Low Energy Nuclear Transmutation In Condensed Matter Induced By D_2 Gas Permeation Through Pd Complexes: Correlation Between Deuterium Flux And Nuclear Products

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Observations of low energy nuclear reactions induced by D_2 gas permeation through Pd complexes (Pd/CaO/Pd) were presented at ICCF-9[1] and in a paper[2] published in the Japanese Journal of Applied Physics (JJAP). 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. When Sr was added to the surface, Mo emerged while the Sr decreased after D_2 gas permeation. The isotopic composition of the detected Mo was different from the natural abundance.

In this paper, recent progress of our research is described. The detected Pr was confirmed by various methods such as TOF-SIMS, XANES, X-ray Fluorescence Spectrometry and ICP-MS. Analysis of the depth profile of Pr indicated that a very thin surface region up to 100 angstroms was the active transmutation zone. Many experimental results showed that the quantity of Pr was proportional to the deuterium flux through Pd complex. The cross section of transmutation of Cs into Pr can be roughly estimated at 1 barn if we consider the deuterium flux as an ultra low energy deuteron beam.

1 Introduction

Anomalous elemental changes have been observed on the Pd complexes, which consist of a thin Pd layer, alternating CaO and Pd layers and bulk Pd, after subjecting the Pd complexes to D_2 gas permeation as we reported at ICCF-9[1] and in the paper[2] in the Japanese Journal of Applied Physics (JJAP).

In this paper, we describe recent progress. The following points have been improved or changed.

1) Pr was identified by XPS, TOF-SIMS, XANES, X-ray Fluorescence and ICP-MS.
2) A quantitative analysis of Pr has became possible using ICP-MS.
3) The correlation between deuterium flux and Pr was investigated.
4) Cs ion injection into Pd complexes (instead of the electrochemical method) was performed.
5) Depth profile and surface distribution of Cs and Pr was obtained by TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry).

Our experimental method can be characterized by the following two main features. The first is the permeation of D_2 gas through the Pd complex, as shown in Fig. 1(a). Permeation of deuterium is attained by exposing one side of the Pd complex to D_2 gas while maintaining the other side under vacuum conditions. On the D_2 gas side of the Pd complex, dissociative absorption causes the D_2 molecules to separate into D atoms, which diffuse through the metal toward the vacuum side, where they emerge from the metal, combine and are released as D_2 gas.

The second feature is the addition of an element that is specifically 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 or Sr is deposited on the surface of the top thin Pd layer, as shown in Fig. 1(b). This Cs or Sr is transmuted. In other words, with this composition, we can provide a deuterium flux through the Pd complex on which a target element is placed as a target to be transmuted. We perform elemental analyses of the given elements after D_2 gas permeation by exhausting the D_2 chamber (by making it into a vacuum chamber). Our experimental method is superior in that it clearly discriminates transmutation products from

contamination because we analyze the products by XPS (X-ray Photoelectron Spectroscopy) in vacuum, in situ during the experiment, without moving or the sample or opening the chamber.
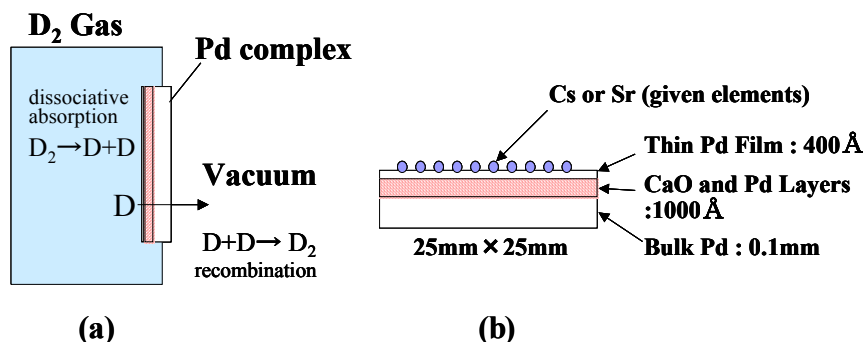

Figure 1. Schematic of the present method: (a)D2 gas permeation of the Pd complex, (b)Structure of the Pd complex deposited with Cs or Sr
.

