

論文

Pd/Zr₃Al₂による重水素吸収機構と耐不純物ガス特性

芦田 完¹・渡辺 国昭¹
寺下 尚克²・多々 静夫²・池野 進³

富山大学水素同位体機能研究センター^{*1}

富山大学工学部物質工学科^{*2}

地域共同研究センター^{*3}

〒930 富山市五福3190

Absorption Kinetics Deuterium by Zr₃Al₂ Covered with Electroless Pd Plating —Durability against Impurity Gases—

Kan ASHIDA¹, Kuniaki WATANABE¹, Naoyoshi TERASHITA²
Sizuo TADA² and Susumu IKENO³

1. Hydrogen Isotope Reseach Center,

2. Material Sci. and Eng., Faculty of Eng.,

3. Center for Cooperative Research,

Toyama University, Gofuku 3190, Toyama 930, Japan

(Received September 7, 1994; accepted November 30, 1994)

Abstract

Electroless Pd plating on Zr₃Al₂ granules was prepared as a protective layer on the getter alloy surface. The absorption of deuterium obeyed the first order kinetics with respect to the deuterium pressure for both Zr₃Al₂ and Pd/Zr₃Al₂. The rate determining step for absorption was the dissociation reaction of gaseous and/or adsorbed deuterium molecules on the surface. The activation energy was evaluated to be 7.4 and 8.9 kJ/mol(D₂) for Zr₃Al₂ and Pd/Zr₃Al₂, respectively. In addition, the durability against impurity gases for deuterium absorption was also demonstrated using CO₂ and N₂ as impurity gases. Exposure to these impurity gases caused a reduction of the absorption rate of deuterium. The extent of the reduction for Pd/Zr₃Al₂ was smaller than that for bare Zr₃Al₂. The effectiveness of the Pd-overlayer against impurity gases was in the order of N₂>CO₂. The results could be explained in terms of different absorption properties of deuterium between Pd and Zr.

1. Introduction

Zirconium alloys are very much active to inorganic gases and adsorb the gases quite rapidly. In addition, they show sufficiently low equilibrium pressure of hydrogen isotopes at room temperature. Because of these properties, they have been used as materials of bulk getter pumps for oil-free ultra-high vacuum systems¹⁻⁵. They also have potential for fuel processing in controlled thermonuclear fusion devices. For this purpose, however, they will have to be improved to meet various requirements, which depend on their applications such as storage⁶⁻⁸, supply^{9,10}, recovery¹¹⁻¹⁵, separation¹⁶ and so on¹⁷⁻²¹.

The applicability of them, however, is rather limited at present. This is due to their high reactivity against impurity gases²²⁻²⁶, especially to oxygen containing molecules as H₂O, CO₂, CO and O₂, which appear most often in vacuum systems. Serious problems arise from those gases owing to the formation of stable overlayers of oxide and carbide²²⁻²⁶. Namely, the active materials are deactivated against hydrogen absorption and desorption. On the other hand, contamination of fuel gases is unavoidable owing to leakage and out-gassing from the wall of the fuel processing system. Therefore, one has to develop new materials inactive to impurity gases but active to hydrogen isotopes.

One solution of this problem is to prepare surface protective layers on active materials which are free from contamination by the impurity gases and act as permeation window for hydrogen isotopes. To develop such protective layers, we have studied physicochemical properties of a Pd-overlayer prepared with electroless plating on Zr₃Al₂. This will be denoted as Pd/Zr₃Al₂ below. Zr₃Al₂ was selected as a model system of hydrogen storage materials for the fuel processing. Parts of the study have been reported previously from view points of surface states and some characteristic features of deuterium desorption²⁷. In this paper, absorption kinetics of deuterium will be compared in detail between Pd/Zr₃Al₂ and bare Zr₃Al₂ surfaces.

2. Experimental

2. 1. Sample preparation

Zr₃Al₂ alloy was purchased from Japan Metals & Chemicals Co. It had been prepared with argon arc melting of the stoichiometric mixture of Zr and Al powder. A lump of the alloy was annealed at 1100°C for 150 min in vacuum, cooled to room temperature with a rate of 150°C/h, and then supplied to sample preparation. First,

grains of the alloys were prepared by hydride formation and sieved to 0.2–0.5mm in diameter. Subsequently, Pd-overlayers were grown over those grains with the electroless plating method. The detailed procedures have been described elsewhere^{2,7}. The bare and Pd-coated Zr₃Al₂ grains were used as samples in the present study.

