Transmutation Reactions Induced by Deuterium Permeation through Nano-structured Pd Multilayer Thin Film

Yasuhiro Iwamura[1], Takehiko Itoh[1], Y.Terada[2] and T.Ishikawa[3]

[1]*Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd., Japan*
3-3-1, Minatomirai, Nishi-ku, Yokohama 220-0012
E-mail: yasuhiro_iwamura@mhi.co.jp
[2]*Japan Synchrotron Radiation Research Institute, Japan*
[3]*Coherent X-ray Optics Laboratory, SPring-8/RIKEN, Japan*

INTRODUCTION

This paper is part of the panel session "Discussion of Low-Energy Nuclear Reactions" and it presents some significant findings in the LENR (Low Energy Nuclear Reaction) field.

Transmutation reactions in nano-structured material have been observed in nano-structured Pd multilayer thin film which are composed of Pd and CaO thin film and Pd substrate, induced by D_2 gas permeation[1]-[3]. 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 systematic experimental study is still insufficient. Replication experiments have been performed by some researchers and similar results have been obtained. Potential applications would be expected for innovative nuclear transmutation method of radioactive waste and a new energy source.

EXPERIMENTAL

Figure 1 shows schematic of our experimental method. Our approach can be characterized by the permeation of D_2 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 D_2 gas while maintaining the other side under vacuum conditions. The 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. The added elements can be transmuted.

Preparation of the multilayer Pd thin film is as follows. A Pd was washed with acetone and annealed in vacuum ($<10^{-5}$ Pa) at 900°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 40nm-thick Pd layer was sputtered on the surface of the CaO 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.

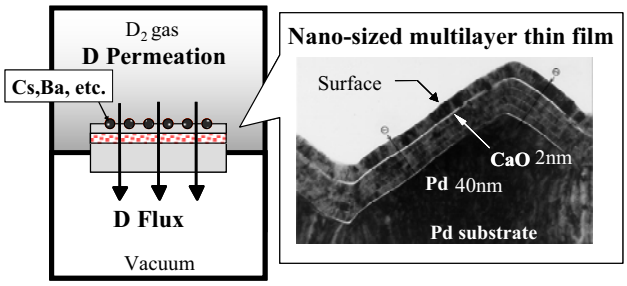

Fig. 1. Experimental Method for Permeation Induced Nuclear Transmutation.

Originally we used an experimental apparatus with XPS (X-ray Photoelectron Spectrometry) shown in Fig. 2. 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 SIMS (Secondary Ion Mass Spectrometry).

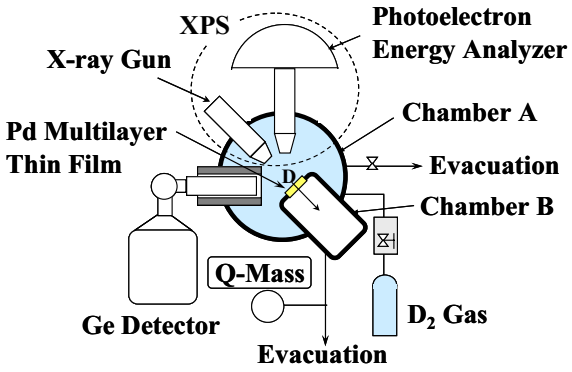

Fig. 2 Experimental set-up with XPS.

Figure 3 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 XRF (X-ray fluorescence spectrometry). Synchrotron orbital radiation X-ray (5.97keV) 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.

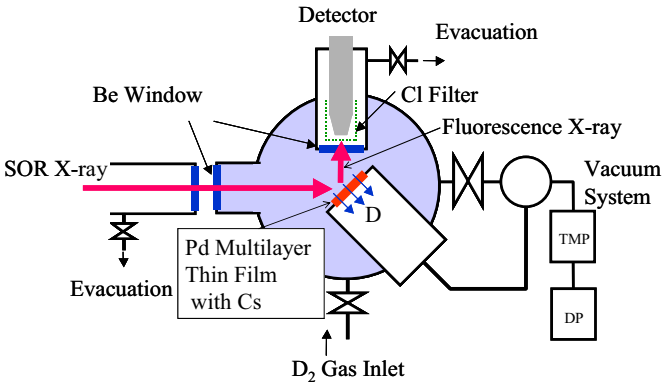

Fig. 3 Experimental set-up for *in-situ* measurement.

RESULTS

Figure 4 shows the first observation of transmutation reaction from Cs into Pr using the experimental set-up shown in Fig. 2. Results for 2 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 was evaluated by XPS spectra. Amount of deuterium permeation was proportional to the elapsed time.

