

Transmutation reactions induced by deuterium permeation through nano-structured palladium multilayer thin film

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Low energy nuclear transmutation reactions have been observed in nano-structured Pd multilayer thin film which is composed of Pd and CaO thin film and Pd substrate, induced by D₂ gas permeation¹⁻⁵. Up to now we have observed transmutation reactions of Cs into Pr, Ba into Sm and W into Pt. Replication experiments have been successfully performed by some researchers and Toyota R&D Center published almost complete replication experiments⁸ on the transmutation of Cs into Pr last year. This new phenomenon would be used as an innovative nuclear transmutation method for radioactive waste⁹⁻¹¹ or a new energy source if we could solve many problems for commercialization.

Keywords: Deuterium, low energy nuclear transmutation, palladium thin film, permeation.

Original method and experimental results

We first observed low energy nuclear transmutation reactions using the method of deuterium gas permeation through palladium (Pd) multilayer thin film¹. Figure 1 shows a schematic of our experimental method. Our approach can be characterized by the permeation of D₂ gas through the nano-structured Pd complex and the addition of an element that is specifically targeted to be transmuted. Permeation of deuterium is attained by exposing one side of the Pd multilayer thin film to D₂ gas, while maintaining the other side under vacuum conditions. The sample is a Pd complex composed of bulk Pd at the bottom, alternating CaO and Pd layers, and a Pd thin film on the top. After fabricating a Pd complex, Cs, Ba, Sr or any other element is deposited on the surface of the top thin Pd layer. The added elements can be transmuted. Preparation of the multilayer Pd thin film is as follows. The Pd substrate is washed with acetone and annealed in vacuum (<10⁻⁵ Pa) at 900°C for 10 h. It is then cooled to room temperature in a furnace and washed with aqua regia to remove impurities on the surface of the Pd plate. The surface of the plate is covered by layers of CaO and Pd,

which are obtained by five times alternately sputtering 2 nm-thick CaO and 20 nm thick Pd layers. Then a 40 nm thick Pd layer is sputtered on the surface of the CaO and Pd layers. These processes is performed by the Ar ion beam sputtering method or the magnetron sputtering method. After fabricating a Pd complex, Cs is deposited on the surface of the thin Pd layer by electrochemical method or ion implantation method.

Originally we used an experimental apparatus with XPS (X-ray photoelectron spectrometry). 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. Figure 2 shows the first observation of transmutation reaction from Cs

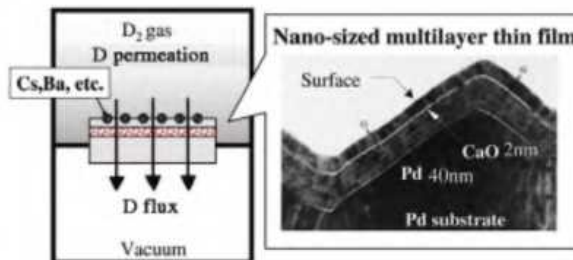


Figure 1. Experimental method for permeation-induced nuclear transmutation.

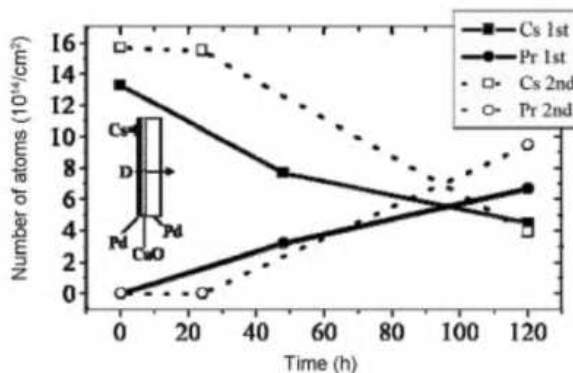


Figure 2. Observation of transmutation of Cs into Pr (ref. 1).

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into Pr using the experimental set-up with XPS. 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 during the experiment. The number of atoms was evaluated by XPS spectra. The amount of deuterium permeation was proportional to the elapsed time.

As the control experiments, (i) H₂ gas permeation experiments using the same Pd multilayer samples (Pd/CaO/Pd); (ii) D₂ gas permeation using the same Pd multilayer samples (Pd/CaO/Pd) without Cs and (iii) D₂ gas permeation using the Pd sample without CaO were performed. These control experiments were performed under the same temperature and pressure as the foreground experiments. No Pr was detected in all the control experiments. This suggests that both deuterium and nano-structured Pd multilayer with CaO are necessary factors to observe transmutation reactions. Pr was confirmed by ICP-MS (inductively coupled plasma mass spectrometry) and TOF-SIMS (time-of-flight secondary ion mass spectrometry; TRIFTTM II; ULVAC-PHI).

