Hydrogen-Induced Vacancy Generation Phenomenon in Pure Pd

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Lattice defects induced by hydriding in pure Pd have been studied by means of positron lifetime spectroscopy. Component analyses of positron lifetime spectra show that a surprising amount of vacancies together with dislocations are generated by the hydriding at room temperature. Vacuum migration in pure Pd after hydriding is observed around 378 K. Dislocations are much more stable and its migration is observed around 873 K. During the vacancy recovery process, secondary defects, that is, dislocation loops are formed.

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1. Introduction

Our laboratory has shown that excess vacancies are generated by the hydrogen absorption transformation (LaNi54, ZrMn55) and NdNi56). The vacancy formation mechanism is not thoroughly explained by existing vacancy formation mechanisms.

In this work, to confirm the anomalous vacancy generation phenomenon and to investigate this mechanism, hydrogen-induced vacancies in pure Pd have been investigated by positron lifetime spectroscopy, which is the most sensitive method to detect vacancy-type lattice defects.

2. Experimental and Computational Procedure

2.1 Experimental procedure

Pure Pd sheet (99.99%) was cut into specimens having a square surface of $10 \times 10$ mm$^2$ and a thickness of 1.0 mm. The specimen was given a fully annealing treatment at 1173 K for 14.4 ks in an Ar atmosphere to eliminate lattice defects induced by rolling. Acid pickling was performed in order to eliminate the surface oxide.

The specimen was fully hydrogenated at 296 K for 1.7 $\times$ 10$^2$ ks at a hydrogen pressure of 5 MPa, which is sufficiently high pressure to form $\beta$ hydride. Subsequently, $\beta$ hydride was subjected to a hydrogen desorption process under a vacuum of 1 $\times$ 10$^{-6}$ MPa at 296 K.

In order to investigate lattice defects formed by the initial hydriding, isochronal annealing in steps was performed. In the temperature range 323 to 523 K, steps of 0.9 ks/25 K were carried out. In the temperature range 548 to 1073 K, steps of 1.8 ks/50 K were carried out. After each annealing, the positron lifetime was measured at 296 K.

The positron lifetime was measured at 296 K using a positron lifetime spectrometer with a time resolution (FWHM) of 167 ps. A 30 $\mu$Ci positron source of $^{22}$NaCl sealed with a Kapton film (1 mg/cm$^2$) was sandwiched between two identical specimens. Each positron lifetime spectrum consists of more than 10$^6$ counts and several spectra were accumulated for each measuring point in order to ensure the reproducibility of the data. The source correction and the resolution functions were evaluated using the code Resolution.7) Lifetime spectra were analyzed using the Positronfit Extended program.8,9)

2.2 Computational procedure

In order to obtain electron density and potential, a DV-X$\alpha$ cluster method using program code SCAT10,11) is employed. In this first-principles calculation, the molecular-orbital wave function is expressed by a linear combination of atomic orbitals (LCAO). As the basis function, we use numerical atomic orbitals obtained by solving the radial part of the Schrödinger equation for each atom in a given environment. Model clusters composed of about 100 atoms are used in this work.

The three-dimensional potential $V_+(r)$ sensed by a positron is constructed as a sum of the electron static potential $V_C(r)$ due to the nuclei and the electrons, and a correlation potential $V_{corr}(n_-(r))$ describing the electron-positron correlation:

$$ V_+(r) = V_C(r) + V_{corr}(n_-(r)) $$

(1)

where $n_-(r)$ is the electron density. For the density dependence of $V_{corr}(n_-(r))$ we have used the interpolation formulas of Bronski and Nieminen12) based on the results of many-body calculations.13) The Schrödinger equation for the positron is solved by the finite-difference method14) employing the periodic boundary conditions for delocalized positron wave functions in the bulk state. In the case of the localized positron at the vacancy, the boundary conditions are the vanishing of the positron wave functions on the surface of a large polyhedron.