2. 2. Absorption measurement

Effects of the Pd-overlayers on the deuterium absorption were observed with the constant volume method using a high vacuum system. Figure 1 shows the schematic illustration of the system used in the present study. It was equipped with a quadrupole mass spectrometer, B-A type ionization vacuum gauge, capacitance manometer and sample tube made of quartz. The system was evacuated with a sputter ion pump and turbomolecular pump backed with an oil-sealed rotary pump. The residual pressure of the system was routinely below 3×10^{-6} Pa.

Each sample was activated by vacuum heating at 800°C for 30min and cooled to a given temperature before the absorption measurements. Deuterium gas was introduced into the closed part of the system enclosed by the valves, v-3, 4 and 5. Subsequently, the valve v-4 was opened quickly, and the time course of pressure decay due to the absorption was measured using the capacitance manometer. The absorption ki-

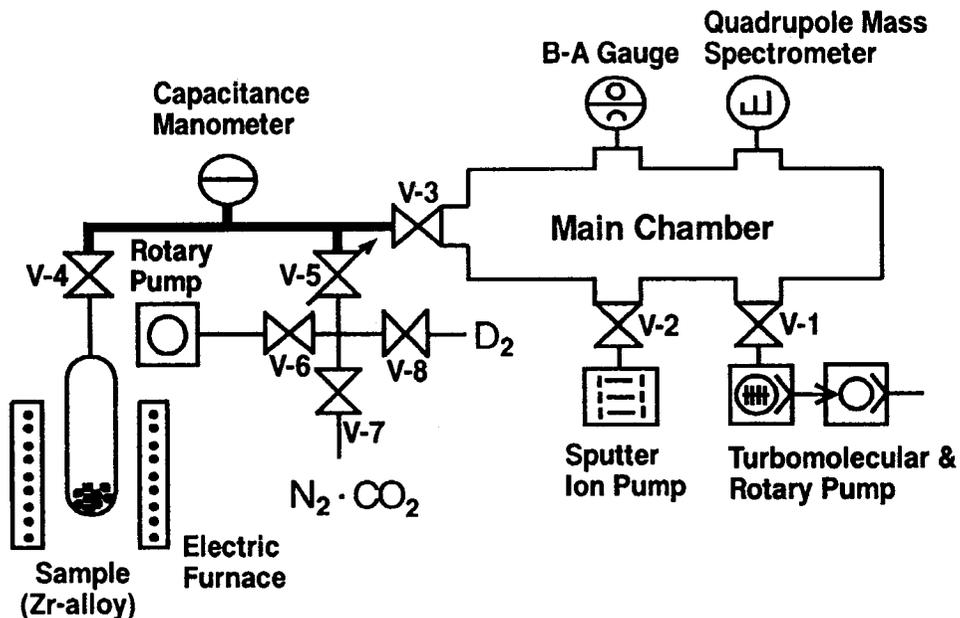


Fig. 1. Schematic illustration of the apparatus used in the present study.

netics was analyzed through the decay curves for various absorption temperatures.

2. 3. Durability test

CO₂ and N₂ were used as impurity gases. Figure 2 shows the procedures of the durability tests of Zr₃Al₂ and Pd/Zr₃Al₂. First, a sample was activated at 800°C for 30 min, and the absorption rate of deuterium, v_0 , was measured at room temperature. Subsequently, the sample was exposed to CO₂ or N₂ under given exposure conditions, and the system was evacuated. Lastly, the absorption rate of deuterium, v_{exp} , was measured under the same conditions as those before the impurity exposure.

