

INFLUENCE OF SURFACE POISONING ON HYDROGEN PERMEATION BEHAVIOR OF PURE ALUMINUM

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Abstract

The permeation behavior of hydrogen through pure aluminum has been investigated in the temperature range of 625 K to 778 K by a gas permeation technique . The permeation rate of hydrogen was strongly affected by the conditions of the surface where the hydrogen was introduced into the sample . They varied characteristically by repeating the permeation run, which was bounded in the temperature range of 690K to 700K . At a higher temperature than 700K, the surface oxide layer was reduced by hydrogen during the permeation run, which resulted in the larger permeation rate of hydrogen in the subsequent permeation runs . At the sensitized surface by the reduction, the temporary poisoning took place and the permeation rate of hydrogen was decreased . The poisoned surface, however, was cleaned by keeping the sample under high vacuum at a higher temperature than 700K . The poisoning was closely related to the presence of carbon and its compounds on the top surface where the hydrogen was introduced into the sample .

Introduction

Solubility and diffusion coefficient of hydrogen in metals are generally determined by hydrogen desorption or hydrogen permeation techniques . However, it is considered that these techniques are affected strongly by surface conditions, such as oxides, of metals . On the interaction between hydrogen and aluminum, many reports have been presented and reviewed^{1,2)} . They are mainly concerned to the diffusivity, the solubility and the trapping of hydrogen in aluminum, whose values have been scattered . It is probable that the scatter has been caused by the influence of the surface conditions of sample in addition to the lattice imperfections such as vacancies, dislocations, grain boundaries and impurities³⁾ . There have been few reports with respect to the effects of the surface on the hydrogen per-

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meation through a pure aluminum . It is important to clarify the relation between the surface conditions and the permeability of hydrogen .

In this study, the permeation behavior of the hydrogen through an aluminum with high purity has been investigated in detail using a gas permeation technique in the temperature range of 625 K to 778 K . Various time dependence of the permeation rate (permeation curves) of hydrogen through the aluminum was observed in spite of the same sample and the same permeation temperature . The variation of the permeation curves was discussed from the standpoint of the hydrogen reduction and the poisoning of the surface introducing the hydrogen .

Experimental Procedure

The material used in the present experiment was zone-refined aluminum whose purity was 99.9999%⁴⁾ . The pure aluminum was cold-rolled into a plate with a thickness of 50-200 μm and cut into disk-shaped samples with 40 mm in diameter . After cutting, the samples were rinsed with acetone and ethanol to clean the surface . To remove the tight oxide layer, just before setting, the surfaces of the sample were slightly scratched using an abrasive paper (corundum , 3000 mesh) in air .

The hydrogen permeation behavior through the pure aluminum was investigated by a gas permeation technique in the temperature range of 625 K to 778 K . The experimental setup is shown schematically in Fig.1^{3,5,6)} . The sample was inserted between an aluminum gasket and an aluminum disk with many small holes to protect the sample from the deformation due to the hydrogen gas pressure, and was mounted at the joint between a hydrogen gas reservoir and an ultra-high vacuum system . The temperature of the sample

