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Combined microtomography, thermal desorption spectroscopy, X-ray diffraction study of hydrogen trapping behavior in 7XXX aluminum alloys

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Abstract

In the present study, combined thermal desorption spectroscopy (TDS), microtomography and X-ray diffraction study has been carried out to identify the hydrogen trap sites in 7XXX aluminum alloys. Through constant heating rate TDS experiments, three distinct trap states have been identified. It is revealed that micropores are the predominant hydrogen trap site in alloys with medium hydrogen content, whereas grain boundaries is the major hydrogen trap site in alloys with low and high hydrogen content. We have clarified that the rate of trap site occupancy in grain boundaries is high compared to dislocations and vacancies. Such high hydrogen coverage at grain boundaries indicates that the hydrogen-assisted fracture would be intergranular.

Keywords: Thermal desorption spectroscopy, Microtomography, XRD, Hydrogen trapping, Hydrogen embrittlement, Aluminum alloys

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1. Introduction

In general, the presence of microstructural imperfections (including grain boundaries, dislocations, vacancies, precipitates etc.) in materials strongly impeded the lattice diffusivity of hydrogen (H). Therefore, the lattice defects and precipitates act as a potential hydrogen trapping sites in any materials system. Depending on the binding energy of hydrogen to the trapping sites, they are classified as: (i) reversible or diffusible trapping sites, and (ii) irreversible or non-diffusible trapping sites [1]. Pressouyre suggested that materials with mostly reversible traps are more sensitive to hydrogen embrittlement and materials with finely distributed irreversible traps are less susceptible to hydrogen embrittlement [2-3].

Hydrogen embrittlement in 7XXX aluminum alloys has been recognized as one of the long-standing technological challenges in the aerospace industry. Until now, many efforts have been carried out by various researchers to increase the strength and toughness as well as to improve the hydrogen embrittlement resistance of 7XXX aluminum alloys through: (i) changes in composition (mainly Zn/Mg/Cu ratios) [4-9], (ii) minimizing the impurity level [10-12], (iii) heat treatment and processing [13-20]. Consequently, a range of microstructural features can be resulted, which can act as H trapping sites. The potential trap sites for hydrogen in aluminum alloys are solute atoms, lattice interstices, dislocations, vacancies, precipitates, high angle grain boundaries, second phase particles and precipitates, micropores [21-22]. It has been reported that the hydrogen-assisted fracture morphology in 7XXX aluminum alloys is frequently intergranular [23-24]. Apart from this, transgranular, mixture of transgranular and intergranular, quasi-cleavage often appears as fractographic features of hydrogen related failure [25-30]. The extent of this fracture mode is mainly influenced by: (i) the nature and distribution of hydrogen trap sites, (ii) the concentration of hydrogen available, and (iii) the possible interaction between

hydrogen and the trap sites. Therefore, identification of the nature and distribution of hydrogen trap sites and the trap binding energy for hydrogen is decisive in determining the likelihood of hydrogen-assisted fracture.

Up to date, very few research works have been carried out to understand the hydrogen trapping behavior of aluminum alloys. Nevertheless, the identification of TDS peaks in terms of the nature of trap sites is mired in controversy. For example, Young and Scully [31] employed thermal desorption spectroscopy (TDS) to study the hydrogen trapping behavior of high purity polycrystalline aluminum and observed three desorption peaks (approximately at 523 K, 673 K, and 793 K, respectively) and proposed that these peaks are due to hydrogen released from lattice interstitial, dislocations and vacancies, respectively. Later on, Izumi and Itoh [32] investigated the hydrogen trapping states of pure aluminum foils and argued that since the diffusion of hydrogen is faster than that of free vacancy, the migration of free vacancy is mainly controlled by the co-diffusion of vacancy/hydrogen pair. Therefore, the first peak observed by Young and Scully at 523 K is due to hydrogen trapped by the vacancies rather than interstitial lattice. They reached the conclusion that the desorption peaks observed at 472 K, 663 K, and 763 K are due to hydrogen trapped at vacancies, dislocations, and blisters, respectively [32]. However, due to the presence of complex microstructures, the hydrogen trapping behavior in practical engineering alloys such as 7XXX aluminum alloys is much complex than that of pure aluminum. To the best of the authors knowledge, hydrogen trapping in 7XXX aluminum alloys has not yet been studied.

