

Behavior of Hydrogen in Aluminum

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Importance of hydrogen in aluminum has been recognized in terms both of molecular state such as porosity in castings and blisters in wrought products and of atomic state in solid solution. Hydrogen is one of the hardest elements to analyze among alloying or impurity elements in aluminum because its content is as low as below 0.2 mass ppm and its atomic number is the smallest. Three methods to elucidate the hydrogen behavior have been briefly introduced: slow strain technique (SSRT) tensile test under moist air, thermal desorption spectroscopy (TDS) and hydrogen microprint technique (HMPT). Then several interesting results recently revealed have been described. By comparing the severity of the atmosphere in terms of hydrogen embrittlement, it was found by means of the SSRT test under air that moist air with relative humidity of 90% is more severe than hydrogen gas with a pressure of 85MPa and that air with relative humidity of 25% is equivalent to hydrogen gas at 70MPa. A TDS study on pure aluminum with different volume fraction of blisters showed that the peak at highest temperature in the desorption spectrum is correspondent to the hydrogen in the blisters and micropores. In an HMPT study on 7075-T6, gaseous hydrogen was found to invade the material and to be emitted at constituent particles, not at the aluminum matrix.

Keywords: *hydrogen, embrittlement, hydrogen microprint technique, thermal desorption spectroscopy, slow strain rate technique*

1. Introduction

Importance of hydrogen in aluminum has been recognized for years in terms of molecular state such as porosity in castings and blisters in wrought products [1-3]. This kind of hydrogen is classified as impurity or internal hydrogen, which is introduced in the course of fabrication process of the materials and already present in the materials prior to the service. Hydrogen atoms in solution have also come to be considered to cause stress corrosion cracking since late 1960's [1]. This type of hydrogen is in a category of environmental or external hydrogen, which invades the materials during the service. Moreover, urgent need to elucidate its behavior has recently occurred since high-pressure hydrogen container composed of aluminum liner has been applied to fuel cell vehicles [4-7]. However, hydrogen is one of the hardest elements to analyze among alloying or impurity elements in aluminum because its content is as low as below 0.2 mass ppm and its atomic number is the smallest. In this paper, three methods to elucidate the hydrogen behavior will be briefly introduced, which include slow strain rate technique (SSRT) tensile test under moist air, thermal desorption spectroscopy (TDS) and hydrogen microprint technique (HMPT). Then several interesting results that have recently been revealed by the author's group will be described.

2. Methods to Elucidate Hydrogen Behavior

2.1 SSRT tensile test under moist air

For the demand of high-pressure hydrogen container, numerous tests are required on the resistance to hydrogen embrittlement, which need large-scale testing facilities in high-pressure hydrogen gas, close attention to safety, long period and large cost. To avoid these difficulties, the author's research group proposed a testing method schematically shown in Fig. 1 where SSRT tensile test is carried out in a moist air [4,5,7,8]. This is based on the principle that a high fugacity of hydrogen is generated through a reaction between aluminum and water vapor [9]:

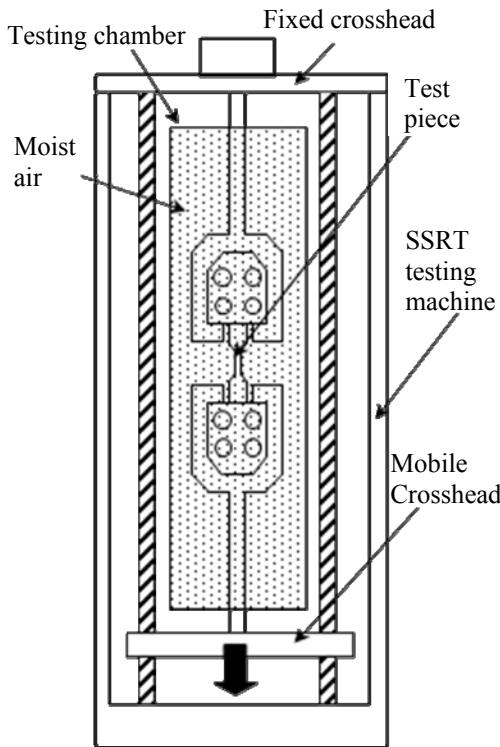
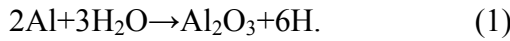


Fig. 1 Schematic of testing apparatus in moist air under SSRT condition.