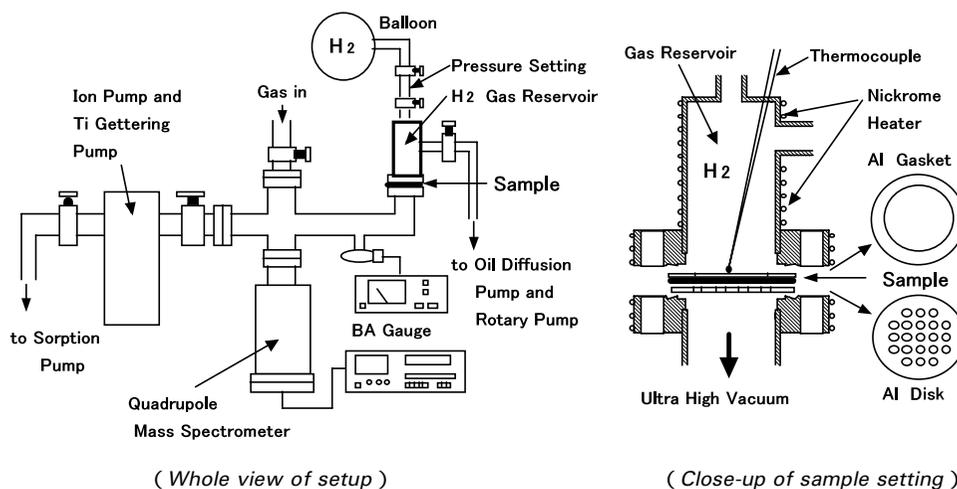


Figure 1 Experimental setup for hydrogen permeation.

was controlled by a nichrome heater wound around the outside walls of the gas reservoir and the vacuum flanges . The used hydrogen gas was nominally 99.99999% in purity and was supplied into the gas reservoir through a liquid nitrogen trap to remove the moisture in hydrogen gas . The initial hydrogen pressures in the gas reservoir were between 2.5 kPa (1/40 atm) and 0.1 MPa (1 atm) , which were estimated by the volume ratio of the reservoir versus the supplied hydrogen gas at the room temperature . The permeation run was performed by supplying the hydrogen into the gas reservoir, after the sample was sufficiently annealed and degassed under a high and ultra high vacuum at a permeation temperature . Hydrogen permeated through the sample was detected as a time dependence of H_2^+ ion current by the quadrupole mass spectrometer (ULVAC MSQ-400) . For some of the permeated aluminum samples, thermal desorption spectroscopic (TDS) analyses and surface analyses by the X-ray photoelectron spectrometry (XPS, KRATOS) were tried.

Results and Discussion

The time dependence of the permeation rate of hydrogen (permeation curve) through aluminum samples was varied by repeating the permeation running, in spite of the same permeation temperature and the same sample . Figure 2 shows the permeation curves through the sample of $56\mu\text{m}$ thickness obtained by hydrogen loading during less than 1minute at the temperatures of 628 , 657 and 683 K, respectively, as is shown in the inset .

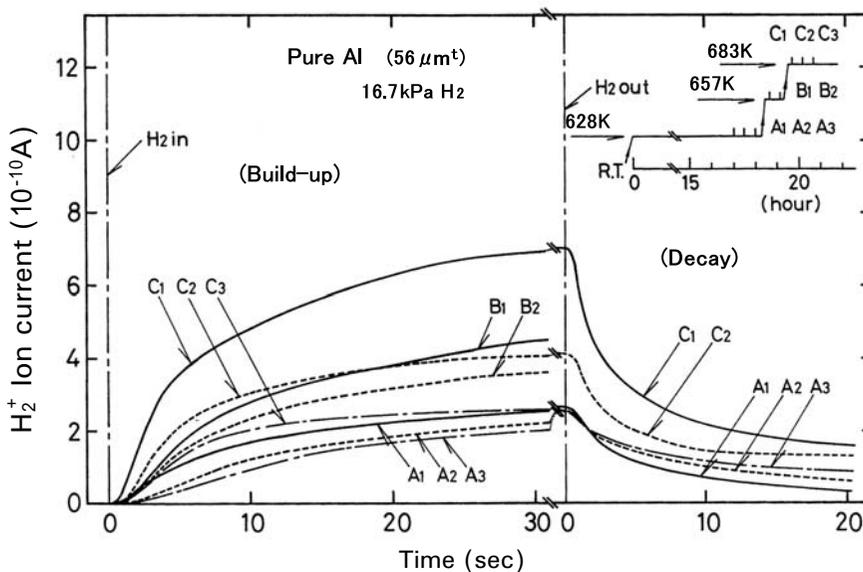


Figure 2 Examples of a series of permeation curves for $56\mu\text{m}$ sample at lower temperature than 700K.

