Proceedings of the 12th International Conference on
Aluminium Alloys, September 5-9, 2010, Yokohama, Japan

pp. 2320-2323

Detection of Hydrogen in Ion-plated Pure Aluminum during Tensile Deformation

Goroh Itoh[1], Hideki Iwahashi[2] and Takahiro Shikagawa[3]

[1]Department of Mechanical Engineering, Ibaraki University, Hitachi, Ibaraki, Japan

[2]Undergraduate Student, Department of Mechanical Engineering, Ibaraki University, Hitachi, Ibaraki, Japan

[3]Graduate Student, Major in Material Science, Ibaraki University, Hitachi, Ibaraki, Japan

An increasing interest has been being taken in hydrogen as a clean energy for solving the global environmental problems. In order to use the hydrogen in safety, investigation on the hydrogen behavior is required. Although hydrogen microprint technique (HMPT) has been known to be effective to investigate the hydrogen behavior, the low detection efficiency of hydrogen was reported. Ion-plating was reported to increase the detection efficiency in HMPT for hydrogen emitted from the specimen by plastic deformation. On the other hand, no such increase was found for hydrogen permeating through the specimen ion-plated with substrate heating in the previous study by the authors. In this study, detection efficiency in HMPT has been investigated on an aluminum ion-plated with or without substrate heating and then plastically deformed. Sheet specimens of aluminum with 99.99% purity were subjected to Ar-ion bombardment in the ion-plating chamber, ion-plated with Sn, covered with photographic emulsion for HMPT, deformed by 5%, photographically treated and then observed with an SEM. It has been found that extrinsic hydrogen that should not be detected is detected when the sample is ion-plated without substrate heating. The detection efficiency was concluded to be improved by the ion-plating with substrate heating.

Keywords: *hydrogen microprint technique, ion-plating, pure aluminum, tensile deformation.*

1. Introduction

In recent years, fuel cell vehicles (FCVs) are being actively developed as a way of solving global environment problems. In the FCVs, high-pressure (35MPa) hydrogen is contained in type-3 cylinders composed of 6061-aluminum-alloy liner and surrounding carbon-fiber-reinforced-plastics layer. Replacing the 6061 alloy with a higher-strength aluminum alloy is demanded to increase the mileage per a filling to the level of the gasoline vehicles by raising the initial pressure to 70MPa. In order to guarantee the safety of the hydrogen cylinder, investigation on the hydrogen behavior as well as on the hydrogen assisted embrittlement is required. Although hydrogen microprint technique (HMPT) has been known to be effective to investigate the hydrogen behavior, the low detection efficiency of hydrogen was reported [1]. Horikawa et al. have reported that ion-plating with Sn increases the detection efficiency in HMPT for the hydrogen emitted from the specimen by plastic deformation [2]. However, in the previous report by the authors, the efficiency of detection was improved only for the ion-plating without substrate heating, not for that with substrate heating, for the hydrogen permeated through pure aluminum foil from hydrogen gas environment [3]. Hence, the discrepancy in the results in the two reports may arise from the method to allow the hydrogen to be emitted from the specimen. In this study, detection efficiency in HMPT will be investigated on a pure aluminum sheet ion-plated with Sn with or without substrate heating and then plastically deformed.

2. Specimens and experimental procedures

2.1 Principle of ion-plating

Surface change of the specimen in the course of ion-plating process is shown in Fig. 1. Firstly, the surface of the specimen is impacted by inert gas (Ar) ions to remove most of the pre-existing oxide film together with contamination, what is called bombardment treatment. After the bombardment, coating substance (Sn) evaporated and ionized is deposited on the specimen with the aid of electrostatic force. In this process, the specimen (substrate) is usually heated. It was reported that the surface of the specimen ion-plated without substrate heating was rough and porous while that with substrate heating was dense and smooth [3]. The ion-plated film will prevent the substrate from further oxidation.

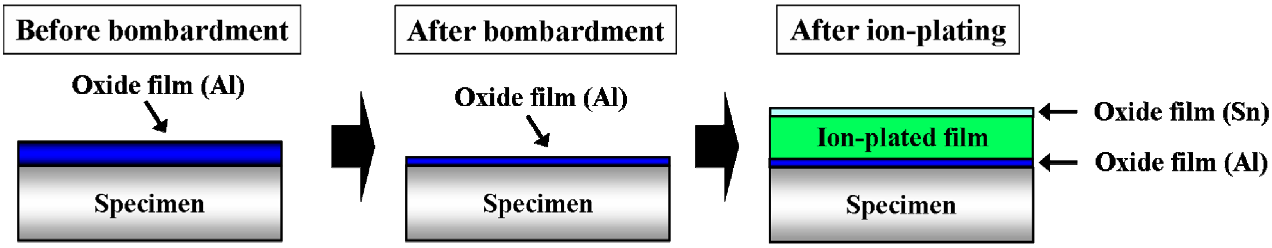

Fig.1 Surface change of the specimen in the course of the ion-plating process.

