Research Article

Observation of Low Energy Nuclear Transmutation Reactions Induced by Deuterium Permeation through Multilayer Pd and CaO thin Film

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Abstract

Low energy nuclear transmutations in condensed matter have been observed in the nano-structured Pd multilayer complex, which are composed of Pd and CaO thin film and Pd substrate, induced by D₂ gas permeation through Pd multilayer complexes. Permeation of deuterium is attained by exposing one side of the Pd complex to D₂ gas while keeping the other side under vacuum conditions. Transmutation reactions of Cs into Pr, Ba into Sm were observed. Especially, transmutation of Cs into Pr has been confirmed by “in-situ” measurements using x-ray fluorescence spectrometry (XRF) at SPring-8 in Japan. Similar experiments have been performed by some researchers and positive results have been obtained in some cases. However, more systematic experiments and theoretical approaches are required to make clear the nature of this phenomenon.

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Keywords: CaO, Deuterium, D₂ gas, Multilayer, Nano-structure, Pd, Permeation, Thin film, Time of flight mass spectrometry, Transmutation, X-ray fluorescence, X-ray photoelectron spectrometry

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1. Introduction

Transmutation reactions in nano-structured material have been observed in Pd complexes which are composed of Pd and CaO thin film and Pd substrate, induced by D\textsubscript{2} gas permeation\cite{1-7}. Experimental data that indicates the presence of transmutation have been accumulated and experimental conditions for inducing low energy transmutation reactions are gradually becoming clear, although it is difficult to make theoretical explanations to this phenomenon and systematic experimental study is still insufficient.

Figure 1 shows schematic of our experimental method. Our approach can be characterized by the permeation of D\textsubscript{2} gas through the nano-structured Pd complex and the addition of an element that is specifically targeted to be transmuted.

Permeation of deuterium, the first feature, is attained by exposing one side of the Pd multilayer thin film to D\textsubscript{2} gas while maintaining the other side under vacuum conditions. On the D\textsubscript{2} gas side of the Pd complex, dissociative absorption causes the separation of D\textsubscript{2} molecules into D atoms, which diffuse through the Pd metal toward the vacuum side, where they emerge from the Pd metal, combine and are released as D\textsubscript{2} gas.

The second feature is the addition of an element targeted to be transmuted. Our sample is a Pd complex composed of bulk Pd on the bottom, alternating CaO and Pd layers, and a Pd thin film on top. After fabricating a Pd complex, Cs, Ba, Sr or other element is deposited on the surface of the top thin Pd layer. We can observe transmutation of the added elements.

In other words, with this experimental method, we can provide a deuterium flux through the Pd multilayer thin film on which an element is placed as a target to be transmuted. We perform elemental analyses of the given elements after D\textsubscript{2} gas permeation by exhausting the D\textsubscript{2} chamber.

2. Experimental

Fabrication of Pd complex is basically the same as before \cite{1-6}. Preparation of the multilayer Pd thin film is shown in Fig. 2a. A Pd was washed with acetone and annealed in vacuum (<10\textsuperscript{-5} Pa) at 900\textdegree C for 10 h. It was then cooled to room temperature in furnace and washed with aqua regia to remove impurities on the surface of the Pd plate. The surface of the plate was covered by layers of CaO and Pd, which were obtained by five times alternately sputtering 2-nm-thick CaO and 20-nm thick Pd layers. Then a 40 nm-thick Pd layer was sputtered on the surface of the CaO

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{D2_gas_permeation.png}
\caption{Schematic of our experimental approach.}
\end{figure}
and Pd layers. These processes were performed by the Ar ion beam sputtering method or the magnetron sputtering method. After fabricating a Pd complex, Cs was deposited on the surface of the thin Pd layer. Cs was deposited by the electrochemical method or the ion implantation method. In the case of SPring-8 experiments, Cs was given by the ion beam implantation method (voltage: 5 kV, dose: $2.5 - 5 \times 10^{14}/\text{cm}^2$).

Cross-sectional view of the fabricated Pd multilayer sample is shown in Fig. 2b. The white lines in the photograph correspond to CaO. We can see that the sample is correctly fabricated by our procedure.

Originally, we used an experimental apparatus with X-ray Photoelectron Spectrometry (XPS) shown in Fig. 3a. Elemental changes on Pd complexes were measured by XPS without taking them out of the vacuum chamber, to prevent contamination from outside of the chamber. Using this experimental set-up, transmutation reactions of Cs into Pr and Sr into Mo were observed. In the case of transmutation experiments of Ba into Sm, the XPS in the chamber was not available at that time so the samples were analyzed before and after D$_2$ permeation using XPS or Secondary Ion Mass Spectrometry (SIMS).

