

Effects of surface modification by ion irradiation on the electrochemical hydrogen absorption rate of Pd

H. Abe^{a,*}, R. Morimoto^b, F. Satoh^b, Y. Azuma^b, H. Uchida^b

^a Department of Material Development, Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

^b Department of Applied Physics, School of Engineering, Tokai University, 1117 Kita-Kaname, Hiratsuka, Kanagawa 259-1292, Japan

Received 4 June 2004; received in revised form 2 December 2004; accepted 9 December 2004
Available online 28 June 2005

Abstract

The effect of ion irradiation on the rate of electrochemical hydrogen absorption rate of palladium (Pd) was investigated. In this study, ion irradiation onto the Pd surface was made with H⁺, He⁺, Ar⁺ and N⁺ in the acceleration energy range from 30 to 350 keV, and for ion doses up to $1 \times 10^{17} \text{ cm}^{-2}$. As the ion dose increased, the initial rate of hydrogen absorption of Pd was increased. The ion irradiation treatment of the surface of a metal induces high concentrations of vacancies. The increased rate of hydrogen absorption may be caused by the introduction of a high concentration of vacancies which traps hydrogen atoms. The ion irradiation was found as an effective way to enhance the rate of the initial activation of the electrochemical hydrogen absorption of Pd.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Palladium; Vacancy; Hydrogen trapping; Ion irradiation; Hydrogen absorbing materials

1. Introduction

Surface modifications are crucial to improve the reactivity of hydrogen with metals because the dissociation of the H₂ molecules in the gas phase or the dissociation of the H₂O molecules in an electrochemical process is the first step of the overall reaction of hydrogen absorption by metals [1]. The dissociation of the H₂ or H₂O molecule is markedly influenced by surface conditions of a metal. So far, we have systematically investigated the effect of surface oxide layers on the kinetics of hydrogen absorption by hydrogen absorbing metals [1,2] and reported several methods of surface modification such as metallic coating [3], fluorination treatment [4,5], and alkaline treatment [6].

In this study, the surface modification of Pd have been made by the ion irradiation using ion beams [7] of proton

(H⁺), helium (He⁺), argon (Ar⁺) and nitrogen (N⁺), and the effect of this modification on the rate of electrochemical hydrogen absorption of Pd was investigated. Ion irradiation onto the surface of a metal effectively induces defects such as vacancies, dislocations, micro cracks or impurities in the surface region of a metal. Defects introduced in Pd by ion irradiations were investigated using positron annihilation spectroscopy [8]. As is well known, vacancies trap hydrogen atoms. The hydrogen trapping effect, for example, induces a marked increase in the hydrogen solubility and the heat of hydrogen solution in Pd [9] or LaNi₅ [10,11]. Hydrogen trapping sites act as the center of segregation of hydrides even in hydrogen solid solution region [12]. Oxide/metal interfaces also tend to act as hydrogen trapping sites and form hydrides in the course of hydrogen absorption [13,14]. Based on these facts, we intentionally induced vacancies with high concentrations by ion irradiation in the surface region of Pd, and investigated the effect of the vacancy formation on the initial rate of hydrogen absorption of Pd in electrochemical process.

* Corresponding author. Tel.: +81 27 346 9323; fax: +81 27 346 9687.
E-mail address: habe@taka.jaeri.go.jp (H. Abe).

2. Experimental

Pd sheets (99.99% purity) with a size of 7.5 mm × 7.5 mm × 0.1 mm were used. Prior to ion irradiation, all samples were annealed for an hour at 1173 K in a flowing pure N₂ gas (99.9998% purity) stream. Ion irradiation was made onto the surface of Pd samples using ion beams of H⁺, He⁺, Ar⁺ and N⁺ in the ranges of an irradiation energy from 30 to 350 keV, and of an ion dose from 1 × 10¹⁴ to 1 × 10¹⁷ cm⁻² at room temperature at the Takasaki Ion Acceleration for Advanced Radiation Application (TIARA), Japan Atomic Energy Research Institute (JAERI). The temperature at the samples surface increased up to 353 K at a beam current of 5 μA, and almost no annealing effect took place during the irradiations.

