Suppressed hydrogen embrittlement of high-strength Al alloys by Mn-rich intermetallic compound particles

Xu, Yuantao
Department of Mechanical Engineering, Kyushu University

Toda, Hiroyuki
Department of Mechanical Engineering, Kyushu University

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

Wang, Yafei
Department of Mechanical Engineering, Kyushu University

他

https://hdl.handle.net/2324/6792843

出版情報：Acta materialia. 236, pp.118110-, 2022-09-01. Elsevier
バージョン：
権利関係：

Suppressed hydrogen embrittlement of high-strength Al alloys by Mn-rich intermetallic compound particles

Yuantao Xu [a,b]*, Hiroyuki Toda [a]*, Kazuyuki Shimizu [c], Yafei Wang [a], Baptiste Gault [d,e], Wei Li [b]*, Kyosuke Hirayama [f], Hiro Fujihara [a], Xuejun Jin [b], Akihisa Takeuchi [g], Masayuki Uesugi [g]

[a]*Department of Mechanical Engineering, Kyushu University, Fukuoka 819-0395, Japan*

[b]*Shanghai Key Laboratory of Materials Laser Processing and Modification, Shanghai Jiao Tong University, Shanghai 200240, PR China*

[c]*Department of Physical Science and Materials Engineering, Iwate University, Morioka 020-8551, Japan*

[d]*Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany*

[e]*Department of Materials, Royal School of Mines, Imperial College, Prince Consort Road, London SW7 2BP, United Kingdom*

[f]*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*

[g]*Japan Synchrotron Radiation Research Institute, Hyogo 679-5198, Japan*

**Corresponding author. Tel.: +81-928023246; E-mail: xu.yuantao.158@m.kyushu-u.ac.jp (Yuantao Xu); toda@mech.kyushu-u.ac.jp (Hiroyuki Toda); weilee@sjtu.edu.cn (Wei Li)*

Abstract

The pursuit of strong and ductile Al alloys with superior resistance to hydrogen embrittlement (HE) is practically significant across the aerospace and transportation industries among others. Unfortunately, effective ways to progress on the strength-HE trade-off for Al-alloys remain elusive. A strategy of suppressing HE by introducing intermetallic compound (IMC) particles to achieve hydrogen redistribution in various trapping sites was proposed. Here, we systematically induce the precipitation of a constant volume fraction of intermetallic compound (IMC) particles by adding one of 14 elements in a ternary Al-Zn-Mg high-strength alloy. We show a strong correlation between hydrogen trapping energies of the IMC obtained from ab initio calculations with the resistance to HE. Mn-rich $Al_{11}Mn_3Zn_2$ particles exhibit the highest hydrogen trapping energy (0.859 eV/atom), leading to a decrease by approximately 5 orders of magnitude in the hydrogen occupancy in η_2 ($MgZn_2$) phase interfaces and grain boundaries, where HE cracks initiate. The Mn-addition did not deteriorate the ductility and most $Al_{11}Mn_3Zn_2$ particles remained intact during plastic deformation which was revealed by in-situ 3D X-ray tomography. Hydrogen-induced strain localization at η_2 phase interfaces and grain boundaries were inhibited due to strong hydrogen trapping capacity of $Al_{11}Mn_3Zn_2$, hence preventing HE cracks initiation. Our approach effectively suppresses hydrogen-induced cracks without sacrificing the ductility, and our strategy can help the design roadmap of HE-tolerant high-strength metallic alloys.

Keywords: Hydrogen embrittlement; Hydrogen trapping; Intermetallic compound particles; Aluminum alloys; Ductility

1. Introduction

Degradation of the mechanical properties of structural materials due to hydrogen intake has become the main concern for key components in many industries, such as nuclear energy [1-4], aerospace [5,6], oil and gas [7]. Hydrogen causes cracking [4,5], hydride precipitation [1-3], embrittlement [8], and other harmful effects [9], thereby limiting the service life of parts, increasing operating costs, and creating potentially unsafe working conditions. Al-Zn-Mg alloys have attracted significant research interest for structural applications in aerospace, transportation, and many other industries owing to their high strength and low density [10,11]. However, their low resistance to stress corrosion cracking and hydrogen embrittlement (HE) severely affects the service life and applications [12-14].

Environmentally assisted HE in high-strength 7xxx series aluminum alloys leads to low ductility and catastrophic failure in structural applications [11,15,16]. The dissolved hydrogen atoms can easily penetrate surface oxide layer and diffuse into various trapping sites (e.g., dislocations, vacancies, grain boundaries, and precipitates) in the Al alloys [17]. Hydrogen not only reduces the ductility but can also change the fracture mode from ductile to brittle, macroscopically featuring as intergranular or transgranular quasi-cleavage fractures [18-20]. Intergranular fracture (IGF) is primarily associated with the hydrogen segregated at the grain boundary that weakens the interface bonding strength (hydrogen-enhanced decohesion (HEDE) [20]). The mechanisms of quasi-cleavage fracture (QCF) remain controversial due to the lack of direct experimental evidence, for which the HEDE mechanism, hydrogen-enhanced localized plasticity (HELP) [21] mechanism, and hydrogen-accelerated spontaneous microcracking at precipitate interfaces have been proposed [22].

The effects of various trapping sites such as micro pores, grain boundaries, dislocations, vacancies, precipitates, and IMC particles on HE mechanism of Al alloys were widely investigated [13,17,22-24]. A high density of micro pores can store hydrogen and contribute to ductile fracture [23]; however, a small amount of dissolved hydrogen can cause brittle fracture [24]. Controlling the distribution of dissolved hydrogen between grain boundaries, dislocations, and vacancies in Al-Zn-Mg alloys was proven ineffective in suppressing HE [17]. The precipitate interfaces (Al-$MgZn_2$) was reported to be a more preferable hydrogen trap site compared to other defects in terms of binding energy and hydrogen partitioning, which leads to spontaneous hydrogen-accumulated QCF [22]. The design concept of IMC particles primarily focused on their role in grain refinement in Al alloys [25-27], whereas little information was reported regarding their role in the HE suppression of Al alloys. A recent study showed that the Al_7Cu_2Fe particles are effective hydrogen traps to reduce the trapped hydrogen at the precipitate interfaces and confirmed to be able to suppress QCF; however, the improvement of the ductility was not satisfactory due to the brittle nature of Al_7Cu_2Fe particles. Therefore, achieving a superior HE resistance without sacrificing the ductility remains a challenge in Al alloys and exploring suitable IMC particles that can realize the balance between hydrogen trapping ability and brittle nature seems a potential route to effectively control HE.

