

Hydrogen Permeation Behaviour in Aluminium Alloys

T.Izumi, G.Itoh, N.Itoh

Graduate Student, Ibaraki University, Naka-Narusawa Hitachi-City Ibaraki, 316-8511 Japan

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Abstract

Aluminium alloys have been regarded as the material of tank for high compressed hydrogen gas using for fuel cell vehicles. However, since the inner surface of the tank is exposed to the hydrogen gas under high pressure, hydrogen embrittlement of the material may occur by hydrogen penetration into the material. In this study, to approach a final goal of elucidating how hydrogen penetration and diffusion in the material take place, hydrogen permeation behaviour was investigated in 5083 and Al-Mg binary alloy sheets by means of hydrogen microprint technique. The effect of plastic deformation on the permeation behaviour was also investigated by applying uni-axial tensile load.

1. Introduction

In recent years, saving the fossil fuel and reducing the amount of carbon-dioxide emission have been demanded and the fuel cell vehicles that use hydrogen as clean energy have been highlighted. To store high compressed hydrogen gas in the vehicle, a tank is needed and aluminium based alloys have been regarded as one of the candidate materials for the tank. During the service of the tank, the inner surface is exposed to the hydrogen gas under high pressure and the outer surface to the air under atmospheric pressure. Since the inner surface subjected to a tensile stress caused by the above-mentioned high pressure, hydrogen embrittlement of the material might occur via hydrogen penetration into it arising from the pressure difference between the two surfaces. However, little knowledge has been obtained so far. In this study, to approach a final goal of elucidating how hydrogen penetration and diffusion in the material take place, hydrogen permeation behaviour was investigated in a 5083 aluminium alloy, which is one of the candidate materials for the tank in marine transportation of liquid hydrogen. Furthermore, to investigate the influence of the second phase particle contained in the 5083 alloy, an Al-4.5mass%Mg binary alloy was prepared and subjected to similar experiments.

2. Experimental Procedures

2.1 Hydrogen Microprint (HMP)

The hydrogen microprint is a technique to visualize hydrogen atom is emitted from the inside of the material, using photographic emulsion covered on one surface of the

specimen as shown in Figure 1. The photographic emulsion consists of silver halide particle. As hydrogen atoms are emitted from the inside by some reason, the following reaction will take place by strong reduction power of the hydrogen atoms.



The unreacted silver halide particle dissolves to the fixing solution, while metallic silver remains on the surface of the specimen at the site where it has reacted. Therefore, the location of the metallic silver indicates the site of the hydrogen atom and the silver particle can be observed by a scanning electron microscope (SEM). In this study, since the emitted hydrogen atoms are assumed to be very small in number, a development was carried out prior to the fixing to improve the detectability. By this process, the whole silver halide particle will become a metallic silver of about $0.1\mu\text{m}$ depending on the original halide particle size even if the number of the silver atoms is very small before development.

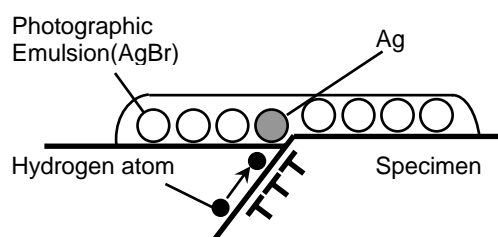


Figure 1: Hydrogen microprint technique.

2.2 Specimens

5083 aluminium and Al-Mg binary alloy specimens were prepared. The composition of the specimens is indicated in Table 1. Noted that the 5083 alloy contains Mn as a minor alloying element in order to inhibit excessive grain growth and Fe and Si as impurities. Hydrogen of about 4 molppm is also expected to be included as an impurity in both specimens[4].