2   Experimental

The experimental method and setup are basically the same as before[1,2]. Therefore we shall omit a detailed description, and describe only the changed and improved aspects of the experiment.

Cs is now added to the surface by the ion injection method, in addition to the electrochemical method, for exact depth profile analysis.

Figure 2 shows the experimental apparatus. The D_2 gas flow rate was estimated by measuring the pressure of the chamber B. (Chamber B is evacuated, but the vacuum is gradually filled with the gas that permeates through the Pd complex.) The calibration curve for pressure versus the D_2 gas flow rate was obtained in advance by letting D_2 gas into the vacuum chamber through a precision gas flow meter.
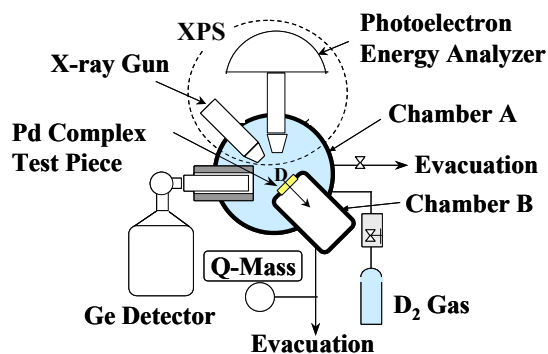

Figure 2. Experimental Setup.

3 Results and Discussion

Let us briefly describe the experimental results presented[2] at ICCF-9. A transmutation reaction converting Cs into Pr is shown in Fig. 3. Results for two runs are shown as examples. The number of Cs atoms decreased while the number of Pr atoms increased over time. No Pr was detected at the beginning of the experiments. At 120 h, the number of Pr atoms exceeded that of Cs atoms.
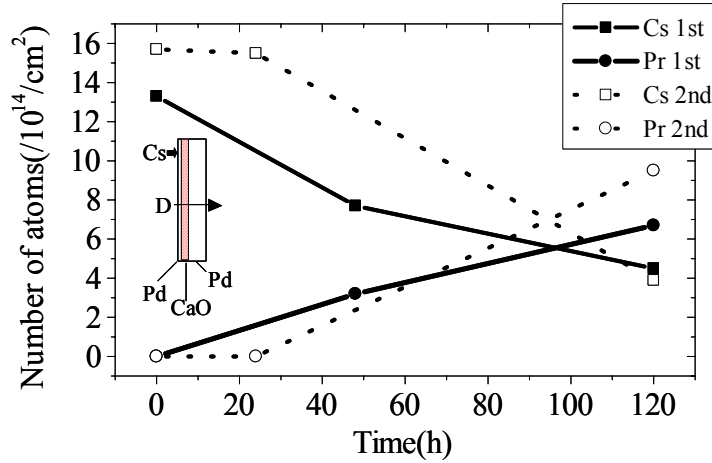

Figure 3. Time variation in the number of Cs and Pr atoms during D_2 gas permeation through Pd complex (Pd/CaO/Pd) deposited with Cs
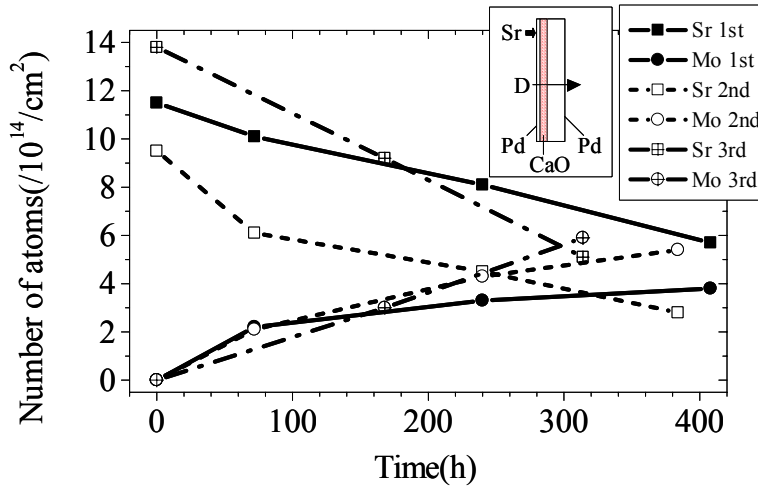

