

Applicability of Pd–Cu alloy to self-developing gas chromatography of hydrogen isotopes

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Abstract

To develop a new material for hydrogen isotope separation, absorption and desorption isotherms of protium (H_1^1) and deuterium (H_1^2) were measured for five kinds of Pd–Cu alloys in the temperature range from 283 to 453 K. Thermodynamic parameters for the formation and decomposition of hydride and deuteride of the alloys, ΔH^0 and ΔS^0 , were evaluated from the temperature dependence of equilibrium pressure in a plateau region of the isotherms for each Pd–Cu alloy. The thermodynamic parameters for Pd–15at.%Cu alloy were almost equivalent to those of the Pd–8at.%Pt alloy which showed good separation performance. Separation tests of the 50% H_2 –50% D_2 mixture were carried out under various conditions by using Pd–15at.%Cu alloy, and significantly high separation efficiency was observed. It was suggested, therefore, that the Pd–Cu alloys are applicable to the separation of hydrogen isotopes near room temperature.

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1. Introduction

Efficient recovery of tritium from exhaust gases of D–T fusion devices such as ITER is one of key issues for economical and safe recovery of tritium. Several isotope separation methods have been proposed for tritium recovery in fuel processing and waste handling [1]. The gas chromatographic separation is one of the promising methods for isotope separation because of simplicity of operation and construction, high separation efficiency. The conventional gas chromatographic separation of hydrogen isotopes is based on the isotope effects on physical adsorption by inert materials such as

molecular sieves near 77 K [2]. It is not easy, however, to apply this method to large scale tritium handling systems, since it requires a huge amount of liquid nitrogen as coolant.

On the other hand, large isotope effects are observed for hydrogen solution and hydride formation by palladium near room temperature or above [3]. The isotope separation based on those isotope effects is possible and has been proposed as replacement gas chromatography for the separation of hydrogen isotopes [4]. Its operation procedures, however, are complicated and the tritium inventory in the column should be fairly large, depending on operation conditions, in comparison with low-temperature gas chromatography [5]. A new separation technique (SDGC: self-developing gas chromatography) for hydrogen isotope mixtures has been recently developed [6], which is based on utilization

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of the isotope effects in the absorption and desorption process of hydrogen isotopes in a separation column material maintained near room temperature. This separation technique is applicable without any replacement gas and cooling at low temperatures. In this new separation technique, Pd–Pt alloys were applied as promising candidate materials for a separation column for SGDC and showed high efficiency for the separation of H₂–D₂ mixture gases in a laboratory scale [7].

However, since the Pd–Pt alloy is an expensive material, it is indispensable to reduce the amount of these novel metals used in a separation column from an economical point of view, taking practical use in a separation system into account. For this requirement, we have proposed a promising new technique to prepare Pd–Pt alloys [8]: namely, Pd and Pt were simultaneously deposited on α -alumina powder using a barrel sputtering device. By using this technique, it was seen that the amount of Pd–Pt alloy could be reduced to about 1/4 in comparison with use of the powdered alloys. To further improve cost performance, it is necessary to seek alternative elements to platinum and to reduce the amount of palladium.

From this viewpoint, the authors have studied the thermodynamic properties of the absorption and desorption process of protium (H₁¹) and deuterium (H₁²) in Pd–Cu alloys to evaluate their applicability to SDGC. In addition, separation tests of a 50%H₂–50%D₂ mixture gas were also carried out using the Pd–15at.%Cu alloy selected based on the thermodynamic properties examined in this study. This paper describes the thermodynamic properties of the Pd–Cu alloys for absorption and/or desorption processes of hydrogen isotopes and the separation behavior under various conditions.

2. Experimental

2.1. Materials

The gases used were H₂, D₂, a 50%H₂–50%D₂ mixture and Ar, whose purities were guaranteed as 99.9999%, 99.6%, 99.9%, and 99.9995%, respectively. Argon was used as carrier gas in the separation experiments.

Purities of palladium and copper used were guaranteed to be above 99.9%. The Pd–Cu alloys (4, 8, 10, 15, and 25 at.%Cu as nominal composition) were prepared from the raw materials employing an arc melting method. They will be denoted hereafter as

Pd–4Cu, –8Cu, –10Cu, –15Cu and –25Cu for simplicity. The prepared alloy ingots were annealed at 1073 K for 10 h before powdering. Their filing below 200 mesh was used to prepare a functional material for measuring absorption and desorption isotherms of H₂ and D₂. To prepare the separation column as an example, the Pd–15Cu alloy powder was mixed with pure copper powder of 100–120 mesh. This is to avoid sintering during heat treatments and to improve the thermal conduction of the powders and the gas flow dynamics in the column.

