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Influence of hydrogen on strain localization and fracture behavior in Al-Zn-Mg-Cu aluminum alloys

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Abstract

Hydrogen-induced dislocation motion is characterized in terms of the microscopic strain distribution in Al-Zn-Mg-Cu aluminum alloys. Hydrogen-induced strain localization was visualized in 3D using X-ray tomography and related microstructural tracking techniques. The strain localization was observed as a form of obliquely aligned shear bands. The strain localization becomes more intense with an increase in holding time at each loading step, indicating that more internal hydrogen is partitioned to the strain localization regions with holding time. In addition, the concentration of hydrostatic strain is observed in the strain localization region. Numerous nano voids were generated after deformation and were determined from the precise interpretation of the measured hydrostatic tension. Direct observation of the nano voids was then successfully performed by employing high-angle annular dark-field (i.e., HAADF) scanning transmission electron microscopy imaging and imaging-type computed tomography (CT) techniques. It is assumed that nano voids can serve a dual role as a fracture origin site and a hydrogen trap site. However, no evidence for hydrogen embrittlement originating from nano voids was observed. Instead, it can be assumed that the most hydrogen was partitioned to nano voids in strain localization regions during deformation due to its high density. A hydrogen embrittlement model was proposed based on these findings, where in-situ hydrogen repartitioning, which is necessary for hydrogen embrittlement to occur, is considered.

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

1. Introduction

The application of aluminum alloys has been undermined by hydrogen embrittlement arising from the high susceptibility of aluminum alloys to degradation in aggressive environments [1,2]. In the presence of hydrogen, hydrogen-induced cracks have appeared as either intergranular cracks [3] or brittle, cleavage-like transgranular cracks [4] leading to unexpected failure under strain levels far lower than the fracture strain of the materials. Therefore, it is reasonable to recognize hydrogen embrittlement as a formidable engineering problem since hydrogen induces the degradation of mechanical properties, especially in the fields of marine science, aerospace and nuclear power.

The resistance to hydrogen embrittlement is influenced by the temperature, chemical compositions and strength of materials [5,6]. The current understanding of hydrogen embrittlement is that hydrogen atoms enter materials, migrate as atomic hydrogen towards high internal stress regions and facilitate the initiation and propagation of cracks at low applied strains [7, 8]. With the help of thermal desorption spectroscopy (TDS), it has been identified that a range of microstructural defects, such as interstitial lattices, dislocations, grain boundaries and vacancies could be hydrogen trap sites in aluminum alloys [9,10]. Futhermore, Pressouyre, et al. revealed that atomic hydrogen tends to migrate from low binding energy trap sites to those with high binding energy, indicating that the migration of atomic hydrogen among various trap sites has a significant influence on hydrogen repartitioning and related hydrogen embrittlement behaviors [8]. Several mechanisms, including hydrogen-enhanced decohesion

(HEDE), hydrogen-enhanced localized plasticity (HELP) and hydrogen-enhanced strain-induced vacancies (HESIV), have been proposed to understand the actual mechanisms of hydrogen embrittlement in different materials [11-13]. According to the HEDE mechanism, hydrogen trapped at the grain boundaries decreases the cohesive atomic bonding strength, promoting crack initiation and propagation along grain boundaries at low applied strains [11]. Additionally, Birnbaum, et al. proposed the HELP mechanism, revealing that hydrogen trapped at dislocations enhances the dislocation mobility [12]. According to the HELP mechanism, it is suggested that slip localization such as planar slip may be promoted in the presence of hydrogen [14]. Finally, in the case of hydrogen-induced nano voids, the effects of hydrogen in the embrittlement process are characterized as the stabilization of vacancies and the promotion of vacancy agglomeration, causing the failure of materials through the coalescence of nano voids in steels [13].

Experimental studies and related finite element method (FEM) simulations have demonstrated that highly localized hydrogen-induced plastic deformation accelerates premature fracturing at low applied strain levels [15-17]. Scully, et al. revealed that hydrogen atoms that are partitioned ahead of a crack tip cause highly localized plastic deformation, accelerating the propagation of hydrogen-induced cracks in ultrahigh-strength steels [15]. Using an FEM simulation in nickel alloys, Liang, et al. proposed that hydrogen atoms trapped at dislocations can localize macroscopic deformation into the shear band [16]. Bhuiyan, et al. revealed that highly localized deformation induced by atomic hydrogen in Al-Zn-Mg-Cu aluminum alloys is time dependent, as evidenced by an increase in the hydrogen concentration ahead of a crack tip with the increase in holding time, and this result is attributed to hydrogen repartitioning ahead of the crack tip [18]. Therefore, the initiation and propagation of a hydrogen-induced crack might be related to the development of internal strain localization and hydrogen repartitioning in the strain localization region.

A 4D strain mapping technique [19], which enables the characterization of time-dependent 3D strain distributions, is thereby employed in the present research to reveal the time-dependent 3D development of hydrogen-induced strain localization during loading and hydrogen repartitioning in the strain localization region in order to identify the microstructural features that lead to the initiation and propagation of hydrogen-induced cracks in Al-Zn-Mg-Cu aluminum alloys.

