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

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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 1×10^{17} 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.

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 H_2 molecules in the gas phase or the dissociation of the H_2O molecules in an electrochemical process is the first step of the overall reaction of hydrogen absorption by metals [1]. The dissociation of the H_2 or H_2O 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 $LaNi_5$ [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.

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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 N_2 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 1×10^{14} to 1×10^{17} 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 1×10^{16} 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

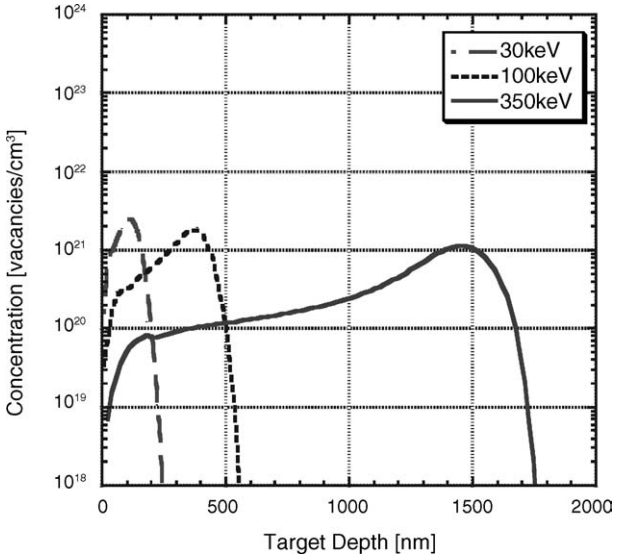

Fig. 1. Distribution of vacancy concentration induced by H^+ ions with a dose of 10^{16} cm^{-2} at irradiation beam energies of 30, 100 and 350 keV.

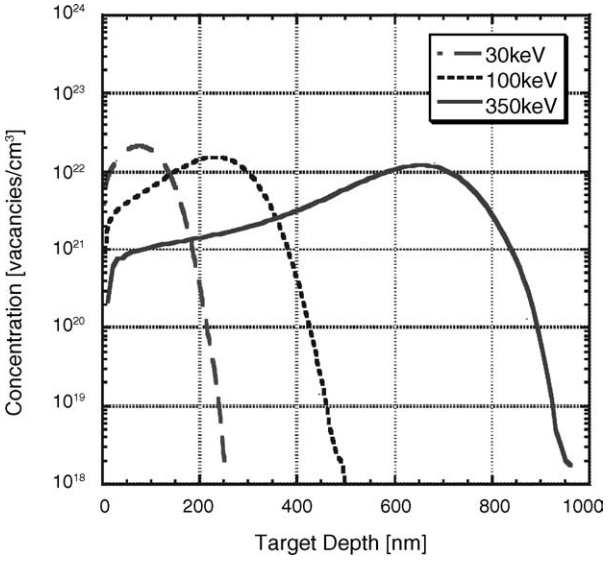

Fig. 2. Distribution of vacancy concentration induced by He^+ ions with a dose of 1×10^{16} cm^{-2} at irradiation beam energies of 30, 100 and 350 keV.

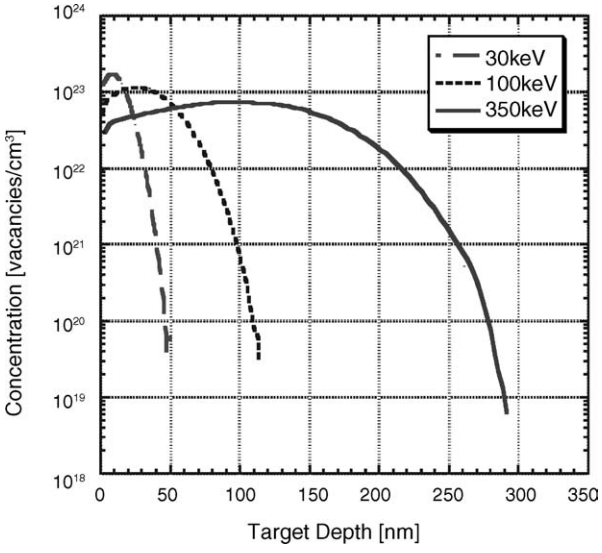

Fig. 3. Distribution of vacancy concentration induced by Ar^+ ions with a dose of 1×10^{16} cm^{-2} at irradiation beam energies of 30, 100 and 350 keV.

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