Figure 4. Time variation in number of Sr and Mo atoms induced by D_2 gas permeation through Pd complex(Pd/CaO/Pd) deposited with Sr

The experimental results for Pd complex test pieces with added Sr are shown in Fig. 4. We observed that Sr decreased while Mo increased over time. Experiments were performed three times and all data are plotted here. 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 with Sr take longer to convert a given mass of Sr into Mo than it takes to convert that mass of Cs into Pr.
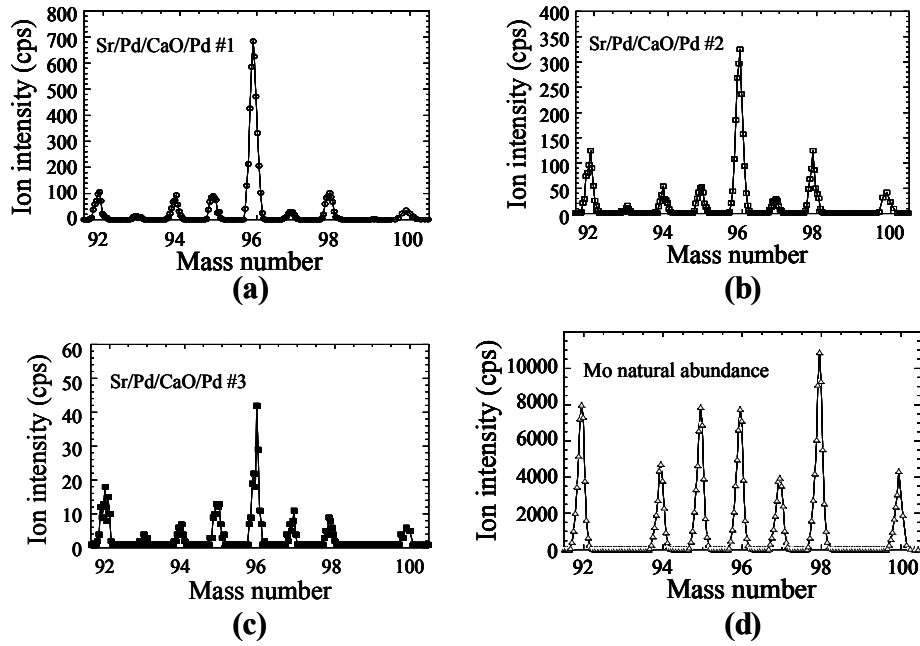
Figure 5. Anomalous isotopic composition of detected Mo: (a) Isotopic composition of detected Mo for run #1, (b)Isotopic composition of detected Mo for run #2, (c)Isotopic composition of detected Mo for run #3, (d) Natural abundance of Mo analyzed by SIMS.

Figures 5(a)-(c) show the results of SIMS analysis for the three samples. 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) that was deposited on a Pd disk is shown in Fig. 5(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.
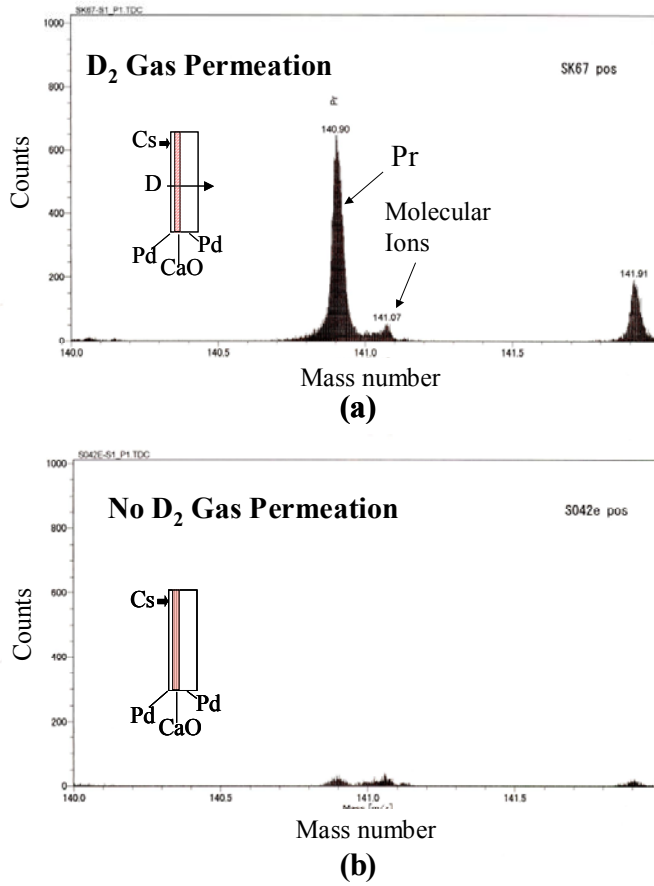
Figure 6. Identification of Pr by TOF-SIMS: (a) Mass number distribution of the sample after D_2 gas permeation, (b) Mass number distribution of the sample without D2 gas permeation