2. Materials and experimental methods

2.1 Materials used

High Zn (10 % mass Zn) Al-Zn-Mg-Cu aluminum alloys were used in the present research. The chemical compositions were 10.00 Zn, 2.40 Mg, 1.50 Cu, 0.15 Zr, 0.04 Ti, 0.05 Si, 0.05 Fe and balance Al in mass%. The ingots were homogenized at 743 K for 24 hours, hot rolled at 673 K, solution treated at 748 K for 2 hours, and artificially aged at 393 K for 6 hours and 423 K for 5 hours, respectively. All the specimens were sampled along the rolling direction by an EDM (electro discharge machine) wire eroder for in-situ tensile tests. The dimensions of an in-situ tensile test specimen are shown in Fig. 1. In addition, hydrogen charging was also performed by the EDM cutting. During the EDM cutting process, numerous hydrogen atoms were absorbed into the materials due to the destruction of the oxide films of aluminum alloys and the absorption of atomic hydrogen from the external environment. According to the previous research, Bhuiyan, et al. revealed that the hydrogen concentration increased up to 6.97 mass ppm due to EDM cutting, which is approximately fifty times higher than that before EDM cutting (0.13 mass ppm) [18].

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

In-situ tensile tests were performed at BL20XU undulator beamline in SPring-8. The synchrotron X-ray beam was monochromated by a liquid nitrogen cooled Si (111) double-crystal monochromator. The applied photon energy was 20 keV. The image detector used in the present research consisted of a 2048 (H) × 2048 (V) element digital CMOS camera (ORCA Flash 4.0, Hamamatsu Photonics K.K.), a single-crystal scintillator (Pr: $Lu_3Al_5O_{12}$) and a 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, scanning 180 degrees in 0.1-degree increments were captured in each scan.

For the in-situ tensile tests, an X-ray tomography scan was first carried out without loading, and then, subsequent scans were performed. The influence of hydrogen repartitioning on the hydrogen embrittlement behavior in Al-Zn-Mg-Cu aluminum alloys was studied by holding an applied displacement for holding times (T_h) of 0.53 ks and 3.34 ks at each step. The specimen were named 10 Zn (T_h=0.53 ks) and 10 Zn

(T_h=3.34 ks), respectively, in the present research.

2.3 Image processing and analyses

Image slices were reconstructed from 1800 radiographs though a series of projections based on the conventional filtered backprojection algorithm. A linear absorption coefficient of -30 to 40 cm^{-1} was collected to fit the 8-bit grayscale from 0 to 255. Various parameters, such as the volume, surface area and diameter, of individual particles and hydrogen micro pores were computed based on the marching cubes algorithm. To eliminate inaccuracies originating from image noise, only features over 9 voxels in volume were recognized as particles and hydrogen micro pores in the present research.

Precise image registration was performed through transformation matrices to minimize the distance of identical particles captured at neighboring loading steps before particle tracking. Identical particles under different loading steps were tracked from the last loading step to the unloading state using microstructural feature tracking (MFT) [19]. Coefficients α, β and γ used for the MFT technique were 0.8, 0.1 and 0.1, respectively. High-density 3D strain mapping was achieved by calculating the displacement of identical particles under different loading steps. Further details of the MFT technique and 3D strain mapping are available elsewhere [19-21].

2.4 Finite element method (FEM) simulation

An image-based 3D FEM simulation is applied for the present research to determine the 3D geometry of a specimen on the hydrostatic strain concentration during the in-situ tensile test. Fig. 2 shows the procedure for generating a 3D FEM model based on the 3D images. A surface triangular mesh model was exported as an STL file and used for mesh generation for an FEM simulation, as shown in Fig. 2b). To suppress the number of elements to a reasonable level, the aspect ratio of the triangular elements was semi-automatically modified. The Ramberg-Osgood model was applied to the FEM simulation [22]. The von Mises yield criterion and isotropic hardening rule were applied in the present simulation. The plastic constitutive behavior was assigned by the true stress-strain curve of over-aged 7150 aluminum alloy, as shown in Fig. 3 a). Young's modulus (E) and Poisson's ratio (v) were set as E=70,200 MPa and v=0.34, respectively [23]. A forced displacement of 100 μm was applied along the z-direction for the present simulation. In addition, various simulation conditions, including boundary conditions, are shown in Fig. 3 b).

2.5 Microstructure observation

3D characterization of nano voids was performed at BL20XU undulator beamline in SPring-8. Imaging-type CT, which offers state-of-the-art resolution ($(62\ \mathrm{nm})^3$ in size), was performed at 20 keV. A detailed illustration of the setup is available elsewhere [24]. The system was composed of a beam diffuser, high precision stages, a center beam stop, a condenser zone plate (CZP), a Fresnel zone plate (FZP), a Zernike phase plate (ZZP) and an X-ray image detector. The X-ray image detector used in the present research consisted of a cooled CMOS camera (as mentioned in Section 2.2), a powder scintillator (Gd_2O_2S: Tb) and a lens. In general, 1800 radiographs scanning 180 degrees in 0.1-degree increments were captured in each scan.

Furthermore, an FEI Tecnai-F20 TEM equipped with a charge-coupled device camera and an HAADF detector, was also applied to observe nano voids at an accelerating voltage of 200 kV. The focused electron probe size for the HAADF-STEM was approximately 0.3 nm to obtain relatively exact Z (atomic number)-contrast images. Specimens for the TEM observation were prepared using a focused ion beam (FIB) micro-sampling technique. All FIB processes were performed at an accelerating voltage of 30 kV using an FEI Quanta 3D 200i FIB. Gluing and mechanical grinding were avoided to prevent any mechanical damage.