The positron lifetime $\tau$ is calculated as the reciprocal value of the positron annihilation rate $\lambda$ by

$$ \lambda = \frac{\pi r_0^2 c}{\tau} \int n_+(r)n_-(r)\gamma(r)dr, $$

(2)

where $r_0$ is the classical electron radius, $c$ is the speed of light, $n_+(r)$ is the positron density, and $\gamma(r)$ is the enhancement...
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\[ \tau_f = 106 \text{ ps} \]

\[ \tau_v = 183 \text{ ps} \]

(a)

(b)

Fig. 1 Calculated positron density in FCC Pd. (a) perfect lattice, (b) Pd vacancy.

factor describing the short-range pileup of the electron at the positron. For the enhancement factor, we have used the interpolation formula by Puska et al.\textsuperscript{12} based on Lantto’s data.\textsuperscript{15}

3. Results and Discussion

3.1 Experimental and computational positron lifetimes of each annihilation state in Pd

Before the hydrogenation of Pd, the positron lifetimes of as-received and fully annealed specimens were measured. The positron lifetime of fully annealed specimen (\( \tau_f \)) was 106 ps. The calculated positron lifetime of the bulk state is 106 ps. This calculated value well corresponds to the experimental value for a fully annealed specimen. This lifetime component comes from free positrons in the matrix.

In the case of the vacancy state in Pd, the calculated positron lifetime (\( \tau_v \)) is 183 ps. Figures 1(a) and (b) show the calculated positron wave functions of the bulk state and vacancy state. Figure 1(a) shows that positrons annihilate with a free electron at the interstitial site because of Coulomb’s repulsive force. Figure 1(b) shows that almost all positrons are localized at the vacancy state because of the positron trapping at the vacancy.

In the non-annealed specimens, the lattice defects (mainly dislocations) are formed by rolling. The positron lifetime of the non-annealed specimen is 160 ps. This value is 54 ps longer than the \( \tau_f \), and is 23 ps shorter than the calculated positron lifetime for the vacancy. Since positron lifetimes for dislocations (\( \tau_d \)) are generally shorter than those for vacancies,\textsuperscript{16} and are longer than those for the matrix (\( \tau_f \)), the positron lifetime component of non-annealed specimens comes mainly from dislocations.

3.2 Recovery process of hydrogen-induced lattice defects on isochronal annealing

Figure 2 shows the change in the mean positron lifetime \( \tau_m \) in degassed Pd on the isochronal recovery process. The \( \tau_m \) for as-degassed Pd was 177 ps, which is longer than for \( \tau_f \) and \( \tau_d \). Generally, positron lifetimes for vacancies and vacancy clusters are longer than those for dislocations. This result implies that vacancies are formed during the hydriding process.

A significant decrease of \( \tau_m \) is observed in the temperature ranges from 423 to 573 K and from 673 to 923 K going down to the positron lifetime value of a fully annealed specimen above 923 K. Therefore, all hydrogen induced lattice defects were removed by annealing at 923 K.

The variance of the fit, \( \chi^2/q \) indicates the fitting accuracy of the analysis. In cases where the value of \( \chi^2/q \) is larger than unity, the result of the analysis is not an adequate representation of the measured spectrum. In the temperature ranges from room temperature to 398 K and from 723 to 873 K, the value of \( \chi^2/q \) is significantly larger than unity. To investigate the recovery process in detail, all positron lifetime spectra were decomposed into multi-components. The positron lifetimes, \( \tau \), the relative intensities, \( I \), and the variances, \( \chi^2/q \) as a function of the isochronal annealing temperature are shown in Fig. 3. The value of \( \chi^2/q \) is almost unity throughout the whole annealing temperature range, indicating that the results of the multi-component analyses are adequate representations of the measured spectra.

The positron lifetime spectrum for as-degassed Pd was resolved into two components, 206 and 142 ps. Since these values are longer than the positron lifetime \( \tau_f \), these positron lifetime components come from lattice defects. The former value is longer than the calculated positron lifetime of the vacancy state (\( \tau_v = 183 \text{ ps} \)) and the latter value is shorter. Therefore, the former positron lifetime component must come from
vacancy clusters, and the latter one must come from dislocations. Figure 4 shows the size dependence for the vacancy clusters of calculated positron lifetimes in Pd. The positron lifetime in vacancy clusters increases from 183 to 286 ps with the cluster size. This result corresponds to the results for Al lifetime in vacancy clusters, and the latter one must come from dislocations. Figure 4 shows the size dependence for the vacancy clusters, and the latter one must come from dislocations. Victoria et al. showed that vacancy migration makes small dislocation loops in Pd.\(^{17}\) This report supports our experimental result. From 498 K, the relative intensity for a dislocation loop decreased gradually and goes down to zero at 673 K. So the annealing temperature of dislocation loop is about 498 K.