Let us move on to new experimental results. Pr, the transmuted product from Cs, was confirmed by many element analysis methods. The first example is the identification of Pr by TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) shown in Fig. 6. The TOF-SIMS device is a model TRIFTTM II made by ULVAC-PHI. The upper figure shows the mass number distribution of the Pd complex (Pd/CaO/Pd) after D_2 gas permeation, and the lower figure is for the Pd complex without D_2 gas permeation. The TOF-SIMS can distinguish small mass difference so that Pr and molecular ions can be clearly separated, as shown in the upper figure. It is confirmed that Pr is detected only for the foreground sample.
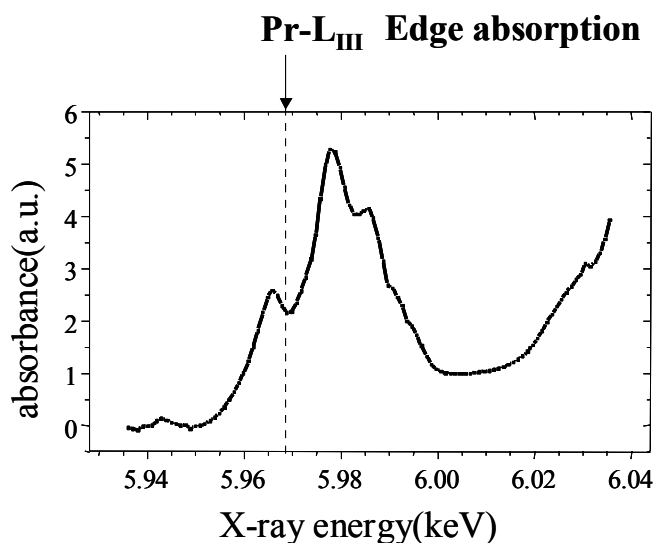
Pr-L$_{III}$ Edge absorption

Figure 7. Identification of Pr by XANES (X-ray Absorption Near Edge Structure) .

Confirmation of Pr by XANES (X-ray Absorption Near Edge Structure) is shown in Fig. 7. This spectrum was obtained at the BL-9A Line at the High Energy Accelerator Research Organization (KEK), located in Tsukuba, Japan (www.kek.jp). A Pd complex sample after D_2 gas permeation, on which Pr was detected by XPS, was examined by XANES. Pr L$_{III}$ Edge absorption was clearly recognized in Fig. 7

Furthermore, Pd complex samples after D_2 gas permeation were examined by X-ray fluorescence spectrometry and ICP-MS (Inductively Coupled Plasma Mass Spectrometry). Although the X-ray fluorescence spectrometry is a bulk analysis method, Pr was detected using strong SOR X-rays. The sensitivity of ICP-MS is so high that quantitative analysis of Pr is performed for all the experiments.
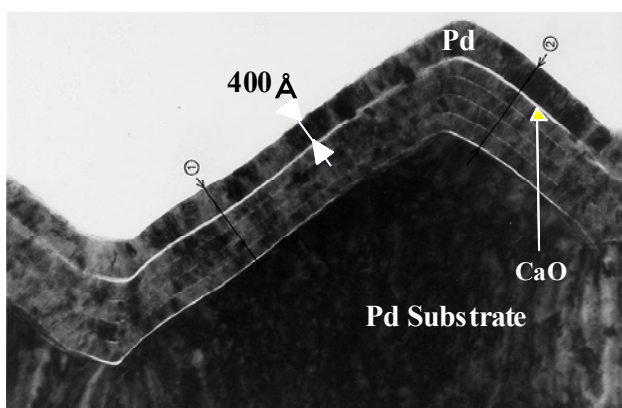

