# OBSERVATION OF LOW ENERGY NUCLEAR REACTIONS INDUCED BY D<sub>2</sub> GAS PERMEATION THROUGH PD COMPLEXES

Yasuhiro IWAMURA\*, Takehiko ITOH, Mitsuru SAKANO and Satoshi SAKAI

Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd. 1-8-1, Sachiura, Kanazawa-ku, Yokohama, 236-8515, Japan \*TAKASAGO Research & Development Center, Mitsubishi Heavy Industries, Ltd, 2-1-1 Shinhama Arai-cho, Takasago, Hyogo, 676-8686, Japan

#### ABSTRACT

Observation of low energy nuclear reactions induced by  $D_2$  gas permeation through Pd complexes, which consist of a thin Pd layer, alternating CaO and Pd layers and bulk Pd, is described. The Pd complex was located in a vacuum chamber and the elemental analysis was performed using an X-ray photoelectron spectroscopy (XPS) apparatus mounted on the chamber. When Cs was added on the surface of a Pd complex, Pr emerged on the surface while Cs decreased after the Pd complex was subjected to  $D_2$  gas permeation at 343K and 1atm for about one week. In the case of adding Sr on the surface, Mo emerged on the surface while the added Sr decreased after  $D_2$  permeation for about two weeks. All the phenomena were reproduced qualitatively. The isotopic composition of the detected Mo exhibited characteristics indicating an isotopic abundance of Sr rather than the natural abundance of Mo

#### 1. INTRODUCTION

We have been investigating the low energy nuclear reactions observed in the palladium-deuterium system. Our experimental results thus far have led to the assumption that necessary conditions which give rise to the phenomena should satisfy the following criteria  $^{1}$ : (i) existence of a low work function material, typically CaO, near the Pd surface; (ii) sufficient diffusion flux of deuterium, (iii) sufficient D on the Pd surface. To check the validity of these assumptions, we have established an experimental method characterized by "permeation of D through Pd complex" as shown in Fig. 1(a).  $D_2$  gas molecules cause a dissociative chemisorption on the  $D_2$  gas side of the Pd complex, and then D atoms diffuse toward the vacuum side, where they combine and are released as  $D_2$  gas. We assume that the above necessary conditions are satisfied on the near surface of  $D_2$  gas side of the Pd complex.

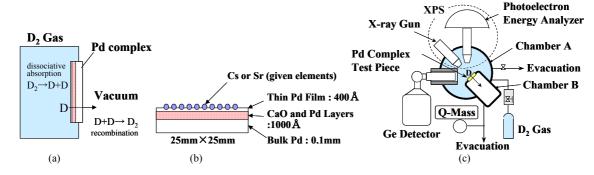


Fig. 1 Schematic of the present method: (a)  $D_2$  gas permeation through the Pd complex, (b) Structure of Pd complex deposited with Cs or Sr on the surface, (c) Experimental apparatus.

The Pd complex is composed of a Pd thin film, alternating CaO and Pd layers and bulk Pd as shown in Fig. 1(b). This composition was determined based on condition (i) above since the work function of CaO is relatively low  $(1.6 \text{ eV}-1.86 \text{ eV})^{2}$ . We assume that  $D_2$  gas permeation satisfies the conditions (ii) and (iii) above. Although the definite physical implications of the above conditions are unclear at present, it

is a fact that the experimental observations described in this paper are consistent with the assumptions.

After forming a Pd complex, Cs or Sr was deposited on the surface of the thin Pd layer as shown in Fig.1(b). Permeation of deuterium through the Pd complex is attained by exposing one side of the Pd complex to  $D_2$  gas while maintaining the other side under vacuum conditions. We perform elemental analyses of the given elements after  $D_2$  gas permeation in a vacuum chamber. Our experimental method described above is superior in that it discriminates the products from contamination because we analyze the products in vacuum during the experiments without moving the products.