A hot-rolled sheet of commercial 5083 alloy of 10mm in the thickness was further hot-rolled at 673K up to 2mm, annealed at 673K for 1h, furnace cooled and cold-rolled to 1mm. The sheet was machined into tensile specimens so that the tensile direction was parallel to the rolling direction. The morphology and size of the specimen are shown in Figure 2. The specimen was annealed at 673K for 1h, furnace cooled, wet-ground to #1500 and finally electro-polished at the parallel portion. The Al-Mg binary alloy with virtually no second phase particle were prepared from a pure aluminium of 99.99% and magnesium of 99.9%, melted in air, cast in an iron mould, homogenized at 703K for 18h, scalped to 10mm in thickness and warm-rolled to 2mm in thickness. The 2mm thick sheet of the binary alloy was processed in the same way as that of the 5083 alloy.

Table1: Composition of the alloys in mass %.

alloy	Si	Fe	Cu	Mn	Mg	Cr	Ti
5083	0.08	0.19	0.02	0.59	4.56	0.05	0.02
Al-Mg	0.007	0.004	0.002	-	4.37	-	-

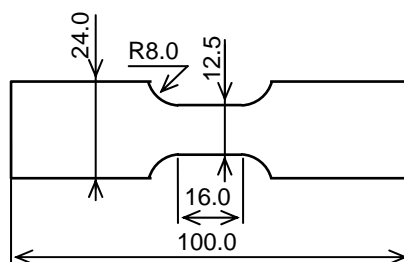


Figure 2: Morphology and dimension in mm of the specimens.

2.3 Experimental Procedure

The specimen was covered with a photographic emulsion, Konica NR-H2, diluted to four times on one of the surfaces by the wire-loop method in the dark room, and then clamped in the experimental device shown in Figure 3. The surface without the photographic emulsion was exposed to the hydrogen gas of 0.2 MPa after evacuating the chamber of this side. During exposure, the specimen was stretched by 10%, using an Instron No.1185 testing machine. To investigate the emission behaviour of impurity hydrogen that is already present in the specimens prior to the exposure to the hydrogen gas, the examination without the exposure to the hydrogen gas was also carried out. In addition, the specimen only exposed for 30min without stretching was prepared as well because it had been considered that the dislocation glide caused by the stretching would influence the emission behaviour of the hydrogen.

As soon as the examination finished, the specimen was soaked in a Fuji SPD developer at 293K for 240s, rinsed, fixed in a Super Fuji Fix solution for 900s, rinsed again in the dark room and finally dried naturally in air. The surface covered with photographic emulsion of the specimen was observed by a Hitachi S-2150 SEM equipped with a Horiba EMAX 1770 energy dispersive X-ray spectroscopy (EDXS) device that can confirm the composition of the observed particle qualitatively.

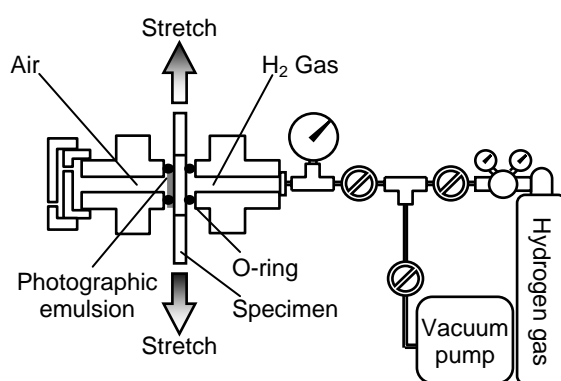


Figure 3: Experimental device.

3. Results

Figure 4 shows an HMP image taken by the SEM of the surface of the Al-Mg binary alloy specimen without stretching or exposure to the hydrogen gas. Any silver particle that

implies the emission of hydrogen was not observed. In the specimen exposed to hydrogen gas without stretching, no silver particle was observed, either. However, in the specimen stretched by 10% without exposure to hydrogen gas, a large number of small particles were observed on slip lines and grain boundaries as shown in Figure 5(a). As a result of EDX analysis, see Figure 5(b), these particles were metallic silver particles. The HMP image of the specimen stretched by 10% during exposure to hydrogen gas was similar to Figure 5(a) as shown in Figure 6, but the number of the silver particles was increased.