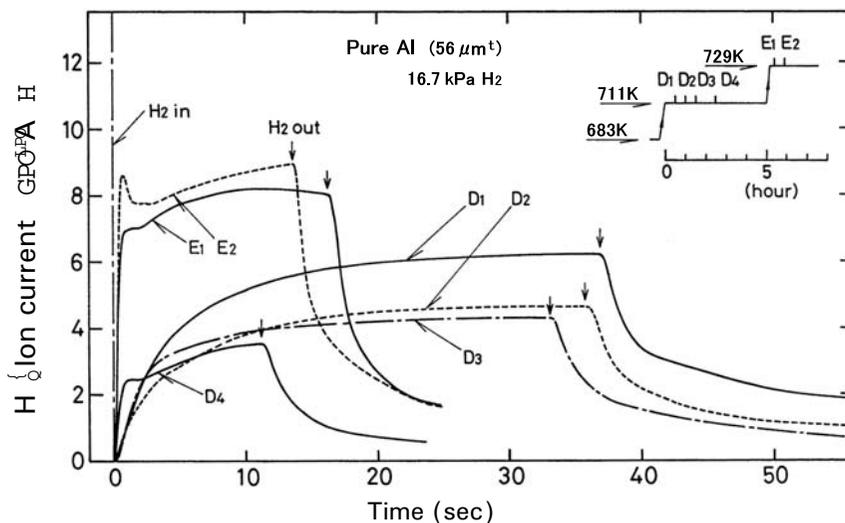


Figure 3 Examples of a series of permeation curves for $56\mu\text{m}$ sample at higher temperature than 700K .

In these temperatures, the permeation rates increased with the temperature of sample, but in the subsequent runs (2nd and 3rd runs) at the same temperature, which were tried at intervals of 30min, they decreased in all cases. However, in the permeation temperature above about 700K , the behavior of the permeation curves differed from ones below that temperature, as is shown in Fig.3. The results showing in both figures were obtained in a series of permeation experiment using same sample. At the temperature of 711K , the permeation rate in the 2nd run decreased in comparison with that of the 1st run, as is same manner in Fig.2. However, it showed a rapid building-up in the 3rd run, and showed a more rapid building-up of the permeation rate at the early period of the permeation in the 4th run, which was tried at interval of 60 minutes after the 3rd run. At the temperature of 729K , the permeation rate of the 2nd run was larger than that of the 1st run, and showed a peaked rate succeeding to the rapid building-up at the early period of the permeation. Such behaviors in the permeation rate of hydrogen above the temperature of 700K was obtained in a sample with different thickness³⁾.

Figure 4 shows the transitions of the building-up of the permeation rate, on and after the 7th run, at the temperature of 753K for the sample with thickness of $54\mu\text{m}$ and $202\mu\text{m}$, respectively. In the 6th run (preceding run), the hydrogen permeation run of 20 minutes was tried for both samples at the same temperature. The sample surfaces, therefore, have been sensitized³⁾. In this figure, all permeation curves presented are for several seconds of the period of building-up, and the numerical values put between curves are time-intervals (minute) of each permeation run, which correspond to the keeping time of the sample under high vacuum ($\sim 10^{-6}\text{Pa}$) after the preceding permeation run. For the sample with $202\mu\text{m}$ thickness, some of permeation runs were tried after keeping the sample under