The distribution of induced vacancy can be simulated [8,15] using a transport of ions in matter (TRIM) code [15] based on L.S.S. theory [16]. Figs. 1–4 show the results of the distributions of vacancy concentration in the Pd surface using a TRIM simulation at an ion dose of 1 × 10¹⁶ cm⁻², and at an irradiation energy from 30 to 350 keV-H⁺, -He⁺, -Ar⁺ and -N⁺, respectively. As the irradiation energy of each ion is increased, vacancies are introduced more deeply. As the mass of an ion is increased from H⁺, He⁺, Ar⁺ to N⁺, the vacancy concentration increases at the same ion beam energy, however, the area of distribution in depth becomes less. The vacancy concentrations are increased with increasing ion dose.

For the electrochemical measurement of hydrogen absorption rate of Pd (cathode), a Pt sheet with a size of 30 mm × 30 mm × 0.3 mm and a purity of 99.98 wt.% was used as an anode. An Hg/HgO electrode was used as the reference electrode in an open cell [17]. The rate of hydrogen absorption of a sample was measured in 6 M-KOH using an

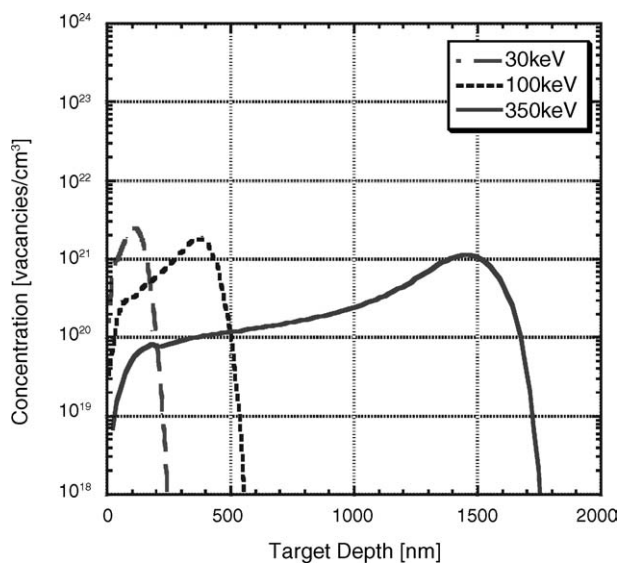


Fig. 1. Distribution of vacancy concentration induced by H⁺ ions with a dose of 10¹⁶ cm⁻² at irradiation beam energies of 30, 100 and 350 keV.

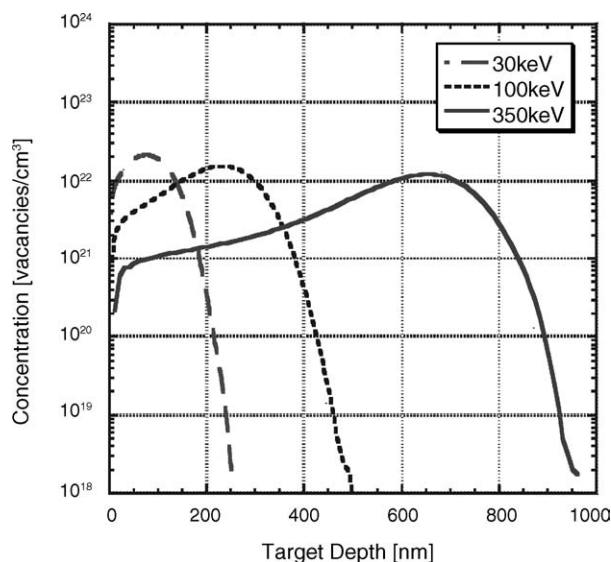


Fig. 2. Distribution of vacancy concentration induced by He⁺ ions with a dose of 1 × 10¹⁶ cm⁻² at irradiation beam energies of 30, 100 and 350 keV.

