Diffusion Coefficient of Hydrogen in Palladium Films Prepared by RF Sputtering*

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Diffusion coefficients of hydrogen in the palladium films of α -phase have been measured between 278 and 323 K by an electrochemical stripping method. Palladium films were deposited on iron by RF sputtering. The values of the diffusion coefficient of hydrogen obtained for the film specimens 0.68 μm and 1.36 μm in thickness were about 2 orders of magnitude lower than those reported for the bulk specimens in the literature, and the temperature dependence of the diffusion coefficients of hydrogen was given by $D_{\text{H}}(\text{m}^2/\text{s}) = 4.16 \times 10^{-9} \exp(-25.7 \text{ (kJ/mol)} / RT)$.

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I. Introduction

Recently, nuclear fusion reactions at room temperature have been reported to occur in palladium bulk specimens charged with deuterium by the electrochemical method⁽¹⁾⁽²⁾, and much attention of scientists is focussed on the behavior of hydrogen isotopes in palladium. The fusion reactions are considered to be caused by the interaction between densely dissolved deuterium atoms, and hence the higher concentration of deuterium in palladium may be more advantageous for the fusion reactions.

It is well known that cold-working of palladium specimens reduces the diffusion coefficient of hydrogen, which is attributed to the trapping of hydrogen by lattice defects such as dislocations⁽³⁾⁽⁴⁾, and the trapping effect of lattice defects in iron causes the increase of hydrogen solubility⁽⁵⁾. Consequently, if introduction of lattice defects into palladium specimens increases solubility of hydrogen isotopes, this may be favorable to the fusion reactions.

Since it is known that thin films have different structures from those of bulk specimens, the diffusion coefficient and solubility of hydrogen in thin film specimens are expected to differ from those in bulk specimens. Though the diffusion coefficient and solubility of hydrogen in palladium have been measured by many workers, the values of them reported in the literature are obtained for bulk specimens and not for thin film specimens⁽⁶⁾⁽⁷⁾.

In the present work, palladium films have been deposited on iron by RF sputtering, and the diffusion coefficients and concentrations of hydrogen in the palladium films have been measured by an elec-

trochemical method. The hydrogen behavior in the palladium films has been discussed by comparing with that in palladium bulk specimens⁽⁶⁾.

II. Experimental Procedure

1. Specimens

The materials used as substrate were pure iron made by vacuum melting of electrolytic iron. They were annealed in vacuum at 1173 K for 10.8 ks and then cooled in the furnace. A thin layer of palladium was deposited on the iron membrane by RF sputtering under argon pressure of 6.7 Pa using targets of commercially pure palladium (99.98 mass%). Substrate temperature was 573 K. The thickness of the palladium films was 0.05–1.36 μm , and the thickness of palladium coated iron specimens was 0.2–0.9 mm. The specimen thickness is comparable with that of the iron membrane.

X-ray diffraction analysis indicated that sputter-deposited palladium was a crystal with fcc structure. When the specimens coated with thin palladium films were immersed into acid solutions, formation of red rusts, i.e., corrosion products containing iron, was observed. This indicates that some orifices exist in the palladium films.

2. Electrochemical stripping method

The diffusion coefficient of hydrogen was determined by an electrochemical stripping method between 278 and 323 K. After hydrogen was introduced into the specimen by cathodic polarization of the surface coated with palladium at $-0.8 \text{ V vs. Ag/AgCl}^{\dagger}$ for a long time, the electrode potential was varied to 0 V. Because this electrode potential, 0 V, is much nobler than the equilibrium potential of hydrogen, hydrogen atoms dissolved in the specimen are extracted by potentiostatical ionization.

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[†] In the present experiment, the values of electrode potential are set against a Ag/AgCl reference electrode.

Time dependence of the ionization current (anodic current) which corresponds to the flux of hydrogen atoms stripped at the palladium surface has been measured. The curves of the anodic current vs. time are referred as "hydrogen stripping curves". The observed hydrogen stripping curves were analyzed to obtain the diffusion coefficient of hydrogen.

The electrolyte was a 0.2 kmol/m³ NaOH aqueous solution of pH 13.