2.2. Apparatus

A conventional system was used to measure the absorption and desorption isotherms of Pd–Cu alloys in the ($\alpha + \beta$) region, where the equilibrium pressure was in the range 1×10^3 – 5.1×10^6 Pa. This system consisted of a sample tube, a standard volume, a pressure gauge, gas reservoirs and a vacuum pump. Details of the measuring system were described elsewhere [9].

A stainless steel tube of 0.3 cm in diameter and 400 cm in length was used to prepare the separation column. It was packed with 1.5 g of Pd–15Cu alloy and 120 g of pure copper powder. Details of the gas chromatographic system were described elsewhere [7]. The system consisted of a separation column, a thermostat, a sample gas inlet and a carrier gas reservoir. They were connected to each other with stainless steel tubes. This system was combined with an ultra-high vacuum system equipped with a conventional quadrupole mass spectrometer. To measure chromatograms, a part of gases eluting from the end of the separation column was introduced into the vacuum system through a separator and was analyzed with the mass spectrometer.

2.3. Procedures

Prior to measurements of absorption and desorption isotherms, the Pd–Cu alloy powders were measured using X-ray diffractometry (XRD) and X-ray fluorescence (XRF) to examine the crystallinity and chemical composition, respectively. Alloy sample (1.3 g) was weighed out to set in the sample tube and the system was evacuated below 10^{-1} Pa. Subsequently, the alloy sample was degassed at 523 K for 2 h and activated by repeating several cycles of hydrogen absorption and desorption processes at 373 K and then the system was again evacuated at 523 K. After the evacuation, the sample was cooled

down and kept at a given temperature with an electric furnace or a water bath. Absorption and desorption isotherms were measured in the temperature range of 283–453 K. The conventional constant volume method was used to obtain the isotherms of the Pd–Cu alloys.

Prior to the separation tests, pre-treatments of the separation column material were conducted to remove adsorbed water and other volatile impurities from the surfaces of both alloy and copper powders packed in a separation column. Alloy and copper powders were heated stepwise from room temperature to 423 K in a flow of argon gas, and then kept at that temperature for 1 h. The flow rate of argon gas was set to 10 cm³/min. During the heating process, about 1 mmol of pure deuterium gas was flowed for several times for final activation. Subsequently, the separation column was cooled to a given operation temperature and then a given amount of the H–D mixture gas was injected into the separation column. Chromatograms were measured by changing the column temperature in the range of 298–413 K, the carrier gas flow rate in the range of 6–14 cm³/min, and the amount of the H–D mixture gas in the range of 0.07–0.5 mmol. To obtain a new chromatogram, temperature of the separation column was raised to 423 K after each separation run, and then about 1 mmol of pure deuterium gas was injected into the separation column two times. This is a process to expel protium dissolved in the alloy during the previous separation experiment. Chromatograms with pure copper powder were also examined under similar conditions for comparison.

3. Results and discussion

X-ray diffraction analyses showed that the Pd–Cu alloy samples prepared had good crystallinity. Diffraction peaks slightly shifted to higher diffraction angle with increasing copper content, and it was seen that the lattice constants estimated from diffraction peaks linearly decreased with increasing copper composition by obeying Vegard's rule. According to XRF analyses, atomic composition of copper in the Pd–Cu alloys prepared was 3.70, 7.92, 10.1, 16.2 and 26.7% for Pd–4Cu, –8Cu, –10Cu, –15Cu and –25Cu alloy, respectively.

3.1. Absorption and desorption isotherms

Fig. 1 shows examples of absorption isotherms of H₂ and D₂ for the Pd–15Cu alloy in the temperature

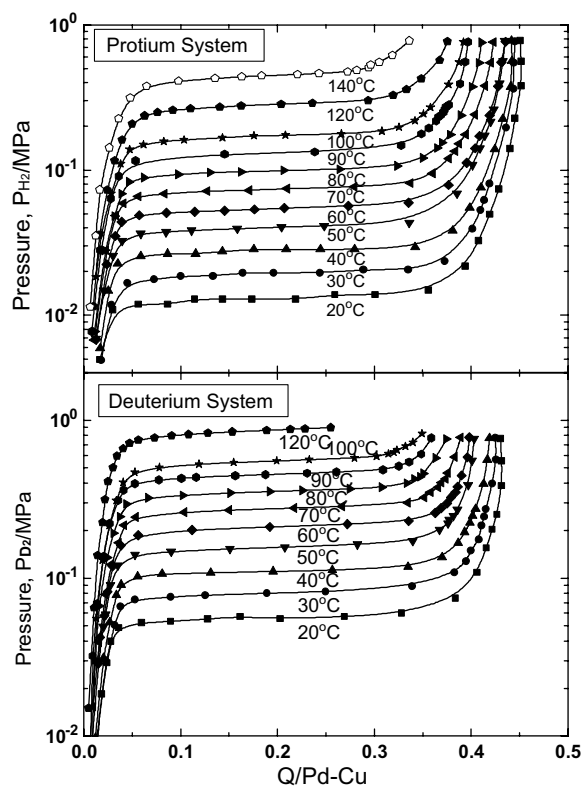


Fig. 1. Absorption isotherms of H₂ and D₂ for Pd–15Cu alloy.

