Improvement of Hydrogen Absorption Characteristics of Pd Using Irradiation of Heavy Ions

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The introduction of vacancies in palladium (Pd) was found to be effective for an increase in the initial hydrogen absorption reaction rate in a previous study. And it also has been reported that the initial hydrogen absorption reaction rate depends strongly on the surface conditions of metals. For the surface modification of materials, ion irradiation is known to be a quite useful method. Especially, heavy ions with keV ranges can create severe damage and high densities of vacancy near the surface of materials. As is further known, the formation of hydride phases can be facilitated by the presence of vacancy since vacancy acts as hydrogen trapping site to form hydrides. Therefore, the hydrogen absorption characteristics of Pd could be heavy ions with an energy range of keV such as chromium (Cr) ions. The Pd sample was irradiated with these ions at room temperature at TIARA (Takasaki Ion Accelerators for Advanced Radiation Application) of JAEA (Japan Atomic Energy Agency). The initial hydrogen absorption reaction rate of Pd was investigated before/after ion irradiations using an electrochemical method at room temperature. As a result, the initial hydrogen absorption reaction rate increase due to ion irradiation and the value became 3 ~ 10 times higher than un-irradiated Pd sample by ion irradiations. In order to obtain the information on electric charge of the hydriding process, the work function (contact potential) was also measured at several spots on the surface of Pd samples before/after ion irradiations by use of Kelvin probe. In this paper, the correlation among ion irradiation conditions, work function and initial hydrogen absorption reaction rate of Pd are reported.

Key words: Palladium, Ion irradiation, Defects, Initial hydrogen absorption reaction rate, Work function

1. INTRODUCTION

Recently, various kinds of environmental concerns such as global warming and air pollution are becoming more serious. And most of the causes for concern are originated with the problems in use of fossil fuel in energy system. The study about the hydrogen energy is performed flourishingly now. For instance, many scientists and the industrial world tried to develop new technologies to achieve low fuel consuming cars and vehicles. As for hydrogen-metal systems, the effect of surface modification on the hydrogen absorbing behavior is also a very important study topic from not only industrial but also fundamental points of view. In terms of the academic point of view, most research has been focusing interest in Pd-H system in ultrafine structured Pd [1 - 5] because of a typical face centered cubic (f. c. c.) metal and which can absorb a large amount of hydrogen [6]. These studies of surface phenomena occur in the process of Pd-H system formation during H₂ interaction with Pd samples. In the process of determination of the electron work function ϕ , one of the most important surface properties of metals provides information concerning the electric

charge of the hydriding process. The change of electron work function was caused by absorption or surface reaction. By definition, surface potential = $-\phi$. The surface potential is an additive property of the absorption/desorption system, and it depends on the change of the electric charge density distribution induced by absorption or chemical reaction on the surface [7]. Hence surface potential is a function of chemical composition and structure of the surface. In previous studies, the induction of vacancy in Pd was found to be effective for an increase in the initial hydrogen absorption reaction rate [8, 9]. Regarding the hydrogen storage in metals, it was reported that the absorption concentration of hydrogen atoms and the hydrogen absorption reaction rate depend strongly on the surface state of metals [8]. As for the surface modification of materials, ion implantation with high and low energy is known to be a quite useful method. These facts give the possibility that the hydrogen absorptivity in Pd can be improved by surface modification using an ion irradiation. In this study, we perform Cr⁺ irradiation into Pd, and the initial hydrogen absorption reaction rate of ion irradiated Pd was

evaluated. Based on the obtained results, we discuss the correlation among ion irradiation, work function and initial hydrogen absorption reaction rate in Pd.

2. EXPERIMENTAL

The samples used in this study were Pd sheets (99.99 % purity, $7.5 \times 7.5 \times 0.1 \text{ mm}^3$). Prior to ion irradiation, all Pd samples were annealed during a flowing pure N_2 gas (99.9998 % purity) stream in the nitrogen atmosphere for an hour at 1173 K.

Cr^+ irradiation onto the Pd samples was made at room temperature using the 400 kV ion implanter at TIARA, JAEA. The acceleration energy of Cr^+ and the maximum fluence were 350 keV and $1 \times 10^{17} \text{ cm}^{-2}$ respectively. Temperature at the Pd surface increased up to about 360 K at a beam current of $\sim 10 \text{ A}$ and almost no annealing effect took place during the ion irradiation [8 - 10]. In this study, 350 keV Cr^+ irradiation was calculated with 97 nm in the Pd sample according to the LET (Linear Energy Transfer) using a TRIM (Transport of Ions in Matter) code [11]. Therefore, it was Cr^+ irradiated between up to 97 nm in the depth direction.

The initial hydrogen absorption reaction rate of the irradiated Pd was investigated by using an electrochemical method. Pd surface was prepared by electrolysis using as a cathode, the opposite electrode of Pt sheet as an anode which size of $30 \times 30 \times 0.3 \text{ mm}^3$, 99.98 % purity. An Hg/HgO electrode was used as the reference electrode in an open cell. The initial hydrogen absorption reaction rate of a Pd sample was measured in 6 M-KOH using an open cell as the change of current density mA (g-alloy)^{-1} at a constant voltage -0.93 V and at room temperature. From the measured current in charging at a constant potential -0.93 V , the hydrogen atoms concentration absorbed by the negative electrode was calculated. In all reactions measured, no gas bubbles were observed during the hydriding. Details of the electrochemical measurements have been reported elsewhere [12].