Here, we propose a hydrogen redistribution approach by introducing IMC particles as strong hydrogen trapping site, which significantly reduces trapped hydrogen at precipitate interfaces and grain boundaries and suppresses QCF and IGF originating from hydrogen segregation. First-principles calculations are employed to calculate the binding energies between hydrogen and various IMC particles formed by adding a fourth alloying element to Al-Zn-Mg alloys. The effect of IMC particles on the hydrogen partitioning behaviors among various trap sites during plastic deformation are investigated by 3D X-ray technique and first-principles calculations. In addition, the role of IMC particles in initiation and propagation of hydrogen-induced QCF and IGF are discussed, and the mechanism of how IMC particles can act as strong hydrogen traps for resisting HE is clarified.

2. Materials and methods

To investigate the effects of IMC particles on the hydrogen partitioning and embrittlement behaviors, various IMC particles were formed by adding a fourth element, such as 1.00 Nb, 0.94 Mo, 1.00 V, 0.15 Ca, 0.09 Y, 0.15 Sr, 0.10 Ni, 1.19 Zr, 0.15 Fe, 0.26 Cr, 1.02 Ti, 0.19 Co, 0.94 Sc, or 1.91 Mn to the Al-10.0 Zn-1.06 Mg (wt.%) Al alloys. The element content was designed to obtain IMC particles with a volume fraction of approximately 0.28%. The detailed thermomechanical treatment process is presented in Figure S1. The corresponding alloys were prepared by homogenization at 500 °C for 24 h after casting and then hot rolling at 450 °C with a rolling reduction of 50%. A solution-aging process was performed as follows: first, a solution treatment was conducted at 500 °C for 5 h. Subsequently, an over-aging treatment was performed at 120 °C for 40 h and 180 °C for 7 h. To investigate the influence of the pre-charged hydrogen content on the embrittlement behavior, specimens with different hydrogen contents were prepared using LH and HH treatments. The specimens with HH content were charged using electrical discharge machining (EDM) cutting in distilled water, while the specimens with LH content were prepared by EDM cutting in oil. The pre-charged hydrogen contents were approximately 6.97 mass ppm and 1.40 mass ppm for the specimens after HH and LH treatments, respectively, the total hydrogen content was analyzed by the vacuum fusion method, which are similar to literature values [13]. The hydrogen concentration in the Mn-added Al alloys after HH and LH treatments were also measured by thermal desorption apparatus (TDA) method, the corresponding desorption curves were shown in Figure S2.

The gauge length of in-situ tensile specimens was 0.7 mm, and these specimens had cross-sectional dimensions of 0.6 mm × 0.6 mm. The deformation and fracture behaviors were observed using high-resolution X-ray tomography during in-situ tensile tests at BL20XU of Spring-8 in Japan; the detailed experimental setup is shown in Figure S3. In-situ tensile tests (strain rate $\sim 3\times10^{-3}$ s^{-1}) were conducted using a DEBEN CT 500 machine at room temperature. 3D images were taken using monochromatic 20 keV X-rays; the detailed methods used for tomography observation and in-situ tensile tests are reported in the literature [13].

Transmission electron microscopy (TEM; JEOL JEM 2100F/ARM 200F) was used to characterize the detailed microstructure of the precipitates, IMC particles, and Al matrix. Scanning electron microscope (SEM) (TESCAN MIRA3) equipped with an electron back-scatter diffraction (EBSD) detector was performed to analyze strain distribution and phase features by transmission Kikuchi diffraction (TKD) technique. Thin foils were prepared for TEM and EBSD observations by electro-polishing using Struers (Tenupol-5) equipment at -30 °C and 15 V; the electrolyte was 7% perchloric acid and 93% ethanol. Atom probe tomography (APT) measurements were performed using a local electrode atomic probe (LEAP 4000 HR) to obtain the spatial distribution of elements and the number density and size of nanoparticles. APT data was obtained at 50 K under ultrahigh vacuum (4.5×10^{-11} Torr), a pulse fraction of 0.2, and a repetition rate of 200 kHz. The APT data was reconstructed using IVAS$^{\mathrm{TM}}$ 3.6.2 software.

Hydrogen trapping at $MgZn_2$ precipitates interface and various intermetallic compound particles was calculated using first-principles calculations. The first-principles calculations were conducted within the DFT framework using the Vienna ab initio simulation package (VASP 5.2) with the Perdew-Burke-Ernzerhof generalized gradient approximation exchange-correlation density functional. The Monkhorst-Pack algorithm was selected for the Brillouin-zone k-point samplings. A plane-wave energy cutoff of 360 eV was used with a first-order Methfessel-Paxton smearing scheme, employing a smearing parameter of 0.2 eV. The total energy converged to 10^{-6} eV in all the calculations. The relaxed atomic configurations were obtained by the conjugate gradient method in which the search terminated when the forces on all atoms were below 0.01 eV/Ang. The crystal structure parameters and sampling k-point mesh of various particles, and the details of calculation process can be found in the Supplementary Materials 1.1.

The hydrogen trap sites in this study were grain boundaries, dislocations, pores, vacancies, precipitate interfaces, and IMC particles. To quantitatively analyze these trap site densities, the area of the grain boundaries, dislocation densities, pore morphology, vacancy concentrations, area of precipitate interfaces, and volume fractions of IMC particles were obtained using a combination of experimental techniques and mathematical models, which are detailed in the Supplementary Materials 1.2.