range 293–413 K. The isotherms showed a steep rise of equilibrium pressure for α -phase absorption, then reached a plateau region of the $\alpha + \beta$ phase and finally rose again sharply. The equilibrium pressure increased with increasing temperature, and the length of plateau region became shorter. In addition, it was observed that the equilibrium pressure of D₂ at the given temperature and concentration was higher than that of H₂ over the whole concentration range. Difference in the equilibrium pressure was dependent on the temperature. Those basic features are also true for the other alloys, although the increase in copper content gave rise to the increase in equilibrium pressure.

Fig. 2 shows examples of desorption isotherms of H₂ and D₂ for the same alloy and temperature range as mentioned above. Equilibrium pressure of desorption isotherms became lower than that of the absorption isotherms, indicating that there is hysteresis in the isotherms. However, the equilibrium pressure of D₂ was higher than that of H₂. This indicates that the isotope effect on the equilibrium pressure is similar in a desorption process.

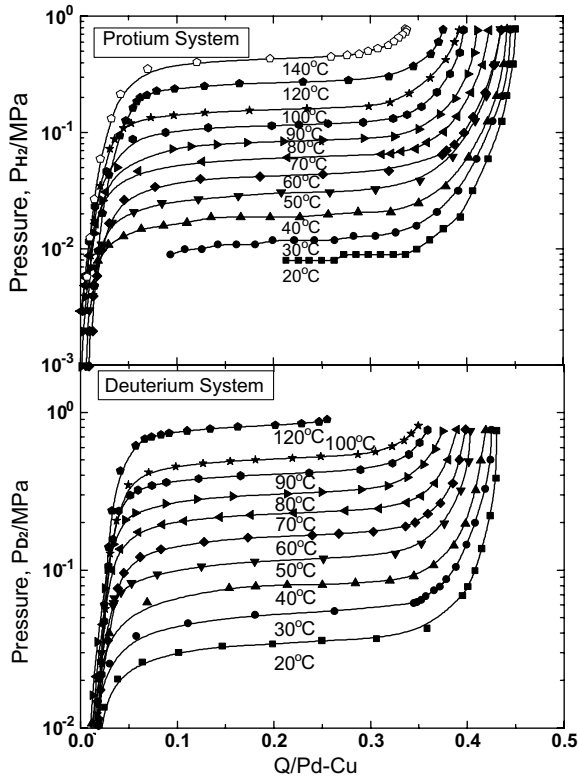


Fig. 2. Desorption isotherms of H₂ and D₂ for Pd–15Cu alloy.

3.2. Thermodynamic parameters such as ΔH^0 and ΔS^0

The temperature dependence of the pressure of a plateau region in absorption and desorption isotherms was examined for all the alloys at the hydrogen concentration of $Q/\text{Pd-Cu} = 0.2$, where Q describes H and D atoms. The van't Hoff plots of H₂ and D₂ for all the alloys resulted in good straight lines. An example of van't Hoff plots for Pd–15Cu alloy is shown in Fig. 3. The standard enthalpy and entropy changes (ΔH^0 and ΔS^0 , respectively) obtained from the van't Hoff plots were as follows: $\Delta H^0 = -29.6$ and -26.3 kJ/mol(Q_2) for H₂ and D₂ of absorption isotherms, and $\Delta H^0 = 33.9$ and 30.6 kJ/mol(Q_2) for H₂ and D₂ of desorption isotherms, respectively. The standard entropy changes were within the range of 84–96 J/K mol(Q_2) for H₂ and D₂ of both isotherms.

