Thermal Desorption Spectroscopy Study on the Hydrogen Trapping States in a Pure Aluminum

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Hydrogen trapping states in pure aluminum foils with 99.99% purity with different amount of blisters have been investigated by means of thermal desorption spectroscopy. Three peaks are seen in the spectra, where the amount of hydrogen from the third peak at the highest temperature range increases with increasing in the volume fraction of the blisters. Hence, the third peak is revealed to arise from the hydrogen in the blisters. The desorption energy of hydrogen released from the blisters is 76.3 kJ/mol. On the other hand, the first peak is inferred to be due to the hydrogen diffusing with vacancy, considering the diffusion distance of the vacancy as well as untrapped hydrogen atom.

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1. Introduction

Hydrogen in aluminum has been known to cause the formation of blisters or pores,¹⁾ and to enhance void formation in ductile deformation and fracture.²⁾ In some alloys, crack propagation process in stress corrosion cracking is reported to be based on a mechanism of hydrogen embrittlement which itself has been claimed to take place in several alloys. However, the behavior of hydrogen in aluminum has not been well understood so far.

Although solid solubility of hydrogen in bulk aluminum under atmospheric hydrogen pressure is extremely low,³⁾ commercial aluminum and its alloys usually contain about ten times as much hydrogen amount as the solubility.⁴⁾ This can be attributed to much larger solubility in liquid aluminum than in solid. The hydrogen atoms are reported to occupy several kinds of sites bound with lattice defects such as vacancies,⁵⁾ dislocations, pores and blisters, as well as interstitial site.⁶⁾ The potential energy of the hydrogen depends on the occupation sites.

Currently, several methods are used to investigate the behavior of hydrogen in metals: thermal desorption spectroscopy (TDS),^{5,7,8)} hydrogen microprint technique,⁹⁾ tritium autoradiography^{10,11)} and secondary ion mass spectroscopy.¹²⁾ The TDS enables to assess the amount and binding energy of hydrogen with a trapping site. Although the hydrogen trapping states in high purity aluminum^{5,7)} and Al-Li-Cu-Zr alloys⁸⁾ have already been investigated by means of TDS, experimental results and discussion on the hydrogen contained in relatively macroscopic defects such as blisters have not been obtained yet. In this study, the behavior of hydrogen in a pure aluminum has been investigated by means of TDS, focusing on the hydrogen contained in macroscopic defects.

2. Experimental

2.1 Principle of TDS

In the TDS, the specimen is heated at a constant heating

Fig. 1 Potential energy diagram of different states of hydrogen in a metal.

rate in a vacuum and the change in hydrogen partial pressure due to hydrogen release from the specimen is monitored as a function of temperature or time. By carrying out the TDS, some desorption peaks corresponding to the trapping sites are visible in the obtained TDS spectrum, partial pressure vs. temperature curve. After acquiring several TDS spectrum at different heating rates, desorption energy for each trapping state can be calculated by¹³⁾

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

where T_p is the temperature of the desorption peak, β the heating rate, E_d desorption energy and R the gas constant. Figure 1 is a schematic illustration showing potential energy of hydrogen at different trapping states in a crystalline metal. Binding energy between a hydrogen atom and a trapping site is the difference between the desorption energy and the potential energy of the hydrogen that is present in an interstitial site of the lattice. This potential energy is equal to migration energy for lattice diffusion.^{5,8)}

Total amount of hydrogen, Q , detected from time t_1 to t_2 can be calculated by

$$Q = \left(\frac{K \cdot S}{V} \right) \int_{t_1}^{t_2} P dt \quad (2)$$

where K , S , V and P are the molecular conversion factor, exhaust rate of the vacuum pump, volume of the sample and partial pressure of hydrogen in the chamber, respectively.

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Fig. 2 Photograph showing surface appearance of the finally annealed foil. (a) Low magnification, (b) high magnification of the squared area indicated in (a).

Fig. 3 Optical microscopic image of the cross-section of a blister.

2.2 Specimens

An ingot with a cross-section of 200×60 mm and length of 300 mm was produced by a DC casting, using a raw aluminum of 99.99% purity. In order to detect hydrogen readily, degasifying treatment was not carried out and some potatoes were added into the melt so that the ingot contained hydrogen of 0.82 massppm, which is much larger than in a usual aluminum, approximately 0.2 massppm. The ingot was homogenized at 590°C for 6 h, scalped by 5 mm on each surface, hot-rolled to 10 mm in thickness, cold-rolled to $130\mu\text{m}$ in thickness, intermediately annealed at 250°C for 2 h, additionally cold-rolled into a foil of $110\mu\text{m}$ in thickness, heated at a rate of 150°C/h and finally annealed at 580°C for 1 h followed by furnace cooling.