3. Results and discussion

3.1 Trapping energies of IMC particles to hydrogen and their HE resistances

Various IMC particles were formed by adding a fourth element such as Nb, Mo, V, Ca, Y, Sr, Ni, Zr, Fe, Cr, Ti, Co, Sc, or Mn to Al-10.0Zn-1.06Mg alloys. First-principles density functional theory (DFT) was employed to calculate the trapping energies of various IMC particles to hydrogen, and the corresponding results are shown in Figure 1. The hydrogen trapping energies of various defect structures, such as edge/screw dislocations [28], grain boundaries [29], vacancies [30], precipitates [22,31], and micro pores [32] are also summarized. The maximum hydrogen trapping energy in the interior of $Al_{11}Mn_3Zn_2$ was 0.859 eV/atom, much higher than that in other IMC particles and defect structures, which indicates that it can be used as a strong hydrogen trapping site for absorbing a large amount of hydrogen at interstitial sites.

The HE resistances of samples with and without IMC particles were evaluated using in-situ tensile tests. In-situ tensile stress–displacement curves for the standard-state, Sc-added, and Mn-added Al alloys after low-hydrogen (LH) and high-hydrogen (HH) treatments are shown in Figure 2(a). The mechanical properties of the standard-state and Sc-added Al alloys were severely affected by the hydrogen content, where the elongation were dramatically reduced after the HH treatment, compared to the LH treatment. However, in the Mn-added alloys, the elongation remained almost unchanged after the HH treatment, compared to the LH treatment, which means that the Mn-added Al alloys overcomes hydrogen-induced ductility loss. Detailed fractography analysis revealed that the fractional areas of IGF and QCF were 50.9% and 46.0% in the standard-state Al alloys and 9.3% and 11.5% for the Mn-added Al alloys after the HH treatment, with 81.7% and 75.0% reduction, respectively. This confirms that the Mn-added Al alloys significantly improves HE resistance (Figure 2(b)). The effect of a fourth element such as Nb, Mo, V, Ca, Y, Sr, Ni, Zr, Fe, Cr, Ti, Co, Sc, or Mn on the HE fracture area is shown in Figure 2(c); the corresponding fracture morphology is presented in Figure 3 and Figure S4. The relationships between hydrogen trapping energies of IMC particles and fractional areas of QCF are summarized in Figure 2(d). Fractional areas of QCF were significantly reduced with the increase of trapping energies of different IMC particles in the Al alloys treated by HH. Compared with the addition of the other elements, the Mn-added Al alloys exhibited the best HE resistance owing to the highest trapping energy between the $Al_{11}Mn_3Zn_2$ particles and hydrogen.

HE occurred in the 7 xxx series Al alloy (Al-10.1Zn-1.2Mg) with hydrogen content of 0.41 mass ppm [12], and also appeared in LH-treated standard-state Al alloys (1.40 mass ppm) in this work (Figure 3). It was reported that the introduction of Mn-rich particles by adding Mn to Al-Zn-Mg alloys under hydrogen-free conditions results in a slight decrease in ductility [33,34]. However, the introduced Mn-rich particles in LH-treated Mn-added Al alloys contributes to a significant increase in ductility compared with LH-treated standard-state Al alloys, which reconfirms that strong hydrogen trapping capacity of $Al_{11}Mn_3Zn_2$ particles.

3.2 Hydrogen partitioning behavior

The microstructures of the standard-state and Mn-added Al-Zn-Mg alloys were investigated (Figure 4(a-b)). The standard-state alloys primarily consisted of $MgZn_2$ and Al matrix, while the Mn-added Al alloys was primarily comprised of $Al_{11}Mn_3Zn_2$, $MgZn_2$, and Al matrix (Figure 4(a-b), Figure S5, and Figure 5), which were identified using high-resolution transmission electron microscopy (HRTEM) and atom probe tomography (APT) analysis. $MgZn_2$ has a hexagonal close-packed (hcp) structure, and its edge and side surfaces of the plate are coherent and semi-coherent along the $[112]_{Al}$ zone axis, respectively. The orientation relationship between $MgZn_2$ and the matrix is $\left[\bar{1}12\right]_{Al}//\left[2\bar{1}\bar{1}0\right]_{MgZn_2}$. $Al_{11}Mn_3Zn_2$ has an orthorhombic structure; the orientation relationship between it and the matrix is $\left[011\right]_{Al}//\left[2\bar{2}1\right]_{Al_{11}Mn_3Zn_2}$. The number density of η_2 ($MgZn_2$) precipitates in standard-state and Mn-added Al alloys are 1.13×10^{23} and 0.78×10^{23} m^{-3}, and their equivalent spherical particle radius are 6.5 and 7.4 nm, respectively, which were determined via APT (Figure 5). The average grain sizes were measured to be 124 and 75 μm for the standard-state and Mn-added Al alloys, respectively (Figure 6). 3D perspective views of IMC particles and micro pores obtained by high-resolution X-ray tomography are shown in Figure 4(c). These parameters were used in the calculation of hydrogen occupancy of the corresponding trap site.

The hydrogen partitioning behavior in the standard-state and Mn-added Al alloys are shown in Figure 4(d). The hydrogen occupancy of a trap site depends on both the trap density and trap binding energy, which were derived from experimental results (Figure 4(a)-4(c)) and first-principles calculations. See the Supplementary Materials 1.2 for detailed calculation procedures of hydrogen occupancy of each hydrogen trap site.

It was found that hydrogen atoms were mainly trapped at micro pores, η_2 precipitates, and vacancies in the standard-state alloys; however, the $Al_{11}Mn_3Zn_2$ particles are the strongest hydrogen trap, which reduced the hydrogen occupancy at other trap sites such as micro pores, η_2 precipitates, vacancies, and grain boundaries. In particular, the hydrogen occupancy of η_2 interfaces and grain boundaries were decreased by approximately 5 orders of magnitude (from 1.15×10^{-1} to 6.20×10^{-7} and from 4.42×10^{-1} to 4.60×10^{-6} atomH/site, respectively), which contributes to the suppression of hydrogen-induced QCF and IGF (Figure 2).