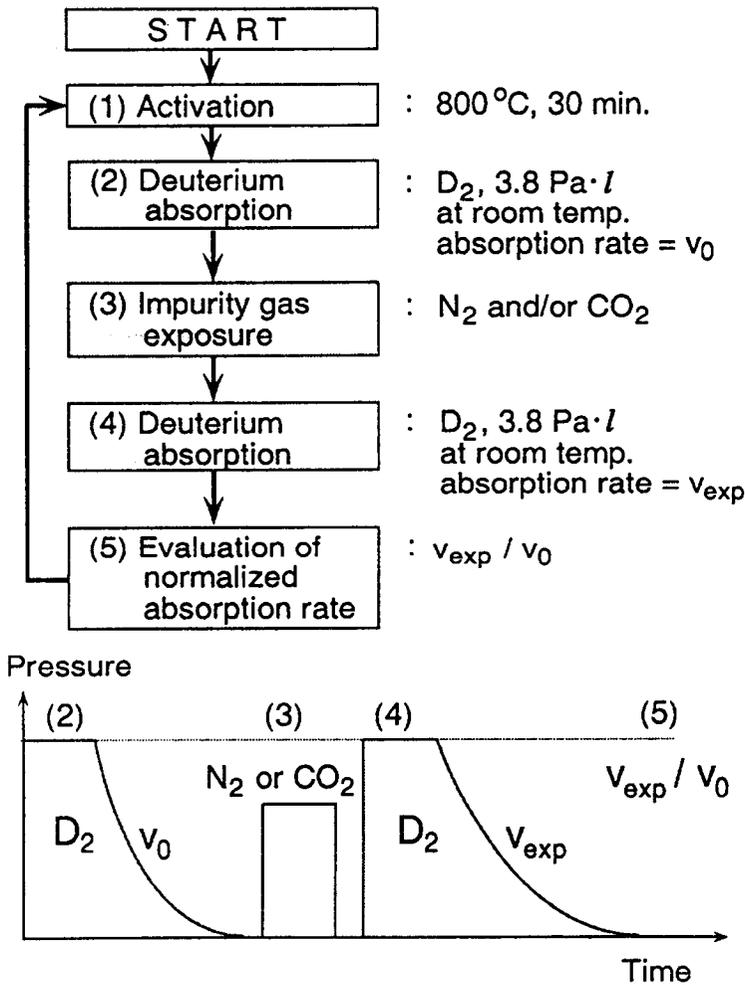


Fig. 2. Flow chart of the durability test against impurity gases, N₂ and CO₂, for the absorption of deuterium gas by Zr₃Al₂ and Pd/Zr₃Al₂.

Changes in the absorption rate with the exposure to impurity gases were evaluated as the normalized absorption rate, v_{exp}/v_0 , for each impurity gas. In the present study, the exposures of CO₂ and N₂ were varied in ranges of 10²-10⁴ and 10⁴-10⁸L, respectively, where L is Langmuir, a unit of gas exposure equivalent to 10⁻⁶ Torr•s.

3. Results and discussion

3. 1. Activation process of samples

Vacuum heating is commonly applied to activate Zr-based alloy getters. Figures 3 and 4 show thermal desorption spectra observed during activation of Zr₃Al₂ and Pd/Zr₃Al₂, respectively. Both of the samples were heated to 800°C with a temperature ramp of 7K/min.

H₂, H₂O, CO and CO₂ were observed for both of the samples. However, the amounts of desorption and the temperatures of the desorption peaks differed from each other. As seen in Fig.3, H₂ was the main desorption species. It consisted of a single desorption peak which appeared around 350°C. The desorption peaks of H₂O, CO and CO₂ were also observed around this temperature, but the amounts of desorption were one or two orders of magnitude smaller than that of H₂. No other desorption peak was observed above 500°C.

On the other hand, CO and CO₂ were main desorption species for Pd/Zr₃Al₂ as shown in Fig.4. In addition, their desorption peaks were observed at higher temperatures around 600°C than those of H₂ and H₂O, which appeared below 500°C.

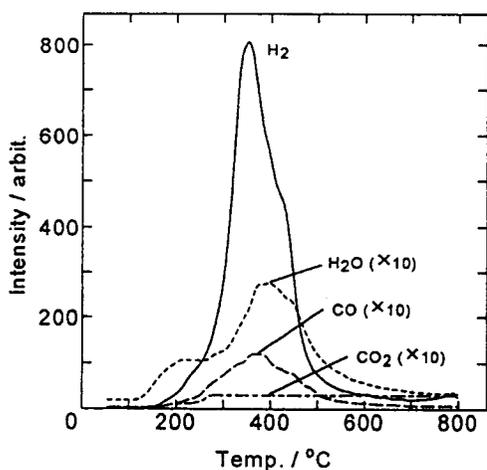


Fig. 3. Thermal desorption of gases from Zr₃Al₂: the ramping rate was 7K/min.