Figure 8. Cross section of Pd complex (Pd/CaO/Pd) observed by TEM (Transmission Electron Microscopy)

Figure 8 shows the cross sectional view of the Pd complex (Pd/CaO/Pd). This image was taken by TEM (Transmission Electron Microprobe). During the process of Pd complex fabrication, the Pd substrate is etched with aqua regia[1,2]. The wave-like shape of the Pd substrate is formed by the etching process. On the Pd

substrate, Pd and CaO complex layer are formed by Ar ion beam sputtering. The white lines correspond to CaO and the black parts to Pd. The 400-angstrom Pd thin film is located on the Pd and CaO complex layer.
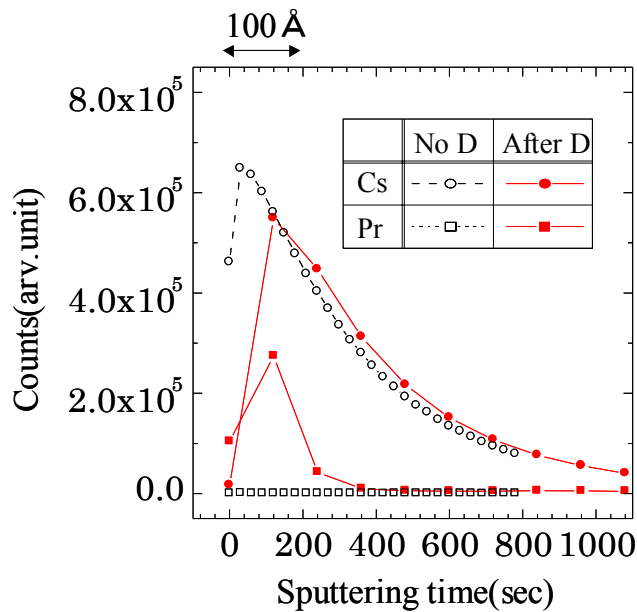

Figure 9. Depth Profiles of Cs and Pr for a Pd complex (Pd /CaO/Pd) sample after D2 gas permeation and a Pd complex (Pd /CaO/Pd) sample without D2 gas permeation

Depth profiles of Cs and Pr were plotted in Fig. 9. Two Pd complex samples were prepared and Cs was injected into them by the ion implantation method. Acceleration voltage and Cs fluence for the ion implantation were the same for the two samples, 18keV and 10^{15} ions/cm^2, respectively. The depth profiles were estimated by TOF-SIMS analysis. Physical Electronics TRIFT II was applied for the analysis and the condition of Ga$^+$ ion was 15keV-600pA. 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. This measurement shows that a 200 sec sputtering time corresponds to 100 angstroms.

Cs and Pr depth profiles for the Pd complex without permeation show normal results in Fig. 9. Cs decreases continuously from the surface and there is no Pr in the sample.

On the other hand, Cs and Pr depth profiles for the Pd complex after D$_2$ gas permeation exhibit interesting results. Cs depth profiles for the foreground and background samples agree in the deep area. However, Cs decreases near the surface after D$_2$ gas permeation. We can see that there is Pr, which is the same order as given Cs, in the near surface area. This experimental fact suggests that Cs transmutation reaction into Pr occurs in the near surface region up to 100 angstrom. This transmutation active zone might be correlated with the D/Pd ratio. Further investigation of the surface region is important. Figure 9 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 imagine that the detected Pr was a concentrated impurity, and not a transmutation product.
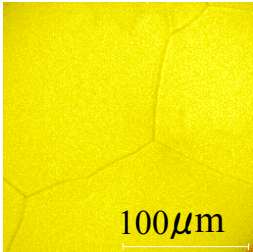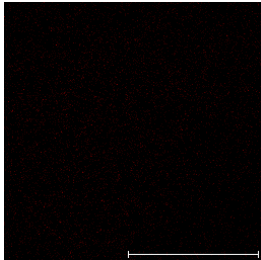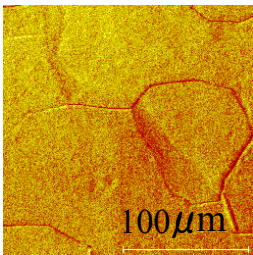
	Cs	Pr
before	100μm	100μm
after	100μm	100μm
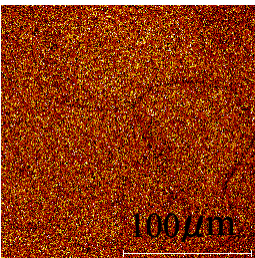
Figure 10. Surface Distributions of Cs and Pr for a Pd complex (Pd /CaO/Pd) sample after D_2 gas permeation and a Pd complex (Pd /CaO/Pd) sample without (before) D2 gas permeation