3. Results

3.1 Hydrogen-induced damage evolution behavior

Stress-strain curves for the in-situ tensile tests are shown in Fig. 4. The vertical drops in the load, shown in Fig. 4, are attributed to the stress relaxation behavior of the material during the CT scans. The fracture strain of Al-Zn-Mg-Cu aluminum alloys is decreased from approximately 15 % to 6 % with an increase in holding time from 0.53 ks to 3.34 ks, as shown in Fig. 4. Decreasing in the fracture strain with the increase in holding time implies that hydrogen-induced fracture is time-dependent, which may be attributed to the hydrogen migration and accumulation ahead of a crack tip.

Fracture surfaces after the in-situ tensile tests are shown in Fig. 5. The fracture surfaces of both the 10 Zn (T_h=0.53 ks) and 10 Zn (T_h=3.34 ks) specimens are composed of quasi-cleavage cracks and fine dimples throughout a crack path.

Quasi-cleavage cracks are initiated near the surface of the specimen, propagated and gradually transformed into ductile dimple fractures with the increase in distance from the specimen surface towards the center, as shown in Fig. 5 a) and b). The areal fraction of quasi-cleavage cracks is 9.7 % in 10 Zn (T_h=0.53 ks) and 18.8 % in 10 Zn (T_h=3.34 ks). The areal fraction of quasi-cleavage cracks increased by approximately 50 % with the increase in holding time, suggesting that the resistance to hydrogen embrittlement drastically decreased with the increase in holding time in the present Al-Zn-Mg-Cu aluminum alloys.

A series of 3D perspective views of hydrogen micro pores and voids near the quasi-cleavage cracks in the 10 Zn (T_h=0.53 ks) specimens under different applied strains are shown in Fig. 6 a)-c). The underlying intermetallic particles and aluminum matrix are not displayed. Hydrogen micro pores are distributed uniformly in the matrix, as shown in Fig. 6 a). Two neighboring quasi-cleavage cracks are initiated near the surface at a strain of 8.3 %, and they propagated and coalesced with an increase in the applied strain levels, as shown in Fig. 6 c). Growth of pre-existing hydrogen micro pores and the nucleation of voids due to the fracture of intermetallic particles are observed ahead of the quasi-cleavage crack tip at an applied strain of 12.0 %, as shown in Fig. 6 c). In contrast, the quasi-cleavage crack was initiated at an applied strain of 1.5 % in the 10 Zn (T_h=3.34 ks) specimen, as shown in Fig. 6 e). The quasi-cleavage crack was initiated just after yielding was reached, and it propagated at a relatively low applied strain range from 1.5 to 5.5 %, as shown in Fig. 6. Almost no growth of pre-existing hydrogen micro pores nor the nucleation of voids was observed during the in-situ tensile tests. The density of dimples ahead of the quasi-cleavage crack in 10 Zn (T_h=0.53 ks) specimen was thereby higher compared to that of the 10 Zn (T_h=3.34 ks) specimen due to the nucleation of voids at high applied strain levels (12.0 %), as shown in Fig. 6 c). Unlike typical brittle fracture in metals, quasi-cleavage cracks were initiated and gradually propagated with an increase in the applied strain, as shown in Fig. 7. The growth rate of the quasi-cleavage crack ($dl/d\varepsilon_a$) in 10 Zn (T_h=3.34 ks) was 0.17 μm, which was approximately 50 % faster than that of 10 Zn (T_h=0.53 ks) (0.12 μm), as shown in Fig. 8. It is noteworthy that the initiation and propagation of the quasi-cleavage cracks accelerated with the increase in holding time, leading to the premature fracture of Al-Zn-Mg-Cu aluminum alloys at an applied strain of approximately 6 %.

3.2 Hydrogen-induced strain localization

The 3D strain mapping observed along the y-z (RD-ND) virtual cross-section of 10 Zn (T_h=3.34 ks) is shown in Fig. 9. Fracture trajectory analysis [25] was applied to quantitatively assess the role of strain localization in relation to the entire fracture. The fracture surface along the y-z (RD-ND) direction was extracted from tomographic images after loading and accurately combined with the equivalent strain map, shown as a solid black line in Fig. 9 a). The strain map reveals a highly heterogeneous strain in all the strain components, especially along the fracture surface in the strain localization region, as shown in Fig. 9. Regions of high equivalent strain appear to be located in a band oriented in an oblique direction (approximately 45°)

with respect to the loading direction. The equivalent strain in the flow localization region is approximately 12 %, which is almost three times higher than the applied strain range ($\triangle\varepsilon_a$=4.4 %), as shown in Fig. 9 a). The concentration and movement behavior of dislocations in the presence of hydrogen are also illustrated in terms of the microscopic strain distribution, as shown in Fig. 9 a). This implies that hydrogen trapped at dislocations accelerates dislocation planar slip and results in microscopic strain localization along the shear direction, as proved by Liang, et al. through an FEM simulation [16]. In addition, the most of high hydrostatic concentration regions are located beneath the entire fracture surface, as shown in Fig. 9 e). Such highly localized hydrostatic tension might be attributed to the heterogeneous formation of vacancies ahead of the quasi-cleavage crack tip in the presence of hydrogen [13].

