Research Article

Effects of Self-poisoning of Pd on the Deuterium Permeation Rate and Surface Elemental Analysis for Nuclear Transmutation

T. Hioki [*], N. Takahashi, J. Gao, A. Murase, S. Hibi and T. Motohiro

Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan

Abstract

Factors affecting the deuterium permeation rate through Pd foils at a temperature as low as 70°C have been studied using X-ray photoelectron spectroscopy. It has been demonstrated that the surface segregation of S from the interior of Pd bulk during the permeation process causes a significant lowering of permeation rate with increasing permeation time, although the concentration of S impurity in Pd bulk is probably less than 10 ppm. The surface accumulated S during D_2 permeation also gives rise to a difficulty in detecting small amount of elements on the surface of Pd after deuterium permeation treatment. For selected nuclear transmutation from Sr to Mo reported by Iwamura group, we have successfully observed Mo on the surface of Sr ion-implanted Pd after a deuterium permeation treatment, by adding a process that removes the sulfur accumulated on the surface of the Pd foil. A time-of-flight secondary ion mass spectroscopy (TOF-SIMS) study on the origin of the observed Mo will be described in a separate paper.
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Keywords: Deuterium permeation, Pd metal, Poisoning, S impurity, Transmutation, X-ray photoelectron spectroscopy

1. Introduction

Deuterium permeation through palladium has been employed as an effective tool to induce low energy nuclear phenomena in condensed matter, although the typical phenomenon of excess heat has been intensively studied using the electrochemical method.

Arata and Zhang invented a double-structure reactor (DS-reactor), in which a nano-Pd sample is loaded with deuterium by gas permeation through the wall of a palladium vessel [1]. They reported that, using the DS-reactor, the existence of cold fusion or excess heat has been verified with efficiency good enough to be utilized as a practical reactor. Modifications of this type of reactor have been made by several research groups to study quantitatively the excess heat effect using the gas loading method [2–4]. It has been suggested that the surface modification of the Pd vessel is an important factor to generate the excess heat effect [3].

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[*]E-mail: hioki@mosk.tytlabs.co.jp

Table 1. Impurities in Pd

Impurity	Concentration (ppm)
Pt	210
Ru	24
Ag	21
Rh	21
Fe	11
Si	11

Iwamura et al. have intensively used deuterium permeation through nanostructure layers of Pd and CaO, to induce the selective nuclear transmutation from Sr to Mo [5], Cs to Pr [5–7], and Sm to Ba [8]. They have claimed a high reproducibility of these nuclear transmutation phenomena, and quite a few reproduction experiments have been reported so far [9–14]. For nuclear transmutation from Cs to Pr, Iwamura et al. [6] have shown that the conversion rate is roughly proportional to the average deuterium gas permeation rate, and that about 50% of Cs atoms deposited on the multi-layer system convert to Pr atoms when the average deuterium permeation rate is about 2 sccm (Standard Cubic Centimeter per Minute). The permeation rates used by the Iwamura group seem to be considerably higher than those reported in the literature [15,16], and the conditions for permeation are not exactly the same.

The hydrogen permeation rate through Pd is known to be strongly affected by surface contamination [17]. In many past studies, because of the practical use of hydrogen purification, hydrogen permeation measurements have largely been conducted at high temperatures greater than a few hundred °C, at which point the effect of surface contamination is comparatively small [18]. Nuclear transmutation experiments by the Iwamura group have been performed at a temperature as low as 70°C.

In the present study, the effects of surface contamination on the deuterium permeation rate through Pd foils at 70°C have been examined using X-ray photoelectron spectroscopy (XPS). It has been demonstrated that the surface segregation of sulfur during the deuterium permeation is the main cause of the observed decrease in the permeation rate with increasing permeation time. A pre-heat treatment to suppress the degradation of the permeation rate is presented. The effects of the surface-segregated sulfur on surface elemental analysis for nuclear transmutation is discussed and a procedure to avoid the effects of sulfur on elemental analysis is also demonstrated for nuclear transmutation from Sr to Mo.

2. Experimental

2.1. Sample preparation

Foil samples of Pd with a purity of 99.97% and thickness of 50 μm were obtained from the Nilaco Corporation. The impurities and their concentrations determined by the supplier are shown in Table 1.

Table 2. Heat treatments before deuterium permeation.

Sample number	Vacuum annealing	Air annealing
No. 1	No	300°C × 10 min
No. 2	No	500°C × 10 min
No. 3	No	1000°C × 10 min
No. 4	No	950°C × 120 min
No. 5	950°C × 120 min	No
No. 6	950°C × 120 min	1000°C × 10 min
No. 7 ([88]Sr ion implanted)	950°C × 300 min	600°C × 10 min

Table 3.   Impurities in D_2 gas.