### 2. EXPERIMENTAL

The Pd complex is composed of a Pd thin film, alternating CaO and Pd layers and bulk Pd. A Pd plate (with purity up to 99.99%; Tanaka Kikinzoku Kogyo K.K.) was washed with acetone and annealed in vacuum (<10<sup>-7</sup> torr) at 900°C for 10 h. It was then cooled to room temperature in furnace and washed with D-based aqua regia (with purity up to 99.9%) to remove impurities on the surface of the Pd plate. The surface of the plate was covered by layers of CaO and Pd (1000 Å). Then a 400-Å-thick Pd layer was sputtered on the surface of the CaO and Pd layers. These processes are performed by Ar ion beam sputtering. Films deposited by ion beam sputtering exhibit the property of low contamination due to the low background pressure that leads to reduced gas incorporation.

After forming a Pd complex, Cs or Sr was deposited on the surface of the thin Pd layer. Cs or Sr atom was deposited by applying an electric field to 1mM CsNO<sub>3</sub> (with purity up to 99.9%) or SrOD (with purity up to 99%) solution. A Pt wire (with purity up to 99.9%) was utilized as a counter-electrode. A 1V negative voltage was applied to the Pd complex for 10 sec.

Figure 1(c) shows a schematic of the experimental apparatus. One advantage of this newly developed apparatus is that we can analyze the surface of a Pd complex sample by X-ray photoelectron spectroscopy (XPS) without removing it from the vacuum chamber, thereby preventing contamination of the test sample. Another advantage is that we can detect the time dependence of the elements on the Pd complex surface. Repeating  $D_2$  gas permeation and XPS analyses, we can obtain information on time variation of the detected elements.

The apparatus consists of two chambers, A and B, an X-ray gun, an electrostatic analyzer for XPS, a mass spectrometer and a Ge semiconductor detector. The mass spectrometer is installed for analyzing the  $D_2$  gas permeating the Pd complex. The Ge semiconductor detector is mounted for the detection of gamma rays. The X-ray gun is non-monochro type and Al-K  $\alpha$  is utilized. The power is 200 W, voltage is 10 kV and current is 20 mA. The electrostatic analyzer is equipped with a five-stage electrostatic lens and the pass energy is 100 eV. The X-ray gun and the electrostatic analyzer were made in our laboratory and the energy was calibrated using Au.

One chamber (Chamber A) is filled with  $D_2$  gas, and the other chamber (Chamber B) is evacuated by a turbo-molecular pump. These two chambers are divided by a Pd complex test piece.  $D_2$  gas is supplied at 1 atm on the Pd film side of the test piece and dissolves in D atoms at the surface. The D atoms intrude into the Pd thin film and diffuse through the Pd complex and then reach the surface of the bulk side, where they combine and are released as  $D_2$  molecules.

The experimental procedure is as follows. The vacuum chambers are baked sufficiently before the experiments. A Pd complex test piece with added Cs or Sr is mounted on a flange in an air environment and then introduced into the vacuum chamber. Step 1: Both of the vacuum chambers are evacuated by a turbo-molecular pump and the test piece is heated to  $70^{\circ}$ C. The ultimate pressure in the vacuum chamber was about  $3\times10^{-8}$  Torr. Step 2: The surface of the test piece is analyzed by XPS to confirm that no other elements on the surface of the Pd test piece are detected except the given element (Cs or Sr), Pd and C. As is widely recognized in the field of surface science, a small amount of C is usually detected on a metal surface even in the vacuum chamber. Step 3: Chamber A is filled with  $D_2$  gas up to 1 atm so that deuterium atoms permeate from this side to Chamber B behind the test piece. Step 4: After a certain period (from two days to one week) of deuterium diffusion through the Pd complex test piece, the  $D_2$  is evacuated from Chamber A and the surface of the Pd test piece is analyzed by XPS in the chamber. New elements that did not exist on the test piece at the beginning of the experiment can be detected. Usually this process is repeated a few times to observe the time dependence of the given or newly generated elements. Step 5: The heater is turned off and all the chambers are filled with 1 atm  $N_2$  gas.

The test piece is removed from the chamber and its surface is analyzed by secondary ion mass spectrometry (SIMS). In this study, we analyzed the Pd complex test piece after an experiment using SIMS to investigate the isotopic compositions of the detected elements. Only surface isotopic compositions were analyzed; we did not measure their depth profiles. SIMS analysis was performed by Probion Analysis, Inc. in France using the Physical Electronics 6600

#### 3. RESULTS

Experimental results are shown in Figs. 2-6. During these experiments, we did not observe statistically significant gamma ray emission and gaseous products exceeding the detection limits (about 1ppm) of the mass spectrometer.