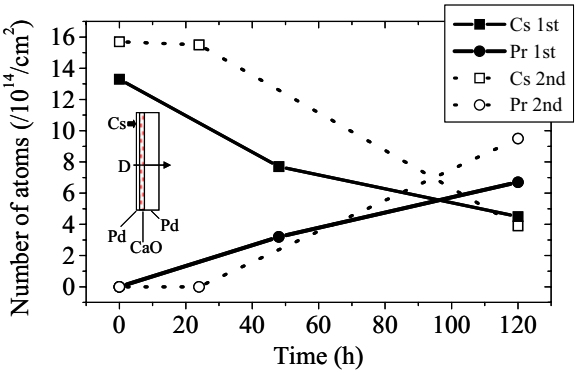

Fig..4 Observation of transmutation of Cs into Pr

Pr was confirmed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) According to ICP-MS, detected Pr ranged from 0.1ng to few 10ng [2]

As the control experiments, 1) H_2 gas permeation experiments using the same Pd multilayer samples (Pd/CaO/Pd), 2) D_2 gas permeation using the same Pd multilayer samples (Pd/CaO/Pd) without Cs, 3) D_2 gas permeation using the Pd sample without CaO were performed. These control experiments were performed under the same temperature and pressure as foreground experiments. No Pr was detected in all the control experiments. It suggests that both deuterium and nano-structured Pd multilayer with CaO are necessary factor to observe transmutation reactions.

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.5. Initial (before D_2 gas permeation) and final (after D_2 gas permeation) XRF spectra are plotted. Cs was injected by the ion beam implantation method (voltage: 5kV, dose: $2.5\times10^{14}/cm^2$). The Cs peaks decreased and the Pr peak emerged after D_2 gas permeation at the shown point in the Fig. 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 this point in the case of this sample.

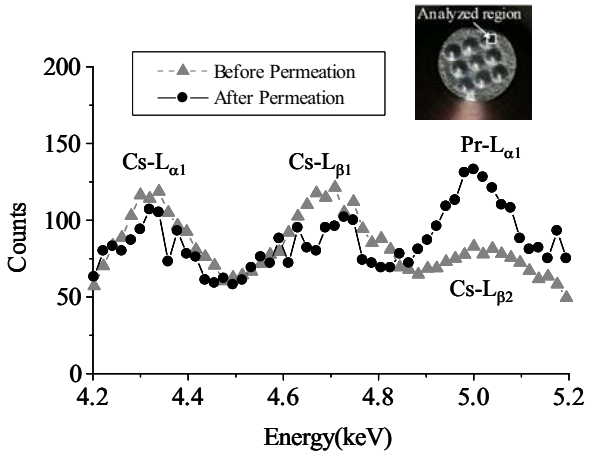

Fig. 5. Observation of transmutation of Cs into Pr by an *in-situ* experiment at SPring-8.

We tried another element transmutation experiments. One is the Ba transmutation experiments using natural Ba and mass 137 enriched Ba[3]. 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. 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).

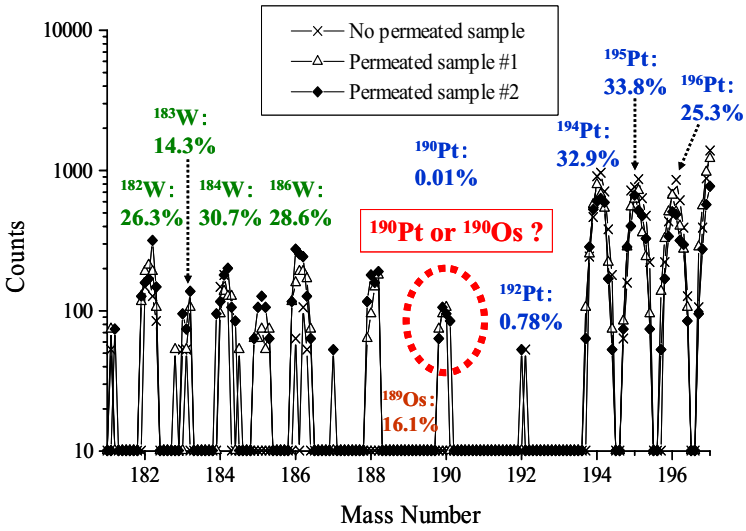

Fig. 6. SIMS Analysis for W transmutation experiments.

Recently, W (tungsten) transmutation experiments were tried using our permeation technique aiming production of Pt or Os. W ion implantation (63kV, $2.5X10^{14}/cm^2$) was applied to Pd/CaO multilayer films, and then permeation experiments were performed several times. Figure 6 shows the SIMS analysis using Cs^+ ions, in which mass spectra were compared between permeated samples and no permeated one. No permeated sample has implanted W and Pt mass numbers. Pt is the major impurity in Pd. Observed spectra have natural W and Pt mass distributions. On the contrary, mass distributions for permeated samples are anomalous. Significant increase for mass 190 should be noticed, although no mass counts of 190 for the No permeated sample. The increase for the two permeated samples can NOT be attributed to natural Os or Pt. We cannot see any mass 189 in the Fig.6 and then expect no contribution to mass 190 by natural Os. Contribution to mass 190 by impurity Pt should be smaller than mass 192 based on the natural mass distribution of 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 W. However, addition of evidences using elemental analysis such as XRF is desirable as a next step research.