In the 5083 alloy specimen without stretching or exposure to hydrogen gas, the silver particle was not observed as in the Al-Mg binary alloy. Only second phase particles of $1 \sim 10 \mu\text{m}$ in size, which were found to be Mg_2Si caused by the impurity Si, were observed. Figures 7 to 9 show the HMP images of the specimens, only stretched by 10%, only exposed to hydrogen, and stretched by 10% during exposure to hydrogen, respectively. In all of these three conditions, small particles, such as arrowed, were observed around Mg_2Si particles and were deduced to be silver particles from EDXS. The number of particles was the largest in the specimen both stretched and exposed (Figure 9) and smallest when only stretched (Figure 7).

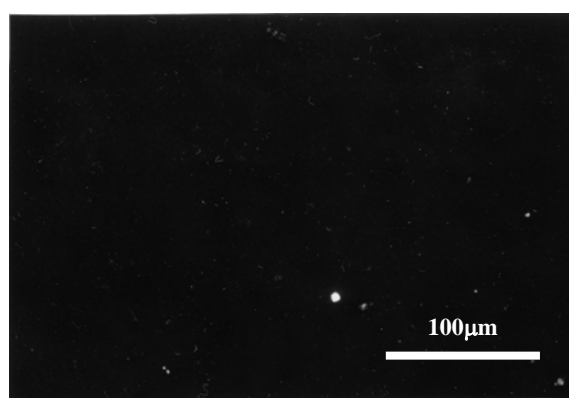


Figure 4: HMP image taken with a scanning microscope of undeformed Al-Mg alloy specimen.

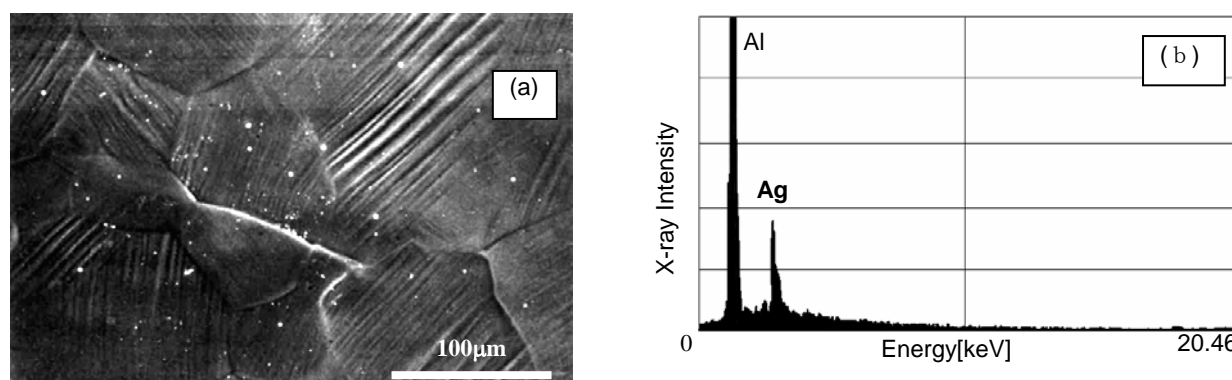


Figure 5: HMP image and EDXS spectrum of a binary alloy specimen stretched by 10% (a)HMP images,(b)EDXS spectrum taken from a white particle shown in (a).

4. Discussion

In both specimens, no hydrogen was confirmed to be emitted only by keeping at room temperature without deformation or exposure to the hydrogen.

