HYDROGEN TRANSPORT IN A 5083 ALUMINUM ALLOY

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ABSTRACT Hydrogen microprint (HMP) technique was applied to 5083 aluminum and Al-4.5%Mg binary alloy sheets to investigate the behavior of internal or impurity hydrogen. In the Al-Mg binary alloy, hydrogen atoms were found to be evolved along slip lines in the specimen surface when heavily deformed. This result was in qualitative accordance with that of pure aluminum reported before, indicating that internal hydrogen atoms move with gliding dislocations in single phase aluminum base materials irrespective of the presence of solute magnesium atoms. Hydrogen atoms were also seen to be evolved along grain boundaries. In contrast, in the 5083 alloy, second phase particles and non-metallic inclusions were found to be a preferential hydrogen evolution site. These results were understood by considering that hydrogen atoms moving with gliding dislocations are trapped and accumulated in the particle/matrix interfaces or grain boundaries, and then move toward the surface by interface or grain boundary diffusion.

Keywords: *5083 aluminum alloy, aluminum-4.5mass% magnesium binary alloy, hydrogen microprint technique, internal hydrogen, gliding dislocation*

1. INTRODUCTION

In recent years, the environmental disruption of the earth has become a crucial problem in a variety of aspects. Among them, prevention of warming of the globe by increasing carbon dioxide is one of the most urgent tasks to be attained. From this point of view, utilization of hydrogen that exhausts no green house effect gas has been projected, which involves marine transportation of liquid hydrogen. To reach the goal of this project, tank material is required to resist possible hydrogen penetration and embrittlement, as well as to have sufficient strength, toughness and corrosion resistance at room and cryogenic temperatures. Hence, it is essential to understand the behavior of hydrogen in the candidate tank material.

Generally, hydrogen related to a structural material can be classified into internal (or impurity) hydrogen and environmental hydrogen. Hydrogen atoms of the former type have been contained from the starting material or picked up during processing, while those of the latter type penetrate from the atmosphere with significant hydrogen gas pressure into the material under tensile stress during the service. Although serious environmental embrittlement of metallic materials by molecular hydrogen has not been reported so far at ambient temperature or below, internal hydrogen atoms have been proved to move with gliding dislocations in pure aluminum[1-4]. In the liquid hydrogen tank shown Fig.1, one side of the sheet material is

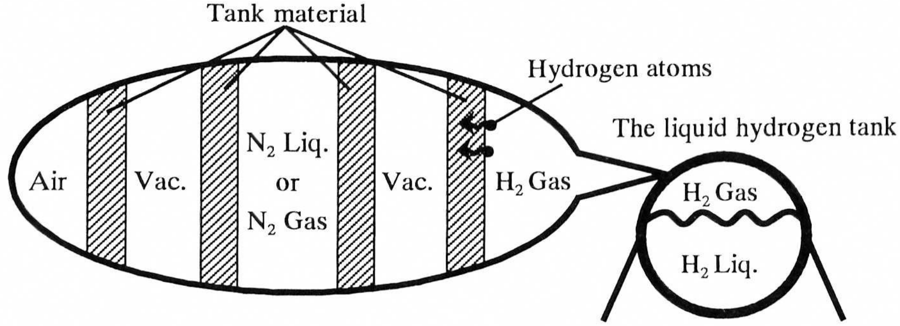

Fig.1 Schematic drawing showing possible penetration of hydrogen atoms into the liquid hydrogen tank material.

exposed to high pressure of hydrogen gas, while no hydrogen partial pressure will be applied onto the other side. The permeation of hydrogen and embrittlement by environmental hydrogen has not been examined in this condition in detail.

In this study, to approach the final goal of elucidating the permeation and migration behavior of hydrogen atoms during loading in the above condition, a preliminary examination on the migration behavior of internal hydrogen atoms has been made by means of hydrogen microprint (HMP) technique on a 5083 aluminum alloy sheet, candidate material for the tank in marine transportation, as well as an Al-Mg binary alloy as a reference material.

2. EXPERIMENTAI PROCEDURE

2.1 Specimens

Hot-rolled plate of a commercial 5083 aluminum alloy of 10mm thickness was further hot-rolled at 400℃ using laboratory mill to 2mm in thickness, annealed at 400℃ for 1h and finally cold-rolled to a 1mm thick sheet. Tensile specimens with gage length of 50mm and gage width of 12.5mm were machined from the above sheet in the longitudinal direction, annealed at 400℃ for 1h and then electro-polished. Constituent particles arising from impurity iron and silicon and dispersoid particles containing mangnese, existing in 5083 alloy, are thought to have some effects on the behavior of internal hydrogen atoms as Tien et al. suggested[5]. To see such effects, an Al-4.5mass%Mg binary alloy with virtually no second phase particles was prepared from raw materials of purity over 99.99%. The alloy was melted in air, cast in an iron mold, homogenized at 430℃ for 1h, warm-rolled from 10mm to 2mm in thickness at 200℃, and then processed into tensile specimens in the same way as in the 5083 alloy. Analyzed composition of the specimens is indicated in Table 1.