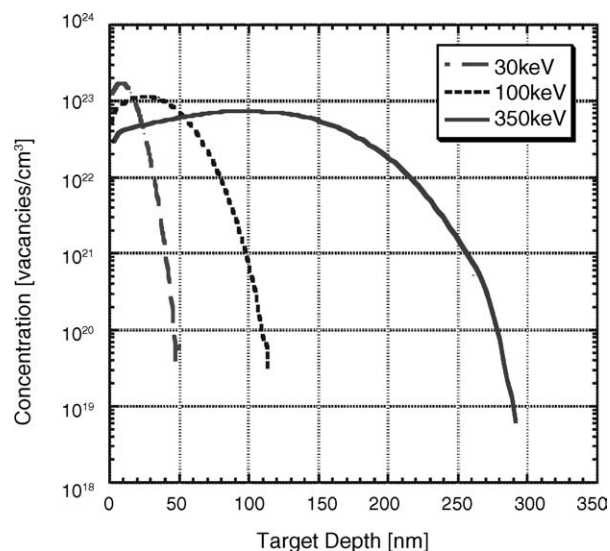


Fig. 3. Distribution of vacancy concentration induced by Ar⁺ ions with a dose of 1 × 10¹⁶ cm⁻² at irradiation beam energies of 30, 100 and 350 keV.

open cell as the change of current density mA(g-alloy)⁻¹ at a constant voltage -0.93 V and at 298 K. In all reactions measured, no gas bubbles were observed during hydrogen absorption. Details of the electrochemical hydrogen absorption rate is reported elsewhere [17].

3. Results and discussions

3.1. Pd-H system

Figs. 5 and 6 show hydrogen absorption curves of Pd samples after H⁺ and He⁺ irradiation at different ion beam energies, respectively. The initial rate of both irradiated samples

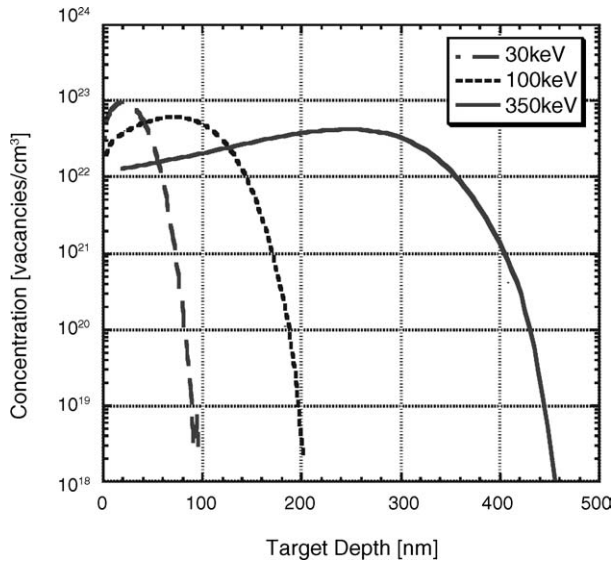


Fig. 4. Distribution of vacancy concentration induced by N^+ ions with a dose of $1 \times 10^{16} \text{ cm}^{-2}$ at irradiation beam energies of 30, 100 and 350 keV.

was increased compared with that of un-irradiated samples. At the initial stage (within 120 min from the start of each reaction), the rate of irradiated samples increased as the ion beam energy increased from 30 to 350 keV. Compared with the result of H^+ , the samples irradiated by He^+ exhibited higher initial rates. As the data of the distribution of vacancy concentration shown in Figs. 1 and 2, He^+ ions induce much higher concentrations of vacancy in the surface than H^+ ions. The higher vacancy concentrations leads to increased numbers of hydrogen trapping sites, resulting in an acceleration of the rate of hydride nucleation and growth in the surface region.

Fig. 7 shows the effect of the dose of Ar^+ on the initial hydrogen absorption rate of Pd irradiated at an energy of