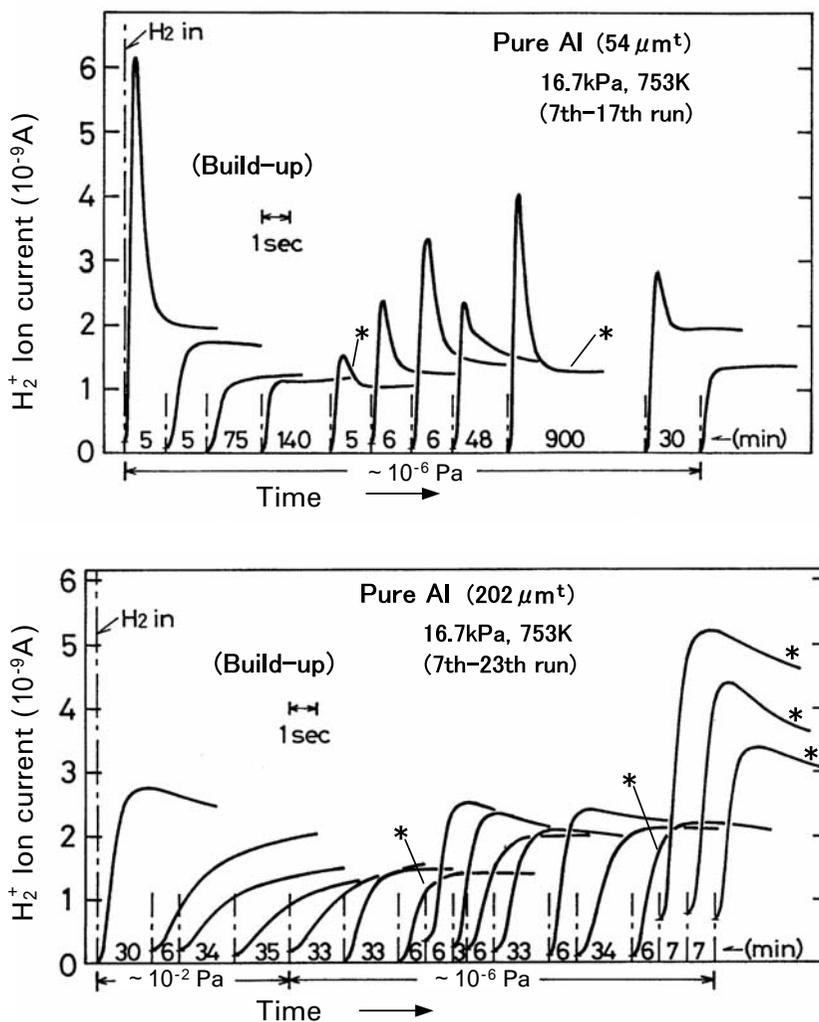


Figure 4 Transitions of the building-ups of permeation rate of hydrogen at 753K. The upper figure is for $54\mu\text{m}$ sample and the lower for $202\mu\text{m}$ one. Long H_2 loading runs are marked by *.

lower vacuum ($\sim 10^{-2}$ Pa), as shown under the transverse axis. Moreover, the permeation runs with long time loading of hydrogen (20 ~ 50 minutes) were tried, which are marked by * in the figure. The peaked building-up curves were obtained in the subsequent permeation run after the preceding run with long loading. The peaked values were increased with the time interval of keeping the sample only under high vacuum ($\sim 10^{-6}$ Pa) after the preceding permeation run, though with some intricacy. It was observed that the sharpness of the peaks depended on the sample thickness and that the decrement beyond the peak for thinner sample was more rapidly than that for the thicker one. These facts

suggest that the variations at the building-up of the permeation curves are mainly caused by a variation of the hydrogen flux penetrated into the sample due to the surface condition of the sample, where the hydrogen is introduced.

The permeation rate of hydrogen varied characteristically by repeating the permeation run, which was bounded in the temperature range of 690 K to 700 K, as is mentioned above. That is, below this temperature range, the permeation rate in the subsequent permeation runs was decreased by the repetition at the same permeation temperature. On the other hand, above the temperature of 700 K, the permeation rate in the subsequent permeation runs was increased by repeating the run and by keeping the sample under high vacuum after the preceding permeation run. And, the variations were conspicuous at the building-up and not at the decay. It is considered that these variations in the permeation rate of hydrogen could be caused by a deformation of sample due to hydrogen pressure supplied and by a variation of the hydrogen flux penetrated into the sample. In order to make sure

