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Visualization of Diffusive Hydrogen in Aluminum

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Close attention has been paid to what is called diffusive hydrogen atoms that have been known to affect directly to hydrogen embrittlement; hydrogen atoms diffuse to the front of crack tip. The behavior of hydrogen in test pieces cut from sheets of aluminum with 99.99% purity, 6061-T6 and 7075-T6 alloys has been investigated by visualizing the hydrogen atoms with respect to the microstructure by means of tritium autoradiography technique. As a result, silver particles that indicate the location of tritium (hydrogen) were always detected on the intermetallic compound particles in 6061 and 7075 alloys and no silver particle was observed in the pure aluminum. Hence, it is deduced that hydrogen atoms invade aluminum alloys through intermetallic compounds. This was not qualitatively affected by the kind of the environment: water and hydrogen gas. The number of silver particles detected was larger in 7075 than in 6061, which may be related to the larger sensitivity of 7075 to hydrogen embrittlement.

Keywords: *environmental hydrogen, pure aluminum, 6061 aluminum alloy, 7075 aluminum alloy, tritium autoradiography*

1. Introduction

In recent years, the use of hydrogen as a clean energy has been paid attention to in terms of the prevention of global warming. Tanks composed solely of steel and of aluminum liner reinforced with carbon-fiber-reinforced plastic in the surrounding are being used to store high-pressure hydrogen gas in hydrogen stations and fuel cell vehicles, respectively. On the other hand, hydrogen embrittlement has been known to occur in some metallic materials under several certain conditions, and must be avoided during the use of the tank. For this purpose, investigations on the behavior of hydrogen in metallic material are needed.

Hydrogen in a metallic material can be classified into two categories: impurity hydrogen and environmental hydrogen. The former is picked up into the material during the manufacturing process, while the latter invades the material during services. It has been generally known that the environmental hydrogen plays major role in hydrogen embrittlement [1,2]. As a technique to visualize the hydrogen atoms in a metallic material, two techniques have been applied: hydrogen microprint technique (HMPT) and tritium autoradiography techniques (TARG). Whereas only the hydrogen discharged from the sample can be detected in HMPT, hydrogen (tritium) that stays in the vicinity of the surface can be detected in TARG. This is based on the principle of TARG that the photographic emulsion spread on the surface of the sample charged with tritium (a radio isotope of hydrogen) is exposed by beta rays radiated from the tritium. In this study, the behavior of environmental hydrogen that invades aluminum from two different environments: tritiated water and tritium gas, has been investigated by means of TARG.

2. Specimens and Procedure

Specimens used in this study are a 0.9mm thick sheet of 99.99% aluminum (4N) and 1.0mm thick sheets of 6061 and 7075 aluminum alloys. Table 1 shows their chemical compositions. The 4N sheet was annealed for 1h at 560°C, while the alloy sheets were solution-heat-treated, quenched, left at room temperature for 2 d, and T6-tempered: at 175°C for 8 h for 6061 and at 120°C for 24 h for 7075.

Samples of 10mm×10mm were cut from the sheets, wet-ground with #1500 abrasive paper, and then mirror-finished with alumina and silica. Dehydrogenation treatment was made on the 4N sample to decrease amount of hydrogen as much as possible before tritium charging, by heating the sample up to 550°C under ultrahigh vacuum.

Tritium was charged to the samples in the above-mentioned two environments. Firstly, tritiated water of about 0.02mL with a radioactivity of 40MBq/mL was placed in contact with a pair of mirror finished sample surfaces, left for 6h at the room temperature, and then rinsed with water. Secondly, the samples were kept for 3h under a gas with a pressure of 573 Pa having a molar composition T/(D+T) (T: tritium, D: deuterium) of 0.17. To diffuse the tritium in the sample, some of the samples were annealed at a heating rate of 20°C /min to 450°C for those charged with tritiated water and to 250°C for those charged with tritium gas, and then air-cooled. Test pieces of 5mm×5mm were cut out from the samples, and their mirror surface was covered with photographic emulsion (Konica-Minolta NR-H2 diluted by 4 times with water) in a darkroom. The surface of some of the test pieces charged with tritiated water was removed by 2.5μm with an NaOH solution, and then covered with the photographic emulsion. After the emulsion covering, the test pieces were exposed in the liquid nitrogen for 14 d and then subjected to photographic development and fixing. The fixed emulsion layer was observed together with the microstructure of the test pieces with a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDXS) device.