Although the fugacity of hydrogen corresponding to Eq. 1 is extremely high (10^{53}Pa in air at 25°C at a relative humidity (RH) of 87% [10]), usually the reaction stops as soon as the passivity (hydro-oxide) film is formed through the reaction in Eq.1. The SSRT tensile testing is presumed to be effective to break the passivity film continuously by plastic deformation, and thus to allow the reaction to take place, leading to invasion of hydrogen into the aluminum specimen.

2.2 TDS

Figures 2 and 3 are schematic view of the apparatus and principle of TDS, respectively. When the specimen in an ultra-high vacuum chamber is heated at a constant heating rate, partial pressure of hydrogen gas emitted from the specimen is continuously measured, and then desorption spectrum such as shown in Fig.3 (a) can be obtained. Activation energy for desorption, E_d , can be obtained from the relationship:

$$\frac{d \ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E_d}{R}. \quad (2)$$

Here, β , T_p and R are heating rate, peak temperature and gas constant, respectively. As shown in Fig.3

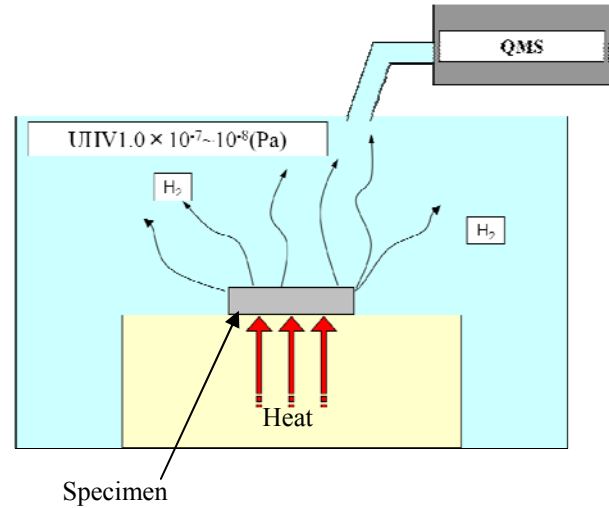


Fig. 2 Schematic view of the apparatus for TDS. UHV: ultra-high vacuum, QMS: quadrupole mass spectrometer.

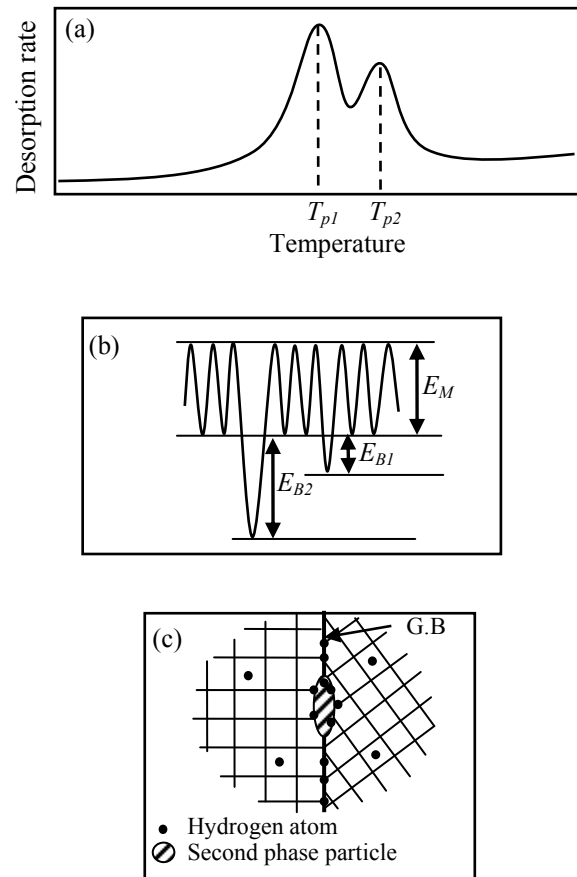


Fig.3 Principle of TDS. (a) desorption spectrum, (b) potential energy related to trapping sites, (c) trapping sites in the microstructure.

(b), E_d is equal to the sum of E_M and E_B , activation energy for lattice diffusion of hydrogen and binding energy of hydrogen with the trapping site, and the former coincides with the desorption energy for the interstitial lattice site.