Figure 3(b) shows the experimental setup for in-situ measurement at SPring-8, which is one of the largest synchrotron radiation facilities, located in the west part of Japan. This setup enables us to observe elemental changes during D$_2$ gas permeation by X-ray fluorescence spectrometry (XRF). Synchrotron orbital radiation X-ray (5.97 keV) is introduced into the permeation chamber through a Be window and attacks on the surface of Pd complex sample. X-ray intensity is about from $10^{12}$ to $10^{13}$ photons/s. Cs-L and Pr-L lines can be detected by a Silicon Drift Detector (SDD). The SDD is covered by a Cl filter which is used for the absorption of intense Pd-L X-ray. XRF was performed during D$_2$ permeation in-situ at the beginning and the end of the experimental runs.

3. Results and Discussion

Transmutations of various elements were tried in our laboratory. In this paper, transmutation of Cs into Pr, Ba into Sm, measurement of distribution of products, the role of CaO, key factors in permeation experiments and replication experiments are described.
4. Transmutation of Cs into Pr

Figure 4 shows the first observation of transmutation reaction from Cs into Pr using the experimental set-up shown in Fig. 3a. Results for two runs are shown as examples. There was no Pr at the beginning of the experiments. The number of Cs atoms decreased while Pr atoms increased as experimental time went by. The number of atoms were evaluated by XPS spectra. Amount of deuterium permeation was proportional to the elapsed time. After 120 h, the number of Pr atoms exceeded that of Cs atoms.

As the control experiments, (1) H\textsubscript{2} gas permeation experiments using the same Pd multilayer samples (Pd/CaO/Pd), (2) D\textsubscript{2} gas permeation using the same Pd multilayer samples (Pd/CaO/Pd) without Cs, and (3) D\textsubscript{2} gas permeation using the Pd sample without CaO were performed. These control experiments were performed under the same temperature conditions.

![Graph showing transmutation reactions from Cs into Pr](image)

**Figure 4.** Observed transmutation reactions from Cs into Pr [1].
We tried Ba transmutation experiments using natural Ba and mass 137 enriched Ba. Natural Ba was deposited by TRIFT™ II made by ULVAC-PHI. Figure 5a shows the mass number distribution of the Pd complex (Pd/CaO/Pd) after D2 gas permeation, and Pr was detected in all the control experiments. It suggests that both 136Y. Iwamura et al. / Journal of Condensed Matter Nuclear Science 4 (2011) 132–144 and Sm 3d and Sm 4d peaks can be seen.

Sm spectra were obtained in both measurements. XPS full spectrum is shown in Fig. 7b. Pd, Ba, C(surface impurity) spectra are shown in Fig. 7a. The measurements were done twice to make sure measurement reproducibility and clear Cs or Sr experiment [1].

In this case, we use 1 mm square X-ray beam. The Cs peaks decreased and the Pr peak emerged after D2 gas permeation as Cs or Sr experiment [1].

Pr detection by TOF–SIMS analysis [4].

The existence of Pr was confirmed by X-ray Absorption Near Edge Structure (XANES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and XRF [2–4]. According to ICP-MS, detected Pr ranged from 0.1 to 100 ng [4].

On the next stage, we tried in-situ measurements with XRF to obtain more confident results. An example of detection of Pr by in-situ measurement is shown in Fig. 6. Initial (before D2 gas permeation) and final (after D2 gas permeation) XRF spectra are plotted. Cs was injected by the ion beam implantation method (voltage: 5 kV, dose: $2.5 \times 10^{14}/cm^2$).

In this case, we use 1 mm square X-ray beam. The Cs peaks decreased and the Pr peak emerged after D2 gas permeation at the shown point in Fig. 6. It can be seen that transmutation of Cs into Pr occurred at this point. However, no Cs was changed and no Pr was seen except this point in the case of this sample. Pr distribution for this sample was measured using micro-sized X-ray as described later.

5. Transmutation of Ba into Sm

We tried Ba transmutation experiments using natural Ba and mass 137 enriched Ba. Natural Ba was deposited by the electrochemical method with 10 mM Ba(OH)2 solution. And mass number 137 enriched Ba was deposited by electrochemical method with 7.3 mM Ba(NO3)2 solution. Applied voltage was 1 V and the time was 10 s as the same as Cs or Sr experiment [1].

