high-resolution X-ray tomography and related microstructural tracking techniques, hydrogen-induced quasi-cleavage cracks and the related strain localization were observed regardless of the content of the intermetallic particles. The area of quasi-cleavage cracks on the fracture surface increased and the strain localization became more intense with a decrease in the content of intermetallic particles, thereby revealing that trapped hydrogen at intermetallic particles increases the resistance to hydrogen embrittlement. In addition, a quantitative assessment of the hydrogen repartitioning taking into account vacancy production and dislocation multiplication during deformation, was applied to characterize the hydrogen embrittlement behavior. Because of the thermal equilibrium among various hydrogen trap sites, internal hydrogen atoms are mainly repartitioned to vacancies and precipitates in the strain localization region during deformation because of their high trap site densities and high hydrogen trap binding energies. Since the concentration of hydrogen trapped at dislocations is extremely limited, it can be assumed that hydrogen repartitioned to precipitates induces decohesion of precipitates along specific crystallographic planes, where quasi-cleavage cracking may originate.

Keywords X-ray tomography, Hydrogen embrittlement, Strain localization, Hydrogen repartitioning, Al-Zn-Mg-Cu aluminum alloy

1. Introduction

Aluminum alloys can absorb hydrogen during high-temperature heat treatment (e.g. a homogenization process) and/or services in aggressive environments due to the destruction of a surface oxide layer [1-3]. The dissolved hydrogen atoms are trapped among various trap sites (e.g. dislocations, vacancies and grain boundaries) and considerably degrade the mechanical properties of aluminum alloys [4, 5]. In particular, hydrogen decreases the ductility and fracture toughness, leading to an unexpected failure at applied strain levels that are far lower than a hydrogen-free material can sustain [6, 7].

In addition to inducing a drastic reduction in ductility and related premature fracture, hydrogen can cause a transition of the fracture mode from ductile (i.e. micro void coalescence) into brittle fractures that appear as either intergranular fractures or transgranular quasi-cleavage fractures [8-10]. Numerous mechanisms have been proposed to explain the effects of hydrogen trapping and concentration on the initiation and propagation of hydrogen-induced cracks. According to Gerberich, et al., hydrogen trapped at grain boundaries reduces the cohesive bonding strength (i.e., the hydrogen enhanced decohesion (HEDE) mechanism), promoting the initiation and propagation of intergranular cracks [10]. Using in-situ transmission electron microscopy (TEM), Birnbaum, et al. proposed the hydrogen enhanced localized plasticity (HELP) mechanism [11], in which hydrogen trapped at dislocations promotes planar slips of dislocations [12], leading to the initiation and propagation of quasi-cleavage cracks in the strain localization region. In addition, Nagumo, et al. revealed that hydrogen trapped at vacancies accelerated the agglomeration of vacancies to form nano voids, resulting in the propagation of hydrogen-induced quasi-cleavage cracks via the coalescence of nano voids (i.e. hydrogen-enhanced strain-induced vacancies (HESIV) mechanism) [13,14]. In previous research, Su, et al. revealed that hydrogen-induced cracks appear as quasi-cleavage cracks initiated on the surface of specimens in Al-Zn-Mg-Cu aluminum alloys [15]. However, the proposed mechanisms for hydrogen-induced quasi-cleavage cracks (e.g. HELP and/or HESIV mechanisms) can not be associated with the hydrogen trapping behavior in Al-Zn-Mg-Cu aluminum alloys since the concentration of hydrogen at the dislocations or vacancies is lower compared with that at other hydrogen trap sites due to its low hydrogen trap binding energy, as determined by Bhuiyan, et al. via performing thermal desorption spectroscopy (TDS) experiments [16].

Additionally, experimental studies and finite element method (FEM) simulations revealed that the initiation and propagation of hydrogen-induced cracks are attributed to the accumulation of dissolved hydrogen atoms in regions with high internal stress and strain during deformation [17-19]. Lee, et al. revealed that hydrogen diffusion and uptake in the strain localization region during deformation increases the growth rate and decreases the threshold stress intensity of hydrogen-induced quasi-cleavage cracks in ultrahigh-strength steels [20]. With the help of FEM simulations, Pañeda, et al. proposed that a high geometry necessary dislocation (GND) concentration in terms of strain gradient plasticity and an elevated hydrostatic stress results in the accumulation of hydrogen ahead of the crack tip, leading to the propagation of hydrogen-induced quasi-cleavage cracks in Ni-Cu superalloys [21]. By applying in-situ tensile tests under high-resolution X-ray tomography, Su, et al. showed that the initiation and propagation of hydrogen-induced quasi-cleavage cracks in Al-Zn-Mg-Cu aluminum alloys are time-dependent due to the accumulation of hydrogen in the strain localization region [15, 22]. In addition, the majority of hydrogen is repartitioned to nano voids in strain localization regions during deformation due to their high trap site density [15], indicating that in-situ hydrogen repartitioning in the strain localization is necessary for hydrogen embrittlement to occur.