Many arrays of blisters parallel to the rolling direction were observed in the finally annealed foil as shown in Fig. 2. Typical cross-section view of a blister is shown in Fig. 3. Volume fraction of the blisters can be calculated by

$$V = \sum_i \left\{ \pi \left(\frac{h_i^3}{6} + \frac{w_i^2 h_i}{8} \right) \right\} / V_s \times 100 \quad (3)$$

where h , w and V_s are height and diameter of a blister and volume of the specimen, respectively. For the TDS tests, square specimens measuring $12 \times 12 \times 0.11$ mm with different volume fraction of blisters were cut out of the foil.

2.3 Experimental procedure

The TDS tests were performed by an EMD-WA1000S/W machine produced by ESCO, Ltd., Japan. Figure 4 shows a skeleton diagram of the TDS machine, which is comprised of three portions, i.e., pre-evacuation chamber, main chamber

Fig. 4 A skeleton diagram of the thermal desorption spectroscopic system, divided into three portions for (i) pre-evacuating and transporting the specimen, (ii) heating the specimen in the main chamber and (iii) detecting hydrogen by QMS (quadrupole mass spectrometer). TC: thermo couple, TMP: turbo-molecular pump, RP: rotary pump, VG: vacuum gage, PS: pressure switch.

with heating unit and quadrupole mass spectroscopic system. A specimen in the pre-evacuation chamber with total pressure less than 1.0×10^{-4} Pa is transferred onto the quartz stage in the main chamber by a carrying device. After the pressure in the main chamber reaches 1.0×10^{-7} Pa, the specimen is (i) kept at 100°C for 30 min in order to remove the moisture adhering to the surface of the specimen and existing in the hydrated oxide film of the specimen, (ii) heated from 100 to 600°C at different constant heating rates ranging from 8 to 50°C/min and cooled in the chamber, and (iii) re-heated under the same conditions as (ii) after the temperature of the specimen reached to room temperature in order to measure the background pressure depending on the temperature. During the test, H_2^+ ion current is electrically measured by the quadrupole mass spectrometer. The heating is indirectly made through the stage baked by infrared radiation.

3. Results and Discussion

Figure 5 shows a hydrogen desorption spectrum of the specimen with blisters of 0.032 vol%, taken at a heating rate of 8°C/min . The spectrum can be separated into three distinct waveforms by Gaussian function. These peaks can be seen at approximately 200, 390 and 490°C . For convenience, these peaks will be referred to as the first, second and third peaks in ascending order of temperature. The spectra of specimens with different volume fraction of blisters, taken at 8°C/min are shown in Fig. 6. Figure 7 shows the height of the third peaks plotted against the volume fraction of blisters. It is to be noted that the 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

Fig. 5 Thermal desorption spectra of the specimens with 0.032 vol% of blisters, taken at a heating rate of 8°C/min.

Fig. 6 Thermal desorption spectra of the specimens with different volume fraction of blisters, taken at a heating rate of 8°C/min.

Fig. 7 Relationship between the volume fraction of blisters, V , and the height of the third peak, N_3 , in Fig. 6.

fraction. This indicates that the third peak is attributed to the desorption of hydrogen in the blisters.¹⁴⁾ For this peak, Young and Scully⁵⁾ insisted that it is due to hydrogen released from vacancies.

Let us consider whether the third peak is due to hydrogen released from vacancies. In the aluminum with hydrogen

atoms in solid solution, two kinds of vacancies can be assumed to be in the thermal equilibrium condition. One is free vacancy and the other is vacancy bound to hydrogen atoms. The atomic fraction of vacancies bound to hydrogen C_{V-H} can be expressed by¹⁵⁾

$$C_{V-H} = (C_H - C_{V-H})(C_V - C_{V-H})Z \exp\left(\frac{E_b}{RT}\right) \quad (4)$$

where Z , T and E_b are the coordination number (six for the face centered cubic lattice), absolute temperature and the binding energy between a hydrogen atom and a vacancy (51.1 kJmol⁻¹), respectively.¹⁶⁾ The total atomic fraction of vacancies C_V is given by

$$C_V = C_{V0} \exp\left(-\frac{E_f}{RT}\right) \quad (5)$$

where C_{V0} and E_f are the entropy factor and the formation energy of a vacancy in pure aluminum (73 kJmol⁻¹), respectively.¹⁷⁾ Ichimura *et al.*³⁾ gives the equation for the hydrogen solubility in the bulk of pure aluminum exposed to hydrogen gas of the atmospheric pressure C_H as

$$C_H = 4 \times 10^{-3} \exp(-7690/T) \quad (6)$$

From eqs. (4), (5) and (6), C_{V-H} at 490°C is estimated to be 1.1×10^{-7} , which is equivalent to approximately 65 percent of solute hydrogen at 490°C. On the other hand, it is known that the vacancy can diffuse and migrate much faster than aluminum atom. The diffusion distance of the vacancy x_V can be estimated by

$$x_V = \sqrt{D_V \cdot t} \quad (7)$$

where D_V and t are the diffusivity of the vacancy and the time, respectively. The D_V is given by