2.3 HMPT

The HMPT is a technique to visualize hydrogen atom emitted from the inside of a metal, using photographic emulsion covered on the surface of the specimen. Figure 4 illustrates the principle of HMPT. If hydrogen atoms are emitted from the inside of the specimen, silver halide particles in the emulsion are converted to metallic silver particles by a strong reduction power of the hydrogen, following the reaction:



The silver halide particles that have not reacted dissolve to the fixer solution during fixing treatment, while the silver particles remain on the surface of the specimen at the site where the reduction reaction has occurred. This indicates that the location of the metallic silver particles, which can be observed by a scanning electron microscope (SEM), coincides with that of the emitted hydrogen atoms. Therefore, HMPT can reveal the emission site in relation to the microstructure. Furthermore, it is also possible to quantify the emitted hydrogen by evaluating the amount of the observed silver particles.

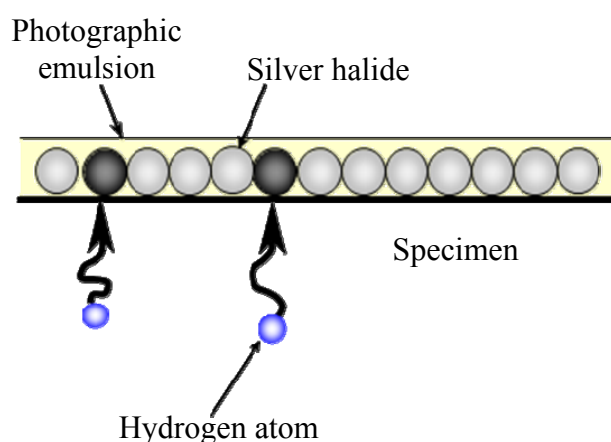


Fig. 4 Principle of HMPT.

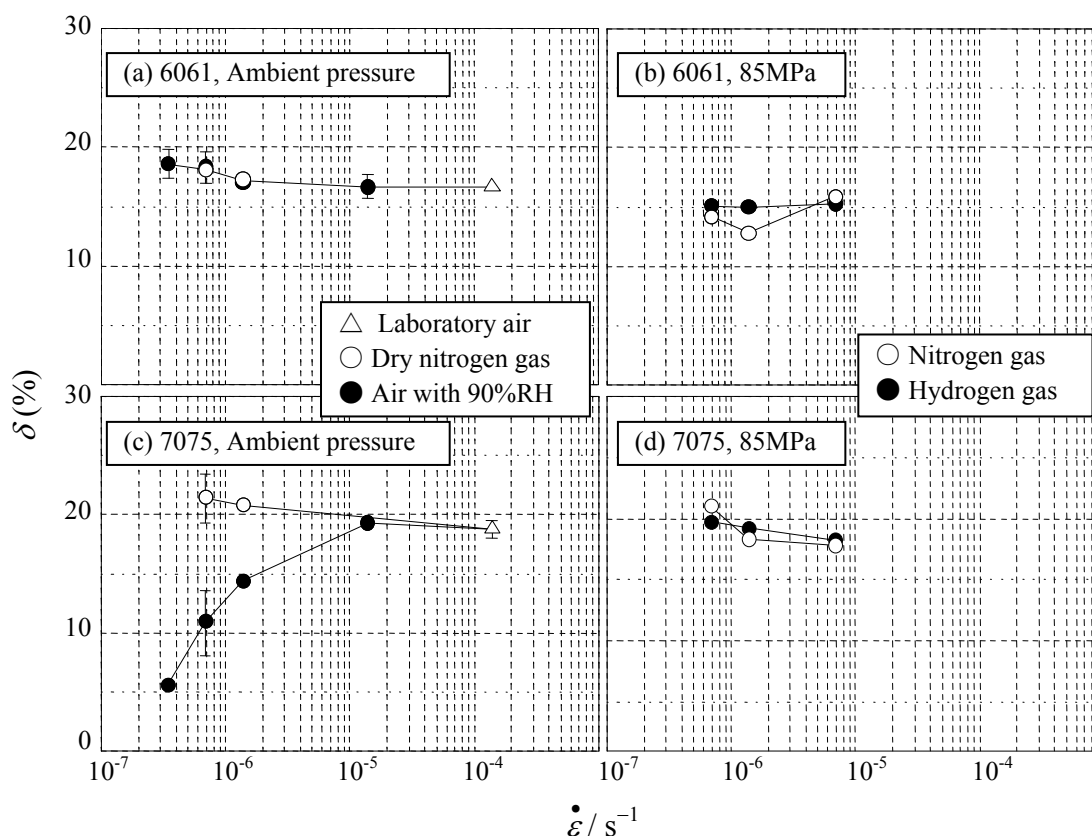


Fig. 5 Relationships between elongation to failure, δ , and strain rate, $\dot{\epsilon}$, in 6061 and 7075 alloys T6-tempered in different atmospheres at ambient pressure and at 85MPa.