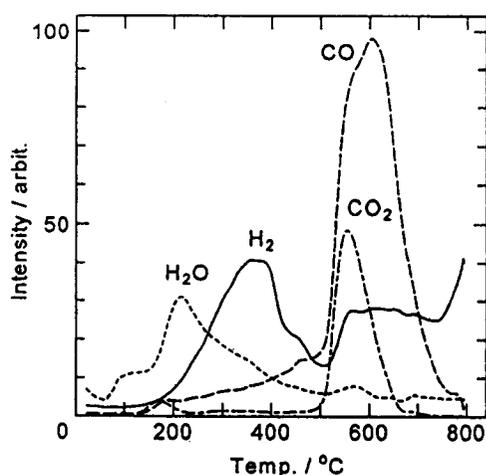
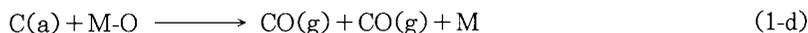


Fig. 4. Thermal desorption of gases from Pd/Zr₃Al₂: the ramping rate was 7 K/min.

H₂ observed in Figs.3 and 4 is considered to arise from hydrogen atoms dissolved in those samples. H₂O would be due to desorption of water adsorbed on the sample surface and/or inner wall of the sample tube. Presence of adsorbed water on those surfaces is plausible, because of the samples and sample tube were exposed to the air before thermal desorption experiments. Concerning to CO and CO₂, a part of them would arise from adsorbed CO and CO₂ from sample surface as



In the above, (a) and (g) denote adsorbed and gaseous state, respectively. Another part of CO and CO₂ is considered due to following reactions on the sample surfaces.



In the above, C(a), M.C. and M-O indicate carbonaceous contaminants and/or adsorbed hydrocarbons (being denoted as surface carbons below), metal carbides and metal oxides, respectively. Metal surfaces are known to be contaminated by surface carbons and other adsorbates^{2,8}. Recent XPS (x-ray photoelectron spectroscopy) measurements^{2,7} suggested that the reactions between surface carbons and metal atoms as indicated in reaction (1-c) and (1-d) took place at high temperatures above 500°C (being denoted as high temperature region). Occurrence of those of surface reactions, of course, largely depend on surface metal elements and its states. Previous XPS measure revealed that Zr-carbide was formed by the surface reaction such as (1-c) at the high temperature region. In addition, desorption of H₂, CO, CO₂ and hydrocarbons was rather in small extent as shown in Fig.3. XPS measurements also revealed that Pd-carbide was not formed even at high temperature region, indicating that the reaction (1-d) would be proceeded. Indeed, CO and CO₂ were desorbed at high temperature region as shown in Fig.4. This would be due to the reaction between surface carbons and oxygen which was diffused to the surface from the inner part of the sample.

3. 2. Absorption rates of deuterium

The absorption rate would be expressed as

$$\begin{aligned} -(\text{dQ}/\text{dt}) &= kP^n \\ &= k_a P^n (k_a = k/V) \end{aligned} \quad (2)$$

where P is the pressure of hydrogen isotopes, k_a the absorption rate constant, V the volume of the system, and n the order of reaction. For many Zr-based alloys, n is known to be unity^{2,9-31}. In this case, equation (2) is rewritten as follows.

$$\ln\left\{\frac{(P_n - P_0)}{(P_{n-1} - P_0)}\right\} = k_a(t_{n-1} - t_n)$$

$$\ln(\Delta P_n / \Delta P_{n-1}) = k_a \Delta t_n \quad (3)$$

Namely, the plots of Δt_n vs. $\ln(\Delta P_n / \Delta P_{n-1})$ give a straight line. Figures 5 and 6 show the plots of Δt_n vs. $\ln(\Delta P_n / \Delta P_{n-1})$ for Zr₃Al₂ and Pd/Zr₃Al₂ at various temperatures, respectively. Each of the plots in Figs 5 and 6 shows fairly well linearity, indicating that the absorption of deuterium obeys the first order kinetics. The rate equation can be expressed as

$$-(dP/dt) = k_a P^{1.0} \quad (4)$$

$$k_a = \nu_a \exp(-E_a/RT) \quad (5)$$

where ν_a is the frequency factor and E_a the activation energy for absorption. The first order kinetics indicates that the rate determining step for absorption is the first order dissociation reaction of gaseous and/or adsorbed deuterium molecules to atomic state on the sample surface.