Impurity gas	Concentration (ppm)
Oxygen	< 5
Nitrogen	< 5
Carbon monoxide	< 1
Carbon dioxide	< 1
Total hydrocarbon	< 1
Water	< 5

The as-received foils were ultrasonically cleaned in alcohol and dried. They were then heat-treated before deuterium permeation as shown in Table 2.

2.2. Deuterium permeation

The deuterium permeation system was the same as that reported by us previously [13]. The upstream side was filled with deuterium at 100–300 kPa. The deuterium gas with purity more than 99.995% was obtained from Takachiho Chemical Industrial Co. Ltd. The impurities and their concentrations in the gas determined by the supplier are shown in Table 3. The concentrations were less than 5 ppm for oxygen, nitrogen and water, and less than 1ppm for others.

The downstream side was evacuated with a dry pump and a turbo molecular pump. The upstream side was connected with a reservoir tank of 1.0 L. The deuterium flow rate was determined from the reduction of the pressure in the reservoir tank. A metal O-ring was used for the vacuum seal.

2.3. Surface elemental analysis

XPS was used to analyze the surface layer elements of the samples. The instrument was a Quantera SXM (ULVAC-PHI INC., 20 kV, 100 W) with a monochromatic Al(Kα) X-ray source (1.438 keV). The size of the incident X-ray beam was $100 \times 1500 \ \mu m^2$.
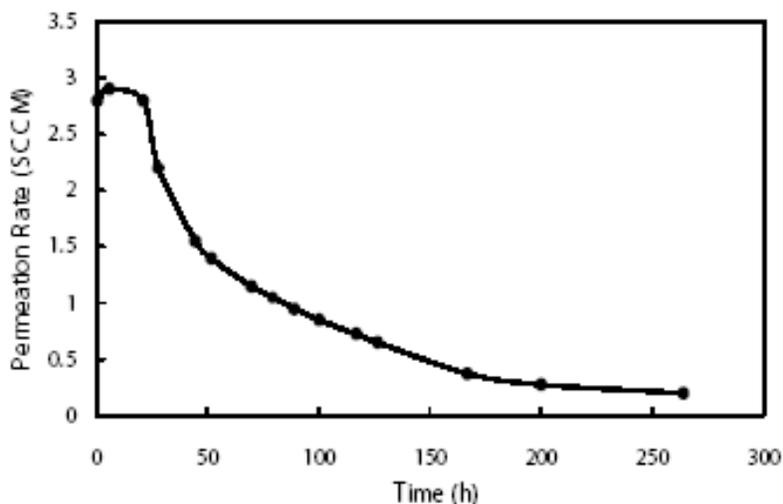
Figure 1.   Variation of permeation rate with time for the Pd foil pre-heat treated in air at 300°C for 10 min (No. 1 sample).
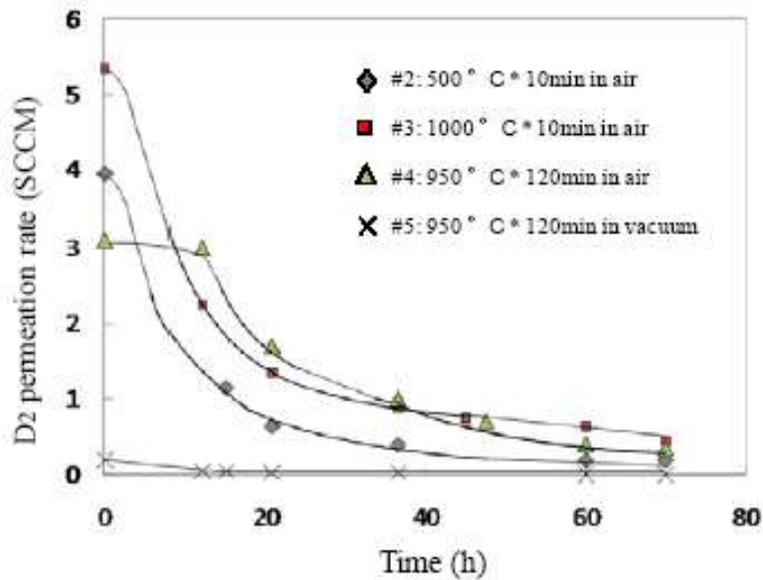
Figure 2. D_2 permeation rate at 70°C as a function of time for foils pre-heat treated in air or in vacuum at various temperatures and periods. The solid lines simply connect the experimental points smoothly.

3. Results and Discussion

3.1. Variation of deuterium permeation rate with time

An example of the deuterium permeation rate as a function of time is shown in Fig. 1. As a pre-heat treatment, this sample (No. 1) was annealed at 300°C in air for 10 min. The pressure of the up stream side was 275 kPa and the temperature of the sample was 70°C.