Therefore, the present work aims to: (i) identify the hydrogen trap sites in 7XXX aluminum alloys, (ii) determine the trap binding energy for hydrogen in each trap, and (iii) quantify the amount of hydrogen trapped in each trap sites. In fact, the ultimate goal of this paper is to clarify the hydrogen embrittlement susceptibility of 7XXX aluminum alloys.

2. Experimental details

2.1 Materials and heat treatment

The material used in the present study was modified 7150 aluminum alloys (with 10 mass% Zn). Three alloys were prepared from the supplied modified 7150 aluminum alloys, where the composition of the materials remains same but the amount of total hydrogen content is varied. Hereinafter, the materials are called material LH, material MH and material HH, respectively. In order to vary the total hydrogen content, TiH₂ was added during the casting of material HH, whereas the homogenization of material LH was performed in a high vacuum chamber that had been evacuated below 3×10^{-4} Pa. The as-cast ingots were first homogenized at 743 K for 86.4 ksec followed by air cooling to room temperature. The ingots were then hot rolled with multiple passes at 673 K. The final thickness of the ingots was 13 mm. The rolled plates were then solution heat treated to for 7.2 ksec at 748 K followed by cold water quenching and artificially aged at 393 K for 21.6 ksec to provide T7651 temper condition. The vacuum fusion method was utilized to measure the total hydrogen content of each material.

2.2. Experimental procedure

X-ray microtomography was used to measure the hydrogen gas trapped in micropores. X-ray microtomography was performed at BL20XU undulator beamline of SPring-8. A monochromatic X-ray beam of 20 keV photon energy generated by a liquid nitrogen cooled Si(111) is used for the observation. The image detector is placed 20 mm behind the specimen and total 1800 radiographs (scanning 180 degrees) were obtained around the loading axis. Image slices were reconstructed from a series of projections based on the conventional filtered back-projection algorithm. An isotropic voxel with a 0.5 μm edge was achieved in the reconstructed slices (with

a resolution of about 1 μm [33-35]). The grey value in each dataset was calibrated so that the linear absorption coefficient of -30 to 50 cm^{-1} fell within an 8 bit gray scale range between 0 to 255. The volume of each micropore and particle at sub-voxel accuracy is estimated by computing pentagonal faceted iso-intensity surfaces from the volumetric data set using the conventional Marching Cubes algorithm [36]. To suppress inaccuracies origination from image noise, only micropores and particles over 9 voxels in volume were counted as microstructural features in the quantitative analysis.

Assuming that micropores are in thermal equilibrium where surface tension, γ , is balanced by an opposing gas pressure inside a micropore, P , hydrogen trapped in all micropores, C_{pore} (mol) is calculated as follows:

$$C_{pore} = \sum \left(\frac{2\pi\gamma d_i^2}{3RT} \right) \quad (1)$$

where d_i is the diameter of the i^{th} micropore, R is the gas constant, T is the temperature, and γ is the surface tension (1.16 Nm^{-1} for (111) face). The diameter of each micropore is known from the tomographic data, hence, C_{pore} can be obtained by using Eq. (1)

The hydrogen desorption and trapping characteristics were studied under thermal desorption spectroscopy (TDS). The TDS spectra for materials LH, MH and HH were obtained by heating the samples from room temperature to 773 K at a constant heating rate of 100 K/h. The activation energy of the different traps were evaluated by heating a sample of material HH at three different heating rates of 50, 100 and 200 K/h, respectively. The activation energy for each trap was estimated by using Kissinger's method from the shift of peaks temperatures with increasing applied heating rate using the relationships [37]:

$$\frac{d(\ln(\varphi/T_m^2))}{d(1/T_m)} = -\frac{E_b}{R} \quad (2)$$

where φ is the heating rate (K^{-1}), T_m is the peak temperature (K), E_b is the desorption energy of each trap ($Jmol^{-1}$), and R is the gas constant ($8.13 JK^{-1}mol^{-1}$). The desorption energy for each trap was calculated from the linear regression of the slope between $d\left(\ln\left(\varphi/T_m^2\right)\right)$ as a function of $d\left(1/T_m\right)$.