Above 673 K, a new positron lifetime component appears. Its lifetime is apparently shorter than that in a fully annealed specimen \((\tau_f)\). When dislocations exist in specimens, the positron lifetime for the matrix is shorter than the \(\tau_f\) because of positron trapping by the dislocations.\(^{18,19}\) This lifetime component comes from free positrons in the matrix. By using the trapping model,\(^{20-22}\) the dislocation density can be estimated. When positrons are trapped by dislocations in a specimen, the following relation is given:\(^{23}\)

\[
k = \mu_d \times C_d = I_d \times \left( \frac{1}{\tau_0} - \frac{1}{\tau_d} \right)
\]

where \(\mu_d\) is the specific positron-trapping rate and \(C_d\) is the concentration of dislocations. We adopt the specific trapping rate of dislocations in most metals of 0.5 cm\(^2\)s\(^{-1}\).\(^{24}\) From the relative intensity for dislocations, about 93% at 673 K, the dislocation density is estimated to be on the order of \(10^{13}\) cm\(^{-2}\). Since the relative intensity for dislocation becomes zero at 923 K, the annihilation of hydrogen-induced dislocations is completed below 923 K.

### 3.3 Concentration of hydrogen-induced vacancies

By using the trapping model,\(^{20-22}\) the concentration of vacancies can be estimated. When positrons are trapped by vacancies or dislocations in a specimen, the following relationship is given:\(^{23}\)

\[
C_{\text{vac}} = \left( I_{\text{vac}}/(1 - I_{\text{vac}}) \right) \times (\mu_{\text{dis}}/\mu_{\text{vac}}) \times C_{\text{dis}}
\]

We adopt here the specific trapping rate for vacancy in most metals of \(2 \times 10^{14}\) S\(^{-1}\).\(^{25,26}\) The expansion of the lattice constant between pure Pd and \(\beta\) hydride is about 3%.\(^{1}\) When a large misfit of the lattice constant exists, it is well known that misfit dislocations are induced. The dislocation density is roughly estimated from Brook’s equation.\(^{3}\) According to Brook’s equation, the density of the misfit dislocation is on the order of \(10^{12}\) cm\(^{-2}\). On the other hand, a transmission electron microscopy (TEM) observation\(^{5}\) shows that the misfit dislocations are induced by hydriding in Pd and the dislocation density is on the order of \(10^{13}\) cm\(^{-2}\). These values are much higher than the density of dislocation induced by normal plastic deformation.

The dislocation density is roughly estimated from Brook’s equation\(^{31}\) to be \(1.0 \times 10^{12}\) cm\(^{-2}\), and the relative intensity for vacancies, 52% just after the initial hydriding treatment, giving us the concentration of vacancies formed by hydriding in Pd to be on the order of \(10^{-3}-10^{-2}\). This value is much larger than the vacancy concentration in thermal equilibrium at the melting point of metals, \(10^{-2}-10^{-3}\). This anomalous vacancy generation phenomenon is accompanied by a large volume change between the matrix and the precipitation phase. The origin of this phenomenon may be the lattice strain.
4. Conclusion

The recovery process of hydrogen induced lattice defects of degassed Pd was investigated by positron lifetime spectroscopy. The following conclusions were drawn:

1. Anomalous vacancy generation phenomenon during the hydriding process was found in Pd. The hydrogen-induced vacancies are possibly formed to relax the misfit strain energy at the interface of solid solutions and hydride phases.

2. The hydrogen-induced vacancies grow up to di-vacancies because of the huge amount of vacancies are formed by hydrogenation. In the recovery process, secondary defects are formed. These are two-dimensional relaxed vacancy clusters or dislocation loops, not three-dimensional vacancy clusters or voids.

3. The concentration of vacancies formed by hydriding in Pd is of the order of $10^{-3}$–$10^{-2}$, which is much higher compared to the vacancy concentration in thermal equilibrium.

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