As seen in the figure, the permeation rate is high at the initial stage of permeation, but it decreases gradually with time. The initial value of the permeation rate and the degree of its decrease with time varied from sample to sample when as-received foils without any pre-heat treatment were used. It has been reported by Yamakawa et al. that the surface impurities that suppress hydrogen permeation through Pd are carbon atoms which may come from hydrocarbons [19]. They have also demonstrated that the contaminants are quickly removed from the Pd surface by heat treatment around 200–300°C in air [18]. The heat treatment of No. 1 sample was conducted following Yamakawa method. As seen in Fig. 1, the initial permeation rate is higher than 2 sccm which is a value expected to induce nuclear transmutation at a high efficiency of ∼50% [6]. The initial high permeation rate is considered to result from the pre-heat treatment removal of hydrocarbons adsorbed on the Pd surface. However, the permeation rate decreases gradually with time and finally reaches a value of about 1/10 of the initial value.

In order to investigate the mechanism of the decrease in the permeation rate with increasing permeation time, Pd foils were pre-heat treated in air or in vacuum at different temperatures and the surface elements were examined with XPS for the foils before and after D2 permeation. Figure 2 shows the permeation rate as a function of permeation time for foil Nos. 2–5. The pressure of the upper stream side was 0.275 MPa, and the sample temperature was 70°C.
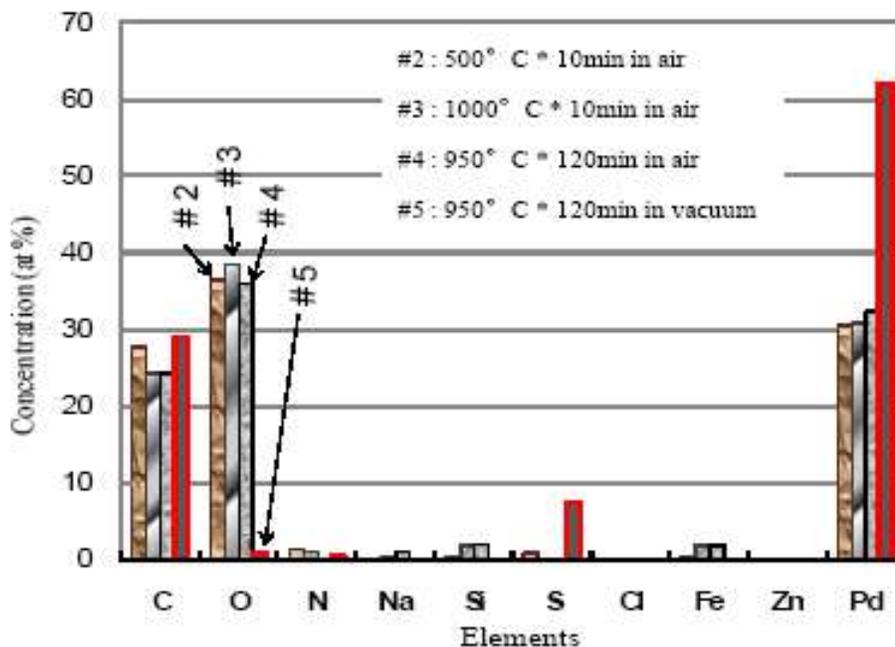
Figure 3.   Elemental concentration on the surface layer of Pd after heat treatments.

It is seen in Fig. 2 that: (i) all the foils heat treated in air show high initial permeation rates larger than 2 sccm, while the foil heat treated in vacuum shows almost no permeation from the beginning of permeation. (ii) The permeation rates of the foils with high initial rates decrease with increasing permeation time and reaches a value less than ∼0.5 sccm at a permeation time of 70 h.

3.2. XPS analysis on Pd surface

Figure 3 compares the concentrations of the elements observed on the surface of Pd foils just after the various heat treatments using XPS. The main elements on the surface layer shallower than about ∼1 nm are Pd, O and C. As impurities, N, Na, Si, S, Cl, Fe and Zn are detected. From Fig. 3, it is seen that the foils annealed in air have high concentrations of O and comparatively lower concentrations of Pd, indicating that the surface layer of Pd is oxidized with the annealing in air. It is noted that the concentrations of C are similar and relatively high for all the samples. Therefore, the existence of C is not the reason why only the vacuum annealed sample shows an extremely low initial permeation rate. What is most remarkable in Fig. 3 is that the concentration of S is significantly high for only the foil sample annealed in vacuum. The concentration of S on the surface reaches a value of 7.5 at.% for the vacuum annealed sample, while it is less than ∼1 at.% for the air annealed samples. Therefore, it is suggested that a surface concentration of S as high as ∼10 at.% results in the extremely low permeation rate for the vacuum annealed sample, as reported by us previously [20]. Sulfur has been known as a poisoning element for the catalytic activities of Pd, i.e., it works to prevent dissociative adsorption of hydrogen molecules on the Pd surface.