3. Determination of diffusion coefficient of hydrogen

If the hydrogen stripping process is controlled by hydrogen diffusion in the palladium film and the diffusion coefficient is independent of the hydrogen concentration (assumption (1)), the diffusion equation is given by Fick's second law as

$$\partial c(x, t_s) / \partial t_s = D_H (\partial^2 c(x, t_s) / \partial x^2), \quad (1)$$

where $c(x, t_s)$ is the hydrogen concentration at the distance x from the palladium surface at any stripping time t_s , and D_H is the diffusion coefficient of hydrogen in palladium. The boundary condition at the palladium surface is assumed to be given by eq. (2) (assumption (2)).

$$c(0, t_s) = 0. \quad (2)$$

If the concentration of hydrogen in the iron substrate is negligible in comparison with that in the palladium film (assumption (3)), transfer of hydrogen to the palladium film through the interface can be considered to be negligible, and hence the boundary condition at the interface is given by

$$(\partial c(x, t_s) / \partial x)_{x=L_{Pd}} = 0, \quad (3)$$

where L_{Pd} is thickness of the palladium film. The concentration of hydrogen is assumed to be uniform throughout the palladium film prior to commencement of hydrogen stripping (assumption (4)). Let C_0 be the uniform hydrogen concentration:

$$c(x, 0) = C_0. \quad (4)$$

Equation (1) is solved with eqs. (2), (3) and (4), and the flux I_H of hydrogen stripped on the surface of palladium film is obtained as

$$I_H = (\partial c(x, t_s) / \partial x)_{x=0} = \frac{C_0 D_H}{L_{Pd}^2} \sum_{n=0}^{\infty} \exp \left(-\frac{(2n+1)^2 \pi^2 D_H t_s}{4 L_{Pd}^2} \right). \quad (5)$$

In the case of large t_s , eq. (5) can be approximated by

$$I_H = (C_0 D_H / L_{Pd}^2) \exp \left(-\pi^2 D_H t_s / 4 L_{Pd}^2 \right). \quad (6)$$

Consequently, a plot of $\log I_H$ vs. t_s is a straight line at large t_s , and the tangent corresponds to the value of $(-\log e) \pi^2 D_H / 4 L_{Pd}^2$, from which the diffusion coefficient of hydrogen, D_H , can be determined.

In order to determine the diffusion coefficient by using eq. (6), the assumptions (1)–(4) described above should be fulfilled in the stripping experiments. These assumptions will be experimentally examined in section III.

4. Measurement of hydrogen content in specimens

When the electrode potential of specimens is varied to 0 V after the cathodic hydrogen charging, hydrogen dissolved in the specimens is extracted by the potentiostatical ionization. The anodic current density takes a maximum value immediately after the potential variation and decreases with the stripping time t_s . Therefore, the amount of dissolved hydrogen was obtained by integrating the anodic current. The integral was taken between the limits of $t_s = 0$ and the time at which the anodic current density was one hundredth of the maximum. The amount of hydrogen increased with charging time and reached a saturation value. This saturation value is called "hydrogen content".

III. Experimental Results and Discussion

1. Concentration of dissolved hydrogen and concentration profile

The hydrogen contents were measured for the specimens of various thicknesses (L) coated with sputter-deposited palladium films of various thicknesses (L_{Pd}). The hydrogen content was independent of L , and the hydrogen content was considered to be proportional to L_{Pd} . This indicates that most of the hydrogen atoms dissolved in the specimen exist in the palladium film and the profile of the hydrogen concentration is uniform in the film. This satisfies the assumptions (3) and (4) described in section II-3.

On the assumption that density of the palladium film is equal to that of palladium bulk, the concentration of hydrogen in the films was calculated from the film thickness and the hydrogen content. Figure 1 shows the thus obtained hydrogen concentration in the palladium films polarized at various electrode potentials (E). The hydrogen concentration is considered to be independent of L and L_{Pd} .

Fig. 1 Dependence of hydrogen concentration in sputter-deposited palladium films on electrode potential E .

According to the phase diagram of the palladium-hydrogen system⁽⁸⁾, the solubility limit of hydrogen in α -phase solid solution is 0.02 H atom/Pd atom at 298 K. When comparing this hydrogen concentration with the data given in Fig. 1, it can be concluded that the concentration of hydrogen in the films polarized at $E > -0.9$ V does not exceed the solubility limit for the α -phase. However, cathodic polarization at $E < -0.9$ V produces β -phase hydride.

