

Behavior of Hydrogen in Electrolytically Charged Aluminum Investigated by Means of Hydrogen Microprint Technique

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In recent years, environmental problems such as global warming, exhaustion of fossil fuels and air pollution have been growing into the serious problems. On this background, fuel cell vehicles using hydrogen as a clean energy have been paid attention to. In the fuel cell vehicles, high-pressure hydrogen gas is stored in a cylinder composed of aluminum alloy liner and shell of carbon fiber reinforced plastic. Only 6061-T6 aluminum alloy is approved for the liner in the current Japanese standard. Application of other alloys having higher strength is considered since higher maximum filling pressure is demanded to achieve longer mileage per fuel filling. However, hydrogen embrittlement has been reported to occur in some aluminum alloys. To guarantee the safety of the fuel cell vehicles, hydrogen embrittlement should be avoided, for which elucidation of hydrogen embrittlement through the investigation on the behavior of hydrogen is needed. Hydrogen microprint technique (HMPT) has been known as an effective method to investigate the hydrogen behavior, in which the reaction between silver bromide emulsion and atomic hydrogen emitted from the sample is used. In the present study, the behavior of electrolytically charged hydrogen in aluminum with 99.99% purity has been investigated by means of HMPT. Annealed samples were cathodically electrolytic-charged in a sulfuric acid solution and subjected to HMPT. By the cathodic charging, hydrogen was found to invade the pure aluminum specimen up to the depth of about 600 μ m, and hydrogen concentration was the highest in surface layer within 100 μ m. In the surface, main hydrogen emission site was grain boundaries.

Keywords: *hydrogen embrittlement, HMPT, electrolytically charging, diffusive hydrogen.*

1. Introduction

In recent years, the fuel cell vehicles using hydrogen as a clean energy have been paid attention to. The 6061-T6 aluminum alloy is being used as a liner material of a high-pressure (35MPa) hydrogen cylinder (Type3) in the current Japanese standard. Application of other alloys having higher strength is considered since higher maximum filling pressure is demanded to achieve longer mileage per fuel filling. However, hydrogen embrittlement has been reported to occur in some high strength aluminum alloys. To solve the cause of hydrogen embrittlement, behavior analysis of hydrogen in the material needed. Main analyzing methods reported so far are tritium autoradiography (TARG), secondary ion mass spectrometry (SIMS), hydrogen microprint technique (HMPT) and atom probe field ion microscopy (AP-FIM). The HMPT is the most convenient technique, and many results based on HMPT have been reported to date.

Hydrogen in a metal material can be classified into two kinds: (i) environmental (external) hydrogen introduced during the service, (ii) impurity (internal) hydrogen introduced during the processing prior to the service. It has been generally known that the environmental hydrogen plays major role in hydrogen embrittlement [1]. Cathodic electrolytic charging is a technique that enhances the invasion of environmental hydrogen into the material. In the present study, the behavior of environmental hydrogen in cathodically electrolytically hydrogen-charged aluminum with 99.99% purity has been investigated by means of HMPT.

2. Specimens and Experimental Procedures

2.1 Principle of HMPT

In HMPT, a hydrogen atom evolved at the specimen surface is visualized as a silver particle using photographic emulsion layer. The principle of HMPT is schematically shown in Figure 1. Following the oxidation-reduction reaction indicated in Eq.1, a silver atom will be produced at the site where a hydrogen atom is emitted.



Silver bromide particle which has not been reacted with hydrogen will dissolve out into the fixer, and finally only the silver particle will remain on the specimen surface. Hence, it is possible to visualize the emission site of the hydrogen by observing the distribution of the remaining silver particle together with metallographic microstructure. It is also possible to assess the amount of emitted hydrogen by measuring the amount of silver particle.