Figure 4 compares the XPS spectra around S 2p and Pd 3d between the samples annealed in air and in vacuum. The intensity of the S 2p peak for the vacuum annealed sample is much stronger than those of the samples annealed in
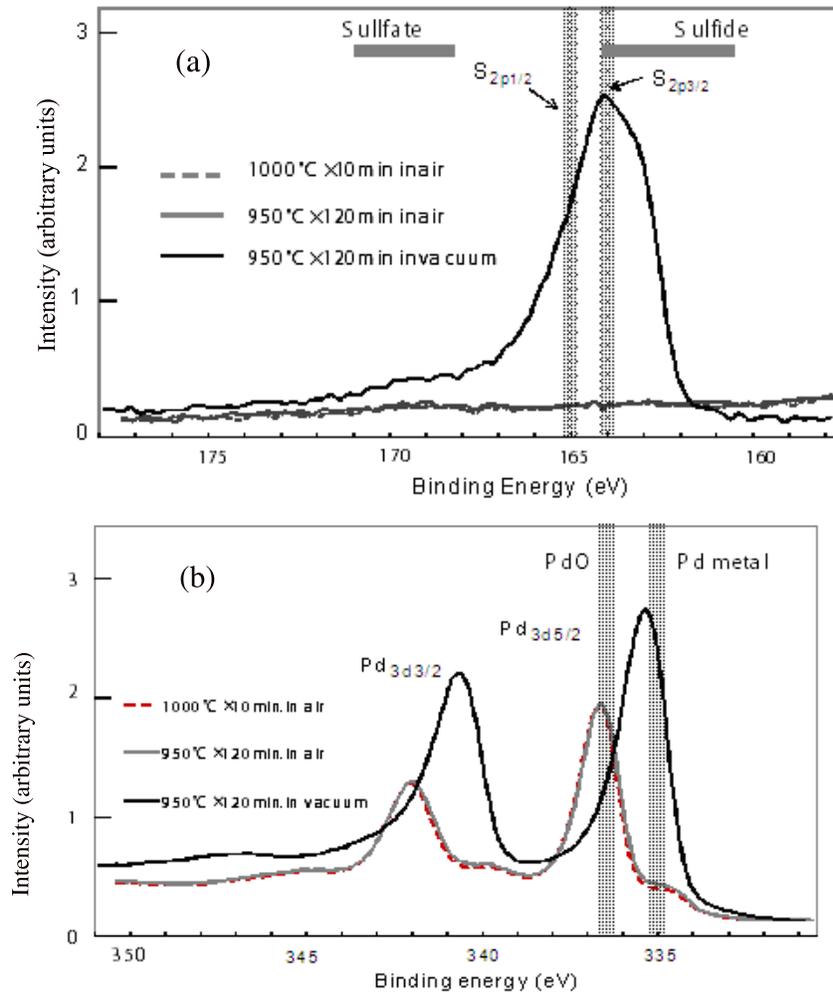
Figure 4. XPS spectra (a) around S 2p and (b) around Pd 3d for foil samples annealed in air (No. 3, No. 4) and in vacuum (No. 5).

air. The observed high concentration of S is considered to result from the surface segregation of S during annealing at 950°C in vacuum. The sulfur probably exists in the Pd bulk as an impurity with a concentration of ∼10 ppm or less. Sulfur does not form a solid solution with Pd even at a concentration close to zero [21]. Therefore, even a very small amount of S impurity in Pd bulk is considered to concentrate on the surface of Pd up to ∼10 at.% with annealing in vacuum at the temperature of 950°C. It is also suggested in Fig. 4 (a) that the chemical form of S is a sulfide.

From the Pd 3d spectra in Fig. 4 (b), it is clearly seen that the surface layer is metallic for the foil annealed in vacuum, while it is oxidized for the foils annealed in air. Since the foils annealed in air have high initial permeation rates as shown in Fig. 2, it is apparent that the formation of PdO in the surface layer of Pd hardly affected the deuterium permeation rate of Pd.