Figure 7 shows XPS spectra for the Pd complex after deuterium permeation for 2 weeks with natural Ba. Sm 3d spectra are shown in Fig. 7a. The measurements were done twice to make sure measurement reproducibility and clear Sm spectra were obtained in both measurements. XPS full spectrum is shown in Fig. 7b. Pd, Ba, C(surface impurity) and Sm 3d and Sm 4d peaks can be seen.
In order to investigate the Sm isotopic distribution, we analyzed the detected Sm by SIMS. Natural abundance of Sm and SIMS spectrum of the detected Sm are shown in Table 1 and Fig. 8, respectively. Natural Sm has seven isotopes and the largest isotope is $^{152}$Sm. However, natural Sm SIMS spectra cannot be seen in Fig. 8, although clear XPS spectra for Sm were obtained on this sample. In Fig. 8, “after permeation” means the Pd multilayer thin film with natural Ba after D$_2$ permeation and “before permeation” means the Pd multilayer thin film with natural Ba without D$_2$ permeation. Mass number 150 for “after permeation” is one order larger than “before permeation” in Fig. 8. This mass

Figure 6. Detection of Pr by an in-situ experiment at SPring-8 [2].

Figure 7. Detected Sm XPS spectra after D$_2$ gas permeation through a Pd complex deposited with natural Ba; (a) XPS spectra for Sm 3d, (b) Full XPS spectrum [3].
number must have been derived from $^{150}\text{Sm}$ according to the XPS analysis.

Let us consider these spectra in Fig. 8 using Table 2 that examines the effects of molecular ions. $^{138}\text{Ba}$ signal for “before permeation” and “after permeation” does not match. We consider this is because of non-uniformity of Ba deposition. Pd$^{40}\text{Ca}$ molecular ion peaks for “before permeation” and “after permeation” are nearly equal. Both $^{110}\text{Pd}(12\%)^{40}\text{Ca}$ and $^{134}\text{Ba}(2.4\%)^{16}\text{O}$ are candidates for mass 150.

In the case of $^{110}\text{Pd}(12\%)^{40}\text{Ca}$, $^{110}\text{Pd}^{40}\text{Ca}$ cannot explain the large mass 150 since the signal for $^{110}\text{Pd}(12\%)^{40}\text{Ca}$ must be lower than $^{106}\text{Pd}(27\%)^{40}\text{Ca}$ and mass 146 is smaller than mass 150.

In the case of $^{134}\text{Ba}(2.4\%)^{16}\text{O}$, the signal of $^{134}\text{Ba}(2.4\%)^{16}\text{O}$ must be one order lower than the signal of $^{138}\text{Ba}(71.7\%)^{16}\text{O}$. However, the mass 150 for the “after permeation” is the same order as $^{138}\text{Ba}(71.7\%)^{16}\text{O}$. Therefore the contribution of $^{134}\text{Ba}(2.4\%)^{16}\text{O}$ cannot explain the mass 150 signal.

Now we consider about the effect of $^{12}\text{C}$ ion. Mass 150 can be created numerically with the combination of $^{138}\text{Ba}$ and $^{12}\text{C}$. If $^{138}\text{Ba}^{12}\text{C}$ might be created, then $^{137}\text{Ba}^{12}\text{C}$ (mass 149) and $^{136}\text{Ba}^{12}\text{C}$ (mass 148) should be created. However, we cannot see any increase of mass 149 and 148 in the “after permeation” signals in Fig. 8. This fact indicates that BaC molecular ions have almost no effects on the SIMS spectra. Therefore the large mass 150 signal cannot be explained by $^{138}\text{Ba}^{12}\text{C}$ formation.

Based on these SIMS considerations and XPS results, it is reasonable that mass 150 for the permeated sample is

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**Table 1.** Natural abundance of Sm.

<table>
<thead>
<tr>
<th>Sm</th>
<th>144</th>
<th>147</th>
<th>148</th>
<th>149</th>
<th>150</th>
<th>152</th>
<th>154</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.2%</td>
<td>15.1%</td>
<td>11.3%</td>
<td>13.8%</td>
<td>7.5%</td>
<td>26.6%</td>
<td>22.5%</td>
</tr>
</tbody>
</table>
derived from Sm. It is strongly suggested that $^{150}$Sm exists on the Pd complex after D$_2$ gas permeation.

In the case of the 137 enriched Ba deposition sample, we could not obtain clear XPS spectra. However, we obtained SIMS data that showed the increase of mass 149. Figure 9 shows two SIMS spectra for Pd complexes with 137 enriched Ba after D$_2$ permeation. About one order increase of mass 149 was observed in the both experiments of Nos. 1 and 2. Table 2 indicates that mass 149 cannot be created by Pd$^{40}$Ca and Ba$^{16}$O. $^{137}$Ba$^{12}$C also cannot explain because BaC molecular ions have almost no effects on the SIMS spectra as described before. These facts imply that $^{149}$Sm exists on the Pd complex if we consider that Sm spectra were obtained by XPS using natural Ba. The 149 mass increase might be caused by $^{149}$Sm.