Figure 10 shows surface distributions of Cs and Pr for the two samples discussed above. Space resolving power is 1 micron. Grain boundaries can be seen in each image. These images show that the surface distribution of Pr basically seems to be uniform and has no correlation with the grain boundaries.

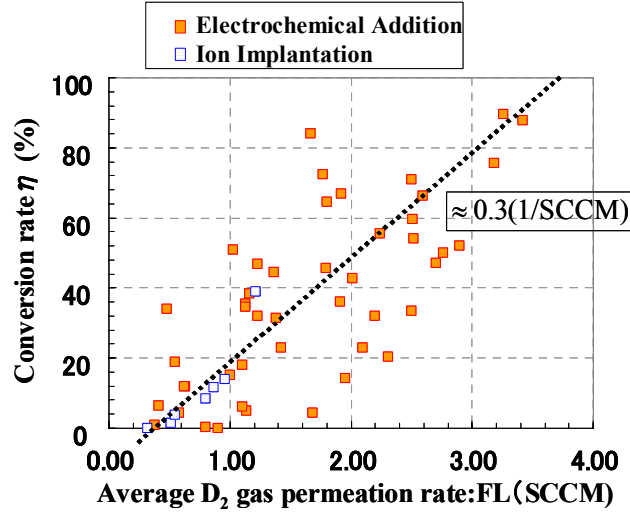Figure 11. Correlation between D_2 permeation rate and conversion rate.

Using ICP-MS analysis, a quantitative estimate of the mass of Pr has been performed. The correlation between D_2 gas permeation rate and conversion rate is shown in Fig. 11.

The conversion rate is defined as

$$\eta = \frac{N_{Pr}}{N_{Cs}} \times 100\% = \frac{N_{Pr}}{N'_{Cs} + N_{Pr}} \times 100\% ,$$

η : conversion rate(%), N_{Pr} : detected Pr(ng), N_{Cs} : given Cs(ng),   (1)
N'_{Cs} : det ected Cs after an experiment(ng).

Since ICP-MS analysis is a destructive analysis method, we cannot measure the starting mass of Cs directly. Assuming that a Cs atom is transmuted into a Pr atom, the sum of the detected Pr and the detected Cs after permeation should be equal to the starting Cs.

Figure 11 suggests that the conversion rate defined as above is proportional to the average D_2 gas permeation rate. Experimental results for both the electrochemical addition and the ion implantation of Cs are plotted in the figure. It seems that they have linear correlation for the both cases.

Let us consider on the situation that D beam irradiates the Pd complex with Cs. The reaction rate is expressed as the following equation.

$$R = \sigma \cdot N_{Cs} \cdot \phi$$

R : reaction rate(event/cm^3/sec), σ : cross section(cm^2), N_{Cs} : number of Cs(1/cm^3),   (2)
ϕ : deuteron beam flux (1/cm^2/sec).

If we regard D_2 gas permeation as a kind of deuteron beam, the following relation is obtained by equation (2).

$$\eta = \int_t (R / N_{Cs}) dt = \int_t (\sigma \cdot \phi) dt = \sigma \int_t \phi dt \approx \sigma \cdot f \cdot FL \cdot T_{exp} / S \qquad (3)$$

FL : flow rate(sccm), T_{exp} : reactiontion time(sec), S : permeation surface area(cm^2).