The influence of strain localization on the initiation and propagation of the quasi-cleavage cracks is illustrated in Fig. 10. In Fig. 10, the local equivalent strain is expressed as normalized equivalent strain ($\varepsilon_{\mathrm{eq}}/\varepsilon_{\mathrm{ave}}$) values to better illustrate the localized deformation behaviors with high viewability. The normalized equivalent strain distribution on the x-z (TD-RD) cross-section, which is marked as a red line on the fracture surface of Fig. 10 a) (10 Zn (T_h= 0.85 ks)) and Fig. 10 d) (10 Zn (T_h= 3.34 ks)) is demonstrated in Fig. 10 b), c), e) and f), respectively. The strain localization region is located in the center of the specimen before the initiation of the quasi-cleavage crack, as shown in Fig. 10 b) and e). With the increase in applied strain levels, the areal fraction of the strain localization region decreases due to the initiation of the quasi-cleavage crack, as shown in Fig. 10 c) and f). The area of the strain localization region decreases and is transformed into a band along the shear direction with the increase in holding time, as shown in Fig. 10 f). It can be inferred that more dislocations are concentrated in a narrower region with the increase in holding time, resulting in a more intense localized plasticity in 10 Zn (T_h= 3.34 ks) compared to that in 10 Zn (T_h= 0.85 ks). This result qualitatively coincides with the modeling approach of Robertson, et al., in which they demonstrated, hydrogen trapped at newly formed dislocations accelerates the planar slip, resulting in shear localization at low applied strain levels [14].

4. Discussion

4.1 Hydrogen-induced time-dependent fracture behavior

Fig**.** **7** and Fig. 8 reveal that quasi-cleavage cracks with a higher growth rate are initiated at a lower applied strain levels in the 10 Zn (T_h= 3.34 ks) specimens compared to that in the 10 Zn (T_h= 0.85 ks) specimens, indicating that the initiation and propagation of quasi-cleavage cracks due to pre-charged internal hydrogen is time-dependent. Subsequent 3D strain mapping revealed that the time-dependent fracture behavior is attributed to a more intense strain localization at lower applied strain levels in the 10 Zn (T_h= 3.34 ks) specimens, as shown in Figs. 9 and 10. According to Albrecht, et al., internal hydrogen atoms tend to migrate and accumulate in the strain localization region through diffusion and dislocation transportation [26]. Consequently, it can be inferred that more hydrogen atoms tend to accumulate and become trapped among various trap sites in the strain localization region with the increase in holding time for each applied displacement. Furthermore, the strain localization region has been observed as a form of obliquely aligned shear bands, revealing the motion and concentration of dislocations in the presence of hydrogen, as shown in Fig. 9. Several studies have observed a microstructure beneath the hydrogen-induced quasi-cleavage cracks and revealed that hydrogen partitioned at dislocations in the strain localization region decreases the initial stress for dislocation motion and accelerates the planar slip of dislocations through locking and immobilizing dislocations to a specific slip system, thereby promoting the initiation and propagation of quasi-cleavage cracks [14,26-29]. The dislocation behavior, in terms of the microscopic strain distribution illustrated in Fig. 9, is consistent with the hydrogen embrittlement mechanism mentioned above. Therefore, it can be inferred that the time-dependent initiation and propagation of hydrogen-induced quasi-cleavage cracks is attributed to the amount of hydrogen accumulated in the strain localization region.

4.2 Hydrogen-induced formation of nano voids

Fig. 11 shows the hydrostatic strain map for 10 Zn (T_h= 0.53 ks) and 10 Zn (T_h= 3.34 ks). A high hydrostatic strain concentration in the strain localization region is observed, especially along the propagation path of the quasi-cleavage crack, indicating volume expansion due to the formation of vacancies in the presence of hydrogen [30,31]. Birnbaum, et al. proposed that the volume expansion of aluminum is attributed to hydrogen traps at interstitial lattices and vacancies [32]. Toda, et al. revealed hydrogen micro pores in aluminum alloys show premature growth, which leads to volume expansion under loading [33]. Therefore, volume expansion ($\frac{\triangle V}{V_0}$) is expressed as:

$$\frac{\triangle V}{V_0} = C_v\frac{\delta_v}{\Omega} + C_H^{lattice}\frac{\delta_H^{lattice}}{\Omega} + V_{mp} + \varepsilon_{\hbar}^{geo} \qquad [1]$$

where C_v is the concentration of vacancies and $\frac{\delta_v}{\Omega}$=0.51 is the magnitude of expansion due to a vacancy in Al [32]. $C_H^{lattice}$ is the concentration of hydrogen trapped in the interstitial lattice and $\delta_H^{lattice}$ is the volume expansion due to the introduction of hydrogen into lattices in an fcc solid with a value of 0.28 nm^3 [32]. For the atomic volume of Al (Ω), this corresponds to $\frac{\delta_H^{lattice}}{\Omega}$=0.168 per H atom [32]. V_{mp} is the volume expansion due to the growth of hydrogen micro pores during the in-situ tensile test, and the value is 19.6×10^{-5} for 10 Zn (T$_{\mathrm{h}}$= 0.53 ks) and 4.9×10^{-5} for 10 Zn (T$_{\mathrm{h}}$= 3.34 ks). $\varepsilon_{\hbar}^{geo}$ is the volume expansion due to the geometric factors of the specimen, and the value is 0.00028.

Wriedt, et al. revealed that the concentration of hydrostatic stress induces an increase in the amount of hydrogen trapped at interstitial lattice sites during deformation, as expressed as [34]:

$$C_H^{lattice} = \mathrm{C}_0 \exp\left(\frac{\sigma_h V_H}{3RT}\right) \qquad [2]$$

where the original hydrogen content C_0=1.01×10^{16} atoms H/cm^3, the hydrostatic stress σ_h=63.6 MPa (obtained from FEM simulation), the partial molar volume of hydrogen V_H= 2 cm^{-3}mol H [35], the gas constant, R=8.314 Jmol^{-1} K^{-1} and temperature T=298 K.

