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Hydrogen permeation behavior in aluminum alloys

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In recent years, fuel cell vehicles have become highlighted. The storage of compressed hydrogen gas has been regarded as one of the method to supply hydrogen for fuel cell vehicles. Since the inner surface of the tank is exposed to the hydrogen gas under high pressure, hydrogen embrittlement of the material for the tank may occur by hydrogen penetration into the material. 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 behavior was investigated in 5083 aluminum and Al-Mg binary alloy sheets by means of hydrogen microprint technique. By this technique, emission site of hydrogen atoms can be detected on one side in relation to the microstructure when the other side is exposed to hydrogen gas. The effect of plastic deformation on the permeation behavior was also investigated by applying uni-axial tensile load. As a result, largest number of hydrogen atoms were emitted around second phase particles and on grain boundaries or slip lines in 5083 and Al-Mg binary alloy stretched by 10% during exposure hydrogen gas, respectively.

Key words : Hydrogen penetration, Hydrogen microprint print technique, Aluminum alloys, Plastic deformation

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 aluminum 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. Because of this situation and a tensile stress caused by the above-mentioned high pressure, hydrogen embrittlement might occur via hydrogen penetration arising from the pressure difference between the two surfaces. However, little knowledge has been obtained on this issue so far. In this study, to approach a final goal of elucidating how hydrogen penetration and diffusion in the material take place, hydrogen permeation behavior was investigated in a 5083 aluminum 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 investigation.

2. EXPERIMENTAL PROCEDURES

2.1 Hydrogen microprint (HMP)

The hydrogen microprint is a technique to visualize hydrogen atom emitted from the inside of the material, using photographic emulsion covered on a surface of the specimen as shown in Fig.1. The photographic emulsion consists of silver halide particles. 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.

$$AgBr+H \rightarrow Ag+HBr$$

Unreacted silver halide particles dissolve to the fixing solution, while metallic silver remains on the surface of the specimen at the site where the above reaction has taken place. Therefore, the location of the metallic silver particle that can be observed with a scanning electon microscope (SEM) indicates the site where the hydrogen atom has been emitted. 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 0.1μm depending on the original halide particle size even if the number of the silver atoms is very small before development.

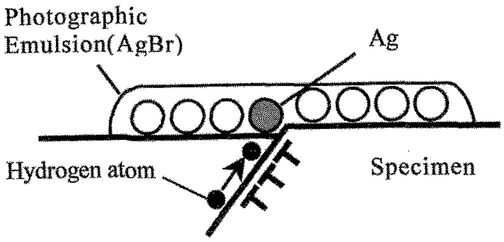

Fig.1 Hydorogen microprint technique.

2.2 Specimens

A 5083 aluminum and Al-Mg binary alloy specimens were prepared. The composition of the specimens is indicated in Table. I . It should be noted that the 5083 alloy contains Mn, as a minor allying element in order to inhibit grain growth, and Fe and Si, as impurities. Hydrogen of about 4 mol ppm is also expected to be included as an impurity in both specimens(1).

A hot-rolled sheet of commercial 5083 alloy of 10mm in thickness was further hot-rolled at 673K up to 2mm in thickness, 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 Fig.2. The specimen was annealed at 673K for 1h, furnace cooled, wet-ground to #1500 and finally electro-polished in theguage area. The Al-Mg binary alloy with virtually no second phase particle were prepared from a pure aluminum of 99.99% and magnesium of 99.9%, melted in air, cast in an iron mold, 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.

Table I 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	-	-

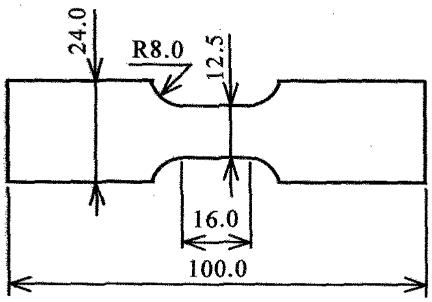

Fig.2 Morphology and dimension in mm of the specimens.