Table 1 Chemical composition of the specimens in mass %

Spesimen	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
4N	0.0016	0.0004	<0.0001	-	-	-	-	-	Bal.
6061	0.63	0.29	0.30	0.05	1.00	0.18	0.01	0.02	Bal.
7075	0.08	0.31	1.87	0.04	2.52	0.22	5.76	0.01	Bal.

3. Results and Discussion

Though the actual photograph is not shown here, no silver particle was observed in 4N test pieces in all of the conditions.

Figure 1 shows a set of examples of autoradiographic images of the surface of the as-charged test pieces of 6061 and 7075 alloys. Silver particles (hydrogen) are detected on intermetallic compound particles commonly in the two alloys, and this was also the case for all the other areas observed. Thus, hydrogen atoms were deduced to invade the aluminum alloy through intermetallic compounds, which is in accord with the result that no silver particle was detected in 4N. From EDXS, the compounds contain Fe and Si in 6061, and Cu and Fe in 7075. The latter compound phase was presumed to be Al_7Cu_2Fe from the literature [3]. No qualitative difference was found with respect to the site of hydrogen invasion between the two ways of charging: water charge and gas charge.

Result of a rough assessment of the number of detected silver particles in each experimental condition is shown in Table 2. The number is larger in the as-charged test pieces than in the annealed test pieces, and is decreased by removing the surface region in the as-charged test pieces. In the annealed 7075, however, the number of silver particles is larger in the test piece of 2.5μm depth than in the surface. With respect to the alloy composition, silver particles are detected more frequently in 7075 than in 6061. This may be related to the tendency that 7075 alloy is more sensitive to hydrogen embrittlement than 6061.

In addition, because the number of detected silver particles was large in 7075, TARG was done after the surface of water-charged 7075 test piece was removed by 10μm. An example of the results is shown in Fig. 2, where silver particles are detected on intermetallic compound particles as well as in the other test pieces of the two alloys, and the number of detected silver particles in this test piece is as large as that of 2.5μm depth. It is thought that the tritium in the surface region is diffused inward as well as emitted outside by annealing.