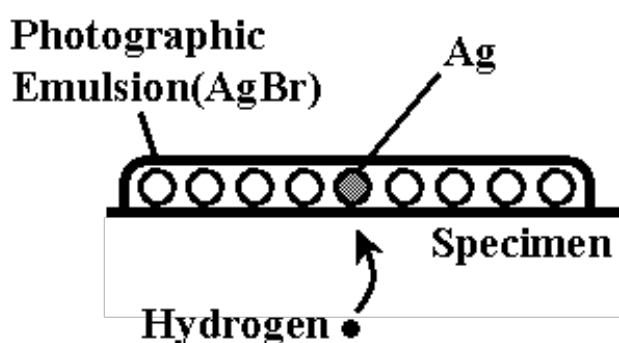


Fig. 1 Principle of hydrogen microprint technique.

2.2 Cathodic electrolytic charging

Cathodic electrolytic charging is the technique that enhances the invasion of environmental hydrogen into the material [2]. A schematic view of the principle of cathodic electrolytic charging is shown in Figure 2. In the cathode, hydrogen atoms are generated following Eq.2, but they usually recombine with each other to form hydrogen gas (Eq.3), without invading the metal.



However, when ions of arsenic, antimony or sulfur are added into the electrolytic solution, recombination reaction is markedly inhibited, leading to a marked promotion of the invasion.

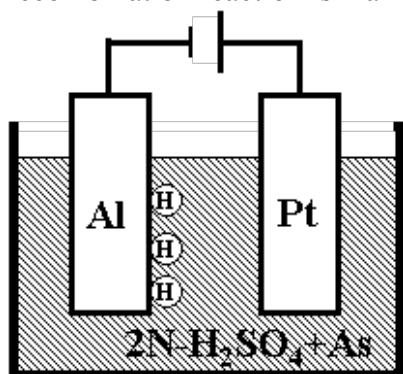


Fig. 2 Cathodic electrolytic charging technique.

2.3 Specimens

A 10mm thick sheet of 99.99%-purity aluminum with the composition shown in Table 1 is used in this study. Specimens of 40mm×15mm were cut from the sheet, annealed for 1h at 560°C, wet-ground with #1500 abrasive paper, cleaned in a 10% NaOH solution for 1 min, desmutted in a 10% HNO₃ solution for 1min, rinsed with distilled water, naturally dried and then electrolytically polished into a mirror surface. This electrolytical polishing was performed in a solution consisting of ethanol (1200ml), hyperchloric acid (90ml) and distilled water (210ml) at 0°C with the use of stainless cathode. The polishing current employed was 2A, while the polishing time was about 30s.

Table 1 Chemical composition of the pure aluminum specimen in mass ppm

Si	Fe	Cu	Al
16	4	<1	Bal.

2.4 Experimental Procedures

In this study, two kinds of specimens were prepared: (i) with electrolytic hydrogen charging, (ii) without hydrogen charging. Hydrogen was introduced in the aluminum specimens by electrolytic cathodic charging. This technique was performed in a solution consisting of 2N-H₂SO₄ with 1g/L of Na₂HAsO₄·7H₂O as hydrogen recombination inhibitor, at room temperature with the use of platinum anodes. The charging current density employed was 10 mA/cm², while the charging time was 30min. Three test pieces of 10mm×15mm were cut out from the two specimens. The first piece was not subjected to surface grinding, the second piece was ground by 40μm from the hydrogen charged surface and the third piece was cut so that the cross section can be observed. To visualize the hydrogen atoms, HMPT was carried out in the following way: the surface of sample was covered in the dark room by means of wire-roopmethod with photographic emulsion consisting of silver bromide (AgBr), Konica NR-H2, distilled by four times [3], naturally dried, left for 24h to allow hydrogen diffusion to occur. After the emulsion with the sample was fixed in a 36% formalin solution for 5s plus in a 15% sodium hyposulfite solution for 8min. Finally, test pieces on the surface were observed with a scanning electron microscope (SEM, Hitachi S-2150) equipped with an energy dispersive X-ray spectroscopy (EDXS, Horiba EMAX 1770) device. After HMPT observation, test pieces were etched by barker liquid and metallographic microstructure was observed with an optical microscope. Finally, the relationship between the location of emitted hydrogen and the microstructure was investigated by comparing the HMPT/SEM image with the optical microscopic image.