With the help of the high-resolution X-ray tomography and the related 4D strain mapping technique, vacancy production and dislocation multiplication in terms of microscopic strain distribution were characterized to precisely estimate the density values for all the hydrogen trap sites during in-situ tensile tests [23]. In addition, Yamaguchi, et al. calculated the hydrogen trap binding energies of dislocations, grain boundaries, vacancies and precipitates in Al-Zn-Mg-Cu aluminum alloys by applying the first-principle simulations [24-26]. By combining the issues mentioned above, the hydrogen repartitioning behavior among various trap sites during plastic deformation and its effect on the initiation and propagation of hydrogen-induced quasi-cleavage were studied in this research.

2. Materials and experimental methods

2.1 Materials

High Zn (10 % mass Zn) Al-Zn-Mg-Cu aluminum alloys were used in this study. To identify the influences of intermetallic particles on the hydrogen partitioning and embrittlement behaviors, two alloys with different Fe and Si contents were applied. The chemical compositions are summarized in Table. 1. The ingots were homogenized at 743 K for 24 hours, hot rolled at 673 K prior to solution treatment at 748 K for 2 hours, and artificially aged at 393 K for 6 hours and then at 423 K for 5 hours. All the specimens for the in-situ tensile tests were sampled along the rolling direction by an electro discharge machine (EDM) wire eroder. The dimensions of the in-situ tensile test specimen are shown in Fig. 1. To determine the influence of the precharged hydrogen content on the embrittlement behaviors in Al-Zn-Mg-Cu aluminum alloys, specimens with different hydrogen contents were prepared. High hydrogen content specimens were charged via EDM cutting in distilled water due to the absorption of hydrogen that was decomposed from distilled water during machining. In contrast, low hydrogen content specimens were prepared by EDM cutting in kerosene to prevent the absorption of hydrogen during the cutting process. The vacuum fusion method was used to measure the total hydrogen content of specimens after EDM cutting [15], and the content of precharged hydrogen was 6.97 mass ppm for the high hydrogen content specimen and 3.26 mass ppm for the low hydrogen content specimen, respectively. Details of the vacuum fusion method used for analyzing the total hydrogen content in aluminum are shown elsewhere [27].

2.2 In-situ tensile test via high resolution X-ray tomography

The in-situ tensile tests were performed at the BL20XU undulator beamline in SPring-8. A monochromatic X-ray beam with a 20 keV photon energy generated by a liquid nitrogen-cooled Si (111) double crystal monochromator was applied for the present research. The image detector used included a 4000 (H) × 2624 (V) element digital CMOS camera (ORCA Flash 2.8, Hamamatsu Photonics K.K.), a single crystal scintillator (Pr: $Lu_3Al_5O_{12}$) and lens (20 ×). The effective pixel size of the detector was 0.5 μm, and it was positioned 20 mm behind the specimen. A total of 1800 radiographs with scanning 180 degrees in 0.1 degree increments, were obtained along the loading axis in each scan. Image slices were reconstructed from the 1800 radiographs using the conventional filtered backprojection algorithm, followed by a conversion process from 16-bit to 8-bit. During this conversion, the gray value of the 8-bit images was calibrated so that the linear absorption coefficients of -30-40 cm^{-1} fell within the 8-bit grayscale of 0 to 255. The isotropic voxels in the reconstructed images were $(0.5\ \mu m)^3$ in size.

Al-Zn-Mg-Cu aluminum alloys with different contents of intermetallic particles and hydrogen, were employed for the in-situ tensile tests. A DEBEN CT 500 in-situ testing stage was used for the in-situ tensile tests, and the strain rate was approximately $5\times10^{-4}\ s^{-1}$. The influence of the intermetallic particles on the hydrogen accumulation and repartitioning behaviors in the Al-Zn-Mg-Cu aluminum alloys under loading was clarified by holding an applied displacement for 3.34 ks at each step (the step size was approximately 0.02 mm between each step). Specimens for the in-situ tensile tests were named as High Fe Si-low H_2, High Fe Si-high H_2 and Low Fe Si-high H_2 specimen, respectively, in the present research.

2.3 Image processing and analysis

The Marching Cubes algorithm was applied to calculate parameters including the volume, surface area and diameter of each particle and hydrogen micro pore at subvoxel accuracy. To suppress the inaccuracies generated from image noise, only hydrogen micro pores and particles that were over 9 voxels in volume were counted as microstructural features in the present research. Precise image registration was performed to minimize the distances of identical particles captured at neighboring loading steps. The microstructural tracking technique (MTT), which enables the visualization of deformation behaviors, was applied by tracking all the particles throughout the deformation. In addition, high-density 4D strain mapping which enables a direct understanding of strain localization mechanisms in the presence of hydrogen, was also achieved by calculating the physical displacement of the identical particles under different loading steps. Further details of the MTT technique and 3D strain mapping are available elsewhere [24,28,29].