Table 1 Composition of the alloy specimens in mass %

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Ti	Al
A5083	0.08	0.19	0.02	0.59	4.56	0.05	0.02	Bal.
Al-Mg	0.007	0.004	0.002	-	4.37	-	-	Bal.

2.2 Hydrogen microprint technique

By mean of HMP technique, microscopic location in the surface where a hydrogen atom has been evolved can be visualized utilizing a reductive reaction of hydrogen atom in metals. First, specimen surface is covered with photographic emulsion consisting of silver halide, and then the reaction

$$Ag^{+} + H \rightarrow Ag + H^{+} \qquad (1)$$

takes place when a hydrogen atom moves by some mechanism and arrives at the surface from the inside; Fig.2 shows an example when hydrogen atoms move with gliding dislocations. A silver grain that is sufficiently large in size for observation can form arising from the silver atom produced by the above reaction, when the emulsion is photographically developed with the specimen. On the other hand, when fixed, remaining silver halide can be dissolved into the fixing solution and removed from the specimen surface. Thus the point in the specimen surface where a hydrogen atom has been evolved can be visualized as a silver grain.

In this study, a collodion layer was placed layer between the photographic emulsion and the specimen. This layer is thought to provide a closer adherence of the emulsion layer to the specimen and to prevent the reaction

$$3Ag^{+} + Al \rightarrow 3Ag + Al^{3+} \qquad (2)$$

between the photographic emulsion and metallic aluminum atoms[6,7]. The specimens were next covered with photographic emulsion Konica NR-H2 (silver bromide grain size, 0.08μm) diluted by four times, by wire loop method in a darkroom as previously reported[7]. Then they were covered with a shading film, and deformed in tension to fracture at room temperature at a constant speed of 2.0 mm/min (initial strain rate, $5.6 \times 10^{-4} s^{-1}$) on an Instron 1185 testing machine. In the present experiment both deformed and undeformed specimens were developed in Fuji SPD and fixed in Super Fuji Fix. The resultant silver grains were observed together with the microstructure on the specimen surface using a Jeol 7330 SEM equipped with an EDXS device.

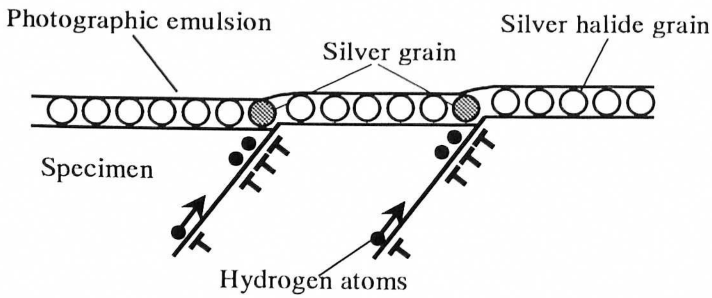

Fig. 2 Principle of hydrogen microprint technique.

Table 2 Properties of the specimens

Specimens	Yield Stress (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	Grain Size (μm)
A5083	133	302	22	18
Al-Mg	80	227	28	120

3. EXPERIMENTAL RESULTS AND DISCUSSION

Prior to HMP technique, usual tensile tests were performed on the two alloy specimens. Table 2 shows the resultant tensile properties together with grain size measured in short-transverse direction on an LT-ST plane by means of mean intercept method. Since Al-Mg binary alloy does not include dispersoid, it has coarser grains and lower strength. Because of the lower strength and the absence of constituent particles, the binary alloy has higher ductility.

Figure 3 shows SEM micrographs of the two alloy specimens HMP-treated without deformation. A few white particles are seen in both specimens, which were found by EDXS to be rich in silicon or sodium but not to contain silver. These particles were regarded as a kind of contaminant, and no silver particle was observed in any other regions. This means that hydrogen atoms are not evolved from the specimen surface unless the specimen is deformed.