Depth profiles of Cs and Pr were plotted in Fig.7. XPS analysis was applied. Cs was injected into all the Pd 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 without permeation show normal and reasonable result as shown in Fig. 7. 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 7 also shows that Cs atoms do not diffuse and migrate with D_2 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.

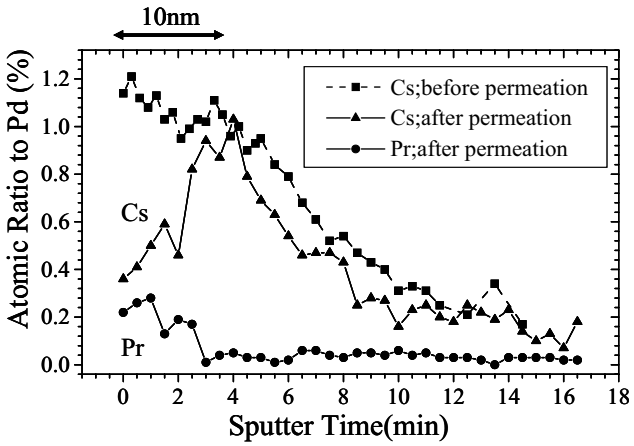

Fig..7 Depth profiles of Cs and Pr for samples after D_2 permeation and before permeation.

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 [3] 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 1. 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 the Table1. Although it is difficult to make conclusive

results, the existence of low work function of intermediate material might have some effects to induce transmutation.

Table1 Correlation between intermediate material in Pd multilayer film and transmutation results.

Intermediate Material	Work Function (eV)	Results for analysis after permeation
CaO	1.2	Pr detected >100cases
Y_2O_3	2.2	Pr detected (3cases)
MgO	3.3	No Pr (3cases)

The obtained experimental results so far suggest that a certain rule seems to exist for this deuterium permeation transmutation. Table 2 summarizes typical transmutation results obtained so far in our experiments. We can notice that 2d, 4d or 6d looks like reacting with deposited elements. From another point of view, it might be consider that α 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.

Table2 Typical Reactions observed so far

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

There are no established theories that can explain the experimental results without any assumptions, although some attractive models and theories have been proposed [4]-[5]. 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.

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[7]. 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 [8]. N. Takhashi et al., the researchers of Toyota Central R&D Labs, presented that they detected Pr from the permeated Pd sample using SOR x-ray at Spring-8 and the detected Pr was confirmed by ICP-MS and TOF-SIMS [8].

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.

ACKNOWLEDGEMENT

This work is supported by Japan Synchrotron Radiation Research Institute (JASRI) and the Thermal & Electric Energy Technology Foundation (TEET). The authors would like acknowledge Prof. A.Takahashi, Prof. Fukutani, Prof. Sekiba, Dr.F. Clelani, Prof. Kasagi, Dr. Nishimura, Dr. T. Hioki, Dr.N.Takahashi, Prof. Yamada, Prof. Narita, Prof. M. Melich, and Dr. K. Grabowski for their supports and valuable discussions.

REFERENCES

1. Y. Iwamura, M. Sakano and T. Itoh, Jpn. J. Appl. Phys. 41, 4642-4648 (2002).
2. Y. Iwamura et al., Proceedings of 12th International Conference on Condensed Matter Nuclear Science, ed. by A.Takahashi et al., Condensed Matter Nuclear Science, World Scientific, New Jersey, pp.178-187 (2006).
3. Y. Iwamura et.al,, J. Condensed Matter Nucl. Sci. vol.4, p. 132–144(2011)
4. A.Takahashi, J. Condensed Matter Nucl. Sci. 33, 33–44 (2009).
5. A. Widom and L. Larsen Eur. Phys. J. C 46. 107 (2006).
6. T. Higashiyama et al.., Proceedings of 10th International Conference on Condensed Matter Nuclear Science, edited by P.H.Hagelstein et al., Condensed Matter Nuclear Science, World Scientific, New Jersey, , pp.447-454(2006).
7. H. Yamada et al., Proceedings of 12th International Conference on Condensed Matter Nuclear Science, ed. by A.Takahashi et al., Condensed Matter Nuclear Science, World Scientific, New Jersey, 2006, pp.196-205.
8. N. Takahashi et al., "Verification of MHI transmutation", #8 Spring-8 Industrial Application Conference, Sep.8-Sep.9,2011, Kobe, Japan, (in Japanese).