3. Results and discussion

3.1 Influence of intermetallic particles on hydrogen embrittlement behaviors of Al-Zn-Mg-Cu aluminum alloys

Nominal stress-strain curves for the in-situ tensile tests of High Fe Si-low H_2, High Fe

Si-high H_2, Mid Fe Si-high H_2 (also shown as 10 Zn (T_h=3.34 ks) specimens in Fig. 4 in Ref [15]) and Low Fe Si-high H_2 specimens are shown in Fig. 2. Due to the stress relaxation behavior of the material during the CT scans, vertical drops in the load are observed in Fig. 2. Due to the existence of brittle intermetallic particles, the fracture strain decreases with an increase in Fe and Si content in the presence of hydrogen. In addition, the fracture strain of the high Fe and Si content specimens decreases from approximately 10 % to 6 % with an increase in the precharged hydrogen content, revealing a high susceptibility to hydrogen embrittlement in Fig. 2.

The fracture surface morphologies of High Fe Si-low H_2, High Fe Si-high H_2, Mid Fe Si-high H_2 [15] and Low Fe Si-high H_2 are shown in Fig. 3. Fracture surfaces of all the specimens are composed of quasi-cleavage cracks and dimple fracture features. Quasi-cleavage cracks are initiated near the surface of the specimen, and gradually transform into dimple patterns with an increase in the distance from the surface to the center of the specimen. Since the precharged hydrogen content in high hydrogen content specimens (6.97 mass ppm) is approximately fifty times higher compared with that before EDM cutting (0.13 mass ppm), it can be inferred that the initiation of quasi-cleavage cracks is attributed to a high hydrogen concentration near the surface of the specimens precharged through the EDM cutting process in distilled water. In addition, the fractional area of quasi-cleavage cracks (A_{Quasi}/A_{Total}) increases with an increase in the precharged hydrogen content and decreases with an increase in the content of intermetallic particles, as summarized in Table. 2.

A series of 3D perspective views of the hydrogen micro pores and voids near the quasi-cleavage cracks for the High Fe Si-low H_2, High Fe Si-high H_2 and Low Fe Si-high H_2 specimen under different applied strains are shown in Fig. 4. The underlying intermetallic particles and aluminum matrix are not displayed. Hydrogen micro pores are distributed uniformly in the matrix at the unloading state, as shown in Fig. 4 a), d) and h). For the High Fe Si-low H_2 specimen, two quasi-cleavage cracks initiate near the surface at an applied strain of 6.3 %, propagate and tend to be coalesced with an increase in applied strain levels as shown in Fig. 4 b) and c). Voids due to the fracture of intermetallic particles are observed at an applied strain of 6.3 % as shown in Fig. 4 b). In addition, micro cracks due to the growth and coalescence of voids are observed ahead of the crack tip with an increase in the applied strain from 6.3 % to 8.6 %, as shown in Fig. 4 c). In contrast, a quasi-cleavage crack initiates just after the yield strain (i.e. the applied strain, ε_a=1.0 %) and propagates at relatively low applied strain levels ranging from 1.0 to 4.4 % in the High Fe Si-high H_2 material, as shown in Fig. 4 e) to f). Since intermetallic particles are the heterogeneous nucleation site for hydrogen micro pores during the homogenization process in aluminum alloys [30], the number density of hydrogen micro pores in the Low Fe Si-high H_2 material is lower than that in the High Fe Si-high H_2 material at the unloading state, compared in Fig. 4 d) and h). In contrast, the diameter of the hydrogen micro pores in High Fe Si-high H_2 is smaller than that in the Low Fe Si-high H_2 material, which is attributed to the restrained effects of intermetallic particles on the growth of hydrogen micro pores during the homogenization process [3, 30] as shown in Fig. 4 d) and h).

Quasi-cleavage cracks initiate at an applied strain of 2.4 % and 4.4 %, respectively, and gradually propagate with an increase in applied strain levels, as shown in Fig. 4 i)-j). With an increase in the content of precharged hydrogen, almost no growth of pre-existing hydrogen micro pores nor the nucleation of voids was observed during the entire in-situ tensile tests, as shown in Fig. 4 d)-j).

Fig. 5 shows the equivalent strain (ε_{eq}) mapping of the RD-ND virtual cross-section of the High Fe Si-low H_2, High Fe Si-high H_2 and Low Fe Si-high H_2 materials under similar macroscopic applied strain levels (the applied strain, $\Delta\varepsilon_a$, was approximately 4.5 %). Fracture surfaces along the RD-ND direction obtained via the fracture trajectory analysis [31] are also shown as a solid black line in Fig. 5 to show the influence of strain localization on the entire fracture of Al-Zn-Mg-Cu aluminum alloys. For the high Fe and Si content materials, the strain localization region is located at the center of the specimen regardless of the precharged hydrogen content, as shown in Fig. 5 a) and b). Isolated, small regions with a high strain concentration that affect the propagation route of the crack are observed in the strain localization region in the High Fe Si-high H_2 specimen, as shown in Fig. 5 b). For the Low Fe Si-high H_2 specimen, the strain localization region appears as a band oriented in an oblique direction (approximately 45°) which is narrower and more intense compared with that in the High Fe-Si high H_2 specimen, indicating that the hydrogen-induced strain localization behavior is suppressed when there is an increase in the content of intermetallic particles, as compared in Fig. 5 b) and c).