The equilibrium potential of hydrogen is -0.99 V under the experimental condition in this work, i.e., at pH 13 and 298 K. The concentration of hydrogen in the films at the equilibrium potential, i.e., the solubility of hydrogen in the films, is 0.5 H atom/Pd atom as shown in Fig. 1, which does not differ much from the solubility of hydrogen in palladium bulk at 298 K, 0.7 H atom/Pd atom⁽⁶⁾⁽⁸⁾.

Because the assumption (1) (cf. section II-3) is satisfied only in the case of low hydrogen concentration, eq. (1) can not be applied to determination of the diffusion coefficient of hydrogen in hydrides. Therefore, the diffusion coefficient of hydrogen has been measured for the α -phase palladium films polarized at -0.8 V.

2. Experimentally obtained hydrogen stripping curves

In the hydrogen stripping experiments, hydrogen atoms at the palladium surface were ionized at 0 V by a potentiostat. The concentration of hydrogen at the palladium surface polarized at 0 V is known to be maintained at none⁽⁹⁾. This satisfies the assumption (2).

Typical hydrogen stripping curve is shown in Fig. 2. At the electrode potential of 0 V, some electrochemical reactions occur in addition to hydrogen ionization, because

Fig. 2 Typical hydrogen stripping curve. In the time range from 1 s to 5 s, the logarithms of anodic current density I are nearly proportional to stripping time t_s .

the electrolyte is exposed to the atmosphere. So the anodic current density I becomes nearly constant at large stripping time t_s . In a certain time range, however, the logarithms of I are nearly proportional to t_s .

If the assumptions (1)–(4) are fulfilled in the stripping experiments, the values of D_H calculated by using eq. (6) should be independent of hydrogen charging time t_c and the thickness of iron substrate (which is nearly equal to specimen thickness L). Thus obtained values of D_H are independent of t_c and L , as shown in Fig. 3 and Fig. 4.

Furthermore, in order to discuss the experimental procedure for determination of D_H , the procedure has been applied to determination of D_H in the annealed palladium bulk specimens about 0.3 mm in thickness. For the bulk specimens, D_H was obtained to be $3.8 \times 10^{-11} \text{ m}^2/\text{s}$ at 298 K. This value is in good agreement with the data reported in the literature⁽⁶⁾ ($4 \times 10^{-11} \text{ m}^2/\text{s}$ at 298 K).

Consequently, the analysis of hydrogen stripping curves and the experimental conditions in the present work are valid for measurements of D_H in the palladium films.

3. Dependence of D_H on film thickness

Figure 5 shows the effect of L_{Pd} on D_H . Though the

Fig. 3 Diffusion coefficients of hydrogen D_H obtained under various charging time t_c .

Fig. 4 D_H obtained for the specimens of various thicknesses (L).

Fig. 5 Dependence of D_H on the thickness of palladium films L_{Pd} .

experimental values of D_H show some scattering, the palladium film specimens of $L_{Pd}=0.68$ and $1.36 \mu\text{m}$ have nearly the same value of D_H , and the films thinner than $0.68 \mu\text{m}$ have smaller values of D_H .

If the structure of films is unchanged by varying the film thickness, D_H should be independent of L_{Pd} . And so, the decrease of D_H in the thin films may be caused by the structure change, though the cause of the thickness dependence of D_H is not clear.

4. Diffusion coefficients of hydrogen in the film and the bulk specimens

Figure 6 shows Arrhenius plots of D_H in the palladium films of $L_{Pd}=0.68$ and $1.36 \mu\text{m}$. The temperature dependence of D_H is given by

$$D_H(\text{m}^2/\text{s}) = 4.16 \times 10^{-9} \exp(-25.7 (\text{kJ/mol})/RT). \quad (7)$$

Many investigators have studied the value of D_H in α -phase palladium bulk, and the temperature dependence can be approximately represented by⁽⁶⁾

$$D_H(\text{m}^2/\text{s}) = 2.90 \times 10^{-7} \exp(-22.2 (\text{kJ/mol})/RT). \quad (8)$$

The pre-exponential factor for the film specimens is 2 orders of magnitude lower than that for the bulk specimens, while the activation energy is larger in the films.