Militzer, et al. proposed that the rate of vacancy formation during deformation is given by [36]:

$$\frac{dC_v}{dt} = \Pi - \eta \qquad [3]$$

where Π is the initiation rate of vacancies and is expressed as:

$$\Pi = \chi \frac{\Omega_0 \sigma}{Q_f} \dot{\varepsilon} + \zeta \frac{C_j \Omega_0}{4b^3} \dot{\varepsilon} \qquad [4]$$

where χ=0.1 is the dimensionless constant [36], σ=703.8 MPa is the flow stress, Ω_0=1.65×10^{-29} is the atomic volume, $\dot{\varepsilon}$ is the strain rate, Q_f is the energy of vacancy formation, b is the Burgers vector, ζ describes the neutralization effect induced by the presence of vacancy emitting and vacancy absorbing jogs, and C_j is the concentration of thermal jogs. Moreover, the vacancy annihilation rate is given by:

$$\eta = \frac{D_v \rho}{\kappa^2} c_v + \frac{D_v}{L^2} c_v \qquad [5]$$

where D_v is the vacancy diffusivity, ρ is the dislocation density, L is the grain size, κ is a parameter representing the distribution of dislocations, and c_{ex} is the excess vacancy concentration.

Eq [4] can be expressed as:

$$\frac{dC_v}{dt} = \chi \frac{\Omega_0 \sigma}{Q_f} \dot{\varepsilon} + \zeta \frac{C_j \Omega_0}{4b^3} \dot{\varepsilon} - \frac{D_v \rho}{\kappa^2} c_v - \frac{D_v}{L^2} c_v \qquad [6]$$

Witzel proposed that the second term is only applied in the temperature range 0.4 above the melting temperature [37], and so, the second term is not considered in the present research performed at room temperature. In the presence of hydrogen, vacancies are stabilized by hydrogen and are not annihilated; therefore, η seems to approach zero as an approximation. The formation rate of vacancies under a high hydrogen concentration is expressed as:

$$\frac{dC_v}{dt} = \chi \frac{\Omega_0 \sigma}{Q_f} \dot{\varepsilon} \qquad [7]$$

By integrating Eq [7], the vacancy concentration under different applied strains is expressed as:

$$\mathrm{C_v} = \chi \frac{\sigma \Omega_0}{Q_f} \varepsilon + C_0 \qquad [8]$$

where ε is the true strain and C_0 is the initial vacancy concentration. In addition, Polatoglou, et al. revealed that the vacancy formation energy at the (111) surface in bulk aluminum is 0.66 eV [38]. In the presence of hydrogen, Mastumoto, et al. proposed that hydrogen decreases the vacancy formation energy to 0.35 eV using a first-principles simulation [39].

A comparison of the volume expansion of the measured value from the hydrostatic strain map (as shown as Fig. 11) and the calculated value using Eq. [1] with a vacancy formation energy of 0.66 eV and 0.35 eV are shown in Fig. 12. The volume expansion increases with the increase in holding time, indicating that the migration and accumulation of hydrogen in the flow localization region is time-dependent. In addition, the volume expansion calculated using Eq. [1] increases with the decrease in the vacancy formation energy. The calculated values using Eq. [1] for the two in-situ tensile test specimens are both approximately 0.0008 for Q_f= 0.66 eV and 0.0010 for Q_f= 0.35 eV, since the macroscopic applied strain range and flow stress are similar for these two in-situ tensile tests. It is worth noting that the calculated value is lower than the measured value, indicating that some unknown microstructural features, in addition to the interstitial lattice, vacancies and micro pores, also promote the volume expansion during deformation in Al-Zn-Mg-Cu aluminum alloys.

TEM observation, is thereby applied to identify microstructural features in the strain localization region during deformation in the present Al-Zn-Mg-Cu aluminum alloys. Microstructural features such as grain boundaries, dislocations and precipitates are observed in the bright field images, as shown in Fig. 13 a) and c). In addition, nano voids that induce volume expansion are distinguished from precipitates and dislocation pileups with the help of HAADF-STEM, which provides a direct interpretation of the chemical order as well as an atomic configuration of the structure, as shown in Fig. 13 b) and d) [13, 40]. At the unloading state, only a few of nano voids, which are 3-5 nm in size, are observed to be located along the grain boundaries, as shown in Fig. 13 b). With the increase in the applied strain to 5 %, both the size and number density of nano voids increase with the increase in the applied macroscopic strain, as shown in Fig. 13 d). The newly formed nano voids, which are approximately 10 nm in size, distribute uniformly in the matrix, and clusters of nano voids are not observed, as shown in Fig. 13 d). Fig. 14 shows the size and number density distribution of voids under different applied strain levels. Voids observed by HAADF-STEM, imaging-type CT and projection-type CT are all applied to identify the initiation and growth of voids under loading. Due to the destruction of an oxide film, various hydrogen atoms enters the materials and become trapped at various trap sites, such as vacancies, interstitial lattices, intermetallic particles, dislocations and grain boundaries, during a casting process. According to Toda, et al, hydrogen micropores are formed during the homogenization process and remain after extensive plastic deformation, such as the rolling process [24,41]. The number density of hydrogen micropores ranges from 10^{10} to $10^{12}/\mathrm{m}^3$, marked as blue points in Fig. 14 a). On the other hand, hydrogen is accumulated and partitioned at newly formed vacancies in the strain concentration region, leading to the stabilization of vacancies and the formation of nano voids during the rolling process. The size of newly formed nano voids distributes from approximately 5 nm to 500 nm, marked as the red and yellow points in Fig. 16 a). With the increase of applied strain to 5 %, nano voids of approximately 5 to 30 nm in size are initiated, as shown in Fig. 13 d) and 14 b). The number density of the newly formed nano voids is around 10^{19} to $10^{20}/\mathrm{m}^3$, which is ten times higher than that for the unloaded state. In addition, it can be seen that the most frequently observed size range of the hydrogen micropores is not remarkably different, only very coarse hydrogen micropores of approximately 8 μm or even larger were observed, due mainly to the growth and coalescence at the applied strain of 5 %.