Based on the issues mentioned above, influences of intermetallic particles on the hydrogen embrittlement and related premature fracture behavior in Al-Zn-Mg-Cu aluminum alloys has been studied. The introduction of intermetallic particles was found to decrease the fractional area of hydrogen-induced quasi-cleavage cracks and retard the hydrogen-induced strain localization behavior at low applied strain levels during deformation, indicating that the role of intermetallic particles is to enhance the resistance to hydrogen embrittlement in Al-Zn-Mg-Cu aluminum alloys, as shown in Fig. 3 to 5.

According to previous research, particles in aluminum alloys are mainly divided into three types including intermetallic particles, dispersoids and precipitates based on their formation temperature ranges. Intermetallic particles are micrometer in size and are incoherent particles that form through a casting process and remain during the subsequent heat treatment such as homogenization and aging processes [32]. In contrast, dispersoids form during the homogenization process and the precipitates are nanometer-sized particles or clusters that form during the aging process [33, 34]. With respect to intermetallic particles, Yamabe, et al. revealed that hydrogen is mainly trapped at the interface between $(Fe,Mn,Cr)_2SiAl_{12}$ intermetallic particles and the aluminum matrix in Al-Mg-Si aluminum alloys by applying secondary ion mass spectrometry (SIMS), and they proposed that an extremely low effective hydrogen diffusivity (i.e., on the order of 10^{-14} m^2/s) and the related high resistance to hydrogen embrittlement is mainly attributed to the hydrogen trapping behavior at intermetallic particles near the surface of the specimen [35]. In addition, Su, et al. studied the effects of the shape and size of intermetallic particles (e.g. Al_7Cu_2Fe particles) on the hydrogen accumulation and related hydrogen micro pore initiation behavior in Al-Zn-Mg-Cu aluminum alloys [3]. It is proposed that hydrogen is prior to accumulate at intermetallic particles with irregular shapes and large sizes due to a high hydrostatic tension concentration at the angular corners and sharp edges of the irregular intermetallic particles, promoting a higher concentration of hydrogen at more complex and irregular particles compared with that at spherical particles. With an increase in both the volume fraction and the size of intermetallic particles, it can be inferred that hydrogen trapped at intermetallic particles leads to a decrease in both the accumulated hydrogen content ahead of the quasi-cleavage crack tip [36] and the trapped hydrogen content at specific hydrogen trap sites (e.g., dislocations [37,38] and vacancies [13]) due to the thermal equilibrium among various trap sites [39]. This results in a higher resistance to hydrogen embrittlement in the High Fe Si-high H_2 specimen compared with that in the Low Fe Si-high H_2 specimen. Although numerous hydrogen atoms are trapped at the interface between intermetallic particles and the matrix in the High Fe Si-high H_2 specimen, almost no voids due to the decohesion of intermetallic particles was observed ahead of the quasi-cleavage cracks during the in-situ tensile test, as shown in Fig. 4 d) to f). This result coincides with the results of Qin, et al., who demonstrated that hydrogen-induced cracking cannot occur at the interfaces when the sizes of MnS inclusions are less than 3.3 μm in austenitic steels since the inclusion-matrix interfaces can not provide sufficient space for crack nucleation [40]. Based on the issues mentioned above, it can be inferred that Al_7Cu_2Fe intermetallic particles with an average diameter of 4.6 μm [41] mainly act as hydrogen trapping sites instead of hydrogen-induced fracture origins in the High Fe Si-high H_2 specimen. Although intermetallic particles are undesirable because they are generally detrimental to the mechanical and damage tolerant properties of structural materials [42], it is reasonable to assume that the resistance to hydrogen embrittlement can be improved through changing the content, chemical compositions, size and shape of intermetallic particles in Al-Zn-Mg-Cu aluminum alloys.

3.2 Hydrogen repartitioning among various trap sites during deformation

As mentioned in Section 3.1, the existence of intermetallic particles affects the hydrogen-induced strain localization behavior and related internal hydrogen redistribution during deformation. Compared to the hydrogen trapping behavior at the unloading state, internal hydrogen atoms are likely accumulated in the strain localization region due to the heterogeneous initiation of dislocations and vacancies during deformation, leading to a localized repartitioning of internal hydrogen among various trap sites and resulting in hydrogen-induced premature fracture in the strain localization region during deformation.

Bhuiyan, et al. revealed that interstitial lattices, dislocations, vacancies, intermetallic particles, precipitates, grain boundaries and hydrogen micro pores are the main hydrogen trap sites in Al-Zn-Mg-Cu aluminum alloys [16]. According to Oriani, et al., hydrogen trapped at each trap site is calculated by assuming that hydrogen trapped at normal interstitial lattices and at other trap sites is in a thermal equilibrium as follows [39]:

$$\frac{\theta_T}{1-\theta_T} = \theta_L exp\left(\frac{E_b}{RT}\right) \qquad [1]$$

where E_b is the trap binding energy (the trap binding energy of each trap site is summarized in Table. 3 [24-26,43,44]), R is the gas constant (8.31 J mole^{-1}K^{-1}), T is the absolute temperature, θ_L is the occupancy of the interstitial sites and θ_T is the occupancy of other trap sites. The total hydrogen concentration, C_H^T, which represents the sum of the hydrogen stored in the normal interstitial lattice and all the trap sites is expressed as:

$$C_H^T = \theta_L N_L + \sum \theta_{Ti} N_{Ti} + C_{pore} \qquad [2]$$

where N_L and N_{Ti} are the trap densities in the normal interstitial lattice and the i^{th} trap sites other than micro pores in atoms per unit volume, respectively.