Usually we etched one-third of the samples after permeation using 4 cm³ HNO₃ (TAMA-Pure-AA-10; 68%) and H₂O 6 cm³ ultra-pure solution for 5 min. Surface area was 1.3 cm² (circle 13 mm in diameter; Cs deposited area). The etched solutions were sent to Toray Research Center for ICP-MS analysis. No molecular ions interfering mass 141(Pr) in this system. The sensitivity of the ICP-MS is ppt (pg/g) order and detection limit for Pr (mass number 141) was about 0.1 ng/cm². According to ICP-MS, the detected Pr ranged from 0.1 to few 10 ng (ref. 2).

Confirmation of Cs transmutation by *in situ* measurements

Figure 3 shows the experimental set-up for *in situ* measurement at SPring-8, which is one of the largest synchrotron radiation facilities located in the western part of Japan. This set-up enables us to observe elemental changes during D₂ gas permeation by XRF (X-ray fluorescence spectrometry). Synchrotron orbital radiation X-ray (5.97 keV) was introduced into the permeation chamber through a Be window, which interacted on the surface of Pd complex sample. X-ray intensity was from 10¹² to 10¹³ photons/sec. Cs-L and Pr-L lines were detected using a silicon drift detector (SDD), which was covered by a Cl filter used for the absorption of intense Pd-L X-rays. XRF was performed during D₂ permeation *in situ* at the beginning and end of the experimental runs.

In situ measurements with XRF were made to obtain more confident results. An example of detection of Pr by *in situ* measurement is shown in Figure 4. 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 × 10¹⁴ cm⁻²). The Cs peaks decreased and Pr peak emerged after D₂ gas permeation at the point shown in Figure 5. 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 at this point in the case of this sample.

The other element transmutation reactions

We tried other element transmutation experiments. One of them is the Ba transmutation experiment using natural Ba and mass 137-enriched Ba (ref. 3). If we put ¹³⁸Ba on the nano-structured Pd film, we obtain ¹⁵⁰Sm by D₂ gas permeation. And if we set ¹³⁷Ba on the Pd complex, we obtain ¹⁴⁹Sm. 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 (Cs ≥ Pr).

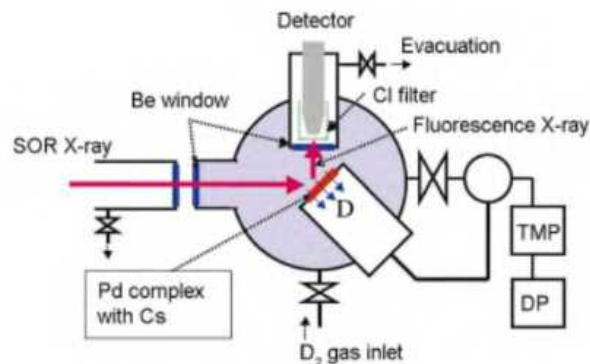


Figure 3. Experimental set-up for *in situ* measurements (ref. 2).

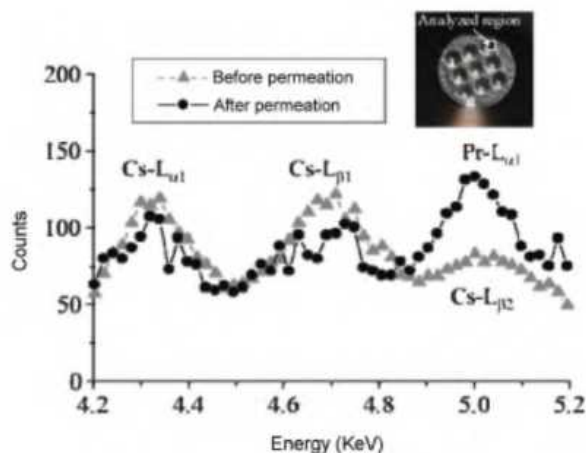


Figure 4. Transmutation of Cs into Pr by *in situ* experiment at SPring-8 (ref. 2).

The other is the tungsten (W) transmutation experiment⁴. W ion implantation (63 kV , $2.5 \times 10^{14} \text{ cm}^{-2}$) was applied to Pd/CaO multilayer films, and then permeation experiments were performed several times. No permeated sample showed natural W and Pt mass distributions. On the contrary, mass distributions for permeated samples were anomalous. Significant increase for mass 190 should be noticed, although no mass counts of 190 for the No permeated sample. The increase in the permeated samples cannot be attributed to natural Os or Pt. Effects of compound species were also considered intensively; however, the increase of mass 190 could not be explained consistently with isotope distributions of each element. Based on these discussions, we consider that the observed increase of mass 190 for permeated samples must be explained by the transmutation of implanted tungsten.