From the slope of each line in figures 5 and 6, the rate constants, k_a , for respective temperatures were evaluated for Zr₃Al₂ and Pd/Zr₃Al₂. Figure 7 shows the Arrhenius plots of the rate constants for Zr₃Al₂ and Pd/Zr₃Al₂. From the slopes of

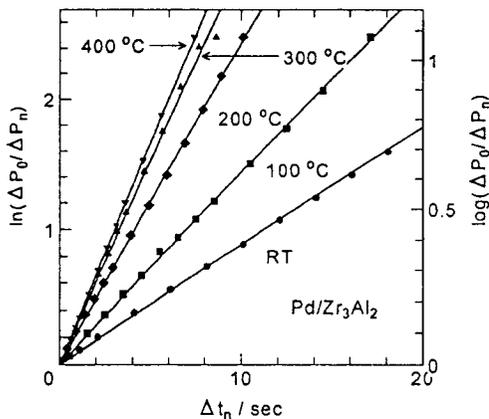


Fig. 5. Plots of $\ln(\Delta P_n / \Delta P_{n-1})$ against Δt_n for the absorption of D₂ by Zr₃Al₂ at various temperatures.

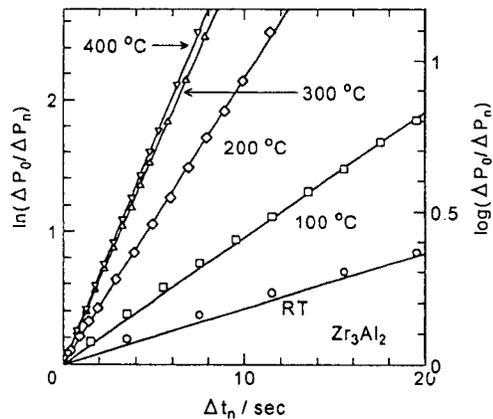


Fig. 6. Plots of $\ln(\Delta P_n / \Delta P_{n-1})$ against Δt_n for the absorption of D₂ by Pd/Zr₃Al₂ at various temperatures.

the plots, the activation energies were evaluated as 7.4 and 8.9 kJ/mol(D₂) for Zr₃Al₂ and Pd/Zr₃Al₂, respectively. The activation energies were quite low and closed each other, indicating that deuterium molecules are easily dissociate into atoms on those surfaces. The frequency factors for absorption could be also evaluated from the intersections of the straight line with vertical axis in the Arrhenius plot diagram. In the present study, however, the apparent values have no physical significance, because the specific surface areas of the samples were not measured.

The desorption kinetics of deuterium for both the Zr₃Al₂ and Pd/Zr₃Al₂ has been confirmed to obey the second order kinetics²⁷. The activation energies for desorption are 106.7 and 134.4 kJ/mol(D₂) for Zr₃Al₂ and Pd/Zr₃Al₂, respectively²⁷. Therefore, the potential energy diagram for the absorption and desorption of deuterium in/from the samples should be drawn schematically as shown in Fig.8. The heat of deuterium solution and/or deuteride formation, ΔH, can be approximated to the difference between the activation energies of absorption and desorption. They were evaluated as 99.3 and 125.5 kJ/mol(D₂) for Zr₃Al₂ and Pd/Zr₃Al₂, respectively. The value for Pd/Zr₃Al₂ is close to the heat of solution of hydrogen in pure Pd³².

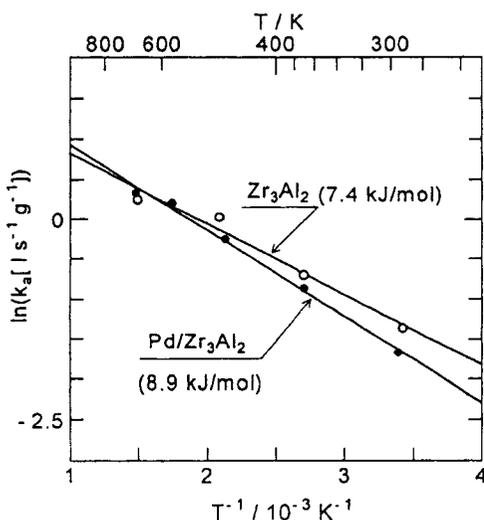


Fig. 7. Arrhenius plots of absorption rate constants for Zr₃Al₂ and Pd/Zr₃Al₂. Open circles are for Zr₃Al₂, and filled circles for Pd/Zr₃Al₂.