At an unloading state, Parker, et al. reported that the dislocation density is 2.5×10^{13} m^{-2} in Al-Zn-Mg-Cu aluminum alloys with the help of the electron back scattered diffraction (EBSD) technique [45]. The average grain size was 20 μm [16] as measured using an optical microscope after etching polished samples by means of the Barker's method. The precipitate density was 2.7×10^{23} m^{-3}, which was determined via the transmission electron microscope (TEM) observations operated at 30 kV [46]. The volume fraction, number density and spatial distribution of both hydrogen micro pores and intermetallic particles were calculated through the X-ray tomography images.

According to Calister, et al., vacancy concentration is expressed as [47]:

$$C_0 = \exp(-\frac{Q_{f1}}{k_B T}) \qquad [3]$$

where the vacancy formation energy Q_{f1} is taken to be 0.66 eV [47] in the absence of hydrogen, k_B is Boltzmann's constant (8.62×10^{-5} eV/atom) and T is the absolute temperature. Both the molecular hydrogen (C_{H_2}) and adsorbed hydrogen ($C_{H_{adsorbed}}$) are trapped within the hydrogen micro pores, and thus, the trapped hydrogen content in the hydrogen micro pore is calculated as [30,48]:

$$C_{pore} = C_{H_{adsorbed}} + C_{H_2} \qquad [4]$$

The content of adsorbed hydrogen in the micro pores is expressed as follows:

$$C_{H_{adsorbed}} = \theta_s N_s \qquad [5]$$

where θ_s is the occupancy of adsorbed hydrogen at the surface of the micro pores and N_s is the trap density of adsorbed hydrogen at the surface of the micro pores. The gas pressure of a hydrogen micro pore is in thermal equilibrium with the surface energy of the aluminum matrix [30], based on Eq. [6]:

$$P = 4\gamma/d \qquad [6]$$

where P is the internal gas pressure, d is the diameter of a pore and γ is the surface energy of aluminum. The surface energy of aluminum is reduced by the adsorbed hydrogen trapped at the surface of a hydrogen micro pore and is expressed as:

$$\gamma = \gamma_0 - \left(E_S + RTln(\theta_L)\right)\frac{N_S\theta_S}{N_A A} \qquad [7]$$

where the original surface energy is γ_0=1J/m^2 [48]. E_S= 67.2 kJ mol^{-1} [44] is the

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$$C_{H_2} = 2N_A \frac{4\gamma V}{dRT} \quad [8]$$

where V is the volume of a hydrogen micro pore.

Huang, et al. reported that the total dislocation density under loading is calculated as [49]:

$$\rho = \rho_{GND} + \rho_{SSD} \quad [9]$$

where ρ_{SSD} is the statistically stored dislocation (SSD) density and ρ_{GND} is the geometrically necessary dislocation (GND) density. SSD tends to be accumulated by trapping other dislocations in a random way while GND is required for compatible deformation of various parts of a material [50]. Brinckmann, et al. proposed the calculation for SSD density as follows [51]:

$$\rho_{SSD} = \frac{\sqrt{3}\ \bar{\varepsilon}^p}{bl} \quad [10]$$

where $\bar{\varepsilon}^p$ is the equivalent plastic strain and the Burgers vector is b=0.286 nm. The mean free path of dislocation motion l is the half of a single dislocation slip distance inside a grain [52]. The value of the mean free path is taken as $l = \frac{\sqrt{2}}{2}\mathrm{D} = 14\ \mu\mathrm{m}$ [16]. According to Paneda, et al. [53], the GND density is calculated as:

$$\rho_{GND} = \bar{r}\frac{\eta^p}{b} \quad [11]$$

where the Nye-factor is $\bar{r}$=1.9 in face center cubic (fcc) alloys [53] and η^p is the equivalent plastic strain gradient.

SSD and GND distributions calculated from the equivalent strain (ε_{eq}) mapping, viewed on the y-z (RD-ND) cross-section in both the High Fe Si-high H_2 and the Low

Fe Si-high H_2 specimens under the applied strain, $\Delta\varepsilon_a$ of 4.5 % are shown in Fig. 6. The SSD distribution is consistent with the equivalent strain distribution, as shown in Fig. 6 b) and e). The high GND concentration regions observed in the High Fe Si-high H_2 specimen are attributed to the isolated, small regions with a high strain concentration located in the strain localization region, as shown in Fig. 6 c). In contrast, high GND concentration regions are mainly located at the interface of the strain localization region in the Low Fe Si-high H_2 specimen, as shown in Fig. 6 f). The average GND density in the Low Fe Si-high H_2 specimen is higher compared with that in the High Fe Si-high H_2 specimen, which is mainly attributed to a more intense strain localization behavior and a higher strain gradient during deformation.