The standard enthalpy changes decreased with increasing ratio of copper, while the standard entropy changes in both absorption and desorption processes were almost constant in the range 80–100 J/K mol(Q_2) for all the Pd–Cu alloys. In addi-

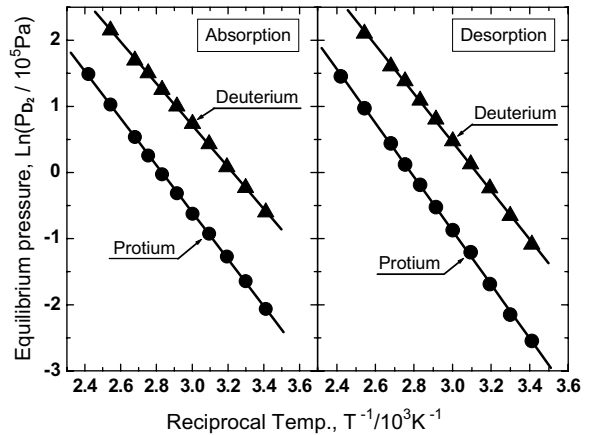


Fig. 3. Temperature dependence of equilibrium pressures of H₂ and D₂ at $Q/\text{Pd-15Cu} = 0.2$ in absorption–desorption isotherms.

tion, the standard enthalpy changes in absorption of H₂ were larger 2–4 kJ/mol(Q_2) than those of D₂, and those in desorption of H₂ were also similarly larger. Among the Pd–Cu alloys examined in this study, thermodynamic parameters for Pd–15Cu alloy were almost equivalent to those for Pd–8at.%Pt alloy: ΔH^0 for absorption of H₂ and D₂ was -29.4 and -26.4 kJ/mol(Q_2), and that for desorption of H₂ and D₂ was 30.7 and 28.3 kJ/mol(Q_2), respectively. It is known that this alloy has good performance for separation of a hydrogen isotope mixture near room temperature [10]. It is suggested, therefore, that Pd–15Cu alloy is a promising candidate for an alternative material to Pd–Pt alloys.

Equilibrium pressure in the plateau region at a given temperature can be estimated from the obtained thermodynamic parameters such as ΔH^0 and ΔS^0 . The temperature dependence of the equilibrium pressure can be described by the following equation:

$$\ln P(Q_2)_e = -(\Delta H^0 - T\Delta S^0)/RT, \quad (1)$$

where $P(Q_2)_e$ indicates the equilibrium pressure of H₂ or D₂, R the gas constant, and T the temperature. The thermodynamic isotope effect between equilibrium pressures of H₂ and D₂, i.e., the ratio of $P(D_2)_e$ to $P(H_2)_e$ is an important factor for estimating separation efficiency of the Pd–Cu alloys. The ratio can be calculated from the thermodynamic parameters obtained in this study by using Eq. (1). It was seen that the ratios are strongly dependent on temperature as well as the ratio of copper, and that the separation efficiency of hydrogen

isotopes considerably increases as the temperature of a separation column packed with Pd–Cu alloys decreases.

3.3. Separation of the H–D mixture

Fig. 4 shows examples of the chromatograms obtained using a separation column packed with pure copper powder (A) or a Pd–15Cu alloy diluted with pure copper powder (b). As for the former column, three sharp peaks corresponding to H₂, HD and D₂ simultaneously appeared, indicating that isotope effects are negligibly small. This was also true for other conditions. Appearance of the hydrogen isotope peaks started at 435 s after injection of the mixture, and this time was dependent on both the flow rate of carrier gas and the temperature. The atomic ratio of protium to deuterium evaluated from peak intensities was 0.49:0.51, which was in fairly good agreement with the atomic composition of the injected H–D mixture.

As clearly seen in the figure, no separation of the mixture can be observed for copper powder, while

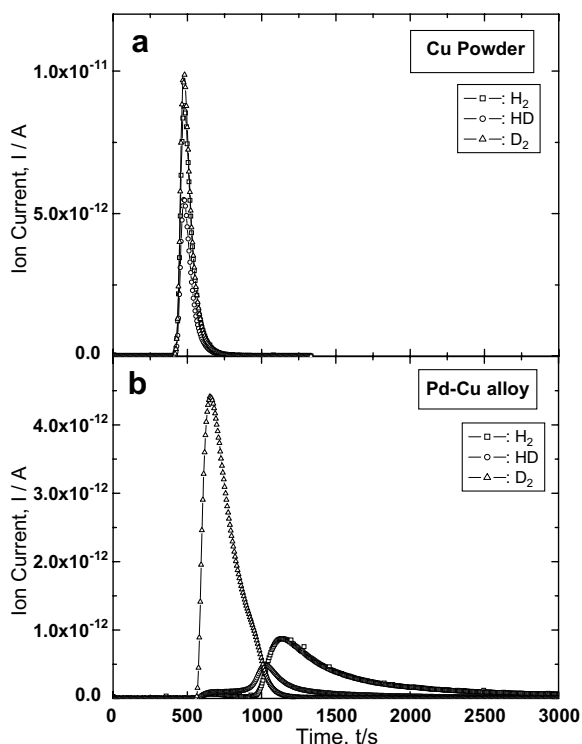


Fig. 4. Examples of chromatograms for the H–D mixture by Cu powder (a) and Pd–15Cu alloy powders (b) column temperature = 320 K, carrier gas pressure = 4 atm, flow rate = 10 cm³ min⁻¹, sample gas = 0.13 mmol.