3.3 Damage behavior of $Al_{11}Mn_3Zn_2$ particles and hydrogen partitioning behavior during deformation

Figure 7(a)-7(h) show the damage behavior of $Al_{11}Mn_3Zn_2$ particles in Mn-added Al alloys after the HH treatment during in-situ tensile tests. 3D images around the crack tip were obtained using high-resolution X-ray tomography. The observation regions ahead of the hydrogen-induced quasi-cleavage crack tip and near the crack ridge were approximately 5.7×10^2 and 4.3×10^3 μm^3, respectively, as shown in Figure 7(i). 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.

The damage ratios, R_d, are defined as follows:

$$R_d(fractured) = n_F / n_{total} \times 100\% \tag{1}$$

$$R_d(debonded) = n_D / n_{total} \times 100\% \tag{2}$$

$$R_d = R_d(fractured) + R_d(debonded) \tag{3}$$

where n_F and n_D are the numbers of fractured and debonded particles, respectively; n_{total} is the total number of IMC particles for each condition.

At a macroscopic tensile strain of 5.7%, the damage ratio of IMC particles near the crack ridge was approximately 7% (2/28). With the further increase of tensile strain to 9%, the damage ratio slightly increased to approximately 20% (2/10). Therefore, most of these IMC particles remained intact during plastic deformation, implying that these particles, with strong hydrogen trapping capacity, did not deteriorate the ductility due to good damage resistance. It is thereby expected that the IMC particles can effectively suppress hydrogen-induced cracks without sacrificing the ductility. This is consistent with the significantly increased fracture strain of the particles-containing Al alloys compared with the particles-free Al alloys (Figure 2(a)).

Figure 7(i) and 7(j) show the hydrogen partitioning behavior during deformation in Mn-added Al alloys after the HH treatment. At the in-situ tensile strain of 3.6%, the volume fractions of IMC particles at the regions ahead of the hydrogen-induced quasi-cleavage crack tip and near the crack ridge were 1.54% and 0.26%, respectively.

Hydrogen partitioning calculations revealed that the hydrogen occupancy of the η_2 interfaces at the region ahead of the crack tip was approximately 8 orders of magnitude lower than that near the crack ridge owing to the higher density of IMC particles. This means that regions with a low density of IMC particles are prone to crack nucleation and propagation (Figure 7(i)). $Al_{11}Mn_3Zn_2$ particles were the main hydrogen trap, and the trapped hydrogen content could reach 2.0×10^{25} atomH·m^{-3} (Figure S6), which was much higher than other tapping sites. The hydrogen occupancy of $Al_{11}Mn_3Zn_2$ particles remained almost unchanged before and after deformation (3.6% strain). Moreover, they exhibited good damage resistance even at high tensile strain (up to 9%). This confirms that the $Al_{11}Mn_3Zn_2$ particles are beneficial for improving the HE resistance without harming the ductility during deformation.

3.4 Suppression of hydrogen-induced strain localization at grain boundaries

Micro-deformation mechanisms of $Al_{11}Mn_3Zn_2$ particles under HH and LH conditions were revealed by transmission Kikuchi diffraction (TKD) technique and TEM (Figure 8). $Al_{11}Mn_3Zn_2$ particles did not deform during tensile failure under HH and LH conditions, strain concentration around $Al_{11}Mn_3Zn_2$ particles mainly resulted from dislocations piled-up. The strain distributions around $Al_{11}Mn_3Zn_2$ and in Al matrix remained almost the same when changing treatment conditions from LH to HH, indicating that hydrogen-induced strain localization caused by the interaction of hydrogen and dislocations was suppressed [13,35-37], which is mainly attributed to strong hydrogen trapping capacity of $Al_{11}Mn_3Zn_2$.

The microstructures near the fracture surfaces of Mn-added and standard-state Al alloys treated by HH after tensile failure are shown in Figure 9. The hydrogen-induced cracks mainly propagated along the grain interiors in the Mn-added Al alloys (Figure 9(a)), while they mainly propagated along the grain boundaries in the standard-state Al alloys (Figure 9(e)). Hydrogen-induced cracks preferably nucleated at IMC-poor regions, and IMC-rich regions could effectively blunt and suppress hydrogen-induced cracks (Figure S7), which is consistent with the result at 3.6% tensile strain (Figures 7(i) and 7(j)). The piled-up dislocations at grain boundaries were significantly reduced during tensile failure after adding Mn in standard-state Al alloys (Figure 9(b)-(d) and 9(f)-(h)), supporting that the trapped hydrogen at grain boundaries were remarkably decreased owing to the introduction of $Al_{11}Mn_3Zn_2$.

3.5 Suppression of hydrogen-induced strain localization at η_2 phase interfaces

As shown in Figure 10, strain maps were plotted by geometric phase analysis (GPA) [38], inverse FFT patterns of HRTEM images were used to characterize dislocations around η_2 phase interfaces. 10 HRTEM images (each image contains 2 precipitates) were collected for the HH-treated Mn-added Al alloys and HH-treated standard-state Al alloys, respectively, and 20 precipitates were counted and analyzed for each condition. Strain concentration around η_2 phase interfaces was not very obvious in HH-treated Mn-added Al alloys subjected to tensile failure, however, the strain values were very high for almost the entire η_2 phase interface in HH-treated standard-state Al alloys subjected to tensile failure (Figure 10(c)-(f) and 10(j)-(m)).

Moreover, more significant dislocations pile up occurred near the η_2 phase interfaces in HH-treated standard-state Al alloys, compared with that in HH-treated Mn-added Al alloys (Figure 10(g) and 10(n)). Based on the analysis results of 20 precipitates under each condition, it can be confirmed that the strain localization at η_2 phase interfaces was effectively suppressed during tensile failure after adding Mn in standard-state Al alloys, which indicates that the trapped hydrogen at η_2 phase interfaces were largely removed by $Al_{11}Mn_3Zn_2$. These results demonstrate that IMC particles inhibit hydrogen-induced strain localization η_2 phase interfaces by consuming most of the hydrogen, hence preventing HE cracks initiation.