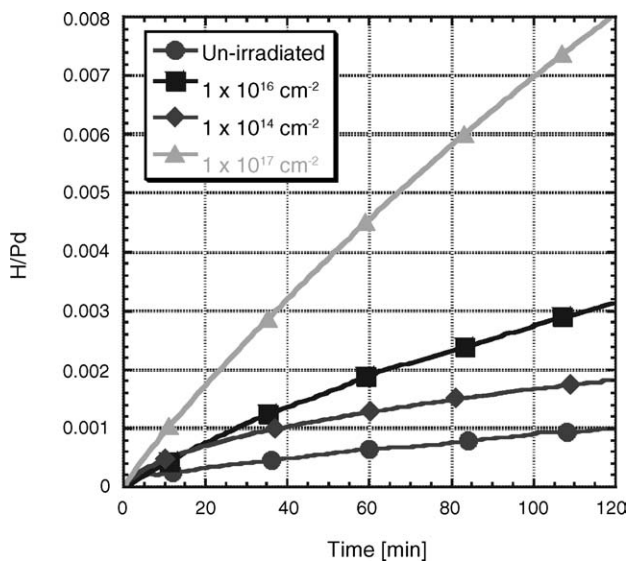


Fig. 5. Hydrogen absorption curves of Pd samples irradiated by H^+ ions with doses of 1×10^{14} , 1×10^{16} and $1 \times 10^{17} \text{ cm}^{-2}$ at an irradiation beam energy of 350 keV.

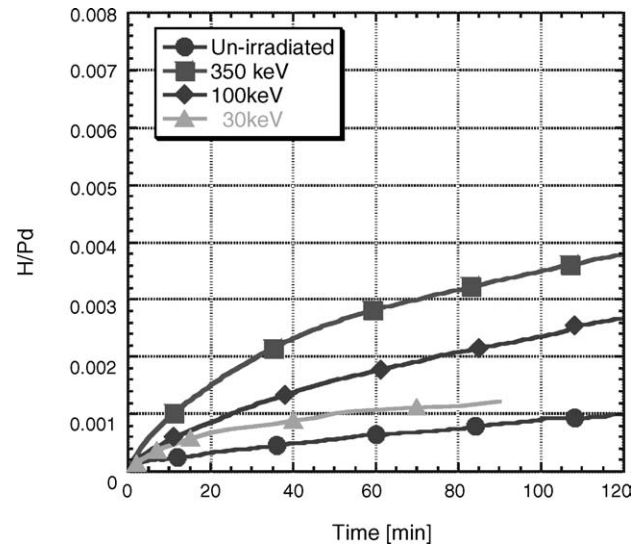


Fig. 6. Hydrogen absorption curves of Pd samples irradiated by He^+ ions with a dose of $1 \times 10^{16} \text{ cm}^{-2}$ at irradiation beam energies of 30, 100 and 350 keV.

350 keV. As the Ar^+ dose was increased from 1×10^{14} to $1 \times 10^{17} \text{ cm}^{-2}$, the rate increased with increasing ion dose. A sample irradiated with a dose of $1 \times 10^{17} \text{ cm}^{-2}$ exhibited a much higher rate than the others, indicating that an increase in the ion dose, namely, an increase in vacancy concentration is effective for enhancing the initial hydrogen absorption rate of Pd.

Fig. 8 shows the results of N^+ irradiation effects on the hydrogen absorption rate of Pd at an irradiation energy of 350 keV. A sample with a higher ion dose exhibited a higher rate, which was measured also in the Ar^+ irradiation. At the reaction time of 120 min, the concentration of hydrogen absorbed by Pd was measured as $[H]/[Pd] > 0.008$. Of the ions

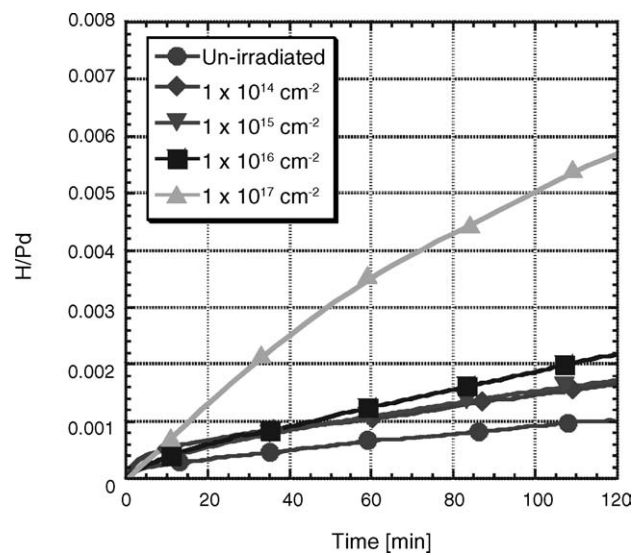


Fig. 7. Hydrogen absorption curves of Pd samples implanted by Ar^+ ions with doses of 1×10^{14} , 1×10^{15} , 1×10^{16} and $1 \times 10^{17} \text{ cm}^{-2}$ at an irradiation beam energy of 350 keV.