Hydrogen-induced nano voids can potentially serve as both a hydrogen trap site and a fracture origin during a hydrogen-induced fracture process. Nagumo, et al. proposed that hydrogen trapped at vacancies stabilizes vacancies and promotes the agglomeration of vacancies to form nano voids, leading to the propagation of hydrogen-induced cracks from the coalescence of nano voids [42]. Martin, et al. have reported that a quasi-cleavage crack is generated from nano voids initiated at slip band intersections which are associated with the strain relaxation process. This occurs after the final decohesion or the separation in a strain localization region in terms of the HELP mechanism [43]. Based on the observation of the quasi-cleavage crack morphology as well as the related underlying microstructure, Neeraj, et al. also revealed dense dislocations and excess nano voids beneath a quasi-cleavage crack. However, the authors have mentioned that the propagation of a quasi-cleavage crack is mainly attributed to the growth and coalescence of nano voids instead of the decohension or separation in the strain localization region [44]. In the present research, both TEM observation (as shown in Fig. 13) and 3D observation via imaging-type CT revealed that nano voids are distributed uniformly in the strain localization region, and neither a localized concentration nor the coalescence of nano voids has been observed during deformation [45]. However, no evidence of hydrogen embrittlement originating from nano voids has been observed. It can be inferred that nano voids mainly act as one of the main hydrogen trap sites in the strain localization region and play a significant role in the repartitioning process of internal hydrogen due to their high density in Al-Zn-Mg-Cu aluminum alloys.

Based on the above mentioned issues in Sections 4.1 and 4.2, a hydrogen embrittlement model considering in-situ hydrogen repartitioning has been proposed, as shown in Fig. 15. The time-dependent behavior of hydrogen-induced quasi-cleavage cracks have revealed that, unlike typical cleavage cracks in steels, there exists a criterion of repartitioned hydrogen in the strain localization region which allows the propagation of quasi-cleavage cracks to occur. With an increase in holding time, a higher concentration of hydrogen is repartitioned in the strain localization region, indicating that more hydrogen atoms are trapped at newly formed dislocations and vacancies, as well as other trap sites in the strain localization region. Vacancies are stabilized, and they coalesce into nano voids in the presence of hydrogen. Additionally, they are reported to be trap sites for both molecular and atomic hydrogen [24,46]. On the other hand, hydrogen atoms trapped at dislocations increase the mobility of dislocation [12], leading to the propagation of quasi-cleavage cracks. In addition, Xie, et al. reported time-dependent dislocation locking/unlocking due to hydrogen-vacancy complexes based on an individual dislocation level observation through TEM, indicating that interactions between dislocations and hydrogen-vacancy complexes suppress the hydrogen-dependent dislocation motion and localized hydrogen embrittlement behavior [47]. Therefore, it is reasonable to assume that hydrogen repartitioning and related embrittlement behavior is strongly dependent on nano voids due to its high hydrogen trap density together with the presence of hydrogen micro pores, vacancies, intermetallic particles and dislocations [17,48]. Importantly, hydrogen repartitioning can be controlled by changing the content and species of microstructural features thereby controlling the resistance to hydrogen embrittlement.

5 Conclusion

The influence of hydrogen on the strain localization and fracture behavior of high Zn (10 mass% Zn) Al-Zn-Mg-Cu aluminum alloys was studied. The following conclusions were obtained:

1. Hydrogen-induced strain localization that results in premature fracture at a low applied strain is observed with the help of a 3D strain mapping technique. With a decrease in the holding time, the location of the strain localization region changes from the center of the specimen to a band along the shear direction. Hydrogen trapped at dislocations in the strain localization region accelerate the dislocation motion, resulting in shear localization in 10 Zn (T_h= 3.34 ks) specimen.
2. The hydrostatic strain concentration along the fracture surface is attributed to the initiation of vacancies and nano voids in the strain localization region during loading. Numerous internal hydrogen atoms are repartitioned at vacancies and nano voids due to their high density in the strain localization region during loading.
3. In-situ hydrogen repartitioning among various hydrogen trap sites such as dislocations, vacancies and nano voids in the strain localization region is considered necessary for hydrogen embrittlement to occur. The hydrogen repartitioning behavior can be controlled to improve the resistance to hydrogen embrittlement by changing the content and species of the hydrogen trap sites.

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Reference

[1] I.W. Huang, B.L. Hurley, F. Yang, R.G. Buchheit, Electrochim. Acta. 199 (2016) 242–253.

[2] R.S. Yassar, D.P. Field, H. Weiland, Acta Mater. 53 (2005) 299.

[3] A. King, G. Johnson, D. Engelberg, W. Ludwig, J. Marrow, Science. 321 (2008) 382–386.