The QCF mechanism induced by hydrogen in structural materials, such as ferritic, martensitic, and austenitic steels, and nickel, can be explained by the HELP model [39], where hydrogen-affected dislocations contribute to structural failure. However, a QCF mechanism assisted by hydrogen in an Al-Mg-Zn alloy was reported [22]; hydrogen atoms tended to be trapped at the interfaces rather than at grain boundaries and dislocations owing to the higher binding energy with hydrogen, which induced hydrogen-accelerated spontaneous microcracking at aluminum-precipitate interfaces. In this work, a similar fracture mechanism caused by precipitate interfaces decohesion can also be used to explain the QCF. The hydrogen occupancy of the η_2 coherent interface decreased from 8.4×10^{-10} in the unloaded state to 8.7×10^{-11} atomH/site at 3.6% in-situ tensile strain (the corresponding hydrogen concentration is 5.3×10^{-10} atomH/nm^2; the hydrogen trap interval for a coherent η precipitate interface is 6.1 atomH/nm^2, assuming that the hydrogen occupancy is equal to one [17,31]). The hydrogen occupancy of the η_2 semi-coherent interface decreased from 1.84×10^{-5} atomH/site in the unloaded state to 1.9×10^{-6} atomH/site (1.2×10^{-5} atomH/nm^2). The interfacial decohesion of η_2 precipitates initiates when the trapped hydrogen density reaches 18.9 atomH/nm^2 [13,17], which is approximately 3.6×10^{10} and 1.6×10^{6} times higher than the hydrogen concentration at the coherent and semi-coherent interfaces of η_2 precipitates in the Mn-added Al alloys, respectively. Moreover, it was observed that hydrogen-induced strain localization at η_2 phase interfaces was suppressed after adding Mn in standard-state Al alloys (Figure 10). As a result, the fractional areas of QCF originating from the hydrogen-induced decohesion of precipitate interfaces was remarkably reduced (Figure 2(b)).

Hydrogen trapped at grain boundaries decreases the cohesion strength of the boundaries (HEDE model) and results in IGF, which is a common HE mechanism in structural materials. The critical hydrogen concentration at the grain boundaries for the initiation of intergranular cracks is approximately 2.8×10^{22} atomH·m^{-3} in Al-Zn-Mg-Cu alloys [30]. The hydrogen content trapped at the grain boundaries in Mn-added Al alloys in the unloaded and 3.6% tensile strain states were 4.04×10^{12} and 4.19×10^{11} atomH·m^{-3}, respectively, which are much lower than the critical value required for hydrogen-induced intergranular cracking. In addition, it was found that hydrogen-induced strain localization at grain boundaries was inhibited after adding Mn in standard-state Al alloys (Figure 9). Therefore, this is the main reason for the significant reduction in the fractional areas of IGF (Figure 2(b)).

Hydrogen-induced strain localization at grain boundaries and η_2 phase interfaces were suppressed due to strong hydrogen trapping capacity of $Al_{11}Mn_3Zn_2$, which could remove hydrogen from the grain boundaries and η_2 phase interfaces. Therefore, the Al alloys with Mn-rich particles exhibited the superior HE resistance by eliminating 75.0% and 81.7% of hydrogen-induced QCF and IGF, respectively, and suppressing hydrogen-induced ductility loss compared to the standard-state Al alloys. Moreover, in terms of HE sensitivity ($El_{loss} = (El_{LH} - El_{HH})/El_{LH} \times 100\%$, El_{LH} and El_{HH} are fracture elongations of LH and HH-treated specimens, respectively), the Al alloys with Mn-rich particles showed lack of HE sensitivity, which indicates that most of the hydrogen is occupied by Mn-rich particles and does not deteriorate the mechanical properties.

IMC particles are often used to inhibit recrystallization during solution heat treatment; however, they are detrimental to the mechanical properties of structural materials, especially the ductility [40]. Although IMC particles such as Al_7Cu_2Fe have been proven to improve the HE resistance due to hydrogen trapping effect, this still cannot solve the problem of ductility deterioration [13].

In this work, we proposed a strategy of suppressing HE by introducing IMC particles to achieve hydrogen redistribution in various trapping sites, rather than eliminating the hydrogen. IMC particles with HH trapping energies were designed using first-principles calculations; Mn-rich $Al_{11}Mn_3Zn_2$ particles exhibit the highest hydrogen trapping energy (0.859 eV/atom), leading to a decrease by approximately 5 orders of magnitude in the hydrogen occupancy in η_2 ($MgZn_2$) phase interfaces and grain boundaries, where HE cracks initiate. Most $Al_{11}Mn_3Zn_2$ particles remained intact during plastic deformation and exhibited good damage resistance. Hydrogen-induced strain localization at grain boundaries and η_2 phase interfaces were suppressed due to strong hydrogen trapping capacity of $Al_{11}Mn_3Zn_2$, hence preventing HE cracks initiation. Superior HE resistance without sacrificing the ductility was achieved through this hydrogen redistribution approach, which can also be applied to a variety of high-strength structural materials containing IMC particles, such as iron, titanium, and zirconium-based alloys.

4. Conclusions

We systematically induce the precipitation of a constant volume fraction of intermetallic compound (IMC) particles by adding one of 14 elements in a ternary Al-Zn-Mg high-strength alloy, the effect of IMC particles on HE resistances and HE mechanisms were investigated. The main conclusions are as follows:

(1) A strong correlation between hydrogen trapping energies of the IMC obtained from ab initio calculations with the resistance to HE was confirmed. The $Al_{11}Mn_3Zn_2$ particles had a trapping energy value (0.859 eV/atom) that was much higher than that of all known hydrogen trap sites, which caused the hydrogen occupancy at other trap sites such as micro pores, η_2 precipitates, vacancies, and grain boundaries to be significantly reduced. In particular, the hydrogen occupancy of η_2 interfaces and grain boundaries were decreased by approximately 5 orders of magnitude compared to the standard-state Al alloys (from 1.15×10^{-1} to 6.20×10^{-7} and from 4.42×10^{-1} to 4.60×10^{-6} atomH/site, respectively).