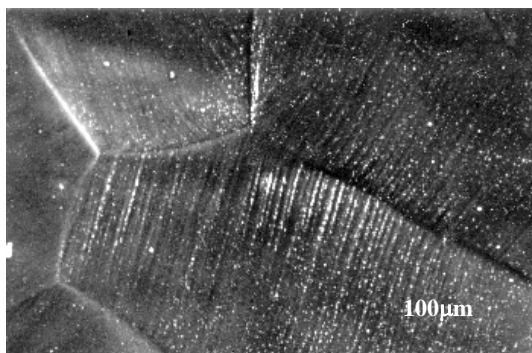


Figure 6: HMP image of a binary alloy specimen stretched by 10% during exposure to hydrogen gas.

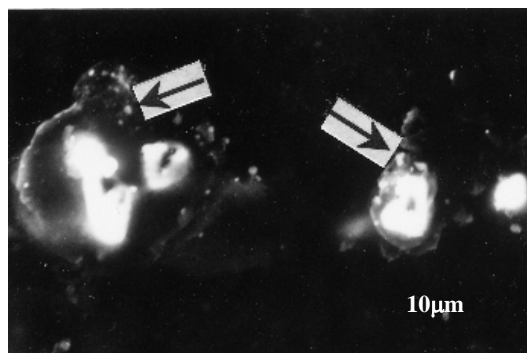


Figure 7: HMP image of a 5083 alloy specimen stretched by 10%.

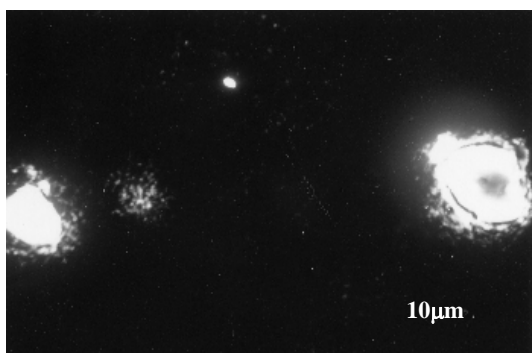


Figure 8: HMP images of a 5083 alloy specimen exposed to hydrogen gas without loading.

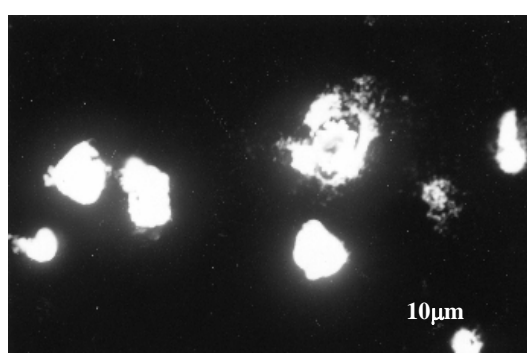


Figure 9: HMP images of a 5083 alloy specimen stretched by 10% during exposure to hydrogen gas.

In contrast, when stretched by 10%, a relatively small number of hydrogen atoms were emitted from the specimens even when not exposed to hydrogen gas. Thus, it is apparent that the hydrogen atoms emitted from the specimens were the impurity hydrogen, as reported in pure aluminum[5]. The emission sites of the impurity hydrogen atoms were slip lines and grain boundaries in the Al-Mg binary alloy, and peripheries of second phase particles in the 5083 alloy. Therefore, it can be deduced that, in the binary alloy, the impurity hydrogen was moved towards the surface of the specimen with gliding dislocations and reached the surface, or moved to the grain boundary with gliding dislocations and reached the surface by grain boundary diffusion. In the 5083 alloy as well, the impurity hydrogen is supposed to be moved with dislocations. However, because of the smaller grain size, slip bands did not develop well, and hence the hydrogen was not detected on the slip lines. Instead, hydrogen atoms are considered to reach the grain boundaries and Mg_2Si particles and then reach the surface by the interface diffusion.