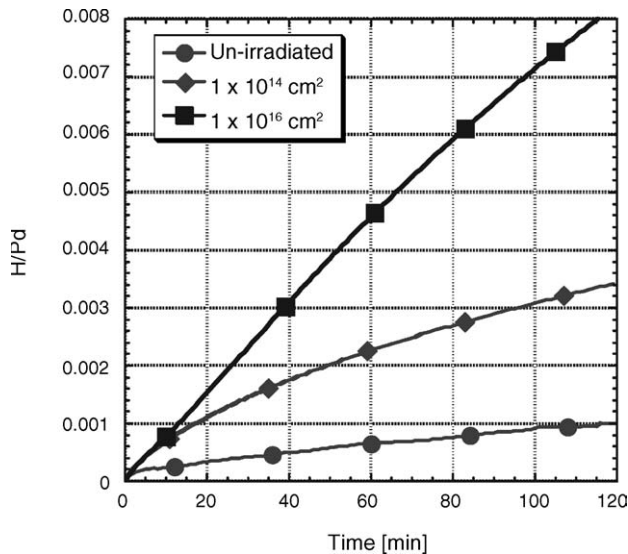


Fig. 8. Hydrogen absorption curves of Pd samples implanted by N^+ ions with doses of 1×10^{14} and $1 \times 10^{16} \text{ cm}^{-2}$ at an irradiation beam energy of 350 keV.

used in this study, the N^+ irradiation was found most effective in the increase of the initial hydrogen absorption rate.

3.2. Change in current density at the initial stage

Fig. 9 shows the change in the current density during the hydrogen absorption in Pd samples irradiated by 350 keV- Ar^+ beams with different doses. As the ion dose increased from 1×10^{14} to $1 \times 10^{17} \text{ cm}^{-2}$, the current density, namely, the initial hydrogen absorption rate was increased. These results correspond to the hydrogen absorption curves in Fig. 6. For a sample with an irradiation of a dose of $1 \times 10^{17} \text{ cm}^{-2}$, with the highest vacancy concentration (see Fig. 3) among

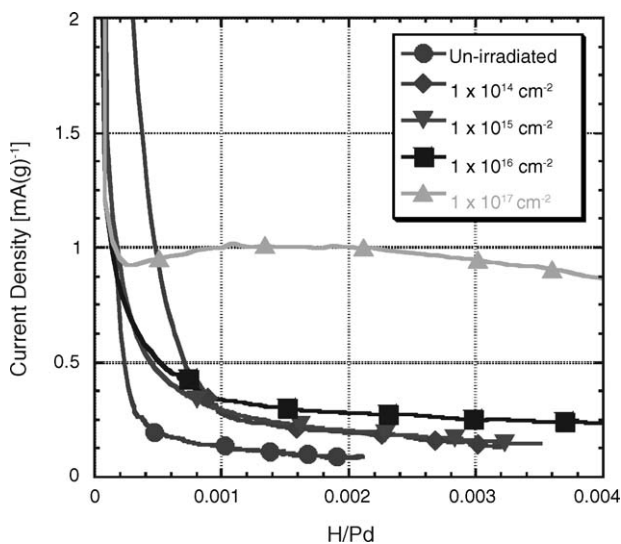


Fig. 9. Change in the current density during the hydrogen absorption of Pd samples irradiated by Ar^+ ions with doses of 1×10^{14} , 1×10^{15} , 1×10^{16} and $1 \times 10^{17} \text{ cm}^{-2}$ at an irradiation beam energy of 350 keV.

the Pd samples used in this study, the highest current density, namely, the highest initial hydrogen absorption rate was measured. The current density measured for this sample with an ion dose of $1 \times 10^{17} \text{ cm}^{-2}$ was extremely high compared to the other samples. In the surface of this sample, the formation of a high concentration of vacancies may trap hydrogen atoms, and may become nucleation sites of hydride formation in the Pd surface. As a hydride phase nucleates and grows on the surface, the lattice expansion and the formation of additional defects take place, and the flux of hydrogen atoms diffusing into the metal becomes higher by the increasing gradient of hydrogen concentration over the surface hydride layers/metal interfaces, resulting in increasing the current density and initial rate.