(2) Hydrogen occupancy and damage ratio of $Al_{11}Mn_3Zn_2$ particles changed

slightly when the tensile strain reached 3.6% and 9% after HH treatment (6.97 ppmw H), respectively, suggesting that they did not deteriorate the ductility. In addition, hydrogen-induced strain localization at grain boundaries and η_2 phase interfaces were suppressed due to strong hydrogen trapping capacity of $Al_{11}Mn_3Zn_2$, hence preventing HE cracks initiation. Therefore, the Al alloys with Mn-rich particles exhibited the superior HE resistance by eliminating 75.0% and 81.7% of hydrogen-induced QCF and IGF, respectively, and suppressing hydrogen-induced ductility loss compared to the standard-state Al alloys.

References

[1] A. T. Motta, et al., Hydrogen in zirconium alloys: A review, J. Nucl. Mater. 518 (2019) 440-460.

[2] S. Sobieszczyk, Hydrogen-enhanced degradation and oxide effects in zirconium alloys for nuclear applications, Int. J. Hydrogen Energy 6 (2011) 8619-8629.

[3] S. Suman, M. K. Khan, M. Pathak, R. N. Singh & J. K. Chakravartty, Hydrogen in Zircaloy: Mechanism and its impacts, Int. J. Hydrogen Energy 40 (2015) 5976-5994.

[4] M. Shahzad, H. Qureshi, H. Waqas & N. Hussain, A case study of environmental assisted cracking in a low alloy steel under simulated environment of pressurized water reactor, Mater. Des. 32 (2011) 5154-5158.

[5] M. P. Brady, et al., Rapid diffusion and nanosegregation of hydrogen in magnesium alloys from exposure to water, ACS Appl. Mater. Interfaces. 9 (2017) 38125-38134.

[6] A. S. H. Kabir, et al., Effect of post-weld heat treatment on microstructure, hardness, and tensile properties of laser-welded Ti-6Al-4V, Metall. Mater. Trans. A 43 (2012) 4171-4184.

[7] Z. Tarzimoghadam, et al., Multi-scale and spatially resolved hydrogen mapping in a Ni-Nb model alloy reveals the role of the d phase in hydrogen embrittlement of alloy 718, Acta Mater. 109 (2016) 69-81.

[8] G. Mcmahon, B. D. Miller & M. G. Burke, High resolution NanoSIMS imaging of deuterium distributions in 316 stainless steel specimens after fatigue testing in high pressure

deuterium environment, Npj Mater. Degrad. 2 (2018) 1-6.

[9] I. I. Chernov, M. S. Staltsov & B. A. Kalin, Some problems of hydrogen in reactor structural materials: A review, Inorg. Mater. Appl. Res. 8 (2017) 643-650.

[10] A. Heinz, A. Haszler, C. Keidel, et al., Recent development in aluminium alloys for aerospace applications, Mater. Sci. Eng. A 280 (2000) 102-107.

[11] J. C. Williams, Jr. E. A Starke, Progress in structural materials for aerospace systems. Acta Mater. 51 (2003) 5775-5799.

[12] 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 (2020) 1-19.

[13] H. Su, H. Toda, K. Shimizu, et al., Assessment of hydrogen embrittlement via image-based techniques in Al-Zn-Mg-Cu aluminum alloys, Acta Mater. 176 (2019) 96-108.

[14] H. Toda, T. Hidaka, M. Kobayashi, et al., Growth behavior of hydrogen micropores in aluminum alloys during high-temperature exposure, Acta Mater. 57 (2009) 2277-2290.

[15] S. K. Dwivedi, M. Vishwakarma, Hydrogen embrittlement in different materials: a review, Int. J. Hydrogen Energy 43 (2018) 21603-21616.

[16] J. T. Burns, S. Kim, R. P. Gangloff, Effect of corrosion severity on fatigue evolution in Al-Zn-Mg-Cu, Corros. Sci. 52 (2010) 498-508.

[17] K. Shimizu, H. Toda, H. Fujihara, et al., Hydrogen partitioning behavior and related hydrogen embrittlement in Al-Zn-Mg alloys, Eng. Fract. Mech. 216 (2019) 106503.

[18] M. L. Martin, B. P. Somerday, R. O. Ritchie, et al., Hydrogen-induced intergranular failure in nickel revisited, Acta Mater. 60 (2012) 2739-2745.

[19] Z. Zhang, G. Obasi, R. Morana, et al., Hydrogen assisted crack initiation and propagation in a nickel-based superalloy, Acta Mater. 113 (2016) 272-283.

[20] W. W. Gerberich, R. A. Oriani, M. J. Lji, et al., The necessity of both plasticity and brittleness in the fracture thresholds of iron, Philosophical Magazine A 63 (1991) 363-376.

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

[22] T. Tsuru, K. Shimizu, M. Yamaguchi, et al., Hydrogen-accelerated spontaneous microcracking in high-strength aluminium alloys, Scientific Reports 10 (2020) 1-8.

[23] H. Toda, H. Oogo, K. Uesugi, M. Kobayashi, Roles of pre-existing hydrogen micropores on ductile fracture, Mater. Trans. 50 (2009) 2285-2290.

[24] M. S. Bhuiyan, et al., Influences of hydrogen on deformation and fracture behaviors of high Zn 7XXX aluminium alloys, Int. J. Fract. 200 (2016) 13-29.

[25] I. Nikulin, A. Kipelova, S. Malopheyev, et al., Effect of second phase particles on grain refinement during equal-channel angular pressing of an Al-Mg-Mn alloy, Acta Mater. 60 (2012) 487-497.

[26] R. Hu, T. Ogura, H. Tezuka, et al., Dispersoid formation and recrystallization behavior in an Al-Mg-Si-Mn alloy, J. Mater. Sci. Technol. 26 (2010) 237-243.