$$\therefore \eta \propto FL$$

This equation agrees with the experimental results shown in Fig. 11. Therefore we can roughly estimate the cross section using the obtained experimental results. If we input experimental parameters into equation (3), we obtain

$$\eta = \sigma \cdot f \cdot FL \cdot T_{exp} / S$$
$$= \sigma \cdot \frac{2 \times 6 \times 10^{23}}{22.4 \times 10^3 \times 60} \cdot FL \cdot 100 \times 3600 / 1.0$$
$$= \sigma [cm^2] \cdot FL[sccm] \cdot 3 \times 10^{23} [1 / cm^2 / sccm]$$

$$(4)$$

The experimental results show the gradient between FL and conversion rate is about 0.3(1/sccm). (The term sccm means standard cubic centimeter per minute.) Therefore the following result is obtained.

$$0.3 \approx \sigma \cdot 3 \times 10^{23} \qquad \therefore \sigma \approx 1 \times 10^{-24} [cm^2] = 1 [barn]$$

This cross section seems to be extremely large if we take it into consideration that the transmutation reaction belongs to multi-body reactions. And we should notice that we regard the deuterium permeation velocity as deuteron velocity, and the deuteron flux is estimated relatively low, leading to very large cross section. If the deuteron behavior on the microscopic level in the Pd thin film could be clarified, a more precise physical model would be developed. In any case, on the macroscopic level deuterium permeation through Pd complex can be regarded similar to an ultra low deuteron beam, and the cross section of transmutation of Cs into Pr is estimated at 1 barn according to our experimental results.

We would like briefly touch on a few points, starting with the problem of discriminating contamination and transmutation products. Since the detected material, Pr, is a rare earth element, it is difficult to imagine that Pr accumulated on the Pd complex test samples by any ordinary process. As mentioned in Fig. 9, Cs atoms do not diffuse and migrate by D_2 gas permeation. Therefore it can be postulated that Pr atoms also do not migrate. The purity of our D_2 gas is over 99.6% and the most of the impurity in it is H_2. Other impurities detected by a mass spectrometer are N_2, D_2O, O_2, CO_2, CO and hydrocarbons; they are all under 10ppm. We analyzed Pd complex test pieces deposited with Cs by ICP-MS mass spectrometry and confirmed that Pr in the test samples was below the detection limit (0.1ng). On the other hand, the detected Pr ranges from 1ng to 100ng. The amount of the detected Pr exceeds the maximum possible contamination of Pr. Therefore we conclude the detected Pr was transmuted from Cs.

Our next point is that the isotope ratio of the synthesized elements is anomalous. The isotopic anomaly of the Mo is particularly strong evidence that this Mo was produced by some nuclear processes. Some might speculate that the anomalous isotope ratios were caused by Mo contamination undergoing some sort of isotopic separation process, leaving only ^{96}Mo to be detected. (See Fig. 5). However, such efficient isotope separation would not be possible.

We noticed that a certain rule exists between starting and produced elements[1,2]. The increase in mass number is 8, and the increase in atomic number is 4 in the case of Cs and Sr. It appears that 4d addition reactions occur. We also observed 2d and 6d addition transmutation reactions[3].

At present, we do not have a complete theory that can explain the experimental results without a few assumptions. The EQPET model [4,5] proposed by Prof. A. Takahashi can basically explain our experimental results, by assuming that a short lived, quasi-particle electron pair like Cooper-pair can be generated. The observed transmutation processes must belong to a new category of nuclear reactions in condensed matter. Therefore much more theoretical investigation is necessary.

4   Concluding Remarks

Nuclear transmutation of Cs into Pr and Sr into Mo can be observed during D_2 gas permeation through Pd Complexes. Pr was identified by various methods such as XPS, TOF-SIMS, XANES, X-ray fluorescence spectrometry and ICP-MS. A very thin surface region up to 100 angstroms was the active transmutation area, as determined by the analysis of depth profile of Pr. The quantity of Pr was proportional to deuterium flux through the Pd complex. The cross section of transmutation of Cs into Pr can be roughly estimated at 1 barn if we regard the deuterium flux as an ultra low energy deuteron beam.

Some replication experiments producing transmutation reactions of Cs into Pr or Sr into Mo were planning or presented for the ICCF10 conference[6,7]. Positive results were obtained not only in a gaseous environment[6] presented by Prof. A. Takahashi *et al.*, but also in an electrochemical environment[7] performed Dr. F. Celani's team.

References

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