$$D_V = D_{0,V} \exp\left(-\frac{E_{a,V}}{RT}\right) \quad (8)$$

where $D_{0,V}$ and $E_{a,V}$ are the frequency factor (10⁻⁴ m²/s), and the activation energy for vacancy migration (50 kJ/mol), respectively.¹⁷⁻¹⁹⁾ Temperature is exposed with heating rate, time and initial temperature T_0 , as

$$T = \beta t + T_0 \quad (9)$$

The relationship between the cumulative diffusion distance of free vacancies and the temperature is shown in Fig. 8, together with that of solute hydrogen atoms calculated using the reported diffusivity of hydrogen¹⁰⁾ instead of D_V in the eq. (7). This indicates that the vacancy as well as hydrogen can already be emitted from the inside of materials 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 to be released from the inside of the specimen at much lower temperature than the 3rd peak temperature. That is, hydrogen will be released at and below 200°C, even if hydrogen is trapped by vacancy, and the 3rd peak is not ascribed to the release of hydrogen trapped by the vacancy. Therefore, it is indirectly supported that the 3rd peak is due to the release of hydrogen in blister as experimentally indicated in this study.

Fig. 8 Temperature dependence of the cumulative diffusion distance of free vacancies, x_V , and untrapped solute hydrogen atoms, x_H .

According to Toda *et al.*,²⁰⁾ recent X-ray CT studies have revealed presence of microscopic pores in many rolled aluminum sheets and plates. The state of hydrogen in pores is the same as that in blisters, gaseous or molecular state. Therefore, although in this study, the 3rd peak has been concluded in relation to macroscopic blisters that are much easier to measure, molecular hydrogen not only in blisters but in pores is inferred to be detected as the 3rd peak. In Fig. 6, the area for the 3rd peak is not proportional to the volume fraction of blisters, which is thought to arise from the presence of microscopic pores that was not able to detect in the present study.

With respect to the 1st peak, on the other hand, Young and Scully⁵⁾ 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, considering the diffusion distance of the hydrogen shown in Fig. 6. 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 1st peak temperature, as discussed above. Therefore, it is presumed that the 1st peak is due to hydrogen not in the untrapped interstitial lattice sites but being trapped by the vacancies.

The second peak is concluded to be caused by the desorption of hydrogen trapped by dislocations for the following reasons: (1) in specimens used in this study, there are very few second phase particles, known as trapping sites for hydrogen,¹¹⁾ (2) high angle grain boundary has been considered to act as short-circuit diffusion path for hydrogen,¹¹⁾ (3) generally, enormous number of dislocations (dislocation densities of more than 10 m/mm³) are present even in well-annealed metals,²¹⁾ (4) dislocation is a trapping site for hydrogen.^{9,22)}

Figure 9 shows hydrogen desorption spectra for the specimens with blisters of approximately 0.03 vol%, obtained at different heating rates. Each peak temperature increases as the heating rate increases. Figure 10 shows $\ln(\beta/T_p^2)$ vs. $1/T_p$ plots of each peak. The straight lines in this figure are the regression lines obtained by the least-square method. For all the three peaks, clear linear correlations

Fig. 9 Thermal desorption spectra at different heating rates in specimens with blisters of about 0.03 vol%. The locations of the 1st, 2nd and 3rd peaks are indicated with $\circ$, $\square$ and $\triangle$, respectively.

Fig. 10 Relationship between $\ln(\beta/T_p^2)$ and T_p^{-1} corresponding to Fig. 9.

between $\ln(\beta/T_p^2)$ and $1/T_p$ can be seen. According to eq. (1), desorption energies for the corresponding trapping states are obtained from the slopes of the peaks by multiplying them by $-R$, resulting in 20.0, 47.3 and 76.3 kJ/mol for the 1st, 2nd and 3rd peaks, respectively. Although the obtained energy values themselves are similar to those reported by Young and Scully,⁵⁾ 15.3, 43.5 and 84.8 kJ/mol, the meaning for the 1st and 3rd peaks are considered to be different in the present study; they are deduced to correspond to co-diffusion of vacancy/hydrogen pair and the desorption of hydrogen in a blister, respectively, as mentioned above. The energy of the 2nd peak can correspond to the desorption energy of hydrogen trapped by dislocation, as reported by them.

4. Conclusion

The behavior of hydrogen in pure aluminum foils with different volume fraction of blisters has been investigated by means of thermal desorption spectroscopy. The main results obtained are as follows.

- (1) Three peaks are observed in the thermal desorption spectra.
- (2) The desorption energies for the three peaks were found to be 20.0, 47.3 and 76.3 kJ/mol.

- (3) The height of the third peak with desorption energy of 76.3 kJ/mol increased with increasing volume fraction of blisters, and this peak was concluded to correspond to hydrogen released from blisters.
- (4) Considering the diffusion distance of vacancies and hydrogen atoms and the reported binding energy between vacancy and hydrogen atom, the first peak with desorption energy of 20.0 kJ/mol was ascribed to the release of hydrogen not in the untrapped interstitial sites but trapped by the vacancy.

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