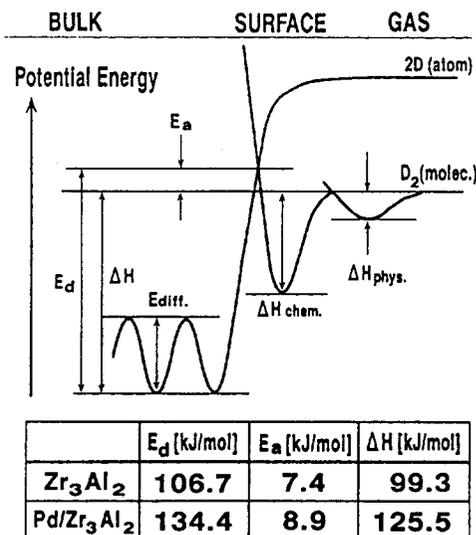


Fig. 8. Schematic potential energy diagram for the ab/desorption of D₂ by/from Zr₃Al₂ and Pd/Zr₃Al₂.

3. 3. Durability against impurity gases

Figure 9-(a) and (b) show plots of the normalized absorption rate of deuterium, v_{exp}/v_0 , as a function of impurity gas exposure. In this figure, open symbols represent results for Zr₃Al₂ and filled ones for Pd/Zr₃Al₂. Circles are the results for CO₂ exposure and squares for N₂, respectively.

Exposures of CO₂ caused the serious reduction of the absorption rate of deuterium for both the Zr₃Al₂ and Pd/Zr₃Al₂. However, the extent of the reduction for Pd/Zr₃Al₂ was always smaller than that of bare Zr₃Al₂. For example, 10⁴L of CO₂ exposure reduced the normalized absorption rates to 0.02 and 0.04 for Zr₃Al₂ and Pd/Zr₃Al₂, respectively. Pd/Zr₃Al₂ is 2.0 times more durable than bare Zr₃Al₂ to 10⁴ L of CO₂ exposure. Namely, the Pd-overlayer acts as protective layer for CO₂. On the other hand, N₂ exposure showed a smaller effect on the absorption rates for both of the samples than CO₂ exposure. However, the effectiveness of the Pd-overlayer was also observed. For example, 10⁴L of N₂ exposure reduced the normalized absorption rates of deuterium to 0.30 and 0.40 for Zr₃Al₂ and Pd/Zr₃Al₂, respectively. Namely, Pd/Zr₃Al₂ was only 1.3 times more durable than bare Zr₃Al₂. However, the effectiveness of the Pd-overlayer against N₂ increased with increasing N₂ exposure. For example, it was 4.1 times more effective in case of 4×10⁸L of N₂ exposure.

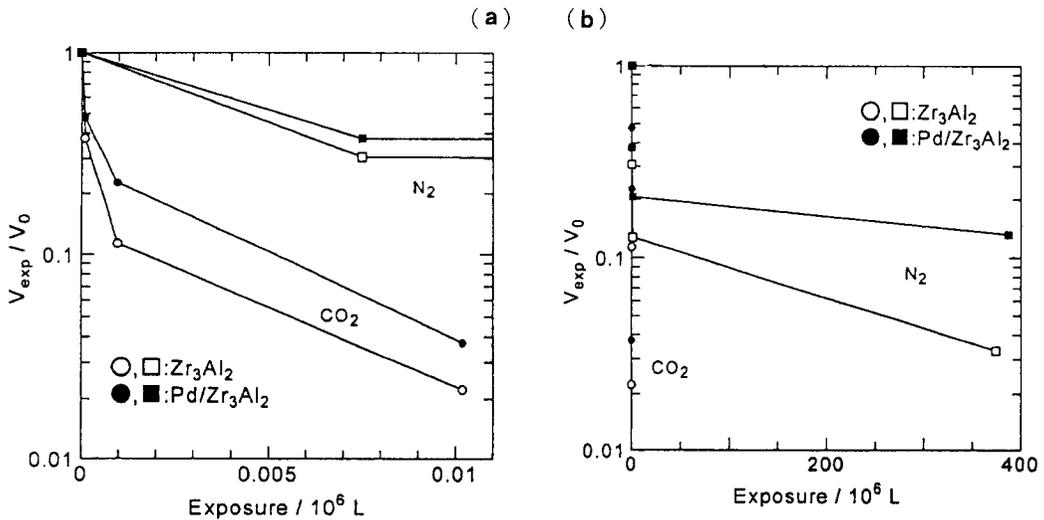


Fig. 9. Change in the normalized absorption rate of D₂ as a function of impurity gas exposure for Zr₃Al₂ and Pd/Zr₃Al₂ in the range of (a): 0-10⁴, and (b): 0-4×10⁸L (L: Langmuir, a unit of gas exposure equivalent to 10⁶ Torr·s). Open symbols represent results for Zr₃Al₂ and filled ones for Pd/Zr₃Al₂. Circles are the results for CO₂ and squares for N₂.