[27] Y. B. Kim, Y. H. Chung, K. K. Cho, et al., Recrystallization behavior of Al-2Li-3Mg-1Cu-0.12Zr-XMn (X= 0, 0.5) alloy, Scr. Mater. 36 (1997).

[28] M. Itakura, M. Yamguchi, K. Ebihara, K. Matsuda, H. Toda, First-principles calculations of hydrogen trapping energy at screw and edge dislocations of aluminum [In preparation].

[29] T. Tsuru, M. Yamaguchi, K. Ebihara, et al., First-principles study of hydrogen segregation at the MgZn2 precipitate in Al-Mg-Zn alloys, Comput. Mater. Sci. 148 (2018) 301-306.

[30] L. Ismer, M. S. Park, A. Janotti, et al., Interactions between hydrogen impurities and vacancies in Mg and Al: A comparative analysis based on density functional theory, Phys. Rev. B 81 (2010) 139902.

[31] T. Tsuru, M. Yamaguchi, K. Ebihara, et al., First-principles study of hydrogen segregation at the MgZn2 precipitate in Al-Mg-Zn alloys, Comput. Mater. Sci. 148 (2018) 301-306.

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

[33] D. S. Park, S. W. Nam, Effects of manganese dispersoid on the mechanical properties in Al-Zn-Mg alloys, J. Mater. Sci. 30 (1995) 1313-1320.

[34] D. H. Lee, J. H. Park, S. W. Nam, Enhancement of mechanical properties of Al-Mg-Si alloys by means of manganese dispersoids, Mater. Sci. Tech. 15 (1999) 450-455.

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

[36] M. Dadfarnia, A. Nagao, S. Wang, et al., Recent advances on hydrogen embrittlement of

structural materials, Int. J. Fracture 196 (2015) 223-243.

[37] I. M. Robertson, P. Sofronis, A. Nagao, et al., Hydrogen embrittlement understood, Metall. Mater. Trans. A 46 (2015) 2323-2341.

[38] M. J. Hÿtch, E. Snoeck, R. Kilaas, Quantitative measurement of displacement and strain fields from HREM micrographs, Ultramicroscopy 74 (1998) 131-146.

[39] M. L. Martin, M. Dadfarnia, A. Nagao, et al., Enumeration of the hydrogen-enhanced localized plasticity mechanism for hydrogen embrittlement in structural materials, Acta Mater. 165 (2019) 734-750.

[40] Q. G. Wang, C. H. Caceres, J. R. Griffiths, Damage by eutectic particle cracking in aluminum casting alloys A356/357, Metall. Mater. Trans. A 34 (2003) 2901-2912.

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.

Additional information

The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to Prof. Toda.

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

Figure Captions

Figure 1 Excellent trapping energies of IMC particles to hydrogen. The trapping energies of various intermetallic compound particles to hydrogen were calculated by first-principles density functional theory (DFT). The hydrogen trapping energies of various defect structures, such as dislocations [28], grain boundaries [29], vacancies [30], precipitates [22,31], and micro pores [32], were derived from references. $Al_{11}Mn_3Zn_2$ shows advantages in hydrogen trapping compared to other IMC particles and defect structures.

Figure 2 Superior HE resistance results from introducing IMC particles. **a,** Stress-displacement curves for standard-state, Sc-added and Mn-added Al alloys after low-hydrogen (LH) and high-hydrogen (HH) treatments, Mn-added Al alloys exhibited a superior HE resistance without sacrificing the ductility after HH treatment. **b,** Fracture morphology of standard-state and Mn-added Al alloys after HH treatment, suppressing hydrogen-induced QCF and IGF by introducing IMC particles was achieved. **c,** Fractional areas of QCF and IGF for standard-state, Nb-added, Mo-added, V-added, Ca-added, Y-added, Sr-added, Ni-added, Zr-added, Fe-added, Cr-added, Ti-added, Co-added, Sc-added and Mn-added Al alloys under HH treatments. **d,** The relationships between the added elements, maximum trapping energies and fractional areas of QCF fracture are summarized, the higher trapping energy with hydrogen, the lower fractional area of QCF, which indicates that QCF was effectively suppressed by introducing IMC particles, especially the IMC particles formed by adding Mn.

Figure 3 Fracture surfaces after preliminary tensile tests of HH and LH specimens. a, Standard state, Sc-added and Mn-added Al alloys after HH treatments. **b,** Standard state, Sc-added and Mn-added Al alloys after LH treatments.

Figure 4 Hydrogen redistribution driven by IMC particles. **a, b,** Distribution and crystal structure of $MgZn_2$ precipitates and $Al_{11}Mn_3Zn_2$ particles in Mn-added Al alloys observed by HRTEM. **c,** 3D perspective views of IMC particles and micro pores obtained by high-resolution X-ray tomography in Zr-added and Mn-added Al alloys. **d,** Hydrogen trapping occupancy before and after adding Mn/Zr elements derived from thermodynamic equilibrium condition and first-principles calculations, the formed $Al_{11}Mn_3Zn_2$ particles after Mn addition caused hydrogen occupancy of the η_2 interfaces and grain boundaries to decrease by approximately 5 orders of magnitude compared to that of the standard-state Al alloys.

Figure 5 APT results. a, Mn-added Al alloys. **b,** Standard-state Al alloys.

Figure 6 EBSD results. a, Standard-state Al alloys. **b,** Mn-added Al alloys.

Figure 7 Damage behavior of $Al_{11}Mn_3Zn_2$ particles and hydrogen partitioning behavior during deformation after HH treatment. a-d, CT images of the Mn-added Al alloys at each nominal strain on a x-z virtual cross section. **e, f,** Corresponding to the partial enlarged view in **a**

and **b**. **g, h,** 3D imaging around crack tip in Zernike imaging in Mn-added Al alloys. **i,** Hydrogen partitioning calculations for the regions ahead of hydrogen-induced quasi-cleavage crack tip and near the crack ridge in Mn-added Al alloys under the in-situ tensile strain of 3.6%. **j,** Hydrogen partitioning behavior among lattice, vacancies, dislocations, grain boundaries, IMC particles, η_2 precipitates and micro pores in Mn-added Al alloys before and after loading.