The dislocation density of each alloy was studied by means of XRD. An automated diffractometer using Cu-K α radiation operating at 40 kV and 30 mA with a wavelength of 0.154 nm was used for XRD. The samples were scanned continuously over a range of 2θ from 20 to 150 deg at a scan rate of 0.01 deg/min. From the XRD data, the value of full width at half-maximum (FWHM) is calculated and substituted into the following modified Williamson-Hall equation [38]:

$$\Delta K^2 \cong \left(\frac{0.9}{D}\right)^2 + \left(\frac{\pi M^2 b^2}{2}\right)\rho K^2 C + O(K^4 C^2) \quad (3)$$

where $K = 2 \sin \theta / \lambda$, and $\Delta K = 2 \cos \theta (\Delta \theta) / \lambda$. Here, θ , λ , $\Delta \theta$, and C are the diffraction angle, the wavelength of the X-ray, FWHM, and average contrast factor of dislocations, respectively. D , ρ , and b are the average grain size, the average dislocation density, and the Burgers vector (0.286 nm in Al [39]), respectively. M is a constant depending on the dislocations, and O indicates higher-order terms.

The average contrast factors of dislocations in a cubic crystal have the following form [40]:

$$C = A + BH^2 \quad (4)$$

where $H^2 = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)$, and A and B are constants which depends on the elastic constants of the material. The value of A is taken as 0.2 [41].

Inserting Eq.(4) into Eq.(3)

$$\frac{[(\Delta K)^2 - \alpha]}{K^2} \cong \beta A + \beta B H^2 \quad (5)$$

where $\alpha = (0.9/D)^2$.

The intercept and the slope of the linear regression between $\frac{[(\Delta K)^2 - \alpha]}{K^2}$ as a function of H^2 are equivalent to βA and βB , respectively. Hence the ratio A/B can be obtained experimentally.

3. Results

3.1 Hydrogen trapped within micropores

Optical micrograph presented in Fig. 1, shows that the grain structure was similar for all the alloys and consisted of almost equiaxed flat shaped grains, elongated in the rolling direction. Table 1 summarizes the average grain size of the three alloys used in the present study. Figure 2 shows the 3D distribution of the micropores in each alloy. Many coarse hydrogen micropores observed in material HH. The quantitative analysis results of both micropores and particles are summarized in Table 2. Interestingly though the average micropore diameter does not differ greatly (2.7 μm for material LH, 2.9 μm for material MH, and 3.6 μm for material HH, respectively) but the volume fraction of micropores is approximately 25 times higher in material HH and 4 times higher in material MH than that of material LH, respectively. In contrast, the volume fraction of particles is approximately 2.70 times higher in material MH and 1.70 times higher in material LH than that of material HH. Variation of the diameter of micropores in

material LH, material MH and material HH is shown in Fig. 3. Many coarser micropores, typically larger than 5 μm , are observed in material HH, whereas majority of micropores are less than 5 μm in both material LH and material MH. The hydrogen trapped within micropores for each alloys was calculated by using Eq. 1 and is shown in Table 3. The total hydrogen content as measured by vacuum fusion method is also shown in Table 3. As can be seen that the total hydrogen content of material MH is about 2.7 times higher than that of LH material, but significantly high amount of hydrogen is found to be trapped in micropores (of about 51%). In contrast, material HH showed about 28% hydrogen is trapped within micropores, whereas material LH showed about 33% hydrogen is trapped within micropores. Recently Toda and his co-workers [42] estimated the hydrogen that was trapped in micropores in Al-5Mg alloy with hydrogen content varied between 0.3 to 5.12 mL per 100 gAl and reported that micropores act as major hydrogen trap site in the Al-5Mg alloys with low hydrogen content (the Al-5Mg alloys with 0.30 mL per 100 gAl total hydrogen content around 53% hydrogen is trapped in micropores, whereas alloy with 4.94 mL per 100 gAl total hydrogen content only 9.1% hydrogen is trapped in micropores). They further reported that the hydrogen micropores are heterogeneously nucleated on particles, and micropore formation can be effectively suppressed in the absence of particles. However, in the present study we observed that material HH, which contain around 8.7 times higher hydrogen than materials LH, only 28% hydrogen is found to be trapped within micropores (which is 1.2 times higher than that of material LH). This difference is attributed due to the lack of heterogeneous nucleation sites for hydrogen to form micropores and also the presence of relatively coarse micropores and their mutual interaction with neighboring micropores.