[4] R.N. Parkins, W.K. Blanchard, B.S. Delanty, Corrosion. 50 (1994) 394–408.

[5] R.N. Parkins, Corros. Sci. 20 (1980) 147–166.

[6] G.A. Young, J.R. Scully, Metall. Mater. Trans. A. 33 (2002) 1297–1297.

[7] A.T. Yokobori. Jr, Y. Chinda, T. Nemoto, K. Satoh, T. Yamada, Corros. Sci. 44 (2002) 407–424.

[8] G.M. Pressouyre, Acta Metall. 28 (1980) 895–911

[9] G.A. Young, J.R. Scully, Acta Mater. 46 (1998) 6337–6344.

[10] T. Izumi, G. Itoh, Mater. Trans. 52 (2011) 130–134.

[11] W.W Gerberich, R.A Oriani, M. Li, X. Chen, T. Foecke. Philos Mag A. 63(1991)363–76.

[12] H.K Birnbaum, P. Sofronis. Mater Sci Eng A. 176(1994)191–202.

[13] M. Nagumo. Mater Sci Technol. 20(2004)940–50.

[14] I. M. Robertson: Eng. Fract. Mech. 68(2001) 671–92

[15] R.L.S. Thomas, J.R. Scully, R.P. Gangloff, Metall. Mater. Trans. A. 34 (2003) 327–344.

[16] Y. Liang, P. Sofronis and N. Aravas: Acta Mater. 51(2003) 2717-30

[17] H. Su, T. Yoshimura, H. Toda, S. Bhuiyan, K. Uesugi, A. Takeuchi, et al., Metall. Mater. Trans. A. 47 (2016) 6077–6089.

[18] M.S. Bhuiyan, Y. Tada, H. Toda, H.Su, K. Uesugi, A. Takeuchi, et al., , Int. J. Fract. (2016) 1-17.

[19] M. Kobayashi, H. Toda, Y. Kawai, T. Ohgaki, K. Uesugi, D.S. Wilkinson, et al., Acta Mater. 56 (2008) 2167–2181.

[20] H. Toda, T. Kamiko, Y. Tanabe, M. Kobayashi, D.J. Leclere, K. Uesugi, et al., Acta Mater. 107 (2016) 310–324.

[21] H. Toda, A. Takijiri, M. Azuma, S. Yabu, K. Hayashi, D. Seo, et al., Acta Mater. 126 (2017) 401–412.

[22] A. Hosokawa, H. Toda, R. Batres, H. Li, O. Kuwazuru, M. Kobayashi, et al., Mater. Sci. Eng. A. 671 (2016) 96–106.

[23] M.M. Sharma, M.F. Amateau, T.J. Eden, Acta Mater. 53 (2005) 2919–2924.

[24] H. Toda, T. Hidaka, M. Kobayashi, K. Uesugi, A. Takeuchi, K. Horikawa, Acta Mater. 57 (2009) 2277–2290.

[25] H. Toda, H. Oogo, K. Horikawa, K. Uesugi, A. Takeuchi, Y. Suzuki, et al., Metall. Mater. Trans. A. 45 (2013) 765–776.

[26] J. Albrecht, A.W. Thompson, and I.M. Bernstein, Metall. Trans. A, 10 (1979)

1759–66.

[27] M.L. Martin, B.P. Somerday, R.O. Ritchie, P. Sofronis, I.M. Robertson, Acta Mater. 60 (2012) 2739–2745.

[28] G.M. Pressouyre, Acta Metall. 28 (1980) 895–911.

[29] X.H. Hu, M. Jain, D.S. Wilkinson, R.K. Mishra, Acta Mater. 56 (2008) 3187–3201.

[30] H. Toda, T. Kamiko, Y. Tanabe, M. Kobayashi, D.J. Leclere, K. Uesugi, et al., Acta Mater. 107 (2016) 310–324.

[31] M. Hatano, M. Fujinami, K. Arai, H. Fujii, M. Nagumo, Acta Mater. 67 (2014) 342–353.

[32] H.K. Birnbaum, C. Buckley, F. Zeides, E. Sirois, P. Rozenak, S. Spooner, et al., J. Alloys Compd. 253–254 (1997) 260–264.

[33] H. Toda, H. Oogo, K. Uesugi, M. Kobayashi, Mater. Trans. 50 (2009) 2285–2290.

[34] H. Wriedt, R.A. Oriani, Acta Metall. 18 (1970) 753–760.

[35] J. Chêne, Mécanismes Mécanique Des Interact. Plast. - Environ. 2007 (2009) 131–145.

[36] M. Militzer, W.P. Sun, J.J. Jonas, Acta Metall. Mater. 42 (1994) 133–141.

[37] W. Witzel, Z. Metallkd. 64 (1973) 585-589

[38] H.M. Polatoglou, M. Methfessel, M. Scheffler, Phys. Rev. B. 48 (1993) 1877–1883.

[39] T. Enomoto, R. Matsumoto, S. Taketomi, N. Miyazaki, Zair. Soc. Mater. Sci.

Japan. 59 (2010) 596–603.

[40] E. Abe, Y. Kawamura, K. Hayashi, A. Inoue, Acta Mater. 50 (2002) 3845–3857.

[41] H. Toda, K. Minami, K. Koyama, K. Ichitani, M. Kobayashi, K. Uesugi, et al., Acta Mater. 57 (2009) 4391–4403.

