九州大学学術情報リポジトリ
Kyushu University Institutional Repository

In-situ 3D observation of hydrogen-assisted particle damage behavior in 7075 Al alloy by synchrotron X-ray tomography

Wang, Yafei
Department of Mechanical Engineering, Kyushu University

Toda, Hiroyuki
Department of Mechanical Engineering, Kyushu University

Xu, Yuantao
Department of Mechanical Engineering, Kyushu University

Shimizu, Kazuyuki
Department of Physical Science and Materials Engineering, Iwate University

他

https://hdl.handle.net/2324/6792838

出版情報：Acta materialia. 227, pp.117658-, 2022-04-01. Elsevier
バージョン：
権利関係：

KYUSHU UNIVERSITY

In-situ 3D observation of hydrogen-assisted particle damage behavior in 7075 Al alloy by synchrotron X-ray tomography

Yafei Wang [a, b, *], Hiroyuki Toda [a], Yuantao Xu [a], Kazuyuki Shimizu [c], Kyosuke Hirayama [d], Hiro Fujihara [a], Akihisa Takeuchi [e], and Masayuki Uesugi [e]

[a] *Department of Mechanical Engineering, Kyushu University, Fukuoka 819-0395, Japan*
[b] *School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China*
[c] *Department of Physical Science and Materials Engineering, Iwate University, Iwate 020-8551, Japan*
[d] *Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*
[e] *Japan Synchrotron Radiation Research Institute, Hyogo 679-5198, Japan*
**Corresponding author: wang.yafei.626@m.kyushu-u.ac.jp; yafeiwang@xjtu.edu.cn.*

Abstract:

We directly captured, classified, and evaluated 3D particle debonding and fracture behavior in a H-charged 7075 Al alloy throughout the entire tensile deformation using synchrotron X-ray tomography and microstructural feature tracking techniques. The effects of particle size, shape, spatial clustering and stress state on strain-dependent particle damage were identified and isolated from each other. Moreover, state-of-the-art imaging and tracking techniques enabled the establishment of spatially and time-resolved hydrogen distributions during deformation. Based on realistic hydrogen partitioning among various nanoscopic trap sites, the contributions of particles to hydrogen trapping and the hydrogen effect at individual damaged particles were assessed quantitatively. Fracturing of coarse and irregular Al_7Cu_2Fe particles was found to be the predominant particle damage mode due to the spatial clustering and brittleness of these particles, but a hydrogen effect was not observed. The debonding of Mg_2Si particles seemed to be the result of competition between hydrogen and clustering-induced stress localization, but detrimental effects of hydrogen on ductile fracture induced by accelerating interfacial debonding were found to be limited. The quantitative evaluation of particle damage in the present model material clarified a viable strategy for mitigating hydrogen embrittlement, which involves introducing and modifying intermetallic particles with strong hydrogen trapping capacities.

Keywords: Hydrogen embrittlement; Al alloy; Debonding; Particle; X-ray tomography.

1. Introduction

Hydrogen is detrimental to the mechanical properties of various metallic materials. This deleterious effect, known as hydrogen embrittlement (HE), is especially dramatic for high strength Al alloys [1, 2]. The hydrogen in Al can either come from fabrication (e.g., aging) [3, 4] or environmental oxidation [5, 6], and it causes a dramatic decrease in ductility and toughness.

Despite extensive prior research, the precise role of hydrogen in triggering premature fracture remains controversial; a variety of HE mechanisms have been proposed, including dislocation-based mechanisms [7, 8], vacancy mechanisms [9, 10], and decohesion mechanisms [11, 12]. These mechanisms may coincide, contradict or interact with each other in different cases [13, 14]. Regardless of the mechanisms involved, the introduction of strong hydrogen traps can mitigate HE by reducing hydrogen concentrations at microstructures responsible for HE. For Al alloys, multiple studies have indicated that micron-scale intermetallic particles trap hydrogen with high binding energies [15, 16]. It was further proven experimentally that hydrogen-induced quasi-cleavage cracks can be suppressed by intermetallic compound particles (i.e., Fe-bearing and Si-bearing particles) [17]. First-principle calculations showed hydrogen trapping in the interior of Al_7Cu_2Fe particles with a binding energy of 54.0 kJ/mol [18] and lent theoretical support for the beneficial effects of these particles in suppressing HE. The authors also confirmed the strong trapping capacity available at incoherent Mg_2Si interfaces.

However, micron-scale particles have been suggested to play a negative role in HE based on the decohesion mechanism, which assumes that hydrogen reduces the cohesive strength of atomic bonds at particle-matrix interfaces [12, 19]. For hydrogen-induced brittle fracture, it was proposed that the hydrogen enhanced decohesion occurring at particle-matrix interfaces promotes embrittlement [19]. For ductile fracture, hydrogen changes the void distribution near the fracture surface [20] and was found to enhance void initiation and/or void growth [21, 22]. Although more convincing evidence is still needed for the effect of hydrogen on particle damage, due to the limitations of traditional characterization methods, it is reasonable to assume that the particles can exhibit dual and opposite effects (hydrogen trapping vs. interface debonding) on HE. Quantitative evaluation of these effects is of great importance.

Moreover, Fe-bearing particles (including Al_7Cu_2Fe) are typically the main initiation sites for damage/cracks in 7XXX Al alloys and are harmful to mechanical properties [23, 24], whereas Mg_2Si particles are much less harmful [25]. These findings have been rationalized in a recent study using micropillar compression tests for 7075-T651 Al alloy, which showed that Al_7Cu_2Fe is completely brittle while Mg_2Si exhibits considerable ductility (up to 10%) [26]. In addition, multiple researchers have investigated the hydrogen-assisted fracture in high-strength Al alloys, in which the damage of intermetallic particles was frequently observed. Using *in-situ* X-ray synchrotron tomography, Sundar et al. [27] confirmed the presence of voids ahead of the corrosion-fatigue cracks in over-aged Al 7075 alloy and these voids were assumed to be initiated from damaged particles. The authors [28, 29] also studied the corrosion damage evolution during the potentiodynamic polarization scan in 7075-T651 alloy using 3D XMT and evidenced pitting initiation from Al_7Cu_2Fe particles, which are generally consistent with the studies of Gudla et al., [30] indicating that, with pre-exposure to corrosive environment, the hydrogen-assisted cracking for 5083 Al alloy is related to the intermetallic particles. However, more rigorous confirmation of void initiation from intermetallic particles and its contribution to hydrogen embrittlement in high-strength Al alloys is still needed due to the difficulty of capturing the onset and evolution of particle damage.

In this study, the 3D debonding and fracture behaviors of Al_7Cu_2Fe and Mg_2Si particles during tensile deformation of a H-charged 7075 Al alloy were directly captured and classified with synchrotron X-ray microtomography (XMT) and related microstructural feature tracking (MFT) technique. This overcomes the misclassifications of particle breakage, debonding and pre-existing voids in conventional 2D observations, providing more convincing evidence for particle damage mechanisms. Through *quasi in-situ* tensile tests with frequent interruptions at very small strain increments (with a total number of up to 24 steps), the onset of particle damage and its strain-dependent evolution as a function of particle diameter and sphericity were investigated in detail. In addition, the 3D statistics and distributions of various hydrogen trap sites (i.e., particles, pores, and dislocations) were determined precisely, which allowed the establishment of spatially and time-resolved hydrogen distributions. In this way, the local strain and local hydrogen occupancy at each particle damaged during the deformation process were obtained based on realistic 3D hydrogen partition behavior, which enables direct quantitative evaluation of the impact of hydrogen on particle damage. This progress was made possible by state-of-the-art imaging and tracking techniques and is expected to contribute to an in-depth understanding of the microdamage and HE mechanisms of Al alloys.