3.2 Hydrogen trap states and activation energy determination

Figure 4 shows the hydrogen evolution curves measured on material LH, MH and HH, respectively, at a heating rate of 100K/h. The TDS spectra of material HH clearly showed the existence of three distinct desorption peaks at approximately 482 K, 584 K and 684 K. In contrast, TDS spectra of material LH and material MH showed that the peak in the higher temperature range 584 K is relatively clear. As shown in Table 3 that significantly high amount of hydrogen is trapped in micropores (33% for material LH and 51% for material MH), therefore, the obtained TDS spectra of material LH and material MH would be due to relatively low trapped hydrogen within the matrix. It has been reported that owing to the varying breadth and height of TDS spectra desorption rate peak, it is possible that overlapped and partially hidden peaks are typical for hydrogen trapping [43]. Therefore, it is reasonable to assume that desorption of hydrogen at relatively low temperature (482 K) may be masked by a larger desorption peak (584 K). Therefore, it is considered that three hydrogen desorption peaks are identified at approximately 482 K, 584 K and 684 K, the TDS spectra of each alloys is analyzed by Gaussian function, and is shown in Fig. 5. Hereinafter, the peaks will be referred to as peak1, peak2, and peak3 in ascending order of temperature. Our microtomography results showed that all alloys contain micropores (as shown in Table 1). Izumi and Itoh [35] reported that the state of molecular hydrogen trapped in micropores is the same as that of blisters. Since the trap site identified by Young and Scully [34] did not take into account the micropores, therefore, the identification of TDS peaks in terms of the nature of trap sites, as proposed by Izumi and Itoh [35] is adopted in the present analysis. Hence, in the 7XXX aluminum alloys, hydrogen resides at trapping sites at vacancies, dislocations, and micropores.

Figure 6 shows hydrogen desorption spectra of material HH at three different heating rates. It can be seen that desorption peaks are shifted to higher temperatures with an increased heating rate.

Figure 7 shows a Kissinger-style plot of $\left(\ln\left(\frac{\varphi}{T_m^2}\right)\right)$ vs $\left(1/T_m\right)$ of each peak together with the linear regression fit. The desorption energy for the corresponding trapping states are 11.4, 17.9, and 31.7 kJ/mol for the vacancy, dislocation, and micropores, respectively.

3.3 Determination of dislocation density and equilibrium vacancy concentration

Figure 8 shows the X-ray diffractogram of the investigated alloys. The crystal indices of each (hkl) reflection are also shown in Fig.8. The FWHM of all the peaks were calculated and is plotted according to the classical Williamson-Hall plot as shown in Figure 9. The ratio of A/B is obtained from the linear regression of the slope and intercept between $\frac{[(\Delta K)^2 - \alpha]}{K^2}$ as a function of H^2 . The values of C is calculated by inserting the value of A and B in Eq. 4. The modified Williamson-Hall plot is shown in Figure 8. The slope of the linear regression is equivalent to $\left(\frac{\pi M^2 b^2}{2}\right) \rho$. Taking $M=0.63$ [39], the dislocation density of each alloys was calculated and is shown in Table 4. The results showed that the dislocation density of each material is approximately 10^{14} order.

The equilibrium number of vacancies, N_v , is evaluated according to [44]:

$$N_v = \left(\frac{\rho N_A}{A_{Al}}\right) \exp\left(-\frac{Q_v}{kT}\right) \quad (6)$$

where, N_A is the Avogadro's number, ρ is the density of aluminum (2.71 g/cm³), and A_{Al} is the atomic weight of aluminum (26.98 amu), Q_v is the energy required for vacancy formation, T is the absolute temperature (K), and k is the Boltzmann's constant (8.62×10⁻⁵ eV/atom).

Since all the materials used in the present study were artificially aged for sufficiently long time, therefore, it is reasonable to assume that vacancy concentration is in equilibrium at room

temperature. The vacancy formation energy, Q_v , is taken to be 0.66eV [45] and the calculated equilibrium vacancy concentration is also shown in Table 4.