Figure 10 shows the mass correlation between given and detected elements. If we put $^{138}$Ba on the nano-structured Pd film, we obtain $^{150}$Sm by D$_2$ gas permeation. And if we set $^{137}$Ba on the Pd complex, we obtain $^{149}$Sm, if we assume that the mass 149 increase of the SIMS spectra are caused by Sm. The observed transmutation reactions of Ba into Sm belong to a reaction category in which the increase of mass number is 12 and the increase of atomic number is 6. Nuclear transmutation induced by our experimental method is not limited to the category in which the increase of mass number is 8 and the increase of atomic number is 4 ($^{210}$Cs $\rightarrow$ Pr, $^{90}$Sr $\rightarrow$ Mo).

We might say that the transmutation of Cs into Pr belongs to 2$\alpha$ capture type reaction and the transmutation of Ba into Sm to 3$\alpha$. At present, it is just a speculation; however, it is important that a certain rule can be noticed for this deuterium permeation transmutation.

### 6. Distribution of Products

Surface distribution of Cs and Pr were measured by the strong synchrotron radiation X-ray at Spring-8. The X-ray was divided by slits and we got rectangular micro X-ray beam. 500-micron, 100-micron and 50-micron X-ray beams were applied for our measurement. The Pd sample was attached on an X–Y stage that could be moved by stepping motors and so 2-dimensional XRF spectra could be obtained. Surface images could be taken by a microscope that was equipped for this 2-dimensional XRF spectrum analysis.

Figure 11 shows surface distribution of Pr and XRF spectra obtained by 100-micron X-ray beam at the point where transmutation of Cs into Pr was observed by the in-situ measurement described in Fig. 6. The amount of Pr changed greatly depending on the locations of the Pd surface. Pr was localized at the specific points as shown in Fig. 11. Surface image for the corresponding region is shown in Fig. 11b. No clear correlation between the localized Pr and surface image could be observed.

These experimental results suggest that transmutation reaction rate varies depending on the Pd surface region. Some uncertain factors, presumably relating to condensed matter effects in the present Pd/D/CaO system, must make a lot of effects on the rate or the process of the reactions. In order to make clear the uncertain factors, it would be necessary to use smaller X-ray beam, although it would take much more time for XRF measurement.
Figure 9. SIMS spectra for Pd complexes with 137 enriched Ba; (a) Spectrum for No. 1 experiment, (b) Spectrum for No. 2 experiment [3].
Depth profiles of Cs and Pr were plotted in Fig. 12. XPS analysis was applied to Fig. 12. Cs was injected into all the Pd complex samples by the ion implantation method. The relation between the sputtering time and the real depth was estimated in advance using a Pd thin film on Si substrate; thickness of the Pd thin film is known.

The Cs and Pr depth profiles for the Pd complex without permeation show normal and reasonable result as shown in Fig. 12. Cs decreases continuously from the surface and there is no Pr in the sample before permeation. On the other hand, Cs decreases and Pr increases within 10 nm region from the top surface. Cs depth profiles in the both samples are nearly equal in deep area. This supports that Cs transmutation reaction into Pr occurs in the near surface region up to 10 nm.

Figure 12 also shows that Cs atoms do not diffuse and migrate with D₂ gas permeation under our experimental conditions. Therefore it is very difficult to postulate that the detected Pr was a concentrated impurity that migrated from the whole Pd multilayer sample.

7. Role of CaO

The authors do not have a definite explanation for the role of the CaO layers in the nano-structured Pd multilayer thin film at present. We have two kinds of explanations for the effects of CaO. The first effect is the increase of deuterium density in the Pd multilayer thin film and the second is the effect for modifying the electronic state of top Pd layer. D⁺ ion bombardment experiments suggest the first effect and the correlation between intermediate material and transmutation reactions implies the second effect.

D⁺ ion bombardment experiment using a Pd complex was performed at Tohoku University. Low energy D⁺ ion beam from 2.5 to 10 keV irradiates the surface of metal and induces D(d, p)T reactions. Proton yield obtained δE − E counter telescope and its energy dependence enable us to estimate screening potential and deuterium density [8].
Figure 11. Surface distribution of Pr using 100-micron X-ray beams. (a) Mapping of Pr by 100-micron beam at the point where Pr was detected by in-situ measurement. (b) Surface image of the sample corresponding to XRF spectra. (c) XRF spectra for three different points [2].

we can see in Fig.13, deuterium density of Pd complex (Pd/CaO) is about one order larger than normal Pd. It suggests that the nano-structured Pd multilayer film contains more deuterium than normal bulk Pd.