2. Materials and methods

2.1 Materials

The material used here was peak-aged A7075-T651 alloy, with a chemical composition in mass % as follows: 5.6 Zn, 2.6 Mg, 1.7 Cu, 0.2 Cr, 0.2 Fe, 0.07 Si, 0.02 Mn, 0.01 Ti and the balance Al. Flat specimens with cross-sectional areas of 0.6 mm × 0.6 mm were used for *in-situ* tensile tests [17]. The specimens were cut from Al plates by electrical discharge machining (EDM) in water, and hydrogen was naturally introduced. Based on thermal desorption analysis (TDA), the hydrogen content after EDM charging was confirmed to be 4.0 mass ppm (Suppl. Mater. Fig. S1). A typical feature of hydrogen-charged Al alloys is that a considerable amount of hydrogen remains in the material after one-round TDA. By using the vacuum effusion method, previous studies demonstrated a total hydrogen concentration of up to 6.97 mass ppm for 7XXX Al alloys after EDM charging, which can result in intergranular fracture with dramatic loss of ductility [31].

2.2 *In-situ* tensile testing via high resolution XMT

In-situ tensile tests were performed using projection-type XMT at the BL20XU undulator beamline in SPring-8. The monochromatic X-ray beam was produced by a liquid nitrogen-cooled Si (111) double-crystal monochromator. The applied photon energy was 20 keV. The image detector consisted of a digital CMOS camera (ORCA Flash 4.0: 2048 × 2048 pixel, Hamamatsu Photonics K.K.), a single-crystal scintillator (Ce: Lu_2SiO_5) and a lens (10×). The effective pixel size of the detector was 0.5 μm, and a sample-to-detector distance of 20 mm was utilized for absorption-contrast tomography.

Tensile tests were performed with a displacement rate of 0.02 mm/s using a miniature test rig (Deben UK Ltd) and yielded the nominal stress-strain curve shown in **Fig. 1**. At each step, the displacement was held constant for 10 min before performing another XMT scan, during which hydrogen redistribution inside the specimen is expected to occur without significant hydrogen loss due to the presence of surface oxide layer [32]. A total of 1800 radiographs, scanning 180° with a 0.1 degree increment, were captured in each scan. In total, 24 tomography scans were performed in the *in-situ* tensile tests, including the first scan in the unloading state. Notably, the fairly small strain increment (~ 1%) utilized in the present study allowed a thorough examination of particle damage behavior at different strain levels throughout the whole deformation process. Since in the present case the microstructural features in the specimen barely change during holding, we refer to such *quasi in-situ* tests with interruptions as *in-situ* tests.

2.3 Image-based particle/void tracking

The filtered back-projection algorithm was used to reconstruct the image slices from 1800 radiographs. The reconstructed 16-bit images were transformed into 8-bit images for subsequent analyses. An absorption coefficient range of -30~60 cm^{-1} was collected from the 16-bit images to fit the 8-bit grayscale from 0 to 255, with other unnecessary absorption coefficients abandoned. The three-dimensional microscopic features, i.e., Al_7Cu_2Fe, Mg_2Si and voids, were segmented by thresholding the grayscale histograms, using the grayscale ranges of 154~255, 52~97 and 0~44, respectively. The XMT images with a size of 2048 × 2048 px^2 were captured, whereas the region of interest for the time-consuming particle damage analysis was in the middle section with a height of 100 μm in the Z direction, and it covered the most severely necked region. Only the features over 9 voxels in volume were analyzed to minimize the effect of noise.

The particles and voids were precisely tracked along different steps based on the MFT technique. Specifically, using such technique the same characteristic features in consecutive 3D images were identified and matched after conducting the quantitative geometric analyses. First, an affine transformation was applied to register the 3D images in two loading steps, which is the key to the success of following tracking analysis. The matching probability parameter (M_p) was defined to evaluate the matching accuracy of particles before and after deformation, by comparing the gravity center, volume and surface area of these two particles, and a threshold M_p value was applied to filter out the mis-matched particles.

The MFT technique enables the 3D strain mapping and the classification of particle damage modes. For the generation of high-density 3D strain maps, the sample interior was divided into numerous tetrahedrons with the tracked Al_7Cu_2Fe particles (with a total number of 11, 460) as vertices. The classification of particle fracture and debonding was achieved in the following steps. First, voids that were successfully tracked from step 0 to step 24 were identified as pre-existing voids. By comparing those voids that could be back-tracked from step 24 to step n and those tracked from step 24 to step n-1, the voids generated at step n were identified. Particle debonding and fracture at different steps were classified by analyzing the voids and their neighboring particles: debonding was confirmed if only one particle was found adjacent to one void; however, particle fracture was identified if two particles were connected to one void. More details of the MFT technique and strain mapping method were provided elsewhere [33, 34].

2.4 Hydrogen partitioning analysis

For the purpose of hydrogen partitioning analysis, the trap site densities for grain boundaries, precipitates and solute Mg atoms were determined by microstructural observations. Grain sizes were determined by electron backscatter diffraction (EBSD) using electropolished specimens and a scanning electron microscope (SEM, JSM-IT800). Spherical aberration-corrected scanning transmission electron microscopy (STEM, JEOL ARM-200F) combined with a high-angle annular dark-field (HAADF) detector operated at an acceleration voltage of 200 kV was used to characterize the sizes, shapes and densities of precipitates. The atomic concentration of solute Mg atoms in the matrix was measured by energy dispersive X-ray spectroscopy (EDX). To avoid misunderstanding, we refer to micron-scale Al_7Cu_2Fe and Mg_2Si as intermetallic compound particles and the nanoscale η-($MgZn_2$) phase as precipitates.

3. Results

3.1 *In-situ* 3D visualization of particle damage

The 3D perspective views of Al_7Cu_2Fe, Mg_2Si and pores (pre-existing voids) in the 7075 Al alloy were obtained from XMT images, which exhibited specific spatial clustering along the rolling direction (Fig. S2). The total numbers of Al_7Cu_2Fe, Mg_2Si and voids in the entire specimen were approximately 1.0×10^5, 2.0×10^4 and 3.0×10^3, corresponding to number densities of 1.5×10^{14}, 3.0×10^{13} and 4.5×10^{12} $1/m^3$, respectively.

Virtual cross-sections in the *x*-*z* plane and the corresponding 3D perspective views with applied strains of 0.00%, 0.79% (yield point), 6.29%, 9.26% (maximum load), 15.6% and 22.2% are shown in **Fig. 2**. One microvoid initiated by Al_7Cu_2Fe via particle fracture can be clearly identified at an applied strain of 6.29% (**Fig. 2c**). The voids gradually grew and coalesced with further increases in strain, as shown in **Fig. 2d, e** and **f**. The 3D rendered image of the final step confirmed the presence of coalesced voids perpendicular to loading direction, but no internal quasi-cleavage cracks or intergranular cracks were observed. The SEM image of the fracture surface (Fig. S3) also shows the ductile fracture.