On the other hand, Clouet, et al. revealed that excess vacancies are formed in the strain localization region due to dislocation plasticity [54]. Militzer, et al. proposed that the vacancy formation rate under loading is expressed as [55]:

$$\frac{dC_v}{dt} = \chi\frac{\Omega_0\sigma}{Q_{f2}}\dot{\varepsilon} + \zeta\frac{C_j\Omega_0}{4b^3}\dot{\varepsilon} - \frac{D_v\rho}{\kappa^2}C_v - \frac{D_v}{L^2}C_v \qquad [12]$$

where

σ is the flow stress, Ω_0=1.65×10^{-29} is the atomic volume, $\dot{\varepsilon}$ is the strain rate, Q_{f2}=0.35 eV is the formation energy of the vacancy in the presence of hydrogen [56], b is Burgers vector, ζ describes the neutralization effect induced by the presence of

Witzel proposed that the second term is only applied in the temperature range over 0.4 of the melting temperature [57], thus, the second term is not considered in the present research, which was performed at room temperature. In the presence of hydrogen, the majority of vacancies are instantaneously trapped and stabilized by hydrogen after initiation. It is therefore reasonable to assume that the vacancies do not annihilate. The formation rate of vacancies under a high hydrogen concentration is then expressed as:

$$\frac{dC_v}{dt} = \chi \frac{\Omega_0 \sigma}{Q_f} \dot{\varepsilon} \qquad [13]$$

By integrating Eq [13], the vacancy concentration under different applied strain is expressed as:

$$\mathrm{C_v} = \chi \frac{\sigma \Omega_0}{Q_f} \varepsilon + C_0 \qquad [14]$$

where ε is the true strain and C_0=8.3 × 10^{-4} [58] is the initial vacancy concentration.

Comparisons of the hydrogen trapping behavior between the whole specimen at the unloading state and the region ahead of the hydrogen-induced quasi-cleavage crack tip (i.e. a selected region that is 20 μm in diameter) at an applied strain, $\Delta\varepsilon_a$ of 4.5 % in the Low Fe Si-high H_2 specimen is shown in Fig. 7. Hydrogen atoms are mainly trapped at interstitial lattice, precipitates and hydrogen micro pores due to their high trap densities and high hydrogen trap binding energies at the unloading state. With an increase in applied strain levels, excess vacancies and dislocations are generated in the strain localization region ahead of the crack tip and hydrogen atoms are mainly trapped at vacancies, precipitates and hydrogen micro pores. Of note, the trapped hydrogen content at vacancies at an applied strain of 4.5 % was approximately 10^6 times higher compared with that at the unloading state, indicating that hydrogen atoms accumulated and mainly repartitioned to vacancies in the strain localization region during loading, as shown in Fig. 7 a). Although hydrogen induced strain localization was observed in the Low Fe Si-high H_2 specimen, Fig. 7 a) reveals that the repartitioned hydrogen content to dislocations was far lower than the content of hydrogen trapped at other trap sites due to its low hydrogen trap binding energy. In addition, the trap site occupancy of dislocation is approximately 10^{-6}, which is approximately 10^4 times lower compared with that at precipitates and vacancies. It can be inferred that the influence of hydrogen trapped at dislocations on hydrogen-induced quasi-cleavage cracks might be negligible considering the repartitioned hydrogen content and hydrogen trap occupancy ahead of the quasi-cleavage crack tip during deformation.

The spatial concentration mapping of the repartitioned hydrogen at dislocations, vacancies and precipitates calculated from the equivalent strain (ε_{eq}) mapping in both the High Fe Si-high H_2 and Low Fe Si-high H_2 specimens are shown in Fig. 8. Fracture surfaces along the RD-ND virtual cross-sections are also shown and are marked as the solid black lines in Fig. 8. The hydrogen-induced strain localization has a significant influence on the content of hydrogen repartitioned to dislocations, vacancies and precipitates during deformation. For instance, hydrogen atoms are repartitioned to dislocations in the strain localization region during deformation, especially along the entire fracture surface, as shown in Fig. 8 a) and d). However, the content of hydrogen repartitioned to dislocations in the strain localization region is approximately 10^7 times lower compared with that repartitioned to vacancies and precipitates, indicating the limited effects of hydrogen concentrated at dislocations to the initiation and propagation of hydrogen-induced quasi-cleavage cracks during deformation.