The contact potential was measured at several spots on the Pd sample surface [13] by use of a Kelvin probe method. Kelvin probe consisted of a vibrating tungsten tip of 1 mm in diameter. The deviation ϕ of the work function ϕ from the standard value of 5.14 eV of standard sample: Au was measured for Pd sample with various surface modifications [7].

3. RESULTS AND DISCUSSIONS

Figure 1 shows the hydrogen absorption reaction rate, 5 cycles, curves of Pd samples before and after 350 keV Cr^+ irradiation with fluence from 1×10^{14} to $1 \times 10^{17} \text{ cm}^{-2}$. The ordinate indicates the ratio of absorbed hydrogen atoms to Pd atoms $[\text{H}/\text{Pd}]$. With increasing Cr^+ fluences up to $1 \times 10^{17} \text{ cm}^{-2}$, the initial hydrogen absorption reaction rate was increased. The irradiated Pd samples at a dose of $1 \times 10^{17} \text{ cm}^{-2}$ exhibited a much higher reaction rate than the others. Therefore, the initial hydrogen absorption reaction rate of the Pd became 5 times higher than that of un-irradiated Pd.

Figure 2 shows the hydrogen absorption reaction rate curves of Pd samples before and after 350 keV Cr^+ irradiation with fluence of $1 \times 10^{17} \text{ cm}^{-2}$ and hydriding cycles from 1 to 10 cycles. These meanings at the

Fig. 1. Hydrogen absorption reaction rate, 5 cycles, curves of irradiated Pd by 350 keV Cr^+ at fluence from 1×10^{14} to $1 \times 10^{17} \text{ cm}^{-2}$.

Fig. 2. Hydrogen absorption reaction rate, from 1 to 10 cycles, curves of irradiated Pd by 350 keV Cr^+ with fluence of $1 \times 10^{17} \text{ cm}^{-2}$.

cycle assume everything from the hydrogen absorption to the following hydrogen desorption to be one cycle. Increasing a hydriding curves, the initial hydrogen absorption reaction rate was increased. The 10 cycle hydriding Pd was 4 times higher than initial hydrogen absorption reaction rate of the 1 cycle hydriding one.

Since vacancy type defects are introduced by ion irradiation and such vacancies might act as hydrogen trapping site, the enhancement of the hydrogen absorption reaction rate obtained in this study can be interpreted in terms of an increase of hydrogen trapping sites near the surface region due to irradiation of Cr^+ into Pd. In other words, relation between hydrogen absorption Pd and ion beam interaction were almost

caused by absorbed in the phase.

Figure 3 shows the relation between the work function of Pd (ϕ) and the initial hydrogen absorption reaction rate (hydriding rate) of Pd before and after Cr^+ irradiation, the value of ϕ is depicted as a shift from un-irradiated Pd sample ($\phi_0 = \pm 0.00$ eV). The fluence of $1 \times 10^{17} \text{ cm}^{-2}$ a much higher reaction rate and a reduced value of the work function with $\phi = -0.11$ eV compared with an un-irradiated Pd sample as a standard sample. The shift of the ϕ is estimated from,

$$\phi = V_E (V - 1)^{-1}$$

where V_E is the peak-to-peak output voltage and V represents the voltage difference between the probe tip and surface of Pd sample. All ion irradiated Pd samples shifted to the negative side. As for the initial hydrogen absorption reaction rate, the work function value increased with increasing fluence of Cr ions. The structure of the Pd surface became revitalization and the defects were formed to the surface phase by Cr^+ irradiation. The work function value shifted to a negative side, it compared with the un-irradiated Pd. Therefore, surface potential of Pd became low and easy to exchange the electron in the electrochemical method. As a result, the initial hydrogen absorption reaction rate of Pd, case with 350 keV, $1 \times 10^{17} \text{ cm}^{-2}$, was 3 times higher absorption reaction rate than un-irradiated one.

These results imply that the work function value decreases and the initial hydrogen absorption reaction rate increases with increasing vacancy concentration in Pd surface. The ion beam modification of the Pd surface using Cr^+ irradiations was found to enhance the initial electrochemical hydrogen absorption in Pd.

Fig. 3. Relationship between the work function of Pd and the initial hydrogen absorption reaction rate (hydriding rate) before and after 350 keV Cr^+ irradiation with fluence from 1×10^{16} to $1 \times 10^{17} \text{ cm}^{-2}$.

4. CONCLUSIONS

It is successful that the hydrogen absorptivity in Pd was improved by surface modifications due to ion irradiation. The measurement of the change in the work function of electrons of the Pd surface and of the initial hydrogen absorption reaction rate measurement of the ion irradiated/un-irradiated Pd suggested the following relation of surface process of initial hydrogen

absorption that the distribution of Cr ions irradiated Pd increasing the ion fluence, the work function value is decreases in the Pd surface. The Cr^+ irradiation causes disorder of the Pd surface structure. As a result, the ion irradiated Pd surface can suppose that the surface activity progress facilitates an approach of the hydrogen atoms.

The Cr^+ irradiation with energies of hundred keV is useful for the improvement of the initial hydrogen absorption reaction rate of Pd.

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