3.2 Strain-dependent particle debonding and fracture

Fig. 3 shows the number densities of fractured and debonded Al_7Cu_2Fe and Mg_2Si particles at different applied strains. For Al_7Cu_2Fe, the numbers of debonded and fractured particles were 40 and 231, and for Mg_2Si, the numbers of debonded and fractured particles were 36 and 37, respectively, in the region of interest with a height of 100 μm along the loading direction. **Fig. 3a** indicates that the number of fractured Al_7Cu_2Fe particles was much higher than that of debonded particles; rose sharply with applied strain, and a peak appeared after necking. For Mg_2Si, however, the numbers of fractured and debonded particles were similar, and they were more easily damaged before the maximum load (**Fig. 3b**). These two particles exhibited significantly different damage behaviors in two main respects. First, while Al_7Cu_2Fe shows preferential particle fracture, the number density of fractured and debonded Mg_2Si particles was similar throughout the whole deformation process; second, while the damage of Al_7Cu_2Fe was dramatically accelerated after necking, the damage of Mg_2Si was not apparently affected by the macrostrain. These observations provide valuable insights into the microdamage mechanisms of these two predominant particles in the present material.

Prior research revealed that particle damage can be strongly influenced by particle size and shape [35-37], spatial distribution [38, 39], mechanical properties of particles and the matrix [40], interfacial strength and hydrogen [19, 41]. The actual damage is thought to result from all of these factors, which can impact each other in complicated ways. One example is that changes in particle size and shape alter local stress distributions and, consequently, the hydrogen concentration and occupancy near particles due to stress-enhanced diffusion [42].

We further separated these related effects based on particle-related 3D quantitative data obtained by synchrotron XMT. First, the dependence of particle damage on particle size and shape was studied. The frequency distributions for damaged particles as a function of diameter and sphericity, as defined below, are plotted in **Fig. 4**.

$$F(\text{total}) = n_\text{i}/n_\text{total} \times 100 \quad (1)$$

$$F(\text{Fractured}) = n_\text{i\_f}/n_\text{damage} \times 100 \quad (2)$$

$$F(\text{Debonded}) = n_\text{i\_d}/n_\text{damage} \times 100 \quad (3)$$

where n_i is the number of particles for each diameter or sphericity, n_total is the total number of particles, $n_\text{i\_f}$ is the number of fractured particles for each diameter or sphericity, $n_\text{i\_d}$ is the number of debonded particles for each diameter or sphericity, and n_damage is the total number of damaged particles.

The frequency distributions shown in **Fig. 4** can be used to quantify the frequency difference between debonding and fracture and also their dependence on particle size and shape. **Fig. 4a** and **b** shows that the frequency distributions for all Al_7Cu_2Fe particles (including both undamaged and damaged particles) exhibited peak frequencies located at approximately $d = 2$ μm and $S = 0.8$, respectively. However, these most characteristic particles ($d = 2$ μm and $S = 0.8$) exhibited a low fracture tendency. Instead, the majority of the fractured Al_7Cu_2Fe particles had a relatively large diameter (d > 3 μm) and low sphericity (S < 0.7). For the debonded Al_7Cu_2Fe particles, however, the frequency distributions were more consistent with those of whole particles in terms of the peak locations. It can be concluded that fracture occurs more easily than debonding for large Al_7Cu_2Fe particles with low sphericity. For Mg_2Si particles, a similar tendency is shown in **Fig. 4c** and **d**: the frequency of fracture is slightly higher than that of debonding for large-diameter, low-sphericity particles.

It is expected that the number and frequency of damaged Al_7Cu_2Fe and Mg_2Si particles are strongly dependent on the total number of each type of particle. To further separate this effect, damage ratio distributions were plotted as a function of particle sizes and shapes, as shown in **Fig. 5**. The damage ratios, R_d, are defined as follows:

$$R_\text{d}(\text{Fractured}) = n_\text{F}/n'_\text{total} \times 100 \quad (4)$$

$$R_\text{d}(\text{Debonded}) = n_\text{D}/n'_\text{total} \times 100 \quad (5)$$

where n_F and n_D are the numbers of fractured and debonded particles, respectively; n'_total is the total number of particles for each diameter or sphericity.

Fig. 5 allows quantification of particle debonding and fracture tendencies as a function of particle size and shape, and these tendencies are not affected by the number of particles. **Fig. 5a** and **b** clearly indicate that the more likely damage mode for Al_7Cu_2Fe is fracture rather than debonding. Extremely high damage ratios, with the maximum value exceeding 60%, were observed for fractured particles with sizes of 12-15 μm, indicating a very high fracture probability for coarse particles. Debonded Al_7Cu_2Fe particles, however, exhibited fairly low damage ratios, regardless of particle diameter. It is clear from **Fig. 5c** and **d** that both fracture and debonding of Mg_2Si were enhanced by increasing particle size and decreasing sphericity. Increases in fracture probability with increasing particle sizes are usually attributed to the lower strengths of large particles, which arise from the higher probability that then contain defects [35]. The dependence of particle damage on sphericity can be explained by increased stress concentration at the sharp edges of irregular particles [43], which facilitates particle damage by either debonding or fracture. For debonding of Mg_2Si, the high damage ratios for large particles can be attributed to the decreases in interfacial strength seen with increasing size, as proposed in some studies employing energetic analyses [44].

Typical morphologies seen for Al_7Cu_2Fe and Mg_2Si particles prior to and after damage are shown in **Figs. 6** and **7**, respectively. The onset of particle damage and the precise locations of voids can be clearly identified. **Fig. 6a** shows that low-sphericity Al_7Cu_2Fe particles were typically coarse, spatially clustered, and prone to fracture. The morphologies of Mg_2Si particles, as presented in **Fig. 7**, indicated debonded and fractured particles with different sizes and shapes. As with Al_7Cu_2Fe, through-thickness microcracks were observed in the interiors of Mg_2Si particles. It is particularly evident from **Fig. 7a** that the Mg_2Si particles themselves underwent noticeable plastic deformation, as indicated by strain-induced elongation along the loading axis; this is consistent with the results of Singh et al. [26] and demonstrates the considerable plasticity of Mg_2Si. The first figure in **Fig. 7b** confirmed the occurrence of particle debonding at the sharp edge of Mg_2Si that is oriented roughly perpendicular to the loading direction, and this debonding is attributable to high local stress concentration at the sharp edges.

Existing studies have suggested, mostly by numerical simulation, that local stress distribution and stress triaxiality affect particle damage [45]. Herein, we summarize the effects of particle debonding and fracture in the uniform deformation and nonuniform deformation stages as a function of particle size and shape, as shown in **Fig. 8**. In general, particle sphericity decreases with increasing particle size. The yellow dots indicated by ‘A’ in **Fig. 8a** and **b** are due to white fringes around voids, which were artifacts inherently originating from particles (Fig. S4). **Fig. 8**a demonstrates rapidly accelerated void nucleation from fractured Al_7Cu_2Fe particles after application of the maximum load, in agreement with **Fig. 3**.

No evidence was observed for the dependence of particle debonding on stress triaxiality for either Al_7Cu_2Fe or Mg_2Si. The numerical predictions in the literature indicate that the critical strain triggering particle debonding can decrease exponentially with increasing stress triaxiality [45, 46]. However, such models are based on the stress-related criterion, which assumes that the critical stress for particle damage is the superposition of von Mises stress and a certain fraction of hydrostatic stress [47]. This assumption intrinsically implies that particle damage must depend on stress triaxiality. More evidence based on other criteria, such as the energy-based criterion, is needed. In terms of experiments, although the dependence of void growth on the stress state has been well reported [48], there is little data describing the effect of the stress state on void initiation. Some experimental observations of void initiation have inevitably included observations of void growth, due to the difficulty of capturing the onset of particle damage [49, 50].