[42] M. Nagumo, M. Nakamura, K. Takai, Metall. Mater. Trans. A32 (2001) 339–347.

[43] M.L. Martin, I.M. Robertson, P. Sofronis,Acta Mater. 59 (2011) 3680–3687.

[44] T. Neeraj, R. Srinivasan, J. Li, Acta Mater. 60 (2012) 5160–5171.

[45] H.Y. Gao, et al. Mater Trans. In press.

[46] R. Kirchheim, B. Somerday, P. Sofronis, Acta Mater. 99 (2015) 87–98.

[47] D. Xie, S. Li, M. Li, Z. Wang, P. Gumbsch, J. Sun, et al., Nat. Commun. 7 (2016) 1–7.

[48] H. Su, M.S. Bhuiyan, H. Toda, K. Uesugi, A. Takeuchi, Y. Watanabe, Scripta. Mater. 135 (2017) 19–23.

Figure captions

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

Fig. 2 Procedure to obtain a 3D FE model; a) 3D rendered image of an in-situ tensile test specimen, b) meshing result and c) magnified views of meshing in the gauge of the specimen.

Fig. 3 Schematic illustration of the FEM simulations; a) Plastic constitutive behavior of the material and b) Typical boundary condition for FEM simulations

Fig. 4 Nominal stress-strain curves for the in-situ tensile tests

Fig. 5 Fracture surfaces after the in-situ tensile tests; a) 10Zn (T_h=0.53 ks) specimen, b) 10Zn (T_h=3.34 ks) specimen, c) magnified views of the quasi-cleavage crack in 10Zn (T_h=0.53 ks) specimen and d) magnified views of the quasi-cleavage crack in 10Zn (T_h=3.34 ks) specimen

Fig. 6 4D observations of the initiation and propagation of the quasi-cleavage crack in 10 Zn (T_h=0.53ks) under different applied strains; a) ε_a = 0.0 %, b) ε_a = 8.3 % and c) ε_a = 12.0 % and that in 10 Zn (T_h=3.34ks) under different applied strains; a) ε_a = 0.0 %, b) ε_a = 1.5 % and c) ε_a = 5.5 %. Hydrogen micro pores are shown in red and the quasi-cleavage crack is shown in yellow

Fig. 7 3D rendered images of a quasi-cleavage crack under different applied strains; a) the quasi-cleavage crack in 10 Zn (T_h=0.53ks) specimen, b) the quasi-cleavage crack in 10 Zn (T_h=3.34ks) specimen

Fig. 8 Growth rates ($dl/d\varepsilon_a$) of the quasi-cleavage cracks during the in-situ tensile tests

Fig. 9 Strain maps on a y-z (RD-ND) virtual cross-section of 10 Zn (T_h=3.34ks). Plastic strain is calculated between applied strain, ε_a, of 1.1 and 5.5 %. Plotted are: a) equivalent strain, ε_{eq}; b) normal strain in the x (TD) direction, ε_{xx}; c) normal strain in the y (ND) direction, ε_{yy}; d) normal strain in the z (RD) direction, ε_{zz}; e) hydrostatic strain, ε_h; f)shear strain in the x-y direction, γ_{xy}; g) shear strain in the y-z direction, γ_{yz} and h) shear strain in the x-z direction, γ_{xz}

Fig. 10 Representation of the normalized equivalent strain distribution (ε_{eq} / ε_{ave}) ahead of the quasi-cleavage crack tip; a) Fracture surface of 10 Zn (T_h=0.53 ks) and extracted x-z cross section used for b) and c) is marked as red line, b) normalized equivalent strain map is calculated between ε_a of 5.1 and 8.4%, c) normalized equivalent strain map is calculated between ε_a of 8.4 and 12.1%, d) Fracture surface of 10 Zn (T_h=3.34ks) and extracted x-z cross section used for e) and f) is marked as red line, e) normalized equivalent strain map is calculated between ε_a of 0 and 3.8% and f) normalized equivalent strain map is calculated between ε_a of 3.8 and 5.5 %. Fracture surface is shown as the blackline in b), c), e) and f).

Fig. 11 Hydrostatic strain (ε_h) distribution viewed on the y-z (RD-ND) cross-section under different test conditions. a) hydrostatic strain map calculated between ε_a of 2.1 and 6.8 % in 10 Zn (T_h=0.53ks), b) hydrostatic strain map calculated between ε_a of 1.1 and 5.5 % in 10 Zn (T_h=3.34 ks).

Fig. 12 Comparisons of total vacancy concentration between the measured value and theoretical calculation. a) is calculated between ε_a of 2.1 and 6.8 % in 10 Zn (T_h=0.53ks), b) is calculated between ε_a of 1.1 and 5.5 % in 10 Zn (T_h=3.34 ks)

Fig. 13 Observations of nano voids in Al-Zn-Mg-Cu aluminum alloys at different applied strains; a) is the bright-field image of the identical cross-section as in b) at the unloading state b) HAADF-STEM image and nano voids are marked by the black arrows, c) is the bright-field image of the identical cross-section as in d) at an applied strain, ε_a, of 5 %, d) HAADF-STEM image and nano voids are marked by the black arrows.

Fig. 14 Changes in the number density and size of nano voids and hydrogen micro pores under different applied strain levels in Al-Zn-Mg-Cu aluminum alloys; a) is at unloaded state and b) is at an applied strain, ε_a, of 5 %

Fig. 15 Schematic illustration of the influence of nano voids on hydrogen partitioning and related crack propagation in a strain localization region