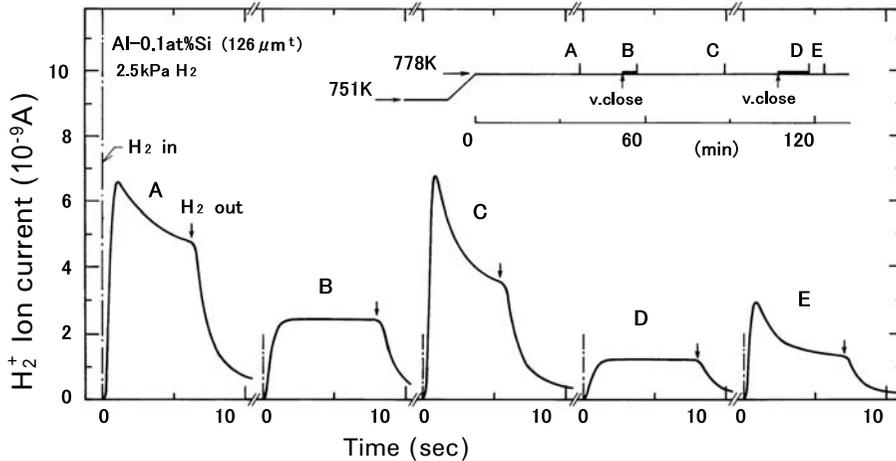


Figure 5 A series of permeation curves for Al-0.1at%Si sample at 778K.

this presumption, a series of permeation run was tried at the temperature of 778K using a sample of an aluminum dilute alloy (Al-0.1at%Si), being hard to deform, under a low hydrogen pressure (2.5 kPa). The results are shown in Fig.5. In this figure, the permeation curves B and D were obtained in the permeation runs in which the evacuating valve of the gas reservoir was closed for 5 and 12 minutes just before the permeation runs, respectively, as is shown in the inset. By the valve-closing, the sample surface which the hydrogen was introduced was exposed to a low vacuum and contaminated. It is obvious that the permeation rate of hydrogen was decreased according to the period of the valve-closing time and tended to recover by keeping the sample under high vacuum at such a high temperature. These results indicate that the main factor for the variation is the surface one.

Transition behaviors of the permeation rates of hydrogen obtained in this experiment are illustrated systematically in Fig.6. The permeation rates decreased by the repetition of

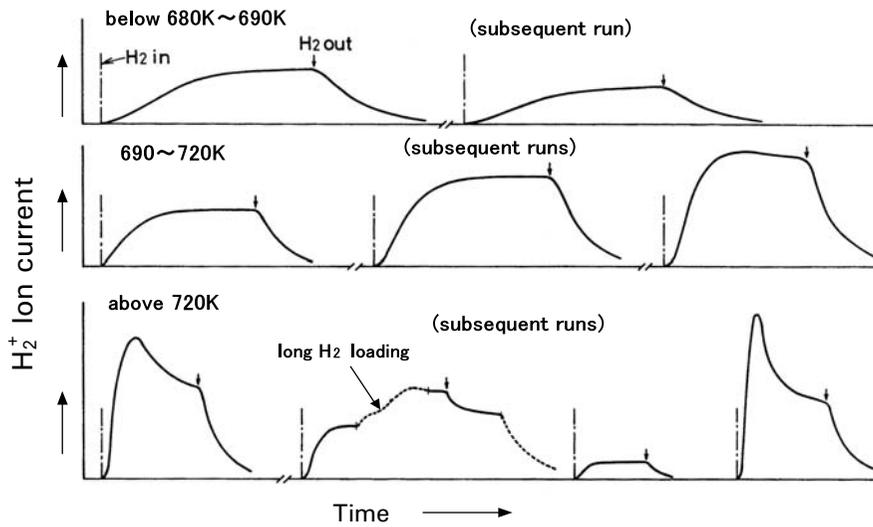


Figure 6 Schematic illustrations of the transitions in the hydrogen permeation curves for each temperature range.