Based on the issues mentioned above, a hydrogen embrittlement model considering the thermal equilibrium among various hydrogen trap sites and related in-situ hydrogen repartitioning in the strain localization region was proposed, as shown in Fig. 9. Due to the vacancy production and dislocation multiplication in the strain localization region, hydrogen atoms migrate, accumulate and repartition among various trap sites in the strain localization during deformation. It is worth noting that the content of repartitioned hydrogen to dislocations is far lower than that to vacancies and precipitates, indicating that the repartitioning of hydrogen is affected by both the hydrogen trap density and the hydrogen trap binding energy of each hydrogen trap site. In addition, Yamaguchi, et al. studied the effects of multiple hydrogen concentrations along grain boundaries on the hydrogen-induced intergranular fracture in Al-Zn-Mg-Cu aluminum alloys by analyzing the cohesion strength of grain boundaries with different grain boundary energies (i.e. $\Sigma3(111)$GB, $\Sigma3(112)$GB and $\Sigma5(012)$GB, etc.) in the presence of hydrogen using first-principles simulations [24]. It is concluded that the cohesion strength of grain boundaries decreases with an increase in the content of hydrogen trapped at the grain boundaries. The critical content of hydrogen atoms concentrated at grain boundaries for the occurrence of hydrogen-induced intergranular crack is approximately 2.8×10^{22} atoms H/m^3, which is approximately 3×10^5 times higher than the content of hydrogen trapped at grain boundaries of Al-Zn-Mg-Cu aluminum alloys at the unloading state (i.e. 9.9×10^{16} atoms H/m^3) [16]. This result indicates that a highly localized repartitioning of hydrogen due to hydrogen-induced strain localization during deformation is necessary for the occurrence of hydrogen-induced cracking. Therefore, the initiation and propagation of hydrogen-induced quasi-cleavage cracks might be attributed to hydrogen repartitioned to precipitates during deformation in the present research.

In the previous research, Wei, et al. studied the hydrogen trapping behavior of TiC precipitates with different interface coherencies in both quenched and tempered 0.05C-0.20Ti-2.00Ni steels, reporting that the trap activation energy (E_a) for hydrogen to semicoherent TiC precipitates and incoherent TiC precipitates is 55.8 KJ/mol and 85.0 KJ/mol, respectively [59]. Takahashi, et al. revealed that hydrogen is mainly trapped at the carbon vacancy on the (001) broad interface between the coherent V_4C_3 precipitates and ferrite matrix in VC precipitation strengthening steels, as observed by atom probe tomography (APT) technique [60]. In addition, Nagao, et al. studied the effects of nano sized (Ti, Mo) C precipitates on the hydrogen trapping and hydrogen-induced fracture behavior in lath martensitic steels [61-62]. It is proposed that hydrogen was trapped at the interface between nano sized (Ti, Mo) C precipitates and the matrix, which promoted the decohesion of precipitates and resulted in the initiation and propagation of hydrogen-induced quasi-cleavage cracks along the {110} lath boundaries during plastic deformation in lath martensite steels. However, neither hydrogen-induced precipitate decohesion nor the propagation of hydrogen-induced quasi-cleavage cracks along the (Ti, Mo) C precipitate/matrix interface was observed in their research. In addition, the hydrogen trap binding energy of high-angle grain boundaries (e.g. 57.4 KJ/mol) is much higher than that of lath boundaries (e.g. 25.7 KJ/mol) and precipitates (e.g. 30.5 KJ/mol) in their research, indicating that hydrogen should be mainly concentrated at grain boundaries instead of at lath boundaries and precipitates due to its high hydrogen trap binding energy [63]. In terms of hydrogen trapping behavior among various trap sites, the mechanism for why the hydrogen-induced fracture process is dominated by the initiation and propagation of quasi-cleavage cracks along the precipitates/matrix interface and lath boundaries instead of by intergranular cracking along grain boundaries remains unclear. Tsuru, et al. studied the hydrogen trapping behavior at $MgZn_2$ precipitates, including both interstitial sites inside the precipitates and at the interface between $MgZn_2$ precipitates and the matrix in Al-Zn-Mg-Cu aluminum alloys using first-principles simulations [26]. It is proposed that hydrogen atoms are mainly trapped at the $[0001]_{MgZn2}//[111]_{Al}$ interface, and they reported that the hydrogen trap binding energy of the most favorable site at the interface is approximately 0.35 eV/H. In addition, it is reported that the cohesion strength of the interface between the precipitates and matrix decreases with an increase in the content of hydrogen trapped at the interface. It is worth noting that the amount of hydrogen for the occurrence of precipitates decohesion is 17.8 atoms H/nm^2, which is approximately 2.5 times higher than the content of hydrogen concentrated at the precipitates (i.e. 7.3 atoms H/nm^2) as calculated through hydrogen repartitioning analysis during plastic deformation in the present research. This difference is mainly because the hydrogen repartitioning analysis only considers the generalized hydrogen behavior for repartitioning to precipitates and the practical hydrogen concentration at each individual precipitate, and in particular, the influence of the size and shape of the precipitates to the localized hydrogen accumulation was not considered in the present research. For individual, plate-shaped precipitate located on the $\{111\}_{Al}$ planes [46], it can be inferred that hydrogen is mainly trapped at the angular corners with the lowest curvature due to the hydrostatic tension concentration during deformation. With an increase in applied strain levels, hydrogen atoms continue to migrate and accumulated at the angular corners of precipitates, leading to a localized decohesion when the content of repartitioned hydrogen exceeds the critical value of 17.8 atoms H/nm^2. As a result, it is reasonable to assume that a hydrogen-induced decohesion of precipitates along the $\{111\}_{Al}$ planes at low applied strain levels during deformation provides both possible fracture initiation sites and a propagation path for hydrogen-induced quasi-cleavage cracks in Al-Zn-Mg-Cu aluminum alloys.