Figure 5 compares the changes in the concentrations of surface elements with the deuterium permeation
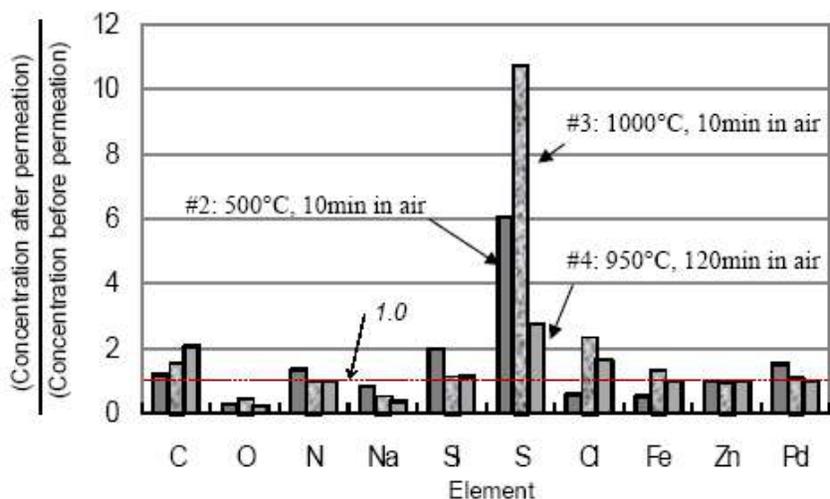
Figure 5.   The ratio of the elemental concentration after D_2 permeation to that before D_2 permeation.

at 70°C for a period of 70 h for the foil samples annealed in air.   From this figure, it is seen that the only element which is remarkably increased with the deuterium permeation is S, while the only element which is remarkably decreased is O. The observed increase in the surface concentration of S suggests that S impurities in the Pd bulk migrates and concentrates onto the surface during deuterium permeation at a temperature as low as 70°C. Since all the foils annealed in air show high initial permeation rates as shown in Fig. 2, it is strongly suggested that the decrease in the permeation rate with increasing permeation time is due to surface segregation of S during deuterium permeation. The remarkable decrease of O after the deuterium permeation indicates that the oxidized surface layer of Pd is reduced by deuterium permeation at 70°C.

Figure 6 compares the XPS spectra around Pd 3d before and after the deuterium permeation. It is clearly seen that the surface layer is initially PdO while it is metallic after the deuterium permeation at a temperature as low as 70°C.

3.3. Improving the degradation of permeation rate

From the results shown above, it has been demonstrated that surface segregation of S strongly affects deuterium permeation through the Pd foil. The surface segregation of S is caused either (i) by annealing in vacuum at a temperature as high as ∼950 °C or (ii) by deuterium permeation for a long time at a temperature as low as ∼70°C. It has also been indicated that the surface concentration of S is small for Pd foils annealed in air at a temperature in the range of 500–1000°C. The surface sulfur seems to evaporate as SOx. As a result, the initial permeation rate of the foils pre-heat treated in air is higher than 2 sccm. Therefore, in order to keep a high permeation rate for a long period of permeation, it is required to suppress the surface segregation of S impurity in Pd or to decrease the concentration of S impurity in Pd.

As a trial to decrease S impurity in Pd bulk, we have tried to intentionally segregate S on to the surface by annealing in vacuum at 950°C for a long time (e.g., 2 h or 5 h), followed by annealing at 1000°C in air for a short time (10 min) to burn the S concentrated onto the surface. Figure 7 compares the permeation behavior for the sample (No. 6)

heat treated with a combination of vacuum-annealing and air- annealing to that for the sample (No. 3) heat treated only with an air-annealing.

It is noted that sample No. 6 maintained a high permeation rate larger than 2 sccm even at a permeation time of 45 h, while the permeation rate of sample No. 3 becomes lower than 2 sccm at a permeation time of 12 h. Figure 8 shows the XPS spectra around S2p for sample No. 6 after the vacuum annealing at 950°C and after the subsequent air annealing at 1000°C. It is confirmed that the intensity of S 2p is very strong just after the vacuum annealing but it becomes almost zero after the subsequent air annealing.

It may be worth mentioning that the S concentrated on the surface during deuterium permeation comes from the interior of the Pd bulk (self-poisoning) and not from the environment, e.g., the deuterium gas. The deuterium gas used in this study is a high purity one and it is not contaminated by any gaseous species containing S as shown in Table 3. If the deuterium gas used in this study contained a very small undetectable amount of S and accumulated on the Pd surface during deuterium permeation, the amount of the accumulated S would have been larger for a foil showing a higher permeation rate. For example, in Fig. 7, the total amount of D_2 passing through the foil of sample No. 6 is about 13 L, while that of sample No. 3 is 5.5 L. Therefore, the amount of S deposited on the Pd surface of the upper stream side of sample No. 6 should be larger by 2.4 times than that of sample No. 3, and the decrease in the permeation rate for sample No. 6 should have been larger than that for sample No. 3. That effect is contrary to the experimental result, as shown in Fig. 7.