The value of D_H at 298 K for the film specimens is $1.3 \times 10^{-13} \text{ m}^2/\text{s}$, which is largely different from the value of D_H at 298 K for the bulk specimens ($3.7 \times 10^{-11} \text{ m}^2/\text{s}$). The large difference between the values of D_H is speculated to be caused by the presence of a large amount of lattice defects in the films, because it is well known that cold-working of palladium and iron specimens, i.e., introduction of lattice defects into the specimens, reduces the value of D_H ⁽⁴⁾. This is reported to be attributed to the trapping of hydrogen by lattice defects⁽⁴⁾⁽⁶⁾⁽¹⁰⁾.

Fig. 6 Arrhenius plots of D_H in α -palladium films of $L_{Pd}=0.68$, $1.36 \mu\text{m}$ obtained in the present work, and D_H in palladium bulk reported in the literature⁽⁶⁾.

In the case of the trapping effect in cold-worked iron specimens, it has been recognized that the lattice defects lower the potential energy of hydrogen and increase the activation energy for hydrogen diffusion, and so the trapping effect causes the increase of the hydrogen solubility and the decrease of the diffusion coefficient⁽⁵⁾⁽⁶⁾. In the case of the palladium specimens described above, however, the values of the solubility of hydrogen in the film are in the same order of magnitude with those of the bulk specimens, while the values of the diffusion coefficient of hydrogen are largely different between the Pd bulk and thin film. This indicates that the variation of the potential energy of hydrogen by introduction of lattice defects differs between iron and palladium specimens.

As described above, the hydrogen solubility in the film specimens does not differ so much from that in the bulk specimens. This implies that the palladium film is not a more favorable material than the palladium bulk for the nuclear fusion reactions at room temperature.

IV. Conclusion

The diffusion coefficients D_H and concentrations of hydrogen in sputter-deposited palladium films were measured between 278 and 323 K by an electrochemical stripping method. The following results were obtained:

- (1) The solubility of hydrogen in the films at 298 K was 0.5 H atom/Pd atom, and this value does not differ much from that in palladium bulk at 298 K.
- (2) Severe cathodic polarization produces hydride,

and hence D_H in palladium films of α -phase can be measured only at appropriate electrode potentials.

(3) In the case of measurement of D_H in the film specimens, the dependence of D_H on film thickness must be considered.

(4) D_H in the α -phase palladium films of 0.68, 1.36 μm in thickness is 2 orders in magnitude lower than D_H in palladium bulk around room temperature, and the temperature dependence of D_H in the films is given by

$$D_H(\text{m}^2/\text{s}) = 4.16 \times 10^{-9} \exp(-25.7 \text{ (kJ/mol)}/RT).$$

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REFERENCES

- (1) M. Fleischmann, S. Pons and M. Hawkins: J. Electroanal. Chem., **261** (1989), 301.
- (2) S. E. Jones, E. P. Palmer, J. B. Czirr, D. L. Decker, G. L. Jensen, J. M. Thorne, S. F. Taylor and J. Rafelski: Nature, **338** (1989), 737.
- (3) H. Hasegawa and K. Nakajima: J. Japan Inst. Metals, **41** (1977), 813.
- (4) Y. Sakamoto and N. Tabaru: J. Japan Inst. Metals, **45** (1981), 1048.
- (5) H. Hagi, S. Asano and N. Ohtani: Bull. Nagoya Inst. Technol., **26** (1974), 273.
- (6) J. Völkl and G. Alefeld: *Diffusion in Solids*, Ed. by A. S. Nowick and J. J. Burton, Academic Press, N.Y., (1975), p. 231.
- (7) R. V. Bucur: Z. Phys. Chem. N. F., **146** (1985), S.217.
- (8) M. Hansen: *Constitution of Binary Alloys*, McGraw-Hill, N.Y., (1958), p. 790.
- (9) H. Hagi, Y. Hayashi and N. Ohtani: J. Japan Inst. Metals, **42** (1978), 801; Trans. JIM, **20** (1979), 349.
- (10) R. V. Bucur: J. Materials Sci., **22** (1987), 3402.