Experimental results obtained for test pieces deposited with Cs are shown in Fig. 2. Figure 2(a) shows the time dependence of the number of Cs and Pr atoms. Results for two runs are shown as examples. No Pr was detected at the beginning of the experiments. The number of Cs atoms decreased while that of Pr atoms increased with increasing experimental time. The amount of deuterium permeation was proportional to the elapsed time. At 120 h, the number of Pr atoms exceeded that of Cs atoms as shown in Fig. 2(a). Similar results were obtained in four other runs, although the initial number of Cs atoms was smaller than that in the Fig. 2(a). The reproducibility of these experiments is thought to be good.

The time variations in XPS spectra for the first run are shown in Figs. 2(b)-2(d) for Cs, Pr and Pd, respectively. All the elements are identified by two binding energy peaks <sup>3)</sup> of 3d<sub>5/2</sub> and 3d<sub>3/2</sub>. It is evident that the two Cs peaks decrease corresponding to the increase in Pr peaks. On the other hand, XPS peaks for Pd do not change. This demonstrates that there is no problem with the stability of the obtained XPS spectra.

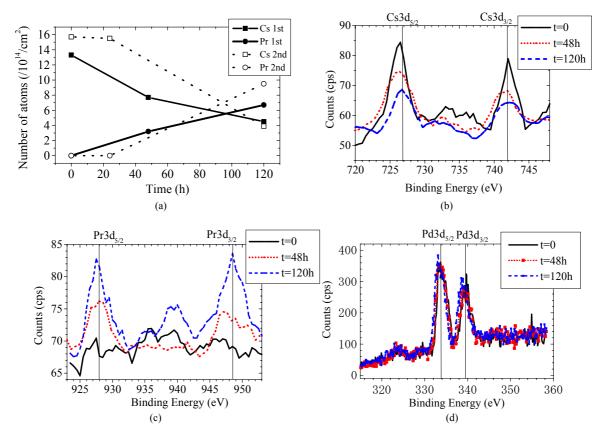


Fig. 2 Experimental results obtained by  $D_2$  gas permeation through Pd complex (Pd/CaO/Pd) deposited with Cs: (a) Time variation in number of Cs and Pr atoms, (b) XPS spectrum of Cs for experiment run #1, (c) XPS spectrum of Pd for experiment run #1.

In contrast, bulk Pd and the thin Pd film test piece with Cs deposition, which does not belong to a Pd complex, do not exhibit anomalous phenomena. All experimental conditions were the same as those of the Pd complex (Pd/CaO/Pd) experiments except for the formation of CaO and Pd layers. The annealing, etching by aqua regia, formation of a 400-Å-thick Pd thin film and deposition of Cs were performed in the same manner. Time variation of the Cs atom number, XPS spectra for Cs and Pr are given in Fig. 3(a). It is clear Cs did not change and Pr never appeared. This experiment indicates that a CaO and Pd complex layer is essential for observing the decrease in Cs and the increase in Pr.

As a comparative study, we used  $H_2$  gas instead of  $D_2$  gas. The experimental results are shown in Fig. 3(b). In this case, only the gas is different; the other experimental conditions are all the same as Fig. 2. We also find that Cs did not change and Pr never appeared. This suggests that deuterium is a necessary factor for observing the anomalous behavior of Cs and Pr.

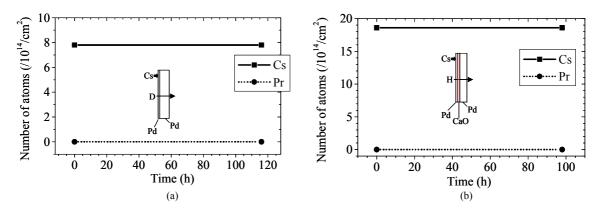


Fig. 3 Results of comparative experiments using Cs: (a) Experimental results obtained by  $D_2$  gas permeation through thin film and bulk Pd with added Cs, (b) Experimental results obtained by  $H_2$  gas permeation through Pd complex (Pd/CaO/Pd) with added Cs

The experimental results for Pd complex test pieces with added Sr are shown in Fig. 4. We observed that Sr decreased while Mo increased with increasing experimental time. Figure 4(a) shows the time variation of the number of Sr and Mo atoms. Experiments were performed three times and all the data are plotted in Fig. 4. At the beginning of the experiments, no Mo atoms were detected, however, Mo atoms increased gradually while Sr decreased correspondingly. It should be noted that runs for Sr are required to be longer to convert Sr to Mo than in the case of Cs to Pr. As can be seen in Fig. 4, qualitative reproducibility of is good. The time variations of XPS spectra for the first run are shown in Figs. 4(b)-7(d) for Sr, Mo and Pd, respectively. All the elements are identified by two binding energy peaks. The peaks of Pd did not change as shown in Fig.4.