3.4. Influence of surface segregated S on surface elemental analysis

As demonstrated by the Iwamura group, XPS is a useful tool for studying nuclear transmutation [5]. This analysis technique has also been employed in the reproduction experiments by a couple of research groups [12,13]. However, as reported by us previously [13] in examining the transmutation from Sr to Mo, it is difficult to detect Mo clearly by XPS, if S atoms exist on the surface of Pd. This is because the peak energy of S 2s comes close to that of Mo 3d and the spectra are composed of a few peaks with different intensities. In Fig. 9, an example of such experimental spectrum (the curve: raw data) obtained for sample No. 7 is shown.
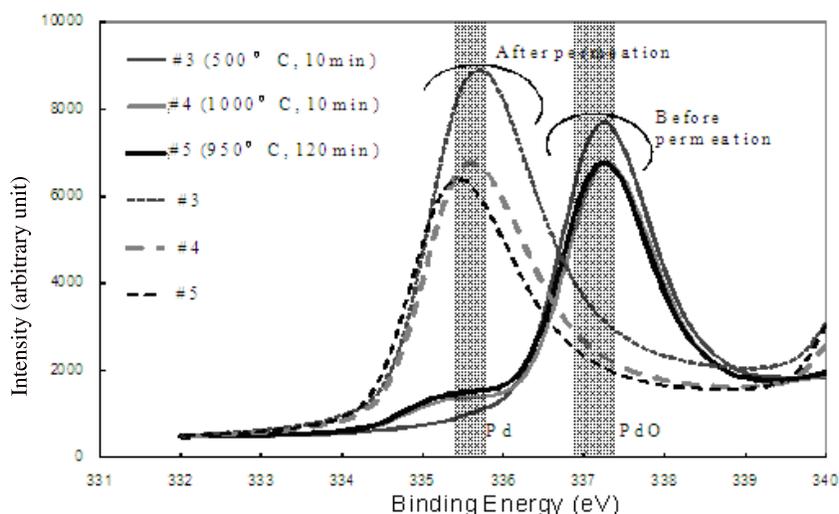
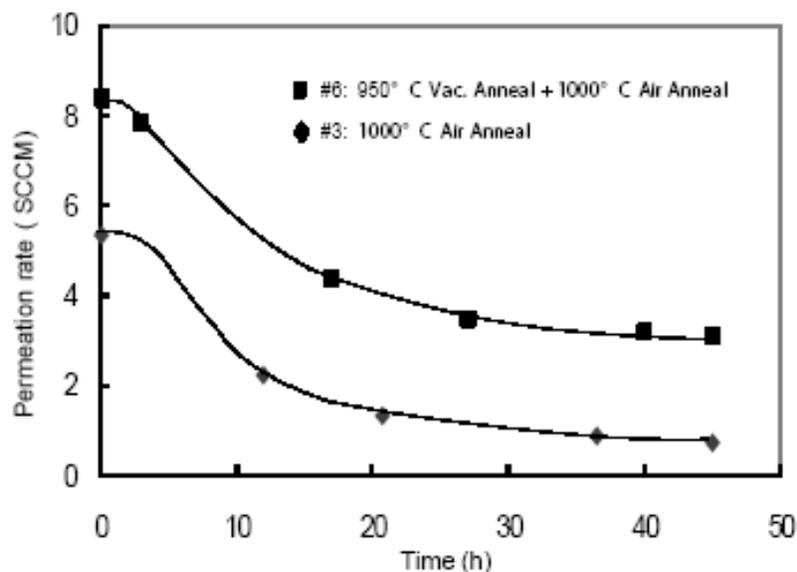**Figure 6.** XPS spectra around Pd 3d5/2 before and after deuterium permeation for samples pre-heat treated in air.

Figure 7. Comparison of the variations of permeation rate with time for samples Nos. 6 and 3.

This sample was implanted with [88]Sr ions and subsequently treated with D_2 permeation at 70°C for ~11 days. As seen in Fig. 9, the experimental spectrum apparently shows two large peaks with an energy difference of ~7 eV which is different from the energy difference between M d3d5/2 and Mo 3d3/2 (3.13 eV). The two large peaks are considered to arise from compounds of sulfur. Actually, as shown in Fig. 10, the experimental spectrum around S 2p for the same sample shows a similar line shape to the raw data in Fig. 9. The experimental spectrum in Fig. 10 is assumed to be composed of four sulfuric compounds: a sulfide, a sulfate, and two other sulfuric compounds. As seen in Fig. 10, the experimental spectrum for S 2p can be well reproduced assuming these four compounds.

Therefore, the experimental spectrum around Mo 3d should also be well reproduced if the spectrum is only composed of S 2s peaks of the four sulfuric compounds. However, as seen in Fig. 9, a small difference is observed between the raw data and the total curve composed of the four S 2s lines calculated from the simulated results in Fig. 10.