It has been confirmed by XPS measurements that the activated Zr-alloy getter surfaces mainly consist of metallic Zr, which is easily deactivated by impurity gases owing to the formation of surface obstacle layers²⁸. On the other hand, plated Pd kept pure metallic state in the range from room temperature to 800°C, although a fraction of the surface was covered with Zr diffused from the inner part of the sample.

The extent of the reduction of absorption rate should largely depend on the adsorption properties of impurity gases. Table 1 shows the classification of metals and semi-metals based on adsorption properties of gases³³. According to the table, the affinity of CO₂ for Zr and/or for Pd is comparable and that of N₂ is in the order of Zr>Pd. Those adsorption properties are in good agreement with the reduction of absorption rate observed in the present study, indicating that the durability of Pd-overlayer against impurity gases depends on the differences in the absorption properties between Pd and Zr³⁴. The change in the normalized absorption rate with increasing temperature will be important to practical applications of Pd/Zr₃Al₂. Further investigation is required on this point.

Table 1. The classification of metals and semi-metals based on absorption properties of gases³³. (+; adsorb, -; not adsorb)

		O ₂	C ₂ H ₂	C ₂ H ₄	CO	H ₂	CO ₂	N ₂
A	Ca, Sr, Ba, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, (Re)	+	+	+	+	+	+	+
B ₁	Ni, (Co)	+	+	+	+	+	+	-
B ₂	Rh, Pd, Pt, (Ir)	+	+	+	+	+	-	-
C	Al, Mn, Cu, Au	+	+	+	+	-	-	-
D	K	+	+	-	-	-	-	-
E	Mg, Ag, Zn, Cd, In, Si, Ge, Sn, Pb, As, Sb, Bi	+	-	-	-	-	-	-
F	Se, Te	-	-	-	-	-	-	-

4. Conclusions

Based on the above mentioned results and discussion, we concluded the followings:

1. The absorption of deuterium obeys the first order kinetics with respect to the deuterium pressure for both Zr₃Al₂ and Pd/Zr₃Al₂. The rate determining step for absorption is the dissociation of deuterium molecules on the sample surface.
2. The activation energies for deuterium absorption were evaluated as 7.4 and 8.9 kJ/mol(D₂) for Zr₃Al₂ and Pd/Zr₃Al₂. The heat of deuterium solution, ΔH, was also evaluated from the proposed potential energy diagram as 99.3 and 125.5 kJ/mol(D₂) for Zr₃Al₂ and Pd/Zr₃Al₂, respectively. The value for Pd/Zr₃Al₂ is close to the heat of solution of hydrogen in pure Pd.
3. Exposure of CO₂ and N₂ caused the reduction of the absorption rate of deuterium. However, the extent of the reduction for Pd/Zr₃Al₂ was smaller than that of bare Zr₃Al₂, indicating that the Pd-overlayer is effective against impurity gases.
4. The order of the effectiveness of the Pd-overlayer against impurity gases was N₂ > CO₂. This could be explained in terms of the differences in the absorption properties of deuterium between Pd and Zr.

Acknowledgment

This work was partially supported by a grant-in-aid from the Ministry of Education, Science and Culture, Japan (#05650705).

References

- 1) T.Yamamoto, T.Yoneoka, S.Kokubo and M.Yamawaki, Fusion Eng. and Design, 7 (1989) 363.
- 2) K.Watanabe, K.Tanaka, M.Matsuyama and K.Hasegawa, *ibid.*, 18 (1991) 27.
- 3) R.-D.Penzhorn, M.Devillers and M.Sirch, J.Nucl. Mater., 170 (1990) 217.
- 4) S.Konishi, T.Nagasaki, N.Yokokawa and Y.Naruse, Fusion Eng. and Design, 19 (1989) 355.
- 5) K.Watanabe, K.Ichimura, K.Ashida, M.Matsuyama and T.Takeuchi, Fusion Technol., 14 (1988) 729.
- 6) E.H.P.Cordfunke, "The Chemistry of Uranium", Elsevier, Amsterdam, 1969.
- 7) T.Yamamoto, T.Yoneoka, S.Kokubo and M.Yamawaki, Fusion Eng. and Des., 7 (1989) 363.
- 8) R.-D.Penzhorn, M.Devillers and M.Sirch, J.Nucl. Mater., 170 (1990) 217.