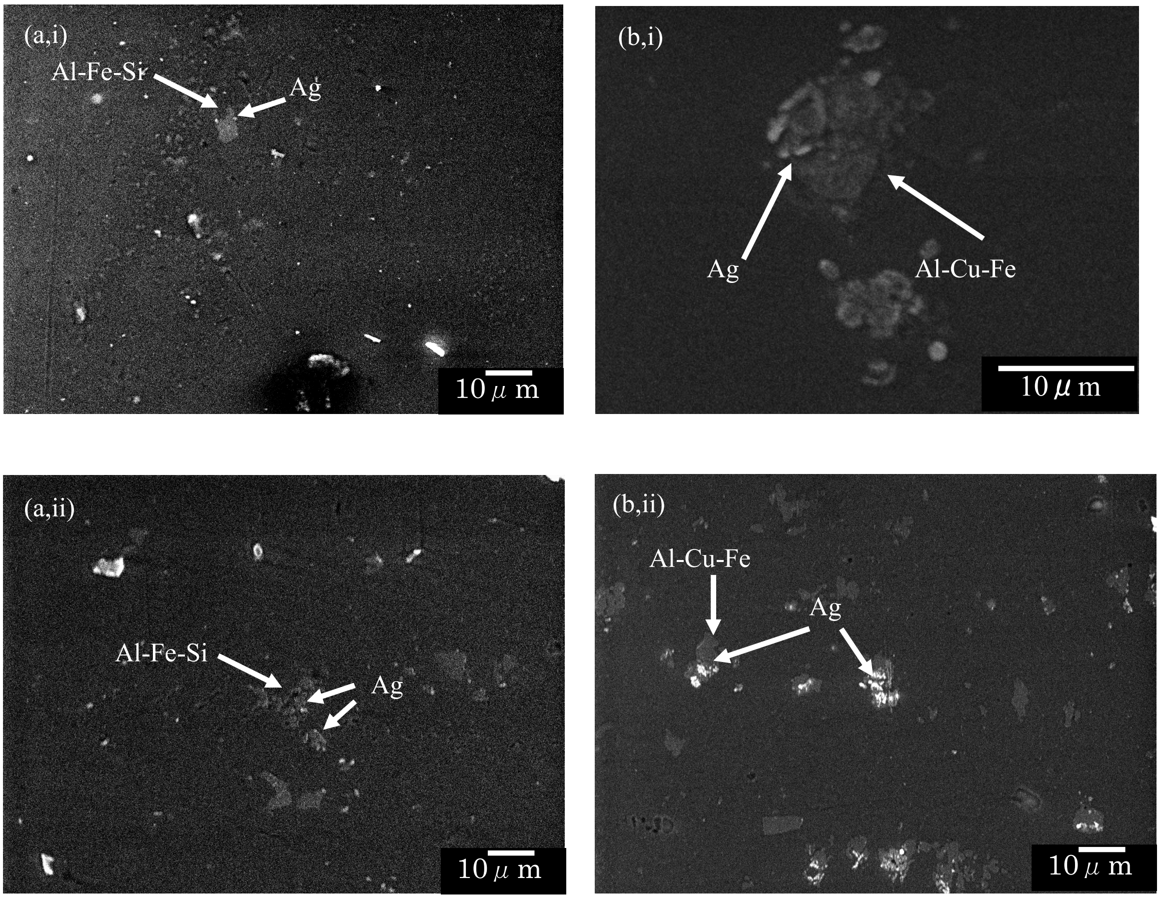

Fig.1 Example of tritium autoradiographs taken using an SEM for two aluminum alloy specimens charged in tritiated water (i) and tritium gas (ii). (a) 6061, (b) 7075.

Table 2 Approximate comparison of detected amount of silver particles in each specimen.

		Water-Charged		Gas-Charged
		Surface	2.5μm from the surface	Surface
4N	As Charged	×	---	×
	Annealed	×	×	×
6061	As Charged	△	×	△
	Annealed	---	×	×
7075	As Charged	○	△	○
	Annealed	×	△	△

○, △, ×: number of particles were large, small and nil, respectively. ---: obervation was not made.

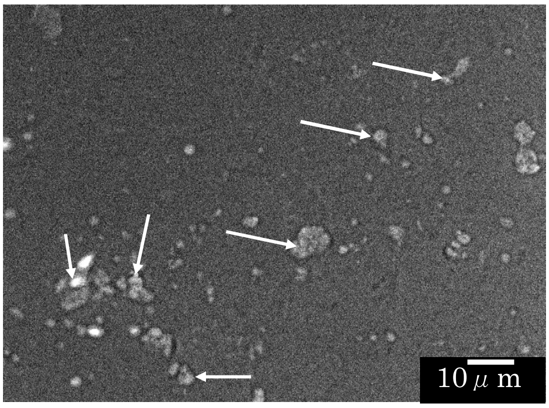

Fig.2 Example of tritium autoradiograph taken using an SEM for water-charged 7075. The surface was removed by 10μm thickness with an NaOH solution. Arrows indicate silver particles.

4. Conclusion

Silver particles were always detected on the intermetallic compound particles in 6061 and 7075 alloys and no silver particle was observed in 4N. Hence, it is deduced that hydrogen atoms invade aluminum alloys through intermetallic compounds. This was not qualitatively affected by the kind of the environment: water and hydrogen gas. The number of silver particles detected was larger in 7075 than in 6061, which may be related to the larger sensitivity of 7075 to hydrogen embrittlement.

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