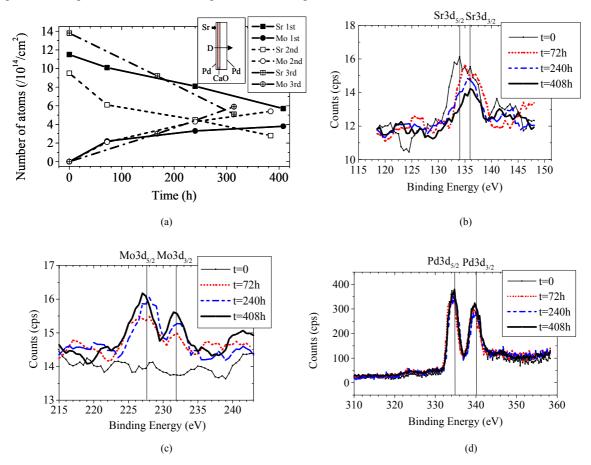


Fig. 4 Experimental results obtained by  $D_2$  gas permeation through Pd complex (Pd/CaO/Pd) with added Sr: (a)Time variation in number of Sr and Mo atoms, (b) XPS spectrum of Sr for experiment run #1, (c)XPS spectrum of Mo for experiment run #1, (d) XPS spectrum of Pd for experiment run #1.

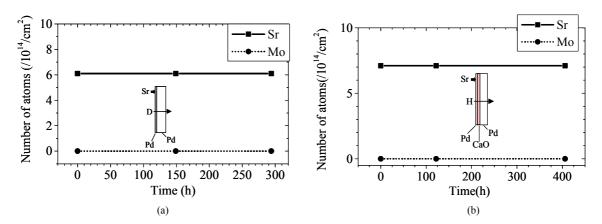


Fig. 5 Results of comparative experiments using Sr: (a) Experimental results obtained by  $D_2$  gas permeation through thin film and bulk Pd with added Sr, (b) Experimental results obtained by  $H_2$  gas permeation through Pd complex (Pd/CaO/Pd) with added Sr.

Figure 5(a) shows the results of the test piece devoid of CaO and Pd layers. All conditions of this comparative experiment were the same as those of the Pd complex (Pd/CaO/Pd) experiments except for the formation of CaO and Pd layers. We can see that Sr did not change and Mo was not detected. Figure 5(b) shows the results of a comparative experiment using  $H_2$  gas for a Pd complex test piece with added Sr. The elements on the surface of the Pd complex test piece did not increase or decrease as expected. The CaO and Pd layers and  $D_2$  gas permeation are considered to be important factors for observing the decrease of Sr and the increase of Mo; this is the same as the case of Cs.

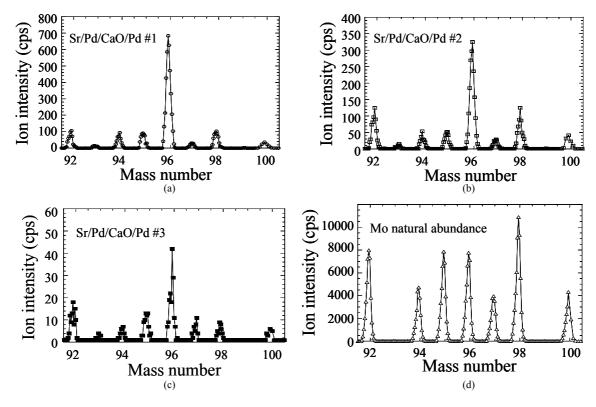


Fig. 6 Anomalous isotopic composition of detected Mo: (a) Isotopic composition of detected Mo for run #1, (b) Isotopic composition of detected Mo for run #2, (c) Isotopic composition of detected Mo for run #3, (d) Natural abundance of Mo analyzed by SIMS.