4. Conclusions

Hydrogen-induced premature fracture and the related hydrogen embrittlement behavior in high Zn (10 mass% Zn) Al-Zn-Mg-Cu aluminum alloys with different intermetallic particle contents were studied in the present research. The following conclusions were obtained:

1. Intermetallic particles are one of the hydrogen trap sites in Al-Zn-Mg-Cu aluminum alloys. The areal fraction of hydrogen-induced quasi-cleavage cracks decreases with an increase in the content of intermetallic particles, indicating an enhancement in the resistance to hydrogen embrittlement due to the existence of intermetallic particles.
2. Quantitative assessment of localized hydrogen repartitioning behavior during deformation was performed to understand the hydrogen embrittlement behavior in Al-Zn-Mg-Cu aluminum alloys. The hydrogen repartitioning behavior is strongly dependent on pre-existing intermetallic particles, vacancies and precipitates instead of dislocations due to their high hydrogen trap densities and high hydrogen trap binding energies.
3. Since the concentration of hydrogen trapped at dislocations is extremely limited, it can be assumed that a high hydrogen concentration at the interface between the precipitates and the aluminum matrix due to the repartitioning of hydrogen results in the decohesion of precipitates along $\{111\}_{Al}$ planes in the strain localization region during deformation, where quasi-cleavage cracking might originate.

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Table captions:

Table.1 Chemical compositions of the three alloys (mass %)

Table.2 Areal fractions of the quasi-cleavage cracks

Table. 3 Hydrogen trap binding energies of each hydrogen trap site in Al-Zn-Mg-Cu aluminum alloys

Figure captions:

Fig.1 Geometry of an in-situ tensile test specimen

Fig. 2 Nominal stress-strain curves for the in-situ tensile tests. It is worth noting that nominal stress-strain curve of Mid Fe Si-high H_2 has already been applied in Ref [15].

Fig.3 Fracture surfaces after the in-situ tensile tests; a) High Fe Si-low H_2 specimen, b) High Fe Si-high H_2 specimen, c) Mid Fe Si-high H_2 specimen [15] and d) Low Fe Si-high H_2 specimen; the quasi-cleavage crack region is identified by yellow solid lines.

Fig.4 4D observations of the initiation and propagation of the quasi-cleavage crack in High Fe Si-low H_2 under different applied strains; a) ε_a = 0.0 %, b) ε_a = 6.3 % and c) ε_a = 8.6 %; in High Fe Si-high H_2 under different applied strains; d) ε_a = 0.0 %, e) ε_a = 1.0 % and f) ε_a = 4.4 % and that in Low Fe Si-high H_2 under different applied strains; h) ε_a = 0.0 %, i) ε_a = 2.4 % and j) ε_a = 6.9 % Hydrogen micro pores are shown in red and the quasi-cleavage crack is shown in yellow

Fig. 5 The equivalent strain (ε_{eq}) distribution under different applied strains, viewed on the y-z (RD-ND) cross-section; a) equivalent strain map calculated between ε_a of 2.1 and 6.3 % in High Fe Si-low H_2, b) equivalent strain map calculated between ε_a of 0 and 4.4 % in High Fe Si-high H_2 and c) equivalent strain map calculated between ε_a of 2.4 and 6.9 % in Low Fe Si-high H_2. Fracture surface is shown as the black line.

Fig. 6 SSD and GND densities calculated from the equivalent strain (ε_{eq}) mapping under different applied strains, viewed on the y-z (RD-ND) cross-section; a) equivalent strain map calculated between ε_a of 2.1 and 6.3 % in High Fe Si-high H_2, b) SSD density calculated from a), c) GND density calculated from a); d) equivalent strain map calculated between ε_a of 2.4 and 6.9 % in Low Fe Si-high H_2, e) SSD density calculated from d) and f) GND density calculated from d). Fracture path is shown as the black line in a) and d).

Fig. 7 Comparisons of the hydrogen trapping behavior between the whole specimen at unloading state and a region ahead of the hydrogen-induced quasi-cleavage crack tip an applied strain of 4.5 % in Low Fe Si-high H_2 specimen; a) trapped hydrogen content and b) hydrogen trapping occupancy

Fig. 8 Hydrogen concentrations at various trap sites including dislocations, vacancies and precipitates that calculated from the equivalent strain (ε_{eq}) mapping at an applied strain, $\triangle\varepsilon_a$ of approximately 4.5 %, viewed on the y-z (RD-ND) cross-section; a) and d) is the hydrogen concentration at dislocations in High Fe Si-high H_2 and Low Fe Si-high H_2 specimen, b) and e) is the hydrogen concentration at vacancies in High Fe Si-high H_2 and Low Fe Si-high H_2 specimen and c) and f) is the hydrogen concentration at precipitates in High Fe Si-high H_2 and Low Fe Si-high H_2 specimen. Fracture surface is shown as the black line.

Fig.9 Schematic illustration of the influence of intermetallic particles to the hydrogen partitioning and related crack propagation in the strain localization region, a) high intermetallic particle content material and b) low intermetallic particle content material