- 9) K.Watanabe, K.Tanaka, M.Matsuyama and K.Hasegawa, *Fusion Eng. and Des.*, **18** (1991) 27.
- 10) K.Ashida, M.Watanabe, C.Takeda, S.Tada, H.Anada, S.Ikeno and K.Watanabe, *Ann. Rept. of Hydrogen Isotope Research Center*, **10/11** (1991) 27.
- 11) C.Boffito, B.Ferrario, P. della Porta and L.Rosai, *J. Vac. Sci. Technol.*, **18** (1981) 1117–1120.
- 12) K.Ichimura, M.Matsuyama, K.Watanabe and T.Takeuchi, *J. Vac. Sci. Technol.*, **A6** (1988) 2541–2545.
- 13) H.F.Dylla, J.L.Cecchi and M.Ulrickson, *J. Vac. Sci. Technol.*, **18** (1981) 1111–1113.
- 14) R.J.Knize, J.L.Cecchi and H.F.Dylla, *J. Vac. Sci. Technol.*, **20** (1982) 1135–1137.
- 15) C.Boffito, B.Ferrario and D.Martelli, *J. Vac. Sci. Technol.*, **A1** (1983) 1279–1282.
- 16) K.Watanabe, K.Ashida, K.Ichimura and T.Takeuchi, *Ann. Rept. of Tritium Res. Center*, **8** (1988) 17–26. (in Japanese)
- 17) H.Albrecht, R.-D.Penzhorn, Th.Kastner and M.Sirch, *Proc. Int. Symp. on Fusion Nucl. Technol.*, Tokyo, Japan, 1988, partC, p.349–354.
- 18) K.Ichimura, K.Ashida and K.Watanabe, *J. Vac. Sci. Technol.*, **A3** (1985) 346–350.
- 19) K.Ichimura, M.Matsuyama and K.Watanabe, *J. Vac. Sci. Technol.*, **A5** (1987) 220–225.
- 20) K.Watanabe, M.Matsuyama, K.Ashida and H.Miyake, *J. Vac. Sci. Technol.*, **A7** (1989) 2725–2729.
- 21) N.J.Clark and E.Wu, *J.Less-Com. Met.*, **163** (1990) 227–243.
- 22) R.-D.Penzhorn, M.Devillers and M.Sirch, *J. Nucl. Mater.*, **179–181** (1991) 863.
- 23) K.Ichimura, K.Ashida and K.Watanabe, *J. Vac. Sci. Technol.*, **A3** (1985) 863
- 24) M.E.Malinowski, *ibid.*, **A3** (1985) 483.
- 25) J.L.Cecchi, P.H.LaMarche, H.F.Dylla and R.J.Knize, *ibid.*, **A3** (1985) 487.
- 26) C.Boffito, B.Ferrario and D.Martelli, *ibid.*, **A1** (1983) 1279.
- 27) K.Ashida, K.Watanabe, S.Morozumi, K.Matsuda and S.Tada, *Ann. Rept. of Hydrogen Isotope Research center*, **12** (1992) 59.
- 28) K.Ichimura, K.Ashida and K.Watanabe, *J. Vac. Sci. Technol.*, **A3** (1985) 346.
- 29) K.Ichimura, N.Inoue, K.Ashida, K.Watanabe and T.Takeuchi, *J. Nucl. Mater.*, **128/129** (1984) 1341.
- 30) K.Ichimura, N.Inoue, K.Watanabe and T.Takeuchi, *J. Vac. Sci. Technol.*, **A2** (1984) 1341.
- 31) K.Watanabe, K.Ichimura, K.Ashida, M.Matsuyama and T.Takeuchi, *Fusion Technol.*, **14** (1988) 729.

- 32) A.W.Aldag and L.D.Schmidt, *J. Catal.*, **22** (1971) 260.
- 33) G.C.Bond, "Catalysis by Metals", Academic Press, 1962, p.66.
- 34) *Catal. Rev.*, **19** (1) (1979) 105–159. (*Heats of Chemisorption of O₂, H₂, CO₂, and N₂ on Polycrystalline and Single Crystal Transition Metal Surfaces*, by I.To-yo-shima and G.A.Somorjai.)