3.4 H trap site calculation

Hydrogen trapped at each trap sites has been calculated assuming that hydrogen trapped in normal interstitial lattices and other trap sites is in equilibrium [46]:

$$\frac{\theta_T}{1-\theta_T} = \theta_L \exp\left(\frac{E_b}{RT}\right) \quad (7)$$

where E_b is the trap binding energy, R is the gas constant equal to $8.31 \text{ J mole}^{-1}\text{K}^{-1}$, T is the absolute temperature, θ_L is the occupancy of the interstitial sites and θ_T is the occupancy of other trap sites. Total hydrogen concentration, C_H^T , represents the sum of the hydrogen stored in normal interstitial lattice and all trap sites, corresponding to the total hydrogen content listed in Table 3:

$$C_H^T = \theta_L N_L + \sum \theta_{Ti} N_{Ti} + C_{pore} \quad (8)$$

where N_L and N_{Ti} are trap densities in the normal interstitial lattice and i^{th} trap sites other than micropores in atoms per unit volume, respectively. C_{pore} represents the total hydrogen atoms per unit volume trapped in micropores, corresponding to the hydrogen in micropores ($M_{H \text{ pore}}$) listed in Table 3.

In this analysis trap binding energy, E_b for solute magnesium was assumed to its upper limit, i.e. 5.8 kJ mol^{-1} [47] and E_b value for high angle grain boundary is 35 kJ mol^{-1} [21]. E_b values for the vacancy and dislocation is taken as 11.4 kJ mol^{-1} and 17.9 kJ mol^{-1} , respectively. Trap site occupancy and the concentration of hydrogen for each trap site are listed in Table 5. It is worth noting that the trap site occupancy is high for grain boundaries ranging from 0.099 to 0.606. It is

interesting to note that grain boundaries are the major trap sites in material LH and material HH, higher than the micropores by a factor of 1.66 and 2.24 for material LH and material HH, respectively. In contrast, micropores is the major trap sites in material MH, higher than grain boundaries by a factor of 1.20.

The estimated value for vacancy trapping has yielded the lowest value in each material. In the present analysis, we have assumed that each vacancy is occupied by a single H atom. Recently Lu and Kaxirus [45] reported that up to 12 H atoms can be trapped at a single vacancy site. Therefore, it is speculated that even such small amount of hydrogen trapped at vacancy can have a strong influence on the fracture. Owing to high hydrogen coverage at grain boundaries, it is reasonable to assume that grain boundaries can have a strong influence on fracture i.e., the hydrogen-assisted fracture could be intergranular.

4. Discussion

This work has shown that vacancies, dislocations, grain boundaries and micropores are the main hydrogen trap sites in 7XXX aluminum alloys. The susceptibility of hydrogen embrittlement of 7XXX aluminum alloys is mainly rooted on the strength and distribution of H traps [3, 48]. The presence of a large population of low binding energy traps provides a reservoir of highly mobile H, thereby exacerbate embrittlement [49]. It has been reported that in aluminum alloys, hydrogen atoms are transported by dislocations [25]. The presence of hydrogen not only enhanced the dislocation mobility but also facilitates dislocation emission from crack tip [50-51]. Therefore, a significant amount of hydrogen can be transported to some sites in the material such as vacancies, grain boundaries, precipitates.

Though the present analysis showed that the trapped hydrogen at vacancy is the lowest in each material, however, the coupling of hydrogen with vacancies lowered the vacancy formation energy and resulted in a drastic increase of vacancy concentration [52-54]. The vacancy defects occupied by H atoms cluster to form platelets on (111) planes of Al and lead to void formation or crack nucleation on (111) plane [45, 55]. Furthermore, the H-induced vacancy formation also facilitates dislocation climb.

It was also observed that the trap site occupancy for grain boundary is high ranging from 0.099 to 0.606 (Table 5). Moreover, desorption energy of hydrogen for dislocation (17.9 kJ mol^{-1}) is lower than that of grain boundary (35 kJ mol^{-1}). When moving dislocations meet grain boundaries, hydrogen will be deposited at grain boundaries. Therefore, the increased hydrogen concentration at grain boundaries enhanced the tendency for intergranular fracture [23-24]. However, intergranular fracture mode is dominant only when a very high concentration of hydrogen is available, otherwise, the fracture mode would be transgranular [25].