When we replaced CaO with MgO, we did not obtain any positive results; we could not observe any transmutation reactions as shown in Table 3. It means that MgO cannot work instead of CaO. Three cases out of the three experiments using MgO show no Pr by ICP-MS measurements, although D2 gas Flow rates were enough (2–3 sccm) in all cases.

However, if we replaced CaO with Y2O3, we could observe transmutation reactions from Cs to Pr. In other words, Y2O3 works like CaO. Work functions for MgO, Y2O3, and CaO are shown in Table 3. Although it is difficult to make conclusive results, the existence of low work function of intermediate material might have some effects to induce transmutation. Anyway, we should continue to make systematic researches to make clear how the CaO layers work.

<table>
<thead>
<tr>
<th>Intermediate Material</th>
<th>Work function (eV)</th>
<th>Results for analysis after permeation</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>3.3</td>
<td>No Pr (3 cases)</td>
</tr>
<tr>
<td>Y2O3</td>
<td>2.2</td>
<td>Pr detected (3 cases)</td>
</tr>
<tr>
<td>CaO</td>
<td>1.2</td>
<td>Pr detected (&gt;100 cases)</td>
</tr>
</tbody>
</table>
8. Key factors in permeation experiments

Transmutation reactions induced by deuterium permeation through nano-structured multilayer Pd were observed for Cs and Ba as described in this paper. Transmutation caused by other elements, for example, Sr, Ca, Na and Li were also observed, though a number of experiments and a number of analysis cross checks are not necessarily enough for these elements. Of course, there are some elements that we could not observe any anomalous transmutation reactions. Based on these experimental results, alkali and alkaline earth elements seem to be transmutable.

There are no established theories that can explain the experimental results without any assumptions, although some interesting models and theories have been proposed [9,10]. The observed transmutation processes must belong to a new category of nuclear reactions in condensed matter. We should continue to work in order to make clear the nature of this new phenomenon experimentally with theoretical approaches. Identification of key experimental factors to induce transmutation reactions would be important to make progress. And more essential factors, such as local deuteron density and electronic structure of Pd–CaO–D system, should be clarified.

The followings are the candidates for key factors in permeation experiments. (1) Deuterium flux through Pd multilayer, (2) target element, (3) local deuterium density, (4) nano-size or nano-structure, (5) temperature, and (6) work function of the intermediate layer. These factors are derived from experimental results obtained so far.

We are now trying to make clear the effect of (3) local deuterium density. A resonance nuclear reaction [11] would give us precise depth profile deuterium near surface. At this moment, we succeed to measure hydrogen 3-dimensional profiles under high pressure (∼1 bar) using 15N ion beam. Local hydrogen density will be able to be detected during permeation through nano-structured Pd multilayer thin film.
9. Replication Experiments

Replication experiments have been performed in some universities or institutes mainly in Japan. T. Higashiyama et al. of Osaka University observed transmutation of Cs into Pr in 2003 [12]. H. Yamada et al. performed similar experiments using Cs and detected increase of mass number 137 by TOF-SIMS. They used a couple of nano-structured Pd multilayer thin film and observed the increase of mass number 141 (corresponding to Pr) only when $^{133}$Cs was given on the Pd sample [13]. T. Hioki et al., the researchers of Toyota Central R&D Labs, recently presented that they detected Pr from the permeated Pd sample using SOR X-ray at Spring-8 and the detected Pr was confirmed by TOF-SIMS [14].

It is not easy to obtain positive results in replication experiments since necessary experimental factors are not completely clarified. Details of experimental conditions can be often varied. If the difference would influence the phenomenon, it might be difficult to observe the same transmutation reactions as ours.

These above replication observations provide important information concerning about the nature of this phenomenon. Their samples were independently fabricated except in the experiments at Osaka University and fabrication conditions, for example, Pd dimension or fabrication method, were different. Nevertheless, similar results were observed. We should investigate how the experimental parameters influence the transmutation reactions more intensively.

10. Concluding Remarks

Low energy nuclear transmutations in condensed matter have been observed in the nano-structured Pd multilayer complex. Transmutation reactions of Cs into Pr, Ba into Sm were observed. Especially, transmutation of Cs into Pr has been confirmed by “in-situ” measurements using XRF at SPring-8 in Japan. Replication experiments have
been performed by some researchers and similar results have been obtained in some cases. However, nature of this phenomenon is not clear at present; we should continue to identify the key experimental factors to induce transmutation reactions experimentally with theoretical approaches.

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