Al_7Cu_2Fe and Mg_2Si particles exhibit different tendencies to experience damage (**Fig. 8**), and this is presumably not due to their sizes and shapes because both Al_7Cu_2Fe and Mg_2Si exhibit similar patterns in the sphericity-diameter plots. Instead, this is attributable to the combined effects of particle mechanical properties, particle clustering and hydrogen. It is well known that particle damage is enhanced by particle clustering due to the marked concentration of stress inside clustered regions [38, 39]. The extent of particle clustering for Al_7Cu_2Fe has been found to be more pronounced than that for Mg_2Si, as previously confirmed in **Fig. 6**. Moreover, particle damage is the result of a competition between particle fracture and debonding. The considerable ductility of Mg_2Si [26] can, to some extent, impede particle fracture and result in damage behavior differing from that of Al_7Cu_2Fe particles.

3.3 3D hydrogen partitioning analysis

In this section, the possible impact of hydrogen on particle damage is evaluated quantitatively by estimating hydrogen partitioning among various nanoscopic hydrogen trap sites. As suggested by thermal equilibrium theory [51], hydrogen atoms in materials are repartitioned among different trap sites and are in equilibrium with the hydrogen at normal lattice sites:

$$\frac{\theta_T}{1-\theta_T} = \theta_L exp\left(\frac{E_b}{RT}\right) \tag{6}$$

where E_b is the trap binding energy, R is the universal gas constant, T is the temperature, θ_T is the occupancy at trap sites, and θ_L is the occupancy at lattice sites.

The total hydrogen concentration, which can be determined from desorption tests, is the sum of hydrogen concentration at various trap sites and lattice sites:

$$C_H^T = \theta_L N_L + \sum \theta_{Ti} N_{Ti} + C_{pore} \tag{7}$$

Although the concept of thermal equilibrium was proposed decades ago, the spatial distribution of hydrogen still remains unclear in most cases. This is largely due to the difficulty in measuring spatial distributions of trap densities for different trap sites accurately. In the present study, the 3D statistics obtained from XMT images enabled spatially- resolved measurements of trap densities for different trap sites, including particles, pores, and dislocations. On this basis, hydrogen partitioning between lattice sites and different hydrogen traps was determined precisely, which enables the realistic and quantitative understanding of hydrogen distributions.

The binding energies for different trap sites used in the present study are: solute Mg atoms, 11.6 kJ/mol [52]; grain boundary, 19.3 kJ/mol [53]; screw dislocation, 10.6 kJ/mol [54]; edge dislocation, 17.4 kJ/mol [54]; vacancy, 28.9 kJ/mol [55]; pore, 67.5 kJ/mol [56]; the interior of Al_7Cu_2Fe particles, 54.0 kJ/mol [18]; coherent $MgZn_2$ interfaces, 7.9-33.9 kJ/mol [57]; semi-coherent $MgZn_2$ interfaces, 53.8 kJ/mol [58]. It should be noted that compared to our recent studies [17, 59], the binding energies of the incoherent Mg_2Si interfaces and semi-coherent $MgZn_2$ interfaces were nearly calculated and taken into consideration here. Specifically, binding energies for incoherent Mg_2Si interfaces can be classified into three categories for both Al-Mg sites and Al-Si sites: unstable interfaces, 77.2 (Al-Mg site) and 53.1 (Al-Si site) kJ/mol;

metastable interfaces, 67.5 (Al-Mg site) and 62.7 (Al-Si site) kJ/mol; and stable interfaces, 63.7 (Al-Mg site) and 33.8 (Al-Si site) kJ/mol, respectively [58]. All six interfaces were considered in the partition calculation, and equivalent proportions were assumed.

The representative cross-sections at the y-z plane were meshed using $20 \times 20 \times 20$ μm^3 unit boxes, assuming that a local equilibrium state was established in each unit box within a holding time of 10 min. The total hydrogen concentration was assumed to be identical, i.e., 4.0 ppm, for all unit boxes and remain constant during plastic deformation. Hydrogen partition analysis was performed for each unit box based on the position-dependent trap densities of various trap sites obtained from 3D quantitative analysis. For Al_7Cu_2Fe, the trap density was calculated based on particle volumes, based on the simulations indicating hydrogen trapping in the interior of particles [18]; for Mg_2Si, the trap density was calculated from the areas of particle surfaces, assuming hydrogen trapping at the interfaces [58]; for pores, the trap density was determined from pore volumes; for dislocations, the trap density was determined from 3D strain maps.

The total dislocation density is the sum of the statistically stored dislocation (SSD) density, ρ_{SSD}, and the geometrically necessary dislocation (GND) density, ρ_{GND}. Based on the strain maps generated at different loading steps, the spatial distributions of SSD and GND can be determined as follows:

$$\rho_{SSD} = \frac{\sqrt{3}\bar{\varepsilon}^p}{bl} \tag{8}$$

$$\rho_{GND} = \bar{r}\frac{\eta^p}{b} \tag{9}$$

where $\bar{\varepsilon}^p$ is the equivalent plastic strain and the Burgers vector is $b = 0.286$ nm [60]; η^p is the equivalent plastic strain gradient, the Nye-factor is $\bar{r} = 1.9$ in face centered cubic (fcc) alloys [61]; and l is the mean free path of dislocation motion, with its value taken as $l = 34$ μm.

Representative equivalent strain maps in the y-z plane calculated from step 1 to step 24 and the corresponding SSD and GND density maps are shown in **Fig. 9a−c**, respectively. A strain localization region is observed, which coincided with the slant-to-shear transition in the case of hydrogen-enhanced ductile fracture. The local equivalent plastic strain can be as large as 60% for the step just before fracture, indicating very intense local plastic deformation. Hydrogen-induced softening, on the basis of the hydrogen-enhanced local plasticity (HELP) mechanism, has been suggested to play an important role in shear fracture [62, 63].

Based on the average grain sizes determined at three different cross-sections by EBSD (Fig. S5), the trap density of the grain boundary was determined to be 1.12×10^{24} sites/m^3. The TEM images, shown in **Fig. 9d** and **e**, indicate disk-like η precipitates with coherent (top/bottom) and semi-coherent (side) interfaces. Both small and large precipitates were observed in the TEM images with equivalent diameters ranging from a few nanometers to over 50 nm and thicknesses ranging from 1 to over 20 nm. It was reported that both η and η' precipitates are visible in the 7075-T651 Al alloy; the η' phase particles were small, and the η phase particles were relatively coarse [64]. An average diameter of 15.5 nm, average height of 6.4 nm, and number density of 1.20×10^{23} 1/m^3 were used for the hydrogen partitioning analysis. In this way, the trap densities of coherent and semi-coherent interfaces at precipitates were determined to be 1.41 × 10^{27} and 2.08× 10^{26} sites/m^3, respectively. The average atomic concentration of solute Mg atoms in the Al matrix was determined to be 2.68% by EDS measurement, corresponding to a hydrogen trap density of 1.61× 10^{27} sites/m^3 at solute Mg atoms.