Figure 8 Micro-deformation mechanisms of $Al_{11}Mn_3Zn_2$ particles under HH and LH conditions. a, Phase, KAM and TEM images of Mn-added Al alloys before tensile deformation, TEM image was taken from 011 crystal zone axis of Al matrix. **b,** Phase, KAM and TEM images taken from the crack tip region of HH-treated Mn-added Al alloys after tensile failure, strain concentration around $Al_{11}Mn_3Zn_2$ particles mainly resulted from dislocations piled-up. **c,** Phase, KAM and TEM images taken from the crack tip region of LH-treated Mn-added Al alloys after tensile failure. **d,** KAM distributions in Al matrix and $Al_{11}Mn_3Zn_2$ particles of HH/LH-treated Mn-added Al alloys before and after tensile failure. The strain distributions around $Al_{11}Mn_3Zn_2$ and in Al matrix remained almost unaffected when changing treatment conditions from LH to HH.

Figure 9 Suppression of hydrogen-induced dislocations piled-up at grain boundaries by $Al_{11}Mn_3Zn_2$. a, e, Microstructures near the fracture surfaces of Mn-added and standard-state Al alloys treated by HH after tensile failure, respectively. The cracks mainly propagated along the grain interiors in Mn-added Al alloys, while they mainly propagated along the grain boundaries in standard-state Al alloys. **b,** TEM BF image cut from area **b** in **a**. **c, d,** TEM BF and DF images corresponding to the area **c** in **b**. **f,** TEM BF image cut from area **f** in **e**. **g, h,** TEM BF and DF images corresponding to the area **g** in **f**. The piled-up dislocations at grain boundaries were significantly reduced during tensile failure after adding Mn in standard-state Al alloys, indicating that hydrogen-induced strain localization at grain boundaries was suppressed by $Al_{11}Mn_3Zn_2$ particles.

Figure 10 Suppression of hydrogen-induced strain localization at η_2 phase interfaces by $Al_{11}Mn_3Zn_2$. a, h, Microstructures near the fracture surfaces of Mn-added and standard-state Al alloys treated by HH after tensile failure, respectively. **b,** TEM BF image cut from area **b** in **a**. **c, d** HRTEM images corresponding to the area **c** and **d** in **b**. **e, f,** Corresponding strain maps of geometric phase analysis (GPA) (in-plane rigid-body rotation, ω_{xy}) for HRTEM images **c** and **d**, respectively. **g,** Inverse FFT and FFT patterns corresponding to HRTEM image **c**, inverse FFT pattern derives from $\left(\bar{1}1\bar{1}\right)$ reflection. **i,** TEM BF image cut from area **i** in **h**. **j, k,** HRTEM images corresponding to the area **j** and **k** in **i**. **l, m,** Corresponding strain maps of geometric phase analysis (GPA) (in-plane rigid-body rotation, ω_{xy}) for HRTEM images **j** and **k**, respectively. **n,** inverse FFT and FFT patterns corresponding to HRTEM image **j**. Strain maps were plotted with respect to an internal reference lattice by $g_1 = \left(11\bar{1}\right)_{matrix}$ and $g_2 = \left(200\right)_{matrix}$. Dislocations mainly bypassed η_2 precipitates in Mn-added and standard-state Al alloys treated by HH. Density of edge dislocations around the η_2 phase interfaces in Mn-added Al alloys is significantly lower than that in standard-state Al alloys after tensile failure, moreover, the results of the strain distributions originating from strain maps are also similar to that. The strain localization at η_2 phase interfaces was effectively inhibited during tensile failure after adding Mn in standard-state Al alloys.

Extended Data Figure S1 Schematic diagrams of the thermomechanical treatment process. a, High-hydrogen treatment. **b,** Low-hydrogen treatment.

Extended Data Figure S2 Desorption curves of the Mn-added Al alloys after HH and LH treatments.

Extended Data Figure S3 Experimental setup for the imaging X-ray microtomography. a, Schematic diagram. **b,** A pneumatic material test rig specially designed for X-ray micro-tomography at the synchrotron radiation facility.

Extended Data Figure S4 Fracture surfaces after preliminary tensile tests of HH specimens. Nb-added, Mo-added, V-added, Ca-added, Y-added, Sr-added, Ni-added, Zr-added, Fe-added, Cr-added, Ti-added and Co-added Al alloys after HH treatments.

Extended Data Figure S5 TEM results. a, Standard-state Al alloys. **b,** Corresponding to the partial area **b** in **a**. **c,** Mn-added Al alloys. **d,** Corresponding to the partial area **d** in **c**.

Extended Data Figure S6 Hydrogen partitioning behavior in HH-treated Mn-added Al alloys during deformation. a, Hydrogen partitioning calculations for the region ahead of hydrogen-induced quasi-cleavage crack tip under the in-situ tensile strain of 3.6%. **b,** Trapped hydrogen contents among lattice, vacancies, dislocations, grain boundaries, IMC particles, η_2 precipitates and micro pores before and after loading.

Extended Data Figure S7 Suppression of hydrogen-induced cracks by $Al_{11}Mn_3Zn_2$. a, Microstructures near the fracture surfaces of Mn-added Al alloys treated by HH after tensile failure. The cracks mainly propagated along the grain interiors in Mn-added Al alloys. **b,** Corresponding to the partial magnification images of the area **1** and **2** in **a**. **c, d,** Corresponding to the partial magnification and mapping images of the area **c** and **d** in **b,** the IMC-rich region can effectively blunt and suppress hydrogen-induced cracks.

Extended Data Figure S8 3D Mapping of equivalent plastic strain, vacancy concentrations and dislocation densities in the Mn-added Al alloys at load strain 0.0 to 3.6% on a x-z virtual section. a, Equivalent plastic strain. **b,** Vacancy concentration. **c,** Geometrically necessary dislocations (GND). **d,** Statistically stored dislocations (SSD).