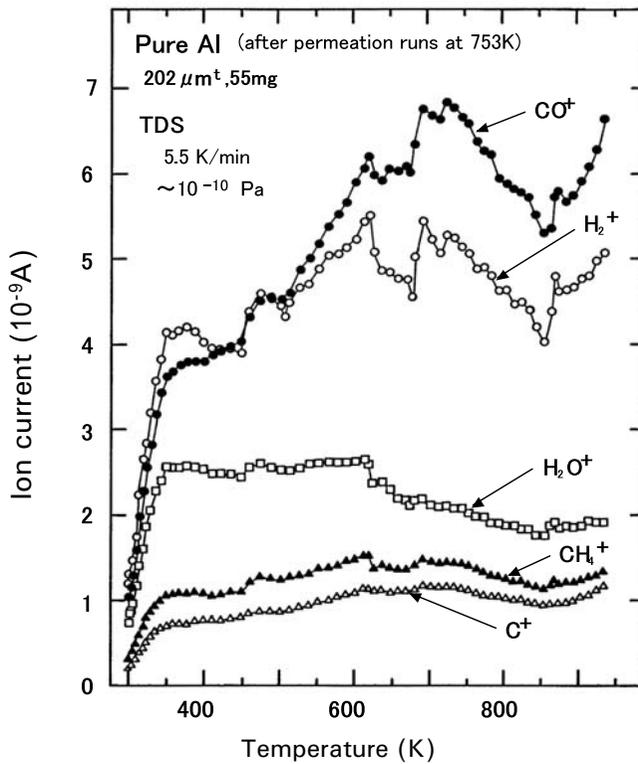


Figure 7 An example of TDS analyses of permeated aluminum samples.

permeation run at a lower temperature than 690K, but increased at a higher temperature than 690 ~ 700K, which needed the repetition of permeation run and the keeping under a high vacuum . Moreover, at a temperature than 720K, the permeation rates behaved as ones with a peak, and the sample surface was more sensitized by long loading of hydrogen resulting in the reduction of surface oxide³⁾ and by the keeping the sample under a high vacuum . To obtain the sensitized surface of the sample in the subsequent runs, a certain extent of the time of keeping under high vacuum was required, as shown in the lowest part of this figure . These facts suggest that the formation of sensitized surface of the sample includes the desorption process of gaseous materials .

Thermal desorption spectroscopy (TDS) for the permeated samples were measured after the permeation experiment to examine the desorbed gases from the sample . Figure 7 shows an example of the TDS results . From this figure, a large desorbed peak of CO was observed at the temperature range of 680K to 760K . This temperature range was coincident with that of the transition in permeation curves of hydrogen . That is, it may be guessed that the temporal poisoning is caused by CO^{7,8)}.

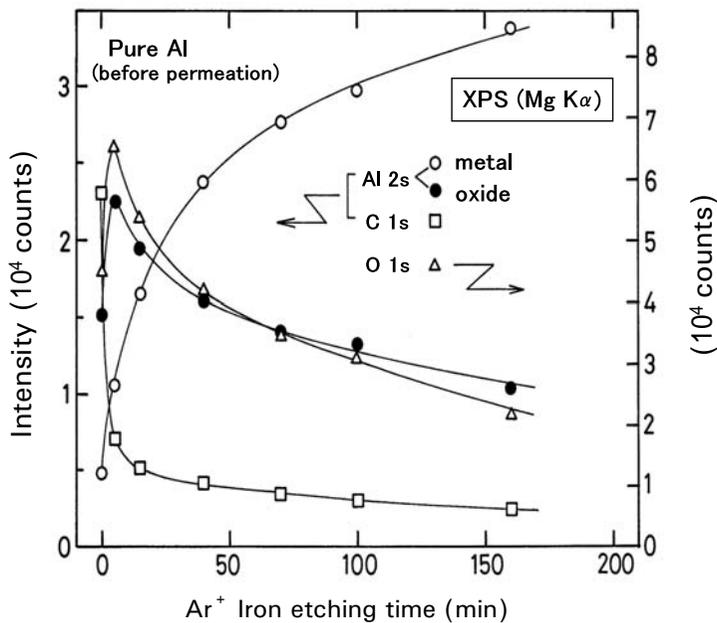


Figure 8 Depth profiles of aluminum, oxygen and carbon analyzed by XPS during argon ion etching.