3. Results and Discussion

Figures 3 and 4 show an example of HMPT/SEM images. In the uncharged specimen (Fig. 3), no silver particle is observed in any test piece. From this result, impurity (internal) hydrogen atoms in this specimen are presumed to have been located in some stable trapping sites and not to be emitted during the holding time of 24h at room temperature. In contrast, in the hydrogen-charged specimen, silver particles can be seen more or less depending on the test piece. In the test piece without surface grinding, a small number of silver particles can be found, while many particles are visible in the test piece ground by 40μm from the surface, together with some other white particles sparsely dispersed. From these particles, a Si peak was detected with the matrix Al peak in the EDXS spectra, which means that these particles are abrasive grains. In the cross section, silver particles are detected within about 600μm from the surface. The amount of emitted hydrogen atoms as a function of depth from the

surface ($0\sim 600\mu\text{m}$) with $100\mu\text{m}$ interval is shown in Fig. 5. It is obvious that the hydrogen amount is highest in the surface region under $100\mu\text{m}$ depth. The reason why the amount of emitted hydrogen was larger at $40\mu\text{m}$ depth (Fig. 4 (b)) than at the very surface (Fig.4(a)) has not been elucidated within the range of the present study. Fraction of detected silver particles (hydrogen atoms) correlated with microstructural location (inside the grain or at the grain boundary) is shown in Table 2 for the test pieces corresponding to Figs 4 (a) and (c). On the cross-section, the data have been averaged throughout the test piece (in the whole depth under $600\mu\text{m}$). On the very surface, 68% of the particles are detected on grain boundaries, which is extremely larger fraction than that of the area fraction of grain boundaries. In contrast, in the cross section, the particles detected in the grain interior account for 98%. The cause of the difference in the site of hydrogen emission is being investigated, considering some artifacts correlated with dislocations brought about by sectioning and grinding.

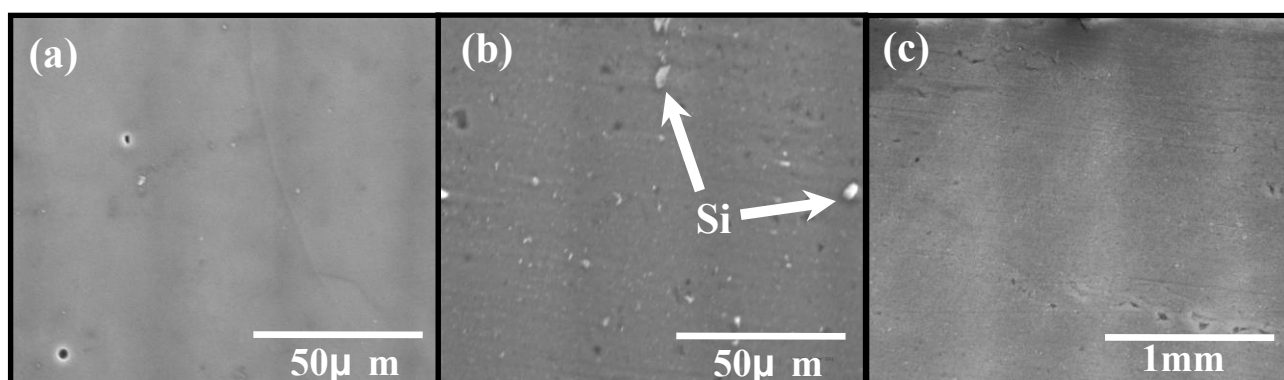


Fig. 3 Example of HMPT/SEM images of the uncharged test pieces. (a) without surface grinding, (b) surface-ground by $40\mu\text{m}$, (c) cross-section.