This difference may mean that Mo atoms exist on the surface after the permeation treatment. However, it is difficult to definitely conclude the existence of Mo from this analysis. This difficulty arises from S which is segregated onto the surface during the deuterium permeation for a long period.

### 3.5. Removing S after the deuterium permeation process

As discussed above (Section 3.3), the sulfur concentrated on the surface of Pd can be removed by annealing in air. Therefore, if the sample after deuterium permeation is again heat treated in air at a temperature of 500–1000 °C for a short time, the sulfur on the surface may be removed and the elements buried under the over layer of sulfuric compounds may be detected. As shown in Fig. 11, this procedure has proven useful for detecting Mo which emerges on the surface of Sr-implanted Pd after the deuterium permeation process.

The energy difference between the two peaks in Fig. 11(c) is 3.13 eV and the intensity ratio of the two peaks is close to 3:2. Therefore, these peaks definitely indicate that Mo atoms are observed on the surface of Pd after the deuterium permeation process.
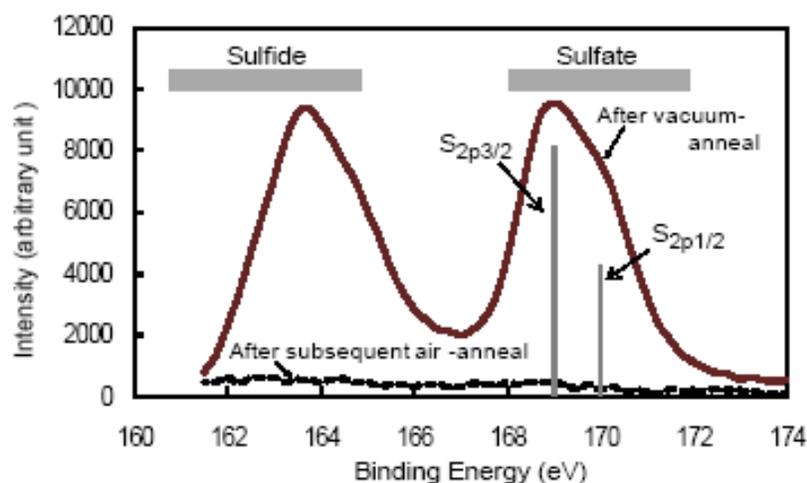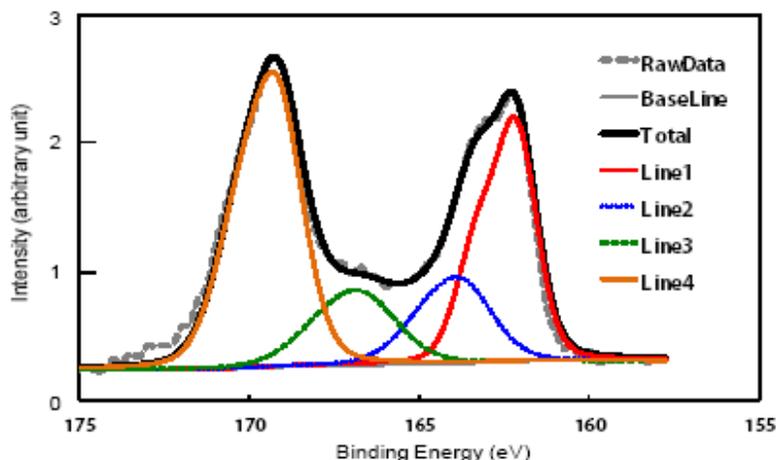
Figure 8. XPS spectra around S 2p for the sample (No. 6) just after annealing in vacuum at 950°C for 2 h and after subsequent annealing in air at1000°C for 10 min.

Similarly, as reported by us previously, Mo has also been detected after deuterium permeation for Pd foils with multi-layers of Pd/CaO being deposited with [88]Sr by ion implantation [14]. Whether the observed Mo is a nuclear transmuted one or not is an important problem to be carefully examined as a next step. As reported by Iwamura et al., to study the isotopic abundance ratio of the observed Mo seems to be useful to identify the origin of the Mo. The TOF-SIMS technique is a powerful tool to measure the isotopic abundance ratio for an atom. We have applied the technique
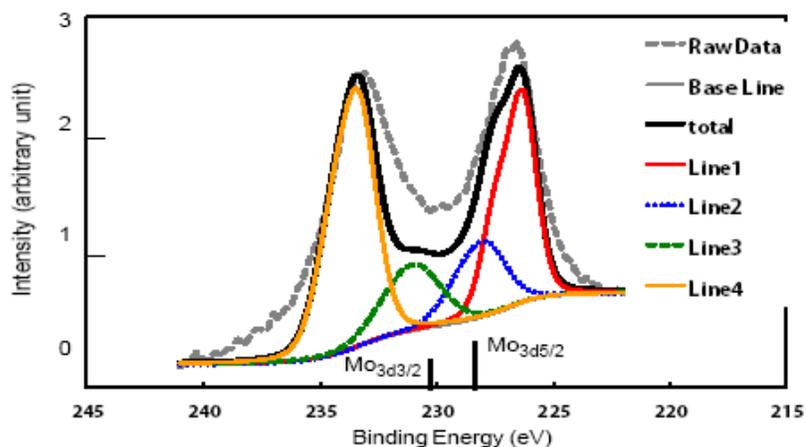
Figure 9. XPS spectrum around Mo 3d for sample No. 7. Raw Data: experimental spectrum; Line 1: S 2s from a sulfide; Line 2: S 2s from a sulfur compound: Line 3: S 2s from a sulfur compound; Line 4: S 2s from a sulfate.