A large number of vacancies could be generated during deformation and serve as effective hydrogen traps [65, 66]. At room temperature the vacancy concentration during deformation, C_v, can be expressed as a linear function of strain, with negligible vacancy annihilation [59]:

$$C_v = \chi \frac{\sigma \Omega_0}{Q_f} \varepsilon + C_0 \tag{10}$$

where χ = 0.1 is a dimensionless constant [67], σ is the flow stress, Ω_0 is the atomic volume, Q_f = 53.1 kJ/mol is the formation energy of vacancies, and $C_0 = 8.3 \times 10^{-4}$ is the initial vacancy concentration at the unloading state [68].

The trap density of hydrogen micropores was precisely calculated based on the volume fraction obtained from quantitative analyses of XMT images and by assuming that the hydrogen gas inside the pores was in equilibrium with the hydrogen atoms at the surfaces of pores. The details for the calculation of the trap density of pores are provided elsewhere [59].

We first examined the hydrogen partitioning behavior at the final step just before fracture. The average hydrogen concentrations and occupancy levels at various trap sites are presented in **Fig. 10a** and **b**. The hydrogen concentrations at lattice sites, GBs, and dislocations were fairly low compared with those of the other trap sites; this was due to their low binding energies, even for the final step with severe local plastic deformation. A very large amount of hydrogen was trapped at Al_7Cu_2Fe particles, and the average hydrogen concentration was more than two orders of magnitude higher than that at incoherent Mg_2Si interfaces. This large difference arose because there were many fewer trap sites present on two-dimensional particle-matrix interfaces than in the interiors of particles. The hydrogen occupancy at Mg_2Si, however, was quite high (close to unity) due to the high binding energies at incoherent interfaces.

Spatially inhomogeneous distributions of different trap sites (e.g., particles, pores and dislocations) can result in position-dependent hydrogen partitioning within a finite period of time. Hydrogen occupancies at semi-coherent $MgZn_2$ interfaces and incoherent Mg_2Si interfaces, i.e., $\theta_{\mathrm{Mg_2Si}}$ and $\theta_{\mathrm{MgZn_2}}$, as well as trap site densities of Al_7Cu_2Fe at different locations, are shown **Fig. 10c**, where they are sequenced from highest to lowest $\theta_{\mathrm{MgZn_2}}$. The increase in the local trap density for Al_7Cu_2Fe particles resulted in a more than three orders of magnitude reduction in $\theta_{\mathrm{MgZn_2}}$, indicating a remarkable hydrogen trapping effect. The discontinuity of the trap density for Al_7Cu_2Fe was due to strong trapping by micropores, which also reduced the occupancy levels at precipitates. Since the hydrogen binding energy at Al_7Cu_2Fe was much higher than that of coherent $MgZn_2$-matrix interfaces, the hydrogen occupancy at precipitates was extremely sensitive to the local volume fraction of Al_7Cu_2Fe. However, $\theta_{\mathrm{Mg_2Si}}$ was not significantly affected by neighboring Al_7Cu_2Fe particles, which was attributable to the higher energy for binding at Mg_2Si. Therefore, the extent to which hydrogen trapping by Al_7Cu_2Fe suppressed interfacial debonding at Mg_2Si was limited. Instead, when the local trap density of Al_7Cu_2Fe particles was high, debonding at Mg_2Si can be accelerated due to clustering-induced concentration of local stress. The debonding of Mg_2Si could be the result of these two opposite effects.

Hydrogen partitioning analyses allowed determinations of local plastic strain and hydrogen occupancy during the exact loading steps and at the exact locations where particle damage was initiated **(Fig. 11)**. Particle damage arising from both fracture and debonding of Mg_2Si particles can occur with both low and high hydrogen occupancy. For particle fracture, there was no apparent correlation between local strain and hydrogen occupancy (**Fig. 11a**). This is because hydrogen was mainly trapped at Mg_2Si interfaces instead of at internal sites and thereby did not affect the fracture behavior [58]. For particle debonding (**Fig. 11b**), the local plastic strain required to trigger particle debonding dramatically decreases with hydrogen occupancy at some loading steps (e.g., steps 15, 16 and 17 marked by the dashed ellipse), implying possible enhancement by hydrogen. However, this effect was not obvious in the preceding loading steps. Other previously discussed factors, including the local stress distribution, which could be affected by particle sizes, shapes and spatial clustering, can also affect particle debonding. Clustering led to a high local stress level arising from the presence of neighboring Al_7Cu_2Fe particles, and this can lead to debonding of Mg_2Si at relatively low levels of hydrogen occupancy and strain.

4. Discussion

4.1 Hydrogen effects on particle damage

It has been proposed by the current authors that intermetallic particles can suppress hydrogen-induced quasi-cleavage cracks due to their high capacity for hydrogen trapping [17, 18]. It is anticipated that hydrogen embrittlement of Al alloys can be effectively controlled by intermetallic particles, despite the necessity for size and shape modifications to reduce stress singularity. It is shown in the analysis of hydrogen partitioning (**Fig. 10**) that Al_7Cu_2Fe particles, unlike Mg_2Si particles, are effective in hydrogen trapping. However, as with the aforementioned hydrogen effect at Mg_2Si, hydrogen might also accelerate the fracture of Al_7Cu_2Fe due to the high energy for hydrogen binding. This hypothesis can also be examined in the present study through statistical analysis of particle damage. Although very few data for hydrogen diffusion inside particles are available in the literature, it is reasonable to assume that hydrogen atoms can reach the centers of smaller particles more quickly, resulting in higher hydrogen occupancies. It is thereby inferred that such a hydrogen effect on embrittlement of Al_7Cu_2Fe particles, if it exists, should be more pronounced for smaller particles. However, **Fig. 5** shows that these small-diameter particles exhibited fairly low damage ratios, implying a negligible hydrogen effect. Therefore, it is reasonable to assume that the Al_7Cu_2Fe particles effectively trapped hydrogen without being embrittled by hydrogen.

4.2 Role of intermetallic particles in HE

The precise roles of hydrogen in triggering premature ductile fracture, quasi-cleavage cracks and intergranular cracks remain controversial. Multiple studies [59, 69] of high Zn-content Al alloys with limited numbers of particles showed that hydrogen caused considerable loss of ductility and the formation of quasi-cleavage cracks accompanying local deformation at the crack tip. Some studies attribute hydrogen-enhanced ductile fracture to accelerated void generation and/or growth at particle-matrix interfaces [21, 70]. Others have argued that the evolution of vacancy-type defects, rather than voids at particles, plays a crucial role in HE. Specifically, strain-induced generation of vacancies was found to be accelerated in the presence of hydrogen and responsible for HE [10, 71]. A similar mechanism favoring a failure pathway involving the hydrogen-vacancy interaction has been proposed, and it was mainly supported by microstructure observations showing nanodimples beneath fracture surfaces [72]. It was also revealed through first-principles simulations [9] that hydrogen vacancies tend to aggregate and form trivacancies on the slip plane of Al, and the trivacancies act as sources of microvoids and cracks. However, Su et al. [32] observed experimentally that hydrogen-induced nanovoids were distributed uniformly in a strain localization region and argued that nanovoids did not cause initiation and propagation of hydrogen-induced quasi-cleavage cracks in Al-Zn-Mg-Cu Al alloys. They also proposed [17] that formation of quasi-cleavage cracks was unlikely because of either the coalescence of hydrogen micropores or the debonding of particles because of their relatively large sizes compared with those of continuous, river-like quasi-cleavage cracks. This agrees with the study of Shimizu et al. [73], which showed that nanovoids do not aggregate on a specific plane to initiate cracking.