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 Fig.3. The surface without the photographic emulsion was exposed to the hydrogen gas of 0.2 MPa after evacuating the chamber of this side. The specimen was exposed for 30min without stretching. To investigate the emission behavior of impurity hydrogen that is already present in the specimens prior to the exposure to the hydrogen gas, the examination only with stretching by 10%, using an Instron No.1185 testing machine, was carried out as well. In addition, the specimen streched by 10% during exposure to hydrogen was also prepared because it had been considered that the dislocation glide caused by the stretching would influence the emission behavior 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.

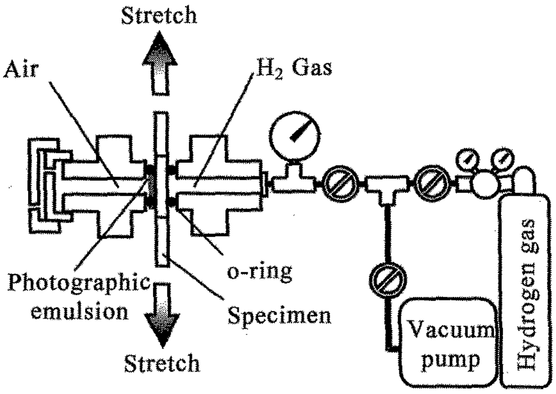

Fig.3 Experimental device

3. RESULTS

Figure 4 shows an HMP image 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 binary 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 Fig.5(a). The result of EDX alalysis, Fig.5(b), shows that these parti-

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

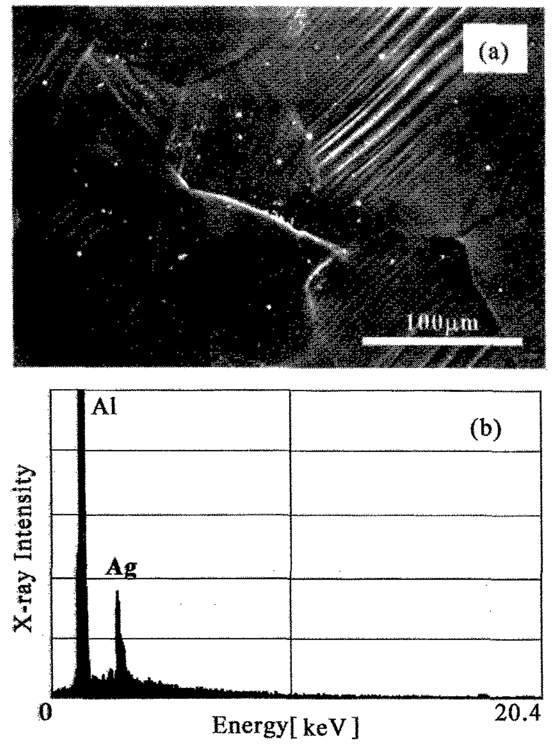

Fig.5 HMP image (a) of a binary alloy specimen stretched by 10%, and EDXS spectrum (b) taken from a white particle shown in (a).

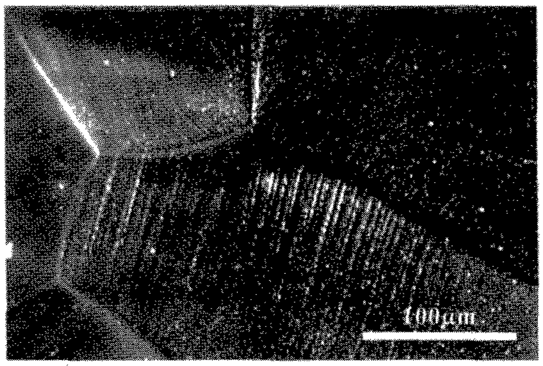

Fig.6 HMP image of a binary alloy specimen stretched by 10% during exposure to hydrogen gas.

-cles were metalic silver particles. The HMP image of the specimen stretched by 10% during exposure to hydrogen gas was similar to Fig.5(a) as shown in Fig.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 1～10μm 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 (Fig.9) and smallest when only stretched (Fig.7).