good separation behavior can be observed for the Pd–15Cu alloy although a small amount of HD molecules appeared at the end of D₂ elution. Most of the injected mixture outflowed within 1 h. In addition, the appearance of a D₂ peak was delayed for 130 s and the width of the peaks became wider in comparison with the case of pure copper powder. These data indicate that the Pd–15Cu alloy was effectively working as an absorption–desorption material for the mixture. Furthermore, it was seen that the thermodynamic isotope effects estimated from the static experiments were fairly kept in a dynamic process.

The atomic ratio of protium to deuterium evaluated from peak intensities in Fig. 4(b) was 0.38:0.62, indicating that a part of protium injected was hard to free from the surface of Pd–15Cu alloy at 320 K. This was also suggested from the result that the total number of protium atoms eluted during a separation run decreased to 66% of the initial loading, while that of deuterium atoms agreed within experimental error. As suggested from the isotherms, the protium retention increased as the temperature of the separation column was decreased. A considerable amount of HD molecules appeared in the eluted gases by the subsequent purges at 413 K with pure deuterium, although the dissolved protium could not be entirely removed by heating. This indicates that the amount of HD molecules can be reduced by pre-purging with deuterium gas at a given temperature.

To evaluate the separation efficiency from the chromatograms, a correlation between the purity and recovery of D₂ was examined. The result is shown in Fig. 5. The purity of D₂ is shown by the atomic percent of the number of deuterium atoms in the outflowed hydrogen isotope gases in a given time. On the other hand, the recovery of D₂ is shown by the atomic percent of the number of deuterium atoms eluted in a given time to the total number of deuterium atoms. In these calculations, it was assumed that relative sensitivities of H₂, HD and D₂ molecules for the mass spectrometer are the same.

As clearly seen from Fig. 5, the deuterium purity was kept at above 97% at deuterium recovery of 90%. The purity sharply decreased, however, to around 60% when recovery increased to 100%. Such high separation efficiency agreed well with the results obtained by Pd–Pt alloys. Therefore, it was concluded that Pd–15Cu alloy is a promising material for self-developing gas chromatography

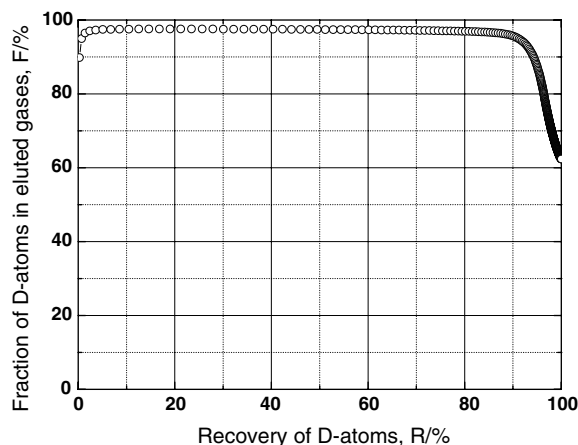


Fig. 5. Apparent separation efficiency of the H–D mixture as a function of deuterium recovery under conditions of Fig. 4(b).

to separate a mixture of hydrogen isotopes near room temperature. Further separation tests, however, are required to examine the separation efficiency for a D–T mixture.

4. Conclusions

To evaluate the applicability of Pd–Cu alloys as alternative material to Pd–Pt alloys for self-developing gas chromatography, thermodynamic properties of the absorption and desorption processes of protium and deuterium for five kinds of Pd–Cu alloys have been examined, and one of the alloys was tested for the separation of a 50% H_2 –50% D_2 mixture in the temperature range from 283 to 453 K. It was seen that the thermodynamic parameters of the Pd–15Cu alloy are similar to those of the Pd–8at.%Pt alloy. On the other hand, separa-

tion tests of the H–D mixture were conducted in the temperature range from 298 to 413 K using the Pd–15Cu alloy powder as an example. As a result, deuterium purity in the gases eluted from the separation column was kept at above 97% at deuterium recovery of 90% below 320 K. Therefore, it was concluded that the Pd–Cu alloys are promising as an alternative to Pd–Pt alloys for self-developing gas chromatography to separate a mixture of hydrogen isotopes near room temperature.

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