4. Conclusion

The ion irradiation treatment of the surface of Pd using H^+ , He^+ , Ar^+ and N^+ ions can enhance the initial rate of electrochemical hydrogen absorption of Pd. Of the ion irradiations using these ions, N^+ ions were found most effective in the enhancement of the hydrogen absorption rate of Pd. The induction of high concentrations of vacancies in the surface of Pd seems to be responsible for the enhancement of the initial rate, where the induced vacancies seem to act as hydrogen trapping sites, resulting in the acceleration of hydride nucleation and growth in the surface. The increasing ion beam energy, and the increasing ion dose are effective to increase the vacancy density, and to enhance the initial rate. The results obtained suggest that the ion irradiation is useful as a surface modification treatment for the activation of hydrogen absorbing metals. A further study is required to elucidate the role of each ion in the induction of vacancy in the surface region of a metal.

References

- [1] H. Uchida, *Int. J. Hydrogen Energy* 24 (1999) 861–869.
- [2] H. Uchida, Y. Ohtani, M. Ozawa, T. Kawahata, T. Suzuki, *J. Less-Common Met.* 172–174 (1991) 983–996.
- [3] E. Fromm, *Poisoning of Hydrogen Reactions*, in: *Kinetics of Metal-Gas Interactions at Low Temperatures*, Springer Verlag, Berlin, 1998, ISBN 3-540-63975-6, Chapter 6.
- [4] H. Uchida, T. Inoue, T. Tabata, S. Seki, H.H. Uchida, F. Aono, T. Nakazawa, H. Kikuyama, R. Hirayama, *J. Alloys Compd.* 253/254 (1997) 547–549.
- [5] H. Uchida, F. Aono, T. Iwamoto, T. Matsu, M. Ito, T. Nakazawa, T. Tabata, A. Kosuge, *Proceedings of the 13th World Hydrogen Energy Conference*, 2 (2000) 1088–1092.
- [6] H. Uchida, K. Yamashita, M. Goto, *J. Alloys Compd.* 330–332 (2002) 622–626.
- [7] H. Abe, H. Uchida, Y. Azuma, A. Uedono, Z.Q. Chen, H. Itoh, *Nucl. Inst. Meth. B* 206 (2003) 224–227.
- [8] H. Abe, A. Uedono, H. Uchida, A. Komatsu, S. Okada, H. Itoh, *Mater. Sci. Forum* 363–365 (2001) 156–158.
- [9] T.B. Flanagan, *The thermodynamics of hydrogen solution in perfect and defective metals and alloys*, in: V.A. Goltsov (Eds.), *Progress in*

- Hydrogen Treatment of Materials, Donetsk State Technical University, Ukraine, 2001, 966-7418-71-5, p. 37.
- [10] H. Uchida, A. Hisano, K. Terao, N. Sato, A. Nagashima, *J. Less-Common Met.* 172–174 (1991) 1018–1027.
- [11] S. Seta, H. Uchida, *J. Alloys Compd.* 231 (1995) 448–453.
- [12] G.H. Kim, A.G. Lee, K.Y. Lee, C.H. Chun, J.Y. Lee, *Acta Metall. Mater.* 43 6 (1995) 2233.
- [13] Y. Ohtani, S. Hashimoto, H. Uchida, *J. Less-Common Met.* 172–174 (1991) 841–850.
- [14] H. Uchida, S. Seki, S. Seta, *J. Alloys Compd.* 231 (1995) 403–410.
- [15] P. Asoka-Kumar, K.G. Lynn, *Appl. Phys. Lett.* 57 (1990) 1634–1636.
- [16] J. Lindhard, M. Scharff, H. Schiott, *Mat. Fys. Medd. Dan. Vid. Selk.* 33 (1963) 1–42.
- [17] H.H. Uchida, Y. Watanabe, Y. Matsumura, H. Uchida, *J. Alloys Compd.* 231 (1995) 679–683.