3. Examples of the results

3.1 Resistance to hydrogen embrittlement assessed by means of SSRT test under moist air

Relationship between elongation to failure and strain rate is shown in Fig. 5 [4,8,11] as a function of testing atmosphere. Specimens of 1 mm thickness of 6061 and 7075 aluminum alloys with T6-temper were tensile-tested at 30°C under moist air with an RH of 90% and hydrogen gas at a pressure of 85 MPa. Results obtained under reference atmospheres (laboratory air, nitrogen gas at ambient pressure and 85 MPa) are also presented. In 6061 alloy, no difference in the elongation is visible between the atmospheres. In 7075 alloy, in contrast, it is found that elongation decreases with decreasing strain rate, that is, hydrogen embrittlement takes place, in the moist air, while embrittlement does not occur in the high-pressure hydrogen gas. From these results, moist air is deduced to be a more severe atmosphere than high-pressure hydrogen gas in terms of assessing the resistance to hydrogen embrittlement, and thus SSRT tensile tests in moist air can be used as a pre-screening method to select safe aluminum-based materials. From the results that numerous other commercial aluminum alloys did not show a sign of embrittlement even in the moist air, they were concluded to be safe materials without any embrittlement in high-pressure hydrogen gas.

In a laboratory-made Al-5.6%Zn-2.5%Mg alloy with no chromium addition, elongation in hydrogen gas at 70MPa was slightly smaller than that in nitrogen gas at the same pressure. Plotting the elongation values obtained in moist air with various RH against square root of RH brought about a linear relationship between the two parameters, and an RH of 25% corresponding to the elongation value obtained in hydrogen at 70MPa was derived. Thus, it was deduced that the RH of 25% is an atmosphere equivalent to the high-pressure hydrogen at 70MPa [12].

3.2 Interpretation of thermal desorption spectra in pure aluminium

Although TDS can provide some information on the trapping site of hydrogen in principle as mentioned in section 2.2, interpretation for the obtained spectrum is still in controversy. Figure 6 [13] shows thermal desorption spectra of pure aluminum specimens having different volume fraction of blisters. For the third peak, Young and Scully [14] insisted that it is due to hydrogen released from vacancies. However, it is to be noted in Fig. 6 that the intensity (height) of the third peak sharply increases as the volume fraction of blisters increases, while that of the other peaks seems to be unaffected by the blister volume fraction. This indicates that the third peak is attributed to the desorption of hydrogen in the blisters or micropores [15]. Furthermore, from the relationship of cumulative diffusion distance of free vacancies and of solute hydrogen atoms versus temperature, it was found that the vacancy as well as hydrogen can already be emitted from the inside of the specimen at 200°C. Since the diffusion of hydrogen is much faster than that of free vacancy, the co-diffusion of vacancy/hydrogen pair should be controlled by the migration of free vacancy. Hence, the vacancy/hydrogen pair is deduced to migrate sufficient distance and to be released from the inside of the specimen at much lower temperature than the third peak temperature. That is, hydrogen will be released at and below 200°C, even if hydrogen is trapped by vacancy, and the third peak is not ascribed to the release of hydrogen trapped by the vacancy. Therefore, it is indirectly supported that the third peak is due to the release of hydrogen in blister and micropores as

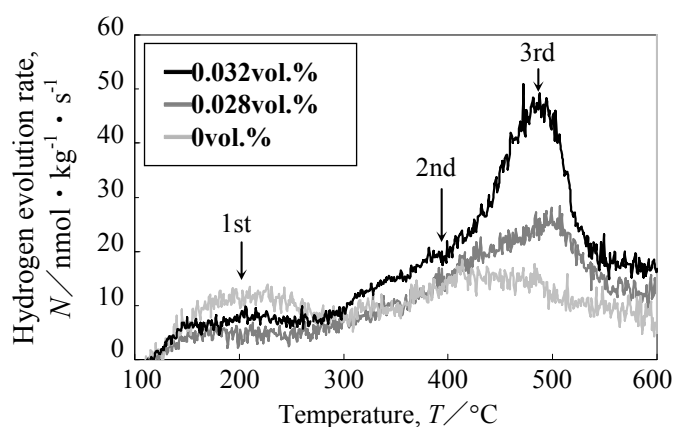


Fig. 6 Thermal desorption spectra of 0.1mm thick aluminum specimens of 99.99% purity with different volume fraction of blisters, taken at a heating rate of 8°C/min.

experimentally indicated in this section.