Figure 10. XPS spectrum around S 2p for sample No. 7. Raw Data: experimental spectrum; Line 1: S 2p from a sulfide; Line 2: S 2p from a sulfur compound: Line 3: S 2p from a sulfur compound; Line 4: S 2p from a sulfate. The total line shape composed of the four S 2p lines corresponding to the assumed four sulfuric compounds well simulates the raw data.

to measure the isotopic abundance ratio of the Mo atoms which emerge in the surface layer of Sr ion-implanted Pd/CaO multi-layer system after deuterium permeation [14]. A more detailed TOF-SIMS study on the origin of the emerged Mo will be published in a separate paper [22].

4. Conclusions

Palladium is often contaminated with a small amount of S. It has been demonstrated that:

  (i) S in the Pd bulk segregates on the surface with annealing in vacuum at a high temperature around 950°C.
 (ii) The deuterium permeation rate at 70°C is drastically lowered if the surface concentration of S is ∼10 at.%.
(iii) The surface segregation of S also occurs with the deuterium permeation process at a temperature as low as 70°C.
 (iv) The lowering of the deuterium permeation rate with increasing permeation time is due to the surface accumulation of S coming from the interior of Pd bulk (self-poisoning).
  (v) To maintain a high permeation rate for an extended period of time, pre-heat treatment of Pd in vacuum at a high temperature around 950°C followed by annealing in air at 500–1000°C has been proved effective.
 (vi) The sulfur accumulated on the surface during deuterium permeation covers the surface of Pd and makes it difficult to detect surface elements of small concentrations with surface analytical methods like XPS.
(vii) By removing the surface-accumulated S by annealing in air at a temperature of 600–1000°C, Mo has been detected clearly on the surface of Sr-ion implanted Pd foils after deuterium permeation treatments.
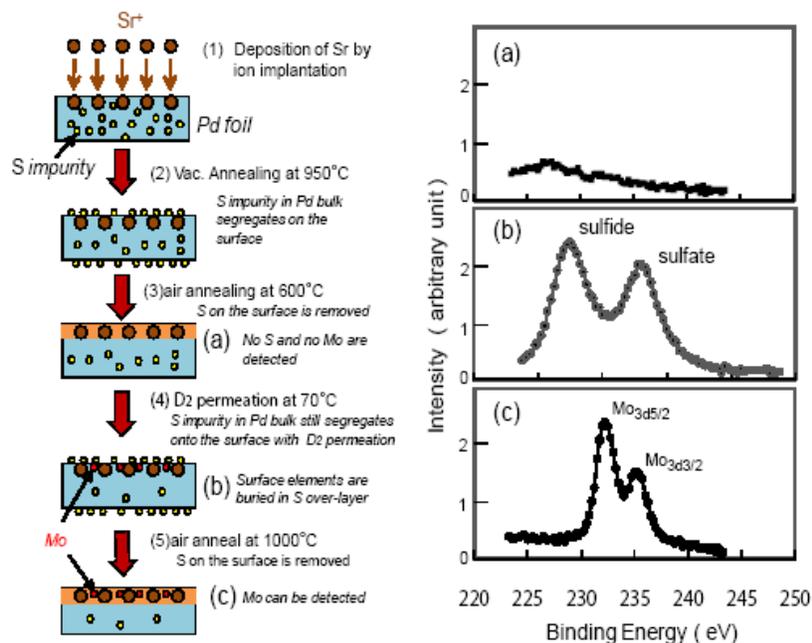
Figure 11. Schematics of the processes to detect Mo on the surface of Sr-ion implanted Pd after the deuterium permeation process, and XPS spectra around Mo 3d, (a) before D_2 permeation, (b) just after D_2 permeation treatment, (c) after adding an air-annealing at $1000°C$ to the D_2 permeated sample.

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