Silver particles that were regarded as the product of HMP technique were observed in only a limited number of areas in the 5083 alloy specimen even though deformed. A rather exceptional example of such HMP images are shown in Fig.4 (a, b). In Fig.4 (a), a number of fine white particles (about 1 μm) are observed in contact with a coarse particle (5 μm) in the middle of the micrograph. Figure 4 (c) shows an EDXS spectrum obtained from one of the fine particles in Fig.4 (a). A strong silver peak implies hydrogen evolution caused by the deformation, while weaker peaks of aluminum, magnesium and silicon are also seen, which are considered to arise from the coarse particle underneath the silver particle. An EDXS spectrum from the matrix is shown in Fig.4 (d), consisting of main aluminum and minor magnesium peaks, corresponding to the alloy composition. The peak height ratios of magnesium and silicon to aluminum in Fig. 4 (c) are far greater than those in Fig.4 (d). Taking this fact and the particle size into account, the coarse particle was deduced to be a constituent Mg_2Si particle. In another area shown in Fig.4 (b), silver particles labeled "S" are also seen in contact with a coarse particle labeled "A". Since no other element than aluminum was detected from the latter

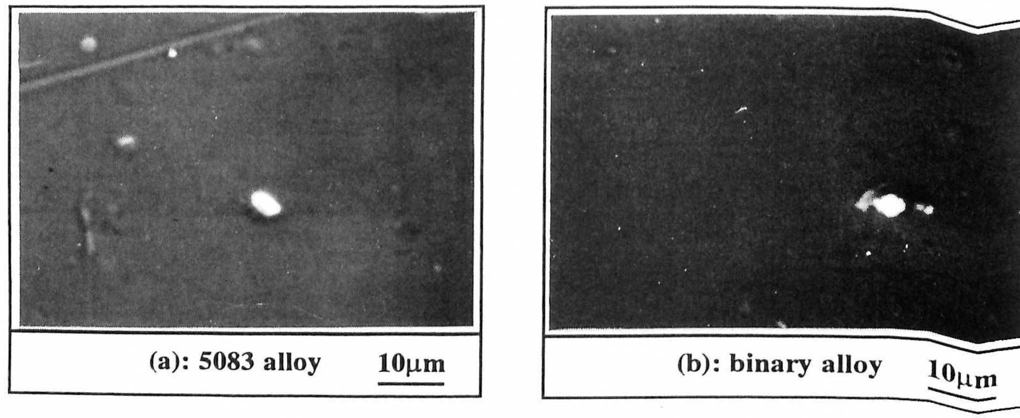

Fig. 3 SEM/HMP images of undeformed specimens.