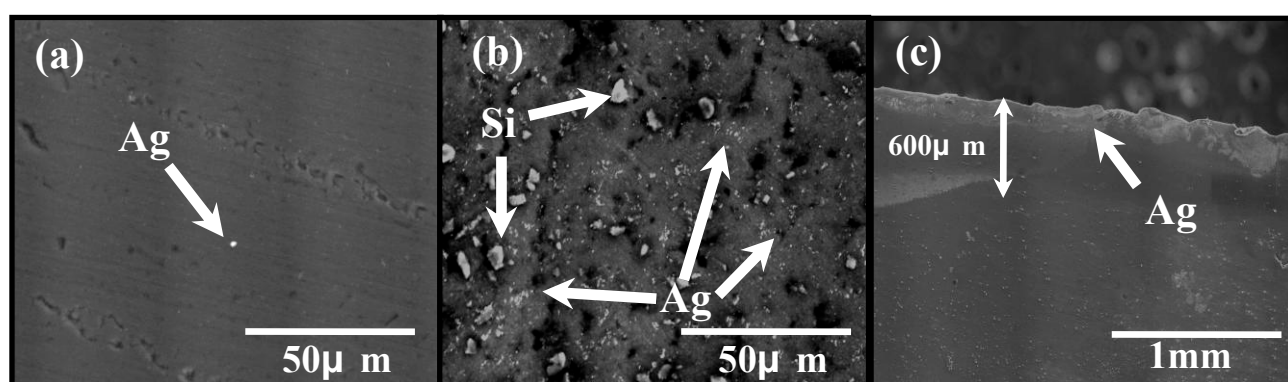


Fig. 4 Example of HMPT/SEM images of the test pieces cathodically hydrogen-charged for 30min. (a) without surface grinding, (b) surface-ground by $40\mu\text{m}$, (c) cross-section

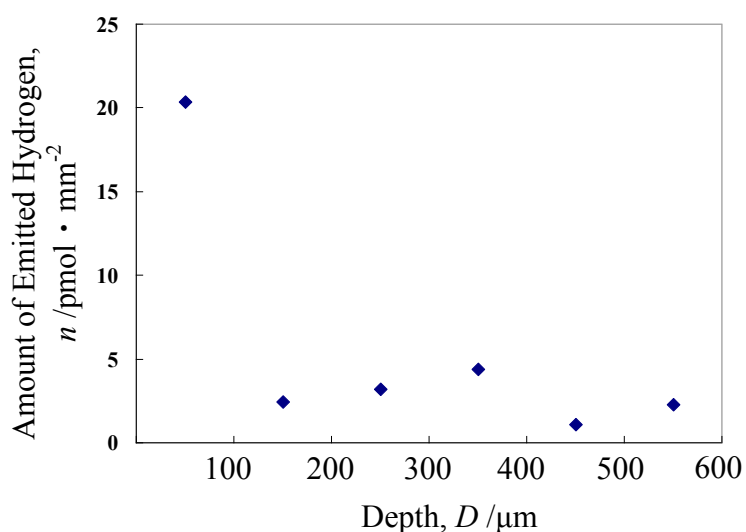


Fig. 5 Amount of emitted hydrogen as a function of depth from the surface in the test piece charged for 30 min. Measurement was made on the cross-section.

Table 2 Fraction of detected silver particles (hydrogen atoms) in the test pieces charged for 30min affected by microstructural location. (a): without surface grinding, (c): cross-section.

(a)	Grain interior	32%
	Grain boundary	68%
(c)	Grain interior	97%
	Grain boundary	3%

4. Conclusions

By the cathodic charging, hydrogen was found to invade the pure aluminum specimen up to the depth of about 600 μm , and hydrogen concentration was the highest in surface layer within 100 μm . In the surface, main hydrogen emission site was grain boundaries.

5. References

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