With respect to the first peak, on the other hand, Young and Scully [14] claimed that it would arise from hydrogen occupying the untrapped interstitial lattice sites. However, it is unlikely that the hydrogen remains in these sites until 200°C, again considering the diffusion distance of the hydrogen. Meanwhile, as for hydrogen trapped by vacancy, the co-diffusion of hydrogen/vacancy pair is slower than the diffusion of the untrapped hydrogen but is still sufficiently fast for the pair to migrate and to be released from the inside of the specimen at the first peak temperature, as mentioned above. Therefore, it is presumed that the first peak is due to hydrogen not in the untrapped interstitial lattice sites but being trapped by vacancies.

The second peak is concluded to be caused by the desorption of hydrogen trapped by dislocations for the following reasons: (i) in specimens used in the study [13], there are very few second phase particles, known as trapping sites for hydrogen [16], (ii) high angle grain boundary has been considered to act as short-circuit diffusion path for hydrogen [16], (iii) generally, enormous number of dislocations (dislocation densities of more than $10^6/\text{mm}^2$) are present even in well-annealed metals [17], and (iv) hydrogen atoms move with gliding dislocations [18].

3.3 Emission site of hydrogen investigated by means of HMPT

Hydrogen atoms that were emitted from one surface of a 7075-T6 specimen were detected by means of HMPT, with the other surface being exposed for 30 min to hydrogen gas with a pressure of 0.2 MPa. An example of resultant HMPT (SEM) images is shown in Fig. 7 [5,19]. Analysis by means of EDXS showed the following facts: (i) the dark area being the background of the image is matrix aluminum; (ii) gray particles, one of which is indicated by the arrow P_1 , are $\text{Al}_7\text{Cu}_2\text{Fe}$ constituent phase that has been formed during solidification and has remained after thermal and mechanical processing; and (iii) white particles, one of which is indicated by the arrow P_2 , are silver particles corresponding to hydrogen emission. From these results, hydrogen has been found to be emitted at constituent particles, not at the aluminum matrix. Since each constituent particle is isolated in the matrix, hydrogen atoms that have entered from hydrogen gas atmosphere must diffuse in the matrix. This means that the matrix must be a path for hydrogen diffusion, and thus the fact that the hydrogen was only detected on the constituent particles can be understood by considering that hydrogen can permeate the surface oxide film of the constituent phase but not of the matrix phase.

4. Summary and Prospect

Although hydrogen has been one of the most difficult elements to analyze among alloying or impurity elements in aluminum, its behavior is being elucidated by means of several experimental techniques. The techniques mentioned in this paper are not very new, but have been sophisticated to achieve the

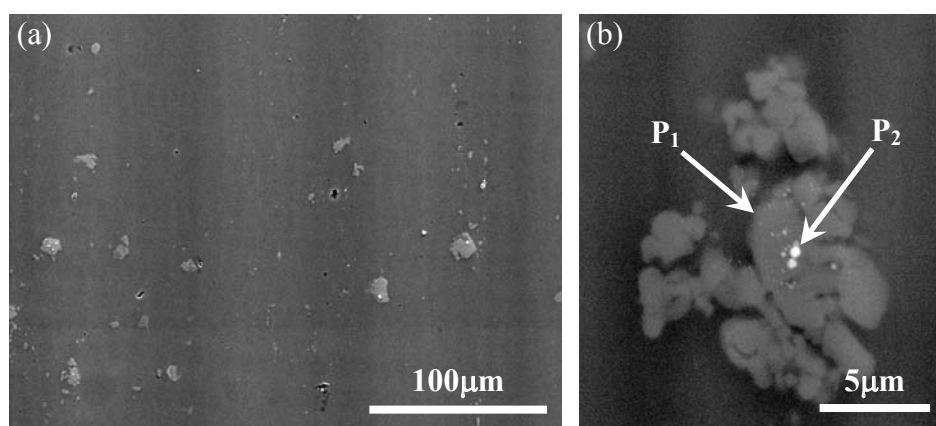


Fig. 7 An example of the hydrogen microprint SEM image in the specimen 7075-T6 alloy specimen exposed to hydrogen gas. (a) low magnification, (b) high magnification.

purpose. Further in detail will be revealed if other techniques for the investigation on hydrogen behavior, such as secondary ion mass spectroscopy and tritium autoradiography, are also modified, and then effective prevention of hydrogen embrittlement or quality increase in aluminum products will be achieved.

Acknowledgement

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