Figure 8 shows the depth profiles of aluminum, oxygen and carbon on the surface layer of the used sample disk, which were analyzed by an X-ray photoelectron spectrometry (XPS) . Here, the etching was performed by using argon ion current of 4.3 ~ 5.5 μ A under 2.5kV . It is obvious that the surface of sample was covered by an aluminum oxide and that the top surface was contaminated by carbon . Such a carbon could act as one of originators

of poisoner during permeation runs . It is considered that, in addition to this carbon, another carbon was originated from the surroundings, the stainless-steel vessel using as a gas reservoir and the oil diffusion pump, during the experiment .

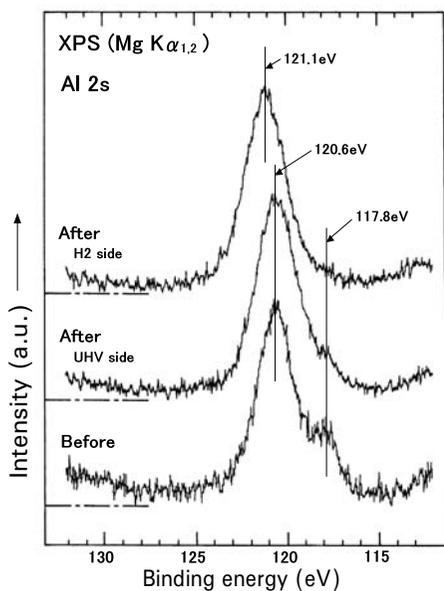


Figure 9 Comparison of the Al2s electron peaks by XPS.

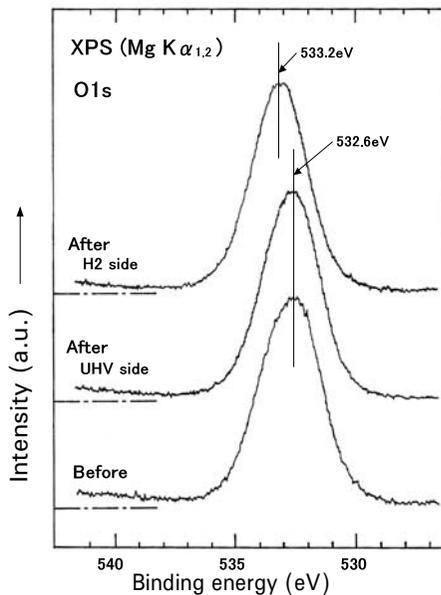


Figure 10 Comparison of the O1s electron peaks by XPS.

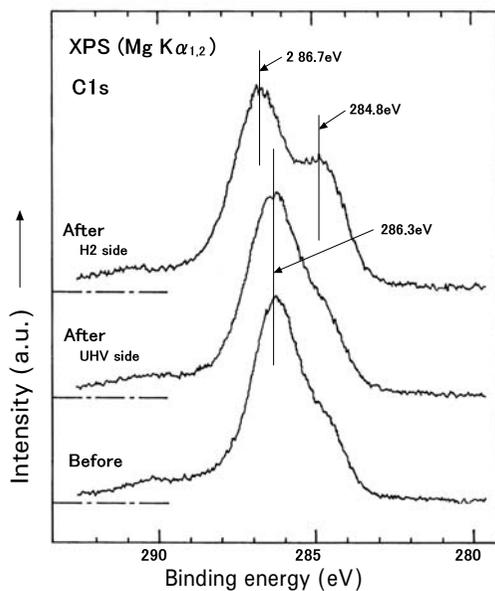


Figure 11 Comparison of the C1s electron peaks by XPS.