2.2 Principle of HMPT

In HMPT, hydrogen atoms emitted from the inside of the metal are visualized, using a photographic emulsion coated on the surface of the specimen. Ag bromide, the major component of the emulsion, is converted into metallic silver with the strong reduction power of atomic hydrogen following Eq. 1.

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

The whole Ag bromide particle that has received several hydrogen atoms is converted to metallic Ag particle by photographic development, and the other Ag bromide particles are dissolved in a fixing solution. The remaining Ag particles can be observed by a scanning electron microscope, SEM, and therefore, the hydrogen emission site can be detected as the location of the metallic Ag particles.

2.3 Specimens

The specimen used in this study was 99.99% purity aluminum sheet of 0.9mm in thickness supplied by Mitsubishi Aluminum Co., Japan in an annealed state. Its chemical composition of the specimen in the as-cast state is shown in Table 1. Samples with and without tensile deformation illustrated in Fig. 2 were cut from the sheet in L direction. The samples were annealed at 560°C for 1 h. Both sides of the samples were wet-ground with #1500 abrasive paper, alkaline-etched and finally electro polished to a mirror surface.

Table 1 Composition of the pure aluminum specimen in mass ppm.

Si	Fe	Cu	H	Al
15	11	49	0.081	Bal.

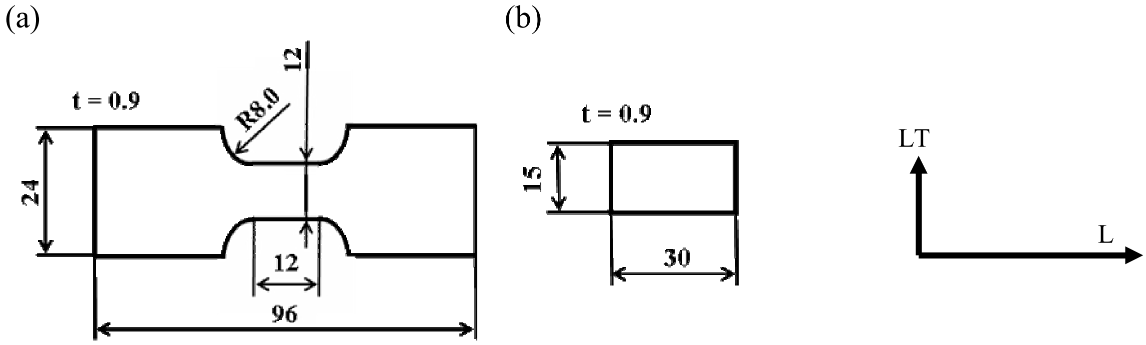

Fig.2 Morphology and dimension in mm of the test pieces to be deformed (a) and undeformed (b).

2.4 Experimental procedures

The condition of ion-plating is shown in Table 2. The sample was placed in the ion-plating apparatus (ULVAC D-330DK), which subsequently was evacuated and back-filled with Ar gas. The sample was subjected to a bombardment treatment under a flow of Ar gas kept at a pressure of about 5Pa by impressing a DC voltage of 300V onto the atmosphere for 90min. After the bombardment, the chamber was re-evacuated to 1.3×10^{-3}Pa, and one of the surfaces of the sample was ion-plated with Sn with or without substrate heating with a bias voltage of 650V. After the ion-plating, the plated surface was covered with a collodion and then photographic emulsion (Konica NR-H2) diluted four times with distilled water, in a dark room by means of wire-loop method [4]. Half of the test pieces were tensile-deformed plastically by about 5% on a screw-driven testing machine at an initial strain rate of $6.94\times10^{-4}s^{-1}$. Then, the emulsion layer was hardened using 36% formalin, developed with photographic developer, fixed in a 15% sodium thiosulphate solution, rinsed and finally dried naturally in air. The silver particles on the surface were observed in a Hitachi S-2150 SEM equipped with Horiba EMAX-1770 energy dispersive X-ray spectroscopy (EDXS) device that can check the composition of the observed particle qualitatively.

Table 2 Parameters of the ion-plating process.