As is well documented in scientific literature, 7XXX aluminum alloys, which have a plethora of microstructural trap sites for hydrogen including solute atoms, dislocations, grain boundaries, vacancies (density of which increases with hydrogen [56-57]), interfaces between matrix and precipitates, micropores, the hydrogen trapping behavior is very complex. Therefore, precise and accurate characterization of hydrogen trapping parameters (such as binding energy, trap density) is of crucial importance. For this purpose, further systematic research has to be carried out by using model materials whose microstructures remain same but the amount of hydrogen content and micropores is varied, to study the interaction of hydrogen with microstructural imperfections and that of micropores separately [58]. Concerning the hydrogen behavior and its interaction with grain boundaries, some investigators claimed that though high angle grain boundary act as

short circuiting diffusion path but has zero or very weak trapping power for hydrogen [59-61]. Therefore, it would be more instructive to use more advanced technique such as three dimensional atom probe (3DAP) to identify the trapped hydrogen at grain boundaries, should they be present, as that would make detection more feasible [62]. Furthermore, in the present study, the desorption energy for vacancy trapping of hydrogen is evaluated under the assumption that hydrogen is desorbed from vacancies together with other hydrogen trap sites such as dislocations. However, there is a possibility that vacancy can migrate to the specimen surface, accompany with the hydrogen and then release the hydrogen. First-principle calculations have to be carried out to clarify details of complex vacancy-hydrogen interaction and evolution of the studied material.

5. Conclusion

The behavior of hydrogen in 7XXX aluminum alloys with different hydrogen content has been investigated by means of thermal desorption spectroscopy, microtomography and X-ray diffraction analysis. Three distinct hydrogen trapping states have been identified in the TDS spectra. Microtomography results revealed that about 51% hydrogen is found to be trapped within micropores in 7XXX alloys with medium hydrogen content. In contrast to this, the absolute amount of hydrogen trapped within grain boundaries in 7XXX alloys with low and high hydrogen content is about 1.66 to 2.24 orders of magnitude higher than micropores. It has also been clarified that the rate of trap site occupancy in grain boundaries is high compared to dislocations and vacancies. Such high hydrogen coverage at grain boundaries indicates that the hydrogen assisted fracture could be intergranular.

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Figure caption:

Fig. 1. Optical micrograph of the alloys investigated.

Fig. 2. 3D perspective views of micropores. Only micropores were extracted and shown here, and underlying aluminum is not displayed.

Fig. 3 (a) Size distributions of micropores in material LH, material MH and material HH, and (b) magnified view of Fig. (a) labeled by red rectangle.

Fig. 4 Thermal Desorption Spectra of material LH (black line), material MH (red line), and material HH (blue line), respectively at a heating rate of 100 °C/h.

Fig. 5 Measured Thermal Desorption Spectra and fitted curve using Gaussian fit of material LH (a), material MH (b), and material HH (c), respectively at a heating rate of 100 °C/h.

Fig. 6 Thermal desorption spectra of material HH at different heating rates. The location of peak1, peak2 and peak3 is indicated with □, ○, and Δ, respectively

Fig. 7 Relationship between $\ln\left(\frac{\varphi}{T_m^2}\right)$ and $1/T_m$ corresponding to Fig. 3.

Fig. 8 X-ray diffractograms of material LH (black line), material MH (red line), and material HH (blue line), respectively.

Fig. 9 The FWHM as a function of K , classical Williamson-Hall plot.

Fig. 10 Peak broadening analysis using the modified Williamson-Hall plot of material LH (black line), material MH (red line), and material HH (blue line), respectively.

Table caption:

Table 1 Grain dimensions of the three modified 7XXX aluminum alloys examined

Table 2 Results of 3D image analysis of micropores and particles

Table 3 The estimated trapped hydrogen within micropores together with the total hydrogen content for each alloys.

Table 4 Summery of the Coefficients of the Fitting Curve in the Modified Williamson-Hall Plot and vacancy concentration.

Table 5 Estimated trap site coverage and the amount of hydrogen at each trap site.