Surface analyses of samples, permeated and no-permeating, were performed for aluminum, oxygen and carbon by XPS. The results are shown in Fig 9, Fig 10 and Fig 11, respectively. In these figures, [Before] corresponds to a no-permeating sample, and [H₂ side] to the surface where the hydrogen was introduced and [UHV side] to other surface of the permeated sample, respectively. The chemical states of these elements at the UHV side surface of the permeated sample were almost unchanged in contrast to the surface of no-permeating sample. In Al-2s electron, the peaks of binding energy about 117.8eV and 120.6eV were originated from metallic and oxidized aluminum, respectively. The peak shift in O-1s electron, similar to Al-2s, was observed only on H₂ side surface. The binding energy was 533.2eV and was in good agreement with that of Al(OH)₃, which is 533.3eV. In C-1s electron, such a change that two peaks, 286.7eV and 284.8eV, appeared was also observed on H₂ side surface. The higher energy was coincident with that originated from carbonyl group (>C=O) and the lower one with that from polyethylene ((CH₂)_n), which is 284.6eV. Here, less peaks of CO, 290.2eV, and CO₂, 291.7eV, were detected. The peak about 286.3eV of UHV side and no-permeating sample was agreement with the binding energy originated from carboxyl group (-COOH), which is 286.2eV. The presence of carboxyl group may be caused by cleaning of the sample surfaces with acetone and ethanol.

These facts suggest that the formation of polyethylene and the carbonylation on the aluminum sample surface with carbon were taken place on loading the hydrogen. The quick decrement of the hydrogen permeability was brought about by these reaction processes that could produce a barrier of the permeation of hydrogen or surface trapping sites of hydrogen. This may be the true character of the temporal poisoning in the hydrogen permeation through an aluminum contaminated by carbon. The poisoned surface has been cleaned by keeping the sample at a higher temperature than 700K under a high vacuum during a certain extent of time, when the poisoner was decomposed as to result in the desorption of CO gas from the sample surface. It is probable that, on the oxidized aluminum surface contaminated by carbon, the hydrogen itself may act a poisoner for its permeation. It is considered that the decrease of permeation rate of hydrogen in curves B and D shown in Fig.5 was caused by poisoning due to residual hydrogen of preceding runs, probably originating from the stainless-steel vessel using as a gas reservoir.

Conclusions

The permeation rate of hydrogen through an aluminum sample was varied characteristically at a temperature bounded by the temperature range of 690K to 700K. Below this range, the permeation rate decreased by the repetition of permeation runs at the same temperature. On the other hand, above this range, it increased by repeating the permeation run and by, subsequently, keeping the sample surface under a high vacuum. This transi-

tion of permeation rate of hydrogen was caused by the variation of sample surface introducing the hydrogen .

In the aluminum sample with surface sensitized by the reduction, which brought about the larger permeation rate of hydrogen in the subsequent permeation run, the permeation rate of hydrogen was remarkably decreased by the temporary poisoning . The poisoning was originated by the reaction of the hydrogen with carbon and its compounds contaminating the top surface of aluminum sample . The poisoned surface was, however, cleaned by keeping the surface under a high vacuum at a higher temperature than 700K after the permeation run . In this process, carbon mono-oxide (CO) was desorbed from the surface, as a result of the thermal decomposition of the carbon compounds on the surface .

References

- 1 . G. A. Young Jr. and J. R. Scully, *Acta mater.* , 46(1998)6337-6349.
- 2 . J. R. Scully, G. A. Young Jr. and S. W. Smith, *Mater. Sci. Forum* 331-337(2000) , 1583-1600.
- 3 . Y. Furuya, A. Takasaki, M. Koga and T. Kino, *Mater. Sci. Forum* 331-337(2000) , 1665-1670.
- 4 . T. Kino, N. Kamigaki, H. Yamasaki, J. Kawai, Y. Deguchi and I. Nakamichi, *Trans. Japan Inst. Met.* , 17(1976)645-650.
- 5 . E. Hashimoto and T. Kino, *J. Phys. F* , 13(1983)1157-1165.
- 6 . Y. Furuya, E. Hashimoto and T. Kino, *Japan. J. Appl. Phys.* , 23(1984) 1190-1196.
- 7 . R. E. Cuthrell, *J. Appl. Phys.* , 49(1978)11.
- 8 . R. A. Outlaw, D. T. Peterson and F. A. Schmidt, *Scripta Metall.* , 16(1982)287-292.