Discussions

The experimental results obtained so far suggest that a certain rule seems to exist for this deuterium permeation transmutation. Table 1 summarizes typical transmutation results obtained so far in our experiments. We can observe that 2d, 4d or 6d may react with the deposited elements. From another point of view, it might be considered that capture reactions occur in deuterium permeation experiments. At present, it is just a speculation; however, it is important that a certain rule seems to exist.

Table 1. Typical reactions observed in our laboratory

Element		Assumed reactions
Cs	4d	$^{133}_{55}\text{Cs} \xrightarrow{4d(2\alpha)} ^{141}_{59}\text{Pr}$
Ba	6d	$^{138}_{56}\text{Ba} \xrightarrow{6d(3\alpha)} ^{150}_{62}\text{Sm}$, $^{137}_{56}\text{Ba} \xrightarrow{6d(3\alpha)} ^{149}_{62}\text{Sm}$
W	4d or 2d	$^{182}_{74}\text{W} \xrightarrow{4d(2\alpha)} ^{190}_{78}\text{Pt}?$, $^{186}_{74}\text{W} \xrightarrow{2d(\alpha)} ^{190}_{76}\text{Os}?$

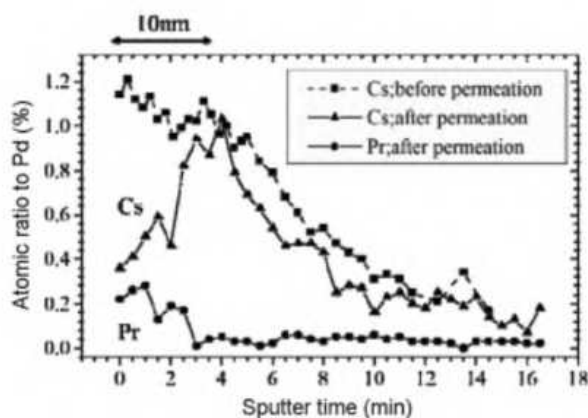


Figure 5. Depth profiles of Cs and Pr for samples after and before D_2 permeation (ref. 3).

Depth profiles of Cs and Pr are plotted in Figure 5 (ref. 3). XPS analysis was applied. Cs was injected into all the Pd samples by the ion implantation method. The relation between the sputtering time and 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 without permeation show normal and reasonable result (Figure 5). 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 5 also shows that Cs atoms do not diffuse and migrate with D_2 gas permeation under our experimental conditions. Therefore, it is difficult to postulate that the detected Pr is a concentrated impurity that migrated from the whole Pd multilayer sample.

At present, the authors do not have a definite explanation for the role of the CaO layers in the nano-structured Pd multilayer thin film. We have two kinds of explanation for the effects of CaO. The first is the increase of deuterium density in the Pd multilayer thin film and the second is the effect of modifying the electronic state of the top Pd layer. D^+ ion bombardment experiments suggest the first effect⁴ and the correlation between intermediate material and transmutation reactions implies the second effect.

When we replaced CaO with MgO, we did not obtain any positive results; we could not observe any transmutation reactions as shown in Table 2. 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 D_2 gas flow rates were enough (2–3 sccm) in all cases. However, if we replaced CaO with Y_2O_3 , we could observe transmutation reactions from Cs to Pr. Work functions for MgO, Y_2O_3 and CaO are shown in Table 2. Although it is difficult to arrive at conclusive results, the existence of low work function of intermediate material might have some effects to induce transmutation.

Replication experiments have been performed in some universities/institutes mainly in Japan. In 2003, Higashiyama *et al.*⁶ (Osaka University) observed transmutation of Cs into Pr. Yamada *et al.*⁷ performed similar

Table 2. Correlation between intermediate material in Pd multilayer film and transmutation results³

Intermediate material	Work function (eV)	Results of analysis after permeation
CaO	1.2	Pr detected >100 cases
Y_2O_3	2.2	Pr detected (three cases)
MgO	3.3	No Pr (three cases)