In terms of dislocations, an obliquely oriented region with substantial plastic strain was observed in the final scan taken just before fracture. The HELP mechanism, which assumes that hydrogen enhances dislocation mobility and favors slip planarity, has been used to explain the flat-to-slanted transitions caused by hydrogen and many other hydrogen-induced brittle fractures [8]. However, it was argued that the contribution of dislocations to the quasi-cleavage crack was limited due to extremely low hydrogen concentrations and occupancies ahead of the crack tip [17]. Other authors have proposed cooperation between multiple mechanisms, e.g., a HELP-mediated decohesion mechanism [13]. In terms of precipitates, first-principles simulations showed that hydrogen can be trapped at NbC/α-Fe semi-coherent interfaces with a high binding energy [74]. This is supported by direct experimental evidence obtained through cryo-transfer atom probe tomography, which indicated the presence of hydrogen (in this case deuterium) at NbC interfaces [75]; this also proves the reliability of first-principles simulations in predicting hydrogen trapping at precipitates. Tsuru et al. [57, 76] demonstrated through first-principles simulations that the cohesive energy of $MgZn_2$ interfaces decreases dramatically with increasing hydrogen occupancy and that spontaneous debonding occurs along $\{111\}_{Al}$ planes when the hydrogen occupancy level reaches unity. Although the maximum hydrogen occupancy observed during plastic deformation in the present research was much lower than the critical value, it is expected that elevated hydrostatic stress at the edges of precipitates could result in higher local levels of hydrogen occupancy and induce debonding. The intermetallic particles, which could trap a great amount of hydrogen (**Fig. 10**), might substantially reduce hydrogen concentrations at precipitates and thereby prevent precipitate debonding. In conclusion, in the presence of such intermetallic particles, hydrogen concentrations and occupancy levels at other trap sites, such as $MgZn_2$ precipitates, vacancies, and dislocations, could be significantly reduced, and this hydrogen trapping could reduce the extent of HE, regardless of the HE mechanisms involved.

5. Conclusions

Hydrogen partitioning analysis indicates that hydrogen occupancy levels at incoherent Mg_2Si interfaces are fairly high due to the high binding energy and insensitivity to other trap sites, such as Al_7Cu_2Fe. Examinations of the local strain and local hydrogen occupancy at damaged Mg_2Si particles indicated possible hydrogen enhancement of some loading steps, whereas no evidence was obtained for hydrogen contributions to particle fracture. It seems that debonding of Mg_2Si particles is the result of a competition between clustering-induced stress and hydrogen-enhanced debonding.

No evidence was obtained for the involvement of hydrogen in the fracture of Al_7Cu_2Fe particles, although high hydrogen occupancy levels at the interiors of particles are expected. Moreover, the presence of Al_7Cu_2Fe particles resulted in a more than three orders of magnitude reduction in hydrogen occupancy at the interfaces of $MgZn_2$ precipitates. Therefore, it is reasonable to assume that modifications of Al_7Cu_2Fe particles can be a viable mechanism for HE mitigation of Al alloys.

The fracture of Al_7Cu_2Fe particles has been confirmed to be the dominant damage mechanism occurring during plastic deformation of the present material. Both the number and damage ratios of fractured Al_7Cu_2Fe particles are extremely high and are substantially increased during nonuniform deformation. For Mg_2Si particles, however, debonding and fracture exhibit similar probabilities and are not apparently affected by necking. This difference in damage behavior for the two types of particles is attributable to the more pronounced spatial clustering of Al_7Cu_2Fe particles and their different mechanical properties (e.g., particle ductility).

Acknowledgments

This work was supported by JST, CREST Grant Number JPMJCR 1995 Japan and JSPS KAKENH Grant Number JP21H04624. The synchrotron radiation experiments were performed at SPring-8 with the approval of Japan Synchrotron Radiation Research Institute through proposal number 2020A1796/1084. The authors would also like to thank Mr. Wataru Masumori for his contribution to the experiment and data analysis.

References

[1] N. Takano, Hydrogen diffusion and embrittlement in 7075 aluminum alloy, Mater. Sci. Eng. A 483 (2008) 336-339.

[2] U. De Francisco, N.O. Larrosa, M.J. Peel, The influence of temperature on hydrogen environmentally assisted cracking of AA7449-T7651 in moist air, Corros. Sci. 180 (2021) 109199.

[3] Q. Han, S. Viswanathan, Hydrogen evolution during directional solidification and its effect on porosity formation in aluminum alloys, Metall. Mater. Trans. A. 33(7) (2002) 2067-2072.

[4] H. Toda, H. Oogo, K. Horikawa, K. Uesugi, A. Takeuchi, Y. Suzuki, M. Nakazawa, Y. Aoki, M. Kobayashi, The true origin of ductile fracture in aluminum alloys, Metall. Mater. Trans. A. 45(2) (2014) 765-776.

[5] G. Kotsikos, J.M. Sutcliffe, N.J.H. Holroyd, Hydrogen effects in the corrosion

fatigue behaviour of the white zone of 7xxx series aluminium alloy welds, Corros. Sci. 42(1) (2000) 17-33.

[6] H. Kamoutsi, G. Haidemenopoulos, V. Bontozoglou, S. Pantelakis, Corrosion-induced hydrogen embrittlement in aluminum alloy 2024, Corros. Sci. 48(5) (2006) 1209-1224.

[7] H.K. Birnbaum, P. Sofronis, Hydrogen-enhanced localized plasticity—a mechanism for hydrogen-related fracture, Mater. Sci. Eng. A 176(1) (1994) 191-202.

[8] A. Barnoush, H. Vehoff, Recent developments in the study of hydrogen embrittlement: Hydrogen effect on dislocation nucleation, Acta Mater. 58(16) (2010) 5274-5285.

[9] G. Lu, E. Kaxiras, Hydrogen embrittlement of aluminum: the crucial role of vacancies, Phys. Rev. Lett. 94(15) (2005) 155501.

[10] M. Nagumo, K. Takai, The predominant role of strain-induced vacancies in hydrogen embrittlement of steels: Overview, Acta Mater. 165 (2019) 722-733.

[11] D.E. Jiang, E.A. Carter, First principles assessment of ideal fracture energies of materials with mobile impurities: implications for hydrogen embrittlement of metals, Acta Mater. 52(16) (2004) 4801-4807.

[12] A. Van der Ven, G. Ceder, The thermodynamics of decohesion, Acta Mater. 52(5) (2004) 1223-1235.

[13] A. Nagao, M. Dadfarnia, B.P. Somerday, P. Sofronis, R.O. Ritchie, Hydrogen-enhanced-plasticity mediated decohesion for hydrogen-induced intergranular and “quasi-cleavage” fracture of lath martensitic steels, J. Mech. Phys. Solids. 112 (2018) 403-430.

[14] I.M. Robertson, P. Sofronis, A. Nagao, M.L. Martin, S. Wang, D.W. Gross, K.E. Nygren, Hydrogen embrittlement understood, Metall. Mater. Trans. B 46(3) (2015) 1085-1103.

[15] H. Kamoutsi, G.N. Haidemenopoulos, V. Bontozoglou, P.V. Petroyiannis, S.G. Pantelakis, Effect of prior deformation and heat treatment on the corrosion-induced hydrogen trapping in aluminium alloy 2024, Corros. Sci. 80 (2014) 139-142.