Coating substance	Sn (99.9%)
Bombardment	300V, 0.1A for 90min
Pressure before bombardment	1.3×10^{-3} Pa
Substrate heating	None or heating(320°C)
Bias voltage, current	650V, 0.001A
Plated thickness	600nm

3. Results and discussion

A set of example of the results of SEM observation on the samples after HMPT is shown in Fig. 3. In the conditions (a) and (b), no Ag particle is detected, with occasional Si and Sn particles, which are thought to arise from abrasive grains and coagulation of plating substance. Although it was reported that hydrogen was not emitted from undeformed aluminum [5], in the condition (c), Ag particles are detected. Thus, in HMPT on the sample ion-plated without substrate heating, hydrogen that should not be detected has been generated by some reaction correlated the ion-plated film, resulting in the detection of extrinsic Ag particles as shown in Fig.3 (c). In the conditions (d), (e) and (f), Ag particles were detected mainly on the slip line. Table 3 shows the density (number of Ag particles per unit area) in the samples corresponding to Fig.3, where the measurement was conducted on an area of $0.25mm^2$ for each sample. Although in the condition (f), the Ag particle density was the highest, extrinsic particles as described above may be included. In contrast, in the condition (e), such extrinsic particles may not be included, and still the density is markedly larger than in (d). Thus it has been concluded that the detection efficiency was increased by the ion-plating with substrate heating for the hydrogen emitted by tensile deformation.

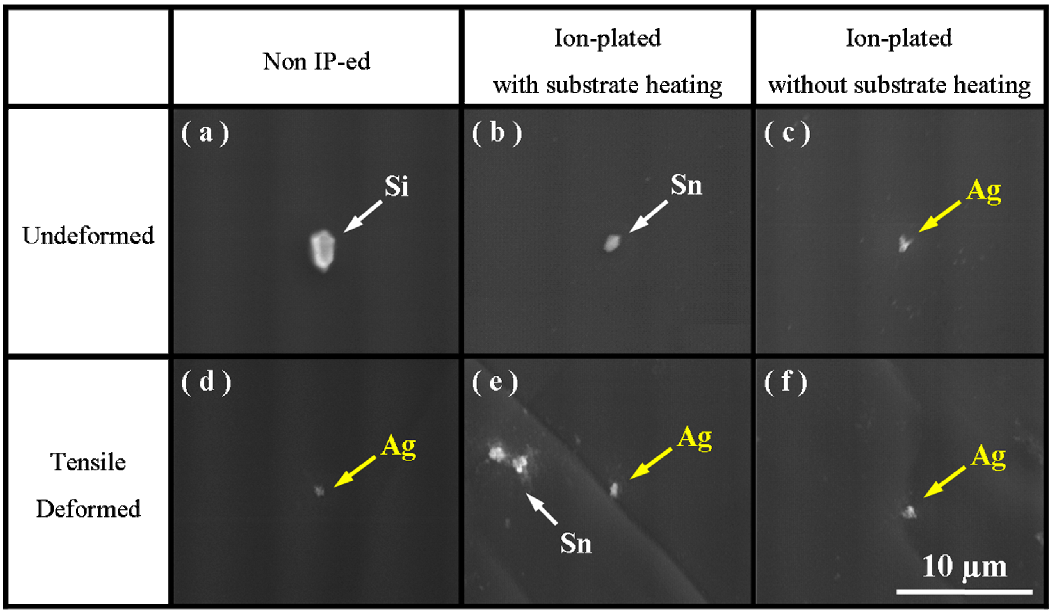

Fig.3 SEM/HMPT images.

Table 3 Ag particle density (mm^{-2}).

	Unplated	Ion-plated with substrate heating	Ion-plated without substrate heating
Undeformed	(a) 0	(b) 0	(c) 12
Tensile-deformed	(d) 4	(e) 24	(f) 36

4. Conclusion

Extrinsic hydrogen that should not be detected was detected when the sample was ion-plated without substrate heating. The detection efficiency was concluded to be improved by the ion-plating with substrate heating for the hydrogen emitted by tensile deformation.

References

[1] K. Ichitani, S. Kuramoto and M. Kanno: Corros. Sci., **45**(2006), 1227-1247.
[2] K. Horikawa, Y. Takeuchi, K. Yoshida and H. Kobayashi: J. JILM, **56**(2006), 10-213.
[3] G. Itoh, T. Shikagawa, Y. Suzuki, I. Nakatsu and N. Itoh: *Processing and Fabrication of Advanced Materials XVIII*(2009), 275-284.
[4] K. Koyama, G. Itoh and M. Kanno: J. Japan Inst. Metals, **62**(1998), 790-795.
[5] K. Izumi and G. Itoh: J. JILM, **56**(2006), 478-482.