In order to investigate the isotopic composition, the samples after the experiment were analyzed by SIMS. Figures 6(a)-6(c) show the results of SIMS analysis for the three samples described in Fig. 4. The primary ions of the SIMS analysis were  $O_2^+$  with the energy of 5.5 keV and the intensity of 30 nA. The area analyzed by SIMS was 150 microns in diameter and mass resolution was 300. The intensities of mass number 96 were the largest for each sample, although the intensities were different. The SIMS mass spectrum for a Mo layer (400 Å thickness) which was deposited on a Pd disk is shown in Figure 6(d). This

spectrum reveals the natural abundance of Mo. Comparing these figures, we can easily recognize that the isotopic compositions of the detected Mo are different from the natural isotopic abundance of Mo.

#### 4. DISCUSSION

The experimental results are summarized as follows: Cs atoms decrease and, correspondingly, Pr atoms emerge on the surface of the Pd complex by permeation of  $D_2$  gas through it. These results were obtained six times and reproducibility was good. However, when we eliminate CaO and Pd complex layers from the Pd complex, or when we let  $H_2$  gas permeate through the Pd complex, we observed no decrease in Cs and no emergence of Pr.

In the case of Cs experiments, the following expression can be derived, as Cs and Pr each have only one isotope.

$$^{133}_{55}Cs \rightarrow ^{141}_{59}Pr \tag{1}$$

It should be noted that the mass number and the atomic number increased by 8 and 4, respectively, in this expression. It is natural to consider that deuterium plays an important role in this phenomenon. This is due to the fact that Cs atoms decrease and, correspondingly, Pr atoms emerge on the surface of the Pd complex as  $D_2$  gas permeates through it.

As indicated in Fig. 4, more permeating time is necessary to convert Sr into Mo than Cs experiments. In other words, Cs is easier to change than Sr. It can be presumed that the cross sections in this low energy transmutation process depend on the type of nuclei. The observed results are expressed by the following expression because Sr and Mo have several isotopes.

$$Sr \to Mo$$
 (2)

As shown in Fig. 6, the characteristic feature of the detected Mo is that mass number 96 is the largest of the isotopes of Mo for all three cases of the Sr experiments. On the other hand, the major isotope of Sr is mass number 88. This fact suggests that the following expression can explain the results of SIMS analysis.

$${}_{38}^{88}Sr \rightarrow {}_{42}^{96}Mo \tag{3}$$

It is also noted that the mass number and the atomic number increased by 8 and 4, respectively, in this expression, as is the case with Cs.

We noticed that a certain rule exists between given and produced elements<sup>1),4)</sup>. The increase in mass number is 8, and the increase in atomic number is 4. At present, we do not have a complete theory that can explain the obtained experimental results without a few assumptions. However, if several assumptions are accepted, they are basically explained by the EINR model<sup>5)</sup>, which is one of the working hypotheses in the investigation of the nature of this phenomenon. The observed transmutation processes belong to the new category of nuclear reactions on the metal surface associated with deuterium and electrons under low energy conditions. However, there are many issues to be resolved, especially theoretical ones, and further investigations by other researchers are necessary.

## **REFERENCES**

- [1] Y. Iwamura, T. Itoh and M. Sakano: *Proc 8th Int. Conf. Cold Fusion* (Italian Physical Society, Bologna, Italy, 2000) p. 141
- [2] Chemical Society of Japan: Kagaku Binran Kisohen Kaitei (Maruzen, Tokyo, 1984) 3rd ed., [in Japanese].T. Mizuno, T. Ohmori and M. Enyo: Electrochemistry **64** (1996) 1160.
- [3] M. Cardona and L. Ley: L. Photoemission in Solid I General Principles (Springer-Verlag, Berlin, 1978) Topics in Applied Physics vol. 26.
- [4] Yasuhiro Iwamura, Mitsuru Sakano and Takehiko Itoh, "Elemental Analysis of Pd Complexes: Effects of D<sub>2</sub> Gas Permeation", Japanese Journal of Applied Physics, Vol.**41**, No.7A, (2002), to be published.
- [5] Y. Iwamura, T. Itoh, N. Gotoh and I. Toyoda: Fusion Technol. 33 (1998) 476.