[16] M. Safyari, M. Moshtaghi, S. Kuramoto, Environmental hydrogen embrittlement associated with decohesion and void formation at soluble coarse particles in a cold-rolled Al–Cu based alloy, Mater. Sci. Eng. A 799 (2021) 139850.

[17] H. Su, H. Toda, K. Shimizu, K. Uesugi, A. Takeuchi, Y. Watanabe, Assessment of hydrogen embrittlement via image-based techniques in Al–Zn–Mg–Cu aluminum alloys, Acta Mater. 176 (2019) 96-108.

[18] M. Yamaguchi, T. Tsuru, K.-i. Ebihara, M. Itakura, K. Matsuda, K. Shimizu, H. Toda, Hydrogen trapping in Mg_2Si and Al_7FeCu_2 intermetallic compounds in aluminum alloy: first-principles calculations, Mater. Trans. (2020) MT-M2020201.

[19] Z. Tarzimoghadam, M. Rohwerder, S.V. Merzlikin, A. Bashir, L. Yedra, S. Eswara, D. Ponge, D. Raabe, Multi-scale and spatially resolved hydrogen mapping in a Ni–

Nb model alloy reveals the role of the δ phase in hydrogen embrittlement of alloy 718, Acta Mater. 109 (2016) 69-81.

[20] Y. Murakami, S. Matsuoka, Effect of hydrogen on fatigue crack growth of metals, Eng. Fract. Mech. 77(11) (2010) 1926-1940.

[21] R. Garber, I. Bernstein, A. Thompson, Hydrogen assisted ductile fracture of spheroidized carbon steels, Metall. Trans. A 12(2) (1981) 225-234.

[22] D.-I. Kwon, R.J. Asaro, Hydrogen-assisted ductile fracture in spheroidized 1518 steel, Acta Metall. 38(8) (1990) 1595-1606.

[23] A. Merati, A study of nucleation and fatigue behavior of an aerospace aluminum alloy 2024-T3, Int. J. Fatigue 27(1) (2005) 33-44.

[24] Y. Xue, H. El Kadiri, M.F. Horstemeyer, J.B. Jordon, H. Weiland, Micromechanisms of multistage fatigue crack growth in a high-strength aluminum alloy, Acta Mater. 55(6) (2007) 1975-1984.

[25] J. Payne, G. Welsh, R.J. Christ, J. Nardiello, J.M. Papazian, Observations of fatigue crack initiation in 7075-T651, Int. J. Fatigue 32(2) (2010) 247-255.

[26] S.S. Singh, E. Guo, H. Xie, N. Chawla, Mechanical properties of intermetallic inclusions in Al 7075 alloys by micropillar compression, Intermetallics 62 (2015) 69-75.

[27] A.S.S. Singaravelu, J.J. Williams, H.D. Goyal, S. Niverty, S.S. Singh, T.J. Stannard, X. Xiao, N. Chawla, 3D time-resolved observations of fatigue crack initiation and growth from corrosion pits in Al 7XXX alloys using in situ synchrotron X-ray tomography, Metall. Mater. Trans. A. 51(1) (2020) 28-41.

[28] S. Niverty, C. Kale, K.N. Solanki, N. Chawla, Multiscale investigation of corrosion damage initiation and propagation in AA7075-T651 alloy using correlative microscopy, Corros. Sci. 185 (2021) 109429.

[29] S. Niverty, N. Chawla, 4D microstructural characterization of corrosion and corrosion-fatigue in a Ti–6Al–4V/AA 7075-T651 joint in saltwater environment, Mater. Sci. Eng. A 825 (2021) 141886.

[30] V.C. Gudla, A. Garner, M. Storm, P. Gajjar, J. Carr, B.C. Palmer, J.J. Lewandowski, P.J. Withers, N.H. Holroyd, T.L. Burnett, Initiation and short crack growth behaviour of environmentally induced cracks in AA5083 H131 investigated across time and length scales, Corrosion Reviews 37(5) (2019) 469-481.

[31] M.S. Bhuiyan, Y. Tada, H. Toda, S. Hang, K. Uesugi, A. Takeuchi, N. Sakaguchi, Y. Watanabe, Influences of hydrogen on deformation and fracture behaviors of high Zn 7XXX aluminum alloys, Int. J. Fracture 200(1) (2016) 13-29.

[32] H. Su, H. Toda, R. Masunaga, K. Shimizu, H. Gao, K. Sasaki, M.S. Bhuiyan, K. Uesugi, A. Takeuchi, Y. Watanabe, Influence of hydrogen on strain localization and fracture behavior in AlZnMgCu aluminum alloys, Acta Mater. 159 (2018) 332-343.

[33] M. Kobayashi, H. Toda, Y. Kawai, T. Ohgaki, K. Uesugi, D.S. Wilkinson, T. Kobayashi, Y. Aoki, M. Nakazawa, High-density three-dimensional mapping of internal

strain by tracking microstructural features, Acta Mater. 56(10) (2008) 2167-2181.
[34] H. Toda, X-Ray CT: Hardware and Software Techniques, Springer Nature2021.
[35] J.J. Williams, Z. Flom, A.A. Amell, N. Chawla, X. Xiao, F. De Carlo, Damage evolution in SiC particle reinforced Al alloy matrix composites by X-ray synchrotron tomography, Acta Mater. 58(18) (2010) 6194-6205.
[36] V.A. Romanova, R.R. Balokhonov, S. Schmauder, The influence of the reinforcing particle shape and interface strength on the fracture behavior of a metal matrix composite, Acta Mater. 57(1) (2009) 97-107.
[37] K. Gall, M. Horstemeyer, D.L. McDowell, J. Fan, Finite element analysis of the stress distributions near damaged Si particle clusters in cast Al–Si alloys, Mech. Mater. 32(5) (2000) 277-301.
[38] A. Ayyar, G. Crawford, J. Williams, N. Chawla, Numerical simulation of the effect of particle spatial distribution and strength on tensile behavior of particle reinforced composites, Comp. Mater. Sci. 44(2) (2008) 496-506.
[39] J. Segurado, J. LLorca, Computational micromechanics of composites: the effect of particle spatial distribution, Mech. Mater. 38(8-10) (2006) 873-883.
[40] L. Babout, Y. Brechet, E. Maire, R. Fougères, On the competition between particle fracture and particle decohesion in metal matrix composites, Acta Mater. 52(15) (2004) 4517-4525.
[41] E.J. McEniry, T. Hickel, J. Neugebauer, Ab initio simulation of hydrogen-induced decohesion in cementite-containing microstructures, Acta Mater. 150 (2018) 53-58.
[42] A.H.M. Krom, R.W.J. Koers, A. Bakker, Hydrogen transport near a blunting crack tip, J. Mech. Phys. Solids. 47(4) (1999) 971-992.
[43] V. Tvergaard, Model studies of fibre breakage and debonding in a metal reinforced by short fibres, J. Mech. Phys. Solids. 41(8) (1993) 1309-1326.
[44] J.-k. Chen, G.-T. Wang, Z.-Z. Yu, Z. Huang, Y.-W. Mai, Critical particle size for interfacial debonding in polymer/nanoparticle composites, Compos. Sci. Technol. 70(5) (2010) 861-872.
[45] G. Testa, N. Bonora, A. Ruggiero, G. Iannitti, D. Gentile, Stress triaxiality effect on void nucleation in ductile metals, Fatigue Fract. Eng. M. 43(7) (2020) 1473-1486.
[46] N. Bonora, G. Testa, A. Ruggiero, G. Iannitti, D. Gentile, Continuum damage mechanics modelling incorporating stress triaxiality effect on ductile damage initiation, Fatigue Fract. Eng. M. 43(8) (2020) 1755-1768.
[47] A. Needleman, A continuum model for void nucleation by inclusion debonding, J. Appl. Mech. (1987).
[48] C. Landron, E. Maire, O. Bouaziz, J. Adrien, L. Lecarme, A. Bareggi, Validation of void growth models using X-ray microtomography characterization of damage in dual phase steels, Acta Mater. 59(20) (2011) 7564-7573.