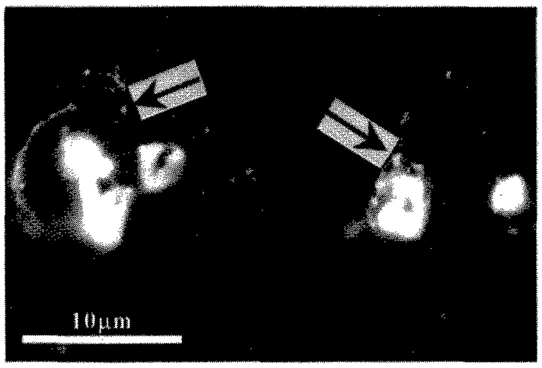

Fig.7 HMP image of a 5083 alloy specimen stretched by 10%.

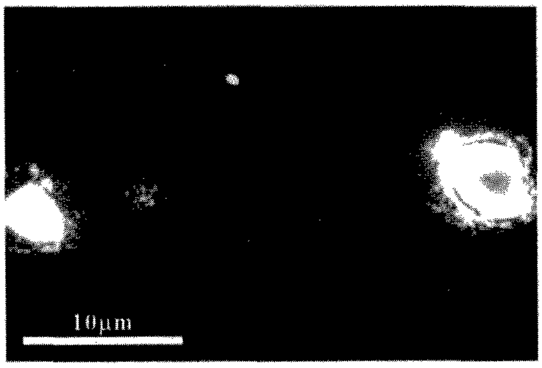

Fig.8 HMP image of a 5083 alloy specimen exposed to hydrogen gas without loading.

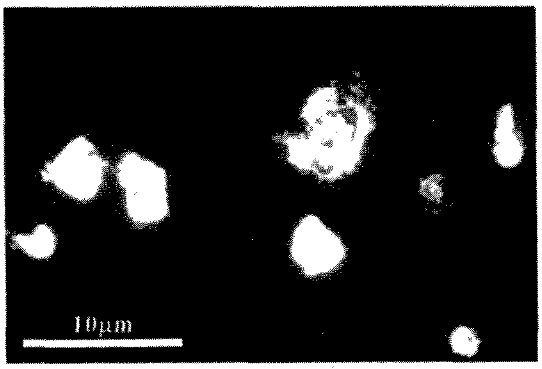

Fig.9 HMP image of a 5083 alloy specimen stretched by 10% during exposure to hydrogen gas.

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.

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 [(2)]. 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 boundary 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 deducted 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 the structure of the films.

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 microscopic 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 Fig.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 by grain boundary diffusion and finally is emitted at the slip line, grain boundary and second phase particle on the other surface.

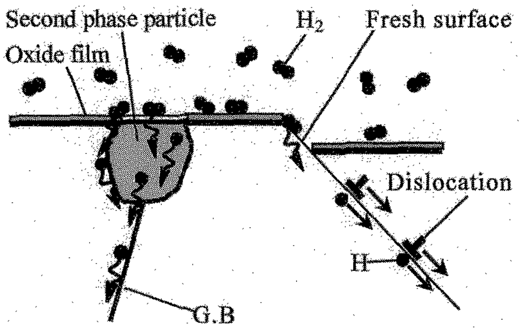

Fig.10 Possible mechanism for the penetration of environmental hydrogen.

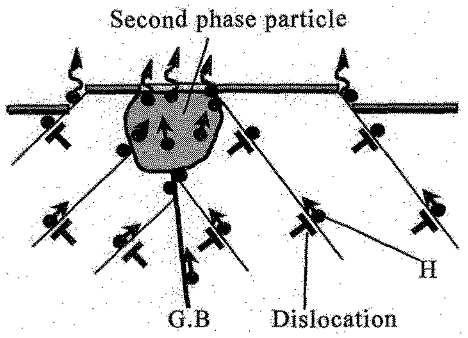

Fig.11 Mechanism for the evolution of hydrogen.

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.

6. REFERENCES

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