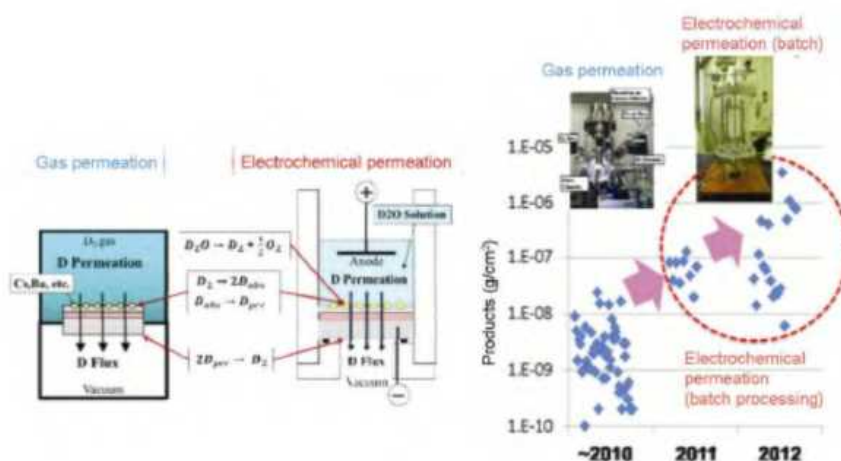


Figure 6. Increase of transmutation products by electrochemical permeation method⁵.

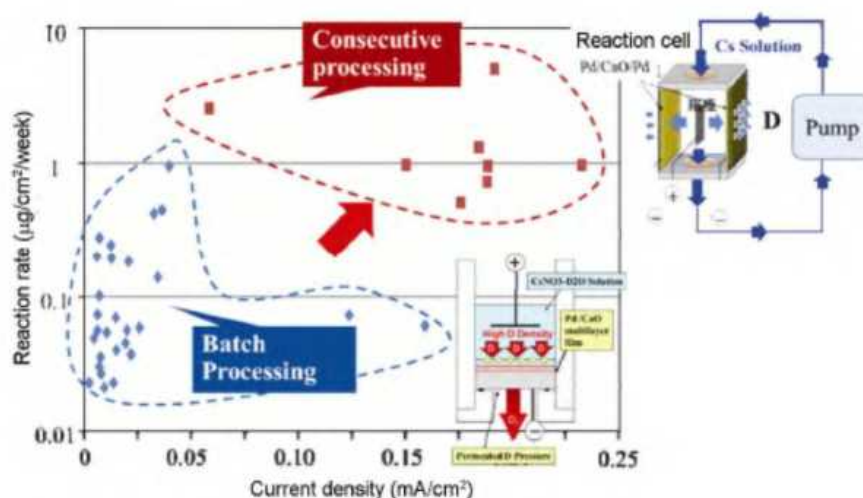


Figure 7. Increase of reaction rate by consecutive processing of electrochemical permeation.

experiments using Cs and detected increase of mass number 137 by TOF-SIMS. They used a couple of nano-structured Pd multilayer thin films and observed the increase of mass number 141 (corresponding to Pr) only when ^{133}Cs was present on the Pd sample. Hioki *et al.*⁸ (Toyota Central R&D Labs), detected Pr using ICP-MS from the permeated Pd sample at ICCF-17.

These replications provide important information about the nature of this phenomenon. Other than Osaka University, the samples were independently fabricated with different Pd dimensions or fabrication techniques. Nevertheless, similar results were observed. These results prove that low energy nuclear transmutation induced by our method really exists, although we have no established theories that can explain the experimental results without any assumptions.

Increase of transmutation products

Increase of transmutation products is important in order to put this deuterium permeation transmutation phenomenon to practical use. This phenomenon would be used as an innovative nuclear transmutation method for radioactive waste or a new energy source if we could solve many problems for commercialization. We have been trying to increase the amount of transmutation products over the years.

The following factors are assumed to be important for inducing deuterium permeation transmutation: (i) local deuteron density and (ii) electronic structure.

Based on this assumption, we applied an electrochemical method to increase the local deuteron density near the surface of the nano-structured Pd multilayer film. Figure 6

shows a comparison between gas and electrochemical permeation. If we apply a voltage more than the decomposition potential between the cathode (Pd multilayer film) and the anode made of Pt, D₂O is decomposed into deuterium and oxygen and deuterium permeates through the cathode. Transmutation products were increased up to $\sim 1 \mu\text{g}/\text{cm}^2$ by this approach, as shown in Figure 6. The amount of products varies widely depending on the experimental condition.

We are now performing another type of electrochemical permeation experiment. Surface temperature seems to rise as the amount of transmutation products increases in the batch electrochemical permeation experiments. So we developed solution circulation type of experimental apparatus shown in Figure 7. The aims of this recent experimental method are as follows: (i) Cooling the Pd surface and (ii) Consecutive transmutation of Cs in the solution.

These recent experimental methods provided increased transmutation products, gamma-ray emissions and new implications on deuterium permeation induced transmutation⁵.

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