In the case of the specimens only exposed to the hydrogen gas, hydrogen atoms were only emitted in the 5083 alloy, but not in the Al-Mg binary alloy. It is deduced that, in the 5083 alloy, the hydrogen atoms invaded from the gas atmosphere to the material at the Mg_2Si particle on the surface moved inside the material by the grain boundary diffusion and was emitted from the particle on the opposite surface. This deduction is based on the following fact and assumptions: that the emission site of the hydrogen atom in the 5083 alloy was around the particle which hardly exists in the Al-Mg binary alloy, that the particle that prevent the grain growth will be present at the grain boundary, and that the hydrogen atom may permeate from the oxide film of the particle more easily than from the oxide film of the matrix because of the difference of their structure.

Although the emission site of the hydrogen in the two specimens stretched by 10% during exposure to the hydrogen gas was the same as in the specimens only deformed, the amount of the silver particles was larger. Thus, the emitted hydrogen atom must be not only the impurity but also the environmental hydrogen, which implies hydrogen invasion from the gas atmosphere. From microscope viewpoint, the invasion site of the environmental hydrogen in Al-Mg binary alloy will be the fresh surface appearing by the fracture of surface oxide film because of the deformation. On the other hand, in the 5083 alloy, the invasion will occur both at the second phase particle as mentioned above and the fresh surface as in the Al-Mg binary alloy.

The invasion and emission behavior of the hydrogen atom is schematically summarized in Figure 10 and 11. As can be seen in these figures, the hydrogen atom, which dissociated on one surface of the material will invade into the material at the fresh surface produced by plastic deformation and at the second phase particle, moves with gliding dislocation and grain boundary diffusion and finally is emitted at the slip line, grain boundary and second phase particle on the other surface.

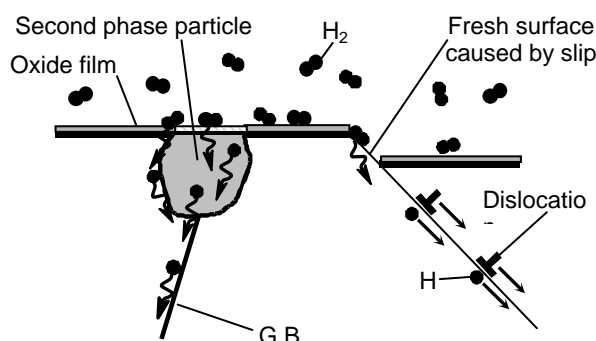


Figure 10: Possible mechanism for the penetration of environmental hydrogen

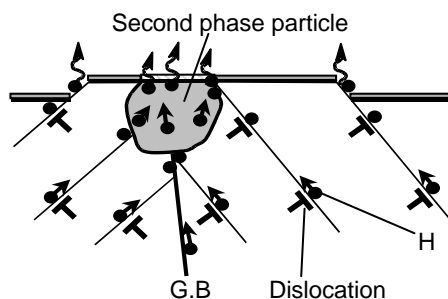


Figure 11: Mechanism for the evolution of hydrogen

5. Summary

In 5083 aluminum and Al-Mg binary alloys, the permeation behavior of the hydrogen atom was investigated by using HMP technique. In both alloys, the hydrogen atom was emitted by a plastic deformation whether the material was exposed to the hydrogen gas or not. The emission sites were around the second phase Mg_2Si particle in the 5083 alloy, and on the slip line and grain boundary in the Al-Mg binary alloy. Since the number of the metallic silver particles in both specimens deformed during exposure to the hydrogen gas was larger than that in the specimens only deformed, it was clear that the environmental hydrogen invaded into the materials. The invasion site in the Al-Mg binary alloy was

presumed to be the fresh surface induced by the deformation because the hydrogen atom was emitted only when the material was deformed. The fact that the hydrogen atom was emitted in the 5083 alloy specimen only exposed to the hydrogen gas suggests that it invades at the Mg_2Si particles in addition to the deformation induced fresh surface. The invading hydrogen atom was deduced to move with the gliding dislocation and by the grain boundary diffusion in the material.

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