[49] N. Pathak, J. Adrien, C. Butcher, E. Maire, M. Worswick, Experimental stress state-dependent void nucleation behavior for advanced high strength steels, Int. J. Mech. Sci. 179 (2020) 105661.

[50] J. He, J. Lian, G. Golisch, A. He, Y. Di, S. Münstermann, Investigation on micromechanism and stress state effects on cleavage fracture of ferritic-pearlitic steel at- 196 C, Mater. Sci. Eng. A 686 (2017) 134-141.

[51] R.A. Oriani, The diffusion and trapping of hydrogen in steel, Acta Metall. 18(1) (1970) 147-157.

[52] T. Tsuru, to be submitted.

[53] M. Yamaguchi, K.-I. Ebihara, M. Itakura, T. Tsuru, K. Matsuda, H. Toda, First-principles calculation of multiple hydrogen segregation along aluminum grain boundaries, Comp. Mater. Sci. 156 (2019) 368-375.

[54] M. Yamaguchi, M. Itakura, T. Tsuru, K.-i. Ebihara, Hydrogen-trapping energy in screw and edge dislocations in aluminum: first-principles calculations, Mater. Trans. 62(5) (2021) 582-589.

[55] T. Enomoto, R. Matsumoto, S. Taketomi, N. Miyazaki., First-principles estimation of hydrogen occupancy around lattice defects in Al, Zair Soc Mater Sci Jpn 59(8) (2010) 596-603.

[56] M. Yamaguchi , T. Tsuru, K. Ebihara, M. Itakura., Surface energy reduction by dissociative hydrogen adsorption on inner surface of pore in aluminum, J Japan Inst Light Met 68(11) (2018) 588-595.

[57] T. Tsuru, M. Yamaguchi, K. Ebihara, M. Itakura, Y. Shiihara, K. Matsuda, H. Toda, First-principles study of hydrogen segregation at the $MgZn_2$ precipitate in Al-Mg-Zn alloys, Comp. Mater. Sci. 148 (2018) 301-306.

[58] M. Yamaguchi, (Unpublished work).

[59] K. Shimizu, H. Toda, H. Fujihara, K. Hirayama, K. Uesugi, A. Takeuchi, Hydrogen partitioning behavior and related hydrogen embrittlement in Al-Zn-Mg alloys, Eng. Fract. Mech. 216 (2019) 106503.

[60] S. Brinckmann, T. Siegmund, Y. Huang, A dislocation density based strain gradient model, Int. J. Plasticity 22(9) (2006) 1784-1797.

[61] E. Martínez-Pañeda, C.F. Niordson, R.P. Gangloff, Strain gradient plasticity-based modeling of hydrogen environment assisted cracking, Acta Mater. 117 (2016) 321-332.

[62] Y. Liang, P. Sofronis, N. Aravas, On the effect of hydrogen on plastic instabilities in metals, Acta Mater. 51(9) (2003) 2717-2730.

[63] P. Sofronis, Y. Liang, N. Aravas, Hydrogen induced shear localization of the plastic flow in metals and alloys, Eur. J. Mech. A-Solid. 20(6) (2001) 857-872.

[64] A. Bendo, K. Matsuda, S. Lee, K. Nishimura, N. Nunomura, H. Toda, M. Yamaguchi, T. Tsuru, K. Hirayama, K. Shimizu, Atomic scale HAADF-STEM study of η′ and η 1 phases in peak-aged Al－Zn－Mg alloys, J. Mater. Sci. 53(6) (2018) 4598-4611.

[65] A.L. Garcia-Garcia, I. Dominguez-Lopez, L. Lopez-Jimenez, J.D.O. Barceinas-Sanchez, Comparative quantification and statistical analysis of η′ and η precipitates in aluminum alloy AA7075-T651 by TEM and AFM, Mater. Character. 87 (2014) 116-124.

[66] Y.-L. Liu, Y. Zhang, H.-B. Zhou, G.-H. Lu, F. Liu, G.-N. Luo, Vacancy trapping mechanism for hydrogen bubble formation in metal, Phys. Rev. B. 79(17) (2009) 172103.

[67] K. Sakaki, T. Kawase, M. Hirato, M. Mizuno, H. Araki, Y. Shirai, M. Nagumo, The effect of hydrogen on vacancy generation in iron by plastic deformation, Script. Mater. 55(11) (2006) 1031-1034.

[68] M. Militzer, W. Sun, J. Jonas, Modelling the effect of deformation-induced vacancies on segregation and precipitation, Acta Metall. 42(1) (1994) 133-141.

[69] K. Carling, G. Wahnström, T.R. Mattsson, A.E. Mattsson, N. Sandberg, G. Grimvall, Vacancies in metals: from first-principles calculations to experimental data, Phys. Rev. Lett. 85(18) (2000) 3862.

[70] K. Shimizu, H. Toda, K. Uesugi, A. Takeuchi, Local deformation and fracture behavior of high-strength aluminum alloys under hydrogen influence, Metall. Mater. Trans. A. 51(1) (2020) 1-19.

[71] H.J. Maier, W. Popp, H. Kaesche, Effects of hydrogen on ductile fracture of a spheroidized low alloy steel, Mater. Sci. Eng. A 191(1) (1995) 17-26.

[72] M. Nagumo, H. Yoshida, Y. Shimomura, T. Kadokura, Ductile crack growth resistance in hydrogen-charged steels, Mater. Trans. 42(1) (2001) 132-137.

[73] T. Neeraj, R. Srinivasan, J. Li, Hydrogen embrittlement of ferritic steels: observations on deformation microstructure, nanoscale dimples and failure by nanovoiding, Acta Mater. 60(13-14) (2012) 5160-5171.

[74] K. Shimizu, H. Toda, C. Kadogawa, H. Fujihara, A. Takeuchi, Influence of nanovoids in the hydrogen embrittlement fracture of Al–Zn–Mg–Cu alloys, Materialia 11 (2020) 100667.

[75] R. Shi, Y. Ma, Z. Wang, L. Gao, X.-S. Yang, L. Qiao, X. Pang, Atomic-scale investigation of deep hydrogen trapping in NbC/α-Fe semi-coherent interfaces, Acta Mater. 200 (2020) 686-698.

[76] Y.-S. Chen, H. Lu, J. Liang, A. Rosenthal, H. Liu, G. Sneddon, I. McCarroll, Z. Zhao, W. Li, A. Guo, Observation of hydrogen trapping at dislocations, grain boundaries, and precipitates, Science 367(6474) (2020) 171-175.

[77] T. Tsuru, K. Shimizu, M. Yamaguchi, M. Itakura, K. Ebihara, A. Bendo, K. Matsuda, H. Toda, Hydrogen-accelerated spontaneous microcracking in high-strength aluminium alloys, Sci. Rep. 10(1) (2020) 1-8.