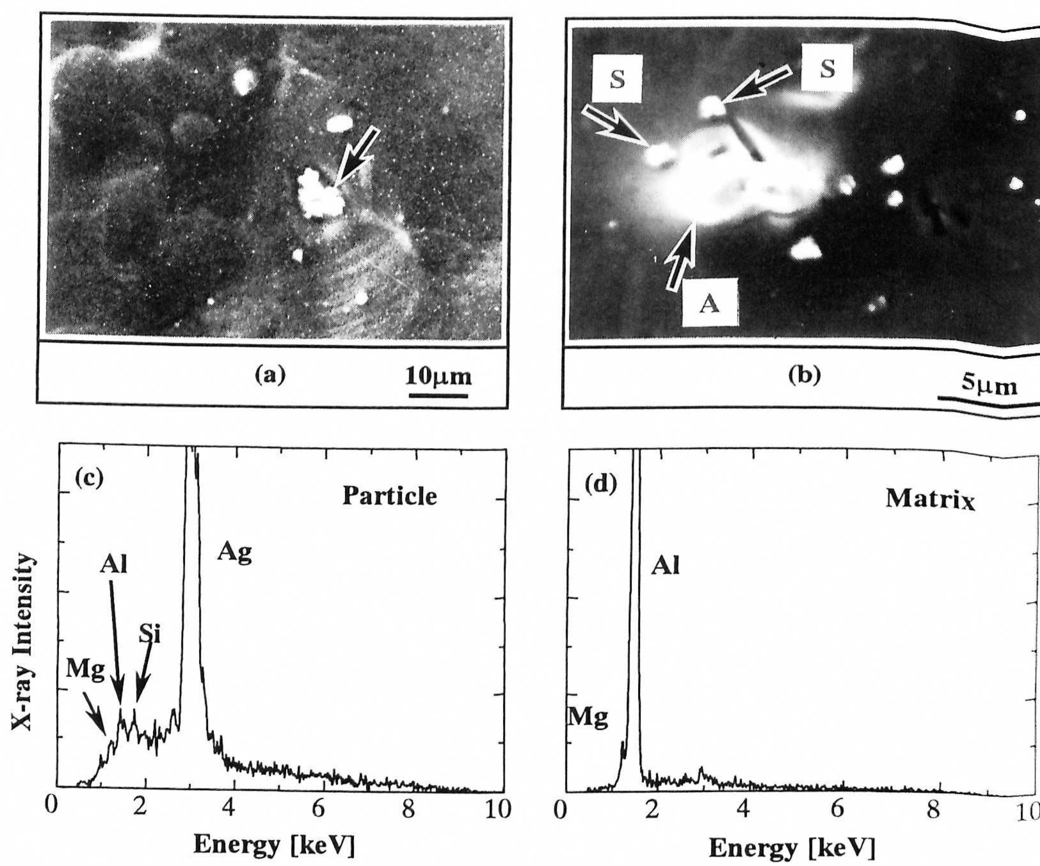

Fig. 4 HMP images (a, b) and EDXS spectra (c, d) of the 5083 alloy specimen stretched to fracture. (c): taken from the white particle indicated by an arrow in (a). (d): taken from the matrix in (a).

particle, this was regarded as non-metallic inclusion of alumina. This means that hydrogen atoms are evolved at the constituent or inclusion particle, or the particle/matrix interface in the 5083 alloy. This will be further discussed later.

An example of HMP image in the Al-Mg binary alloy specimen stretched to failure is shown in Fig.5 (a). An array of white particles is revealed on the grain boundary, while a few particles are visible on slip lines. An EDXS spectrum as shown in Fig.5 (b) was obtained from any of both types of particles, meaning that all of them are silver particles. This result is in accord with that reported in pure aluminum[1-4]. The silver particles on slip lines indicate that hydrogen atoms move with gliding dislocations in the binary alloy, as well as in pure aluminum. The silver particles on grain boundary have not been discussed so far in detail, but can be well understood by assuming that hydrogen atoms, which have reached the grain boundary inside the specimen with gliding dislocations, move toward the surface by grain boundary diffusion. Hydrogen atoms detected in contact with constituent and inclusion particles in the 5083 alloy are presumed to be evolved in the following process: (i) first hydrogen atoms move with gliding dislocations as in the binary alloy, (ii) then they are trapped and accumulated at the particle/matrix interface when the dislocations interact with the particle, (iii) and finally they migrate toward the surface by interface diffusion, leading to the evolution from the surface.

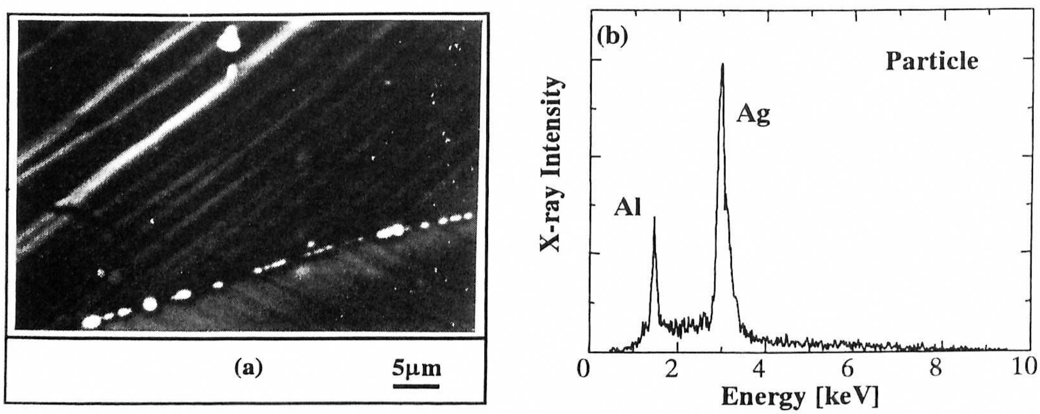

Fig. 5 HMP image and EDXS spectrum of a binary alloy specimen stretched to fracture. (a): HMP image, (b): EDXS spectrum taken from a white particle shown in (a).

4. SUMMARY

The behavior of internal or impurity hydrogen was investigated by means of hydrogen microprint technique on 5083 aluminum and Al-4.5mass%Mg binary alloys. It was confirmed that internal hydrogen atoms moved with gliding dislocations, and were evolved at slip lines on the surface in the binary alloy. This is in accord with the result previously reported in pure aluminum, and hence is regarded as a common feature in single phase material. Hydrogen evolution was also detected at a grain boundary in the binary alloy and at the interface between second phase or inclusion particle and the matrix in the 5083 alloy. This can be understood by assuming that hydrogen atoms moving with gliding dislocations were trapped at the grain boundary or the particle/matrix interface and that they diffused out along the boundary.

ACKNOWLEDGMENT

This work was financially supported by the Iwatani Naoji Foundation's Research Grant, which is highly acknowledged. The authors would like to thank Mr. K. Nagamine, a bachelor course student, for his experimental assistance, and the Furukawa Electric Co., Ltd. for the offer and composition analysis of the specimens.

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