Element Analysis of the Surface Layer on the Pd and Pd-Y Alloy after Deuterium Permeation

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Abstract

ToF-SIMS analysis showed that new elements appeared on the surface layer of a palladium sample and on a palladium-yttrium alloy sample after permeation of deuterium through the surface. It agrees with the similar experimental results at the Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd. Our experiment showed that this phenomenon may appear at higher temperatures even when there is no multiple layer coating on the sample surface.

Keywords Condensed Matter Nuclear Science, Pd, Pd-Y, ToF-SIMS, deuterium permeation

Introduction

In contrast with early experiments using a palladium cathode in electrolytic cell, we have been using the gas loading method to study abnormal phenomena in palladium deuterides since 1989. We observed that when deuterium gas was pumped out from a palladium wire there was an abnormal heat flow. When a high-precision calorimeter was used to detect the heat flow, we found that there was a correlation between the abnormal deuterium flux and the heat flow in the D/Pd system[1]. Y. Iwamura *et al.* have observed nuclear transmutations with a deuterium gas flux[2]. They confirmed their result by delivering their samples to France for ToF-SIMS analysis, while at their own laboratory they used on-line XRF (X-Ray Fluorescence spectrometry). Fortunately, in our National Key Laboratory for Surface Physics and Chemistry there is a gas purifying and gas-solid reaction system equipped with a ToF-SIMS for on-line analysis. It provided an opportunity to examine the Iwamura effect *in situ*. In a distinct difference from Iwamura's method, we simply loaded the deuterium flux to the surface of Pd without multiple layer coating. Despite this difference we still observed new elements on the surface layer of Pd or Pd-Y alloy. Moreover, our system is able to heat the samples to much higher temperatures than Iwamura can achieve, but even at high temperatures we still observed anomalous nuclear phenomena after deuterium permeation.

Apparatus and Experiment

The gas purifying and gas-solid reaction system (Fig. 1) was used to perform deuterium permeation experiments and analysis on line. The reaction chamber vacuum can reach 10^{-8} Pa, and the heating platform offered program-controlled heating from room temperature to 1200°C. In the analysis chamber, a time of flight mass spectrograph was used for on-line analysis. The samples were first degassed in the vacuum and then they absorbed deuterium gas at room temperature. After that, they were heated to 400°C and cooled to room temperature in the D_2 atmosphere. When heated, they released the deuterium; and when cooled, they absorbed deuterium again[3]. The D_2 gas was finally pumped out before the SIMS analysis. In this whole process, the samples absorbed and released deuterium twice; hence, we achieved the required deuterium permeation flux twice, in two directions.

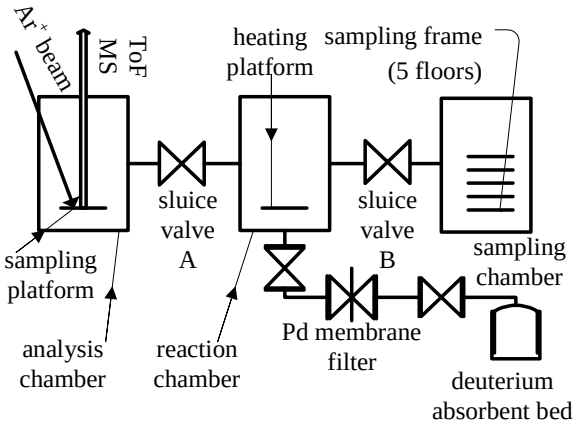

Fig. 1. Schematic of purification and gas-solid reaction system.

Two kinds of samples were used: Pd samples (No. 1 and 2) supplied by Research Institute of Aeronautical Materials (99.98% purity); and Pd-Y samples (Nos. 3, 4 and 5) supplied by the Key Laboratory. Sample No. 3 and 4 contain Y 8.27 at. %, and No. 5 contains Y 7.64 at. %. The size of the samples is about 1 cm^2 with thickness of 0.1 mm.

The samples were glued to stainless steel blocks and polished with #2000 sandpaper in pure water. Then they were finely polished with a Metallographic Polishing Machine (model GPV-2) at a speed of 940 r/min. The samples were separated from the blocks by dipping them into acetone for about 2 hours, and then carefully cleaned with acetone. A small piece was cut from each sample for background analysis.

On the first day, before the deuterium loading, the vacuum in the sampling chamber was 5.5×10^{-6} Pa, while in the reaction chamber it was 6.0×10^{-7} Pa. Each of the samples was placed on a stainless steel plate. Sample No. 1 was put into the reaction chamber, while others remained in the sampling chamber. Sluice valve B closed, and the reaction

chamber was continuously pumped, while the sampling chamber was pumped for only 24 hours. On the fifth day, the sampling chamber was at 3.9 Pa and the reaction chamber was at 3.4×10^{-7} Pa. After this, the sampling chamber was pumped again for about 12 hours, down to a vacuum of 8.6×10^{-6} Pa. During all of these processes, the vacuum of the reaction chamber and the analysis chamber remained almost unchanged.

From 21:50 pm on the fifth day to 5:13 am on the sixth day, sluice valve B was kept open, and the samples were shifted between the sampling chamber and the reaction chamber one after another to undergo the process of absorbing and releasing deuterium gas. The deuterium gas absorbent (uranium) bed was heated to 420°C for 30 minutes to release the deuterium. The deuterium gas was purified through a Pd membrane filter first; then, it entered the reaction chamber and sampling chamber. After the samples were saturated with D_2, the vacuum reached 3.0×10^{-4} Pa.

The main parameters of the heating program are listed in table 1.

Table 1. Parameters of the heating program

Heating segment	*Temperature setting/(°C)*	*Time/(min.)*
1	200	20
2	200	5
3	400	20
4	400	300

The experiment steps were under program control. The heating platform reached 400°C in 45 minutes and was kept at 400°C during the following processes. Sample No. 1 was fetched back to the sampling chamber after 30 minutes where it cooled down naturally. Then, samples No. 2 through 5 samples was shifted into the heating platform to be heated for 30 minutes and returned back to the sampling chamber one by one. Finally, sample No. 5 stayed on the platform after being heated, and the heater was shut off. Then it was cooled down to 50°C in 80 minutes. The cooling speed of sample No. 5 should be the slower in comparison with that of the other 4 samples that cooled in the sampling chamber. The deuterium gas was then pumped out by the uranium absorbent bed. The sampling chamber and reaction chamber were pumped to high vacuum again. Then the samples were shifted into the analysis chamber for analysis using the ToF-SIMS.

The primary ion of SIMS is Ar^+, the intensity of which is adjustable from 300 nA to 20 mA. The mass resolution of the ToF-SIMS is 5000 FWHM; the ion beam footprint on the sample is 0.01 mm^2; the sensitivity is 1×10^8/cc for aluminum or 2.4×10^{12}/cc for copper.

Results

1. Thallium (Tl) observed in Pd-Y alloy after deuterium permeation

The elemental analysis of sample No. 5 (Pd-Y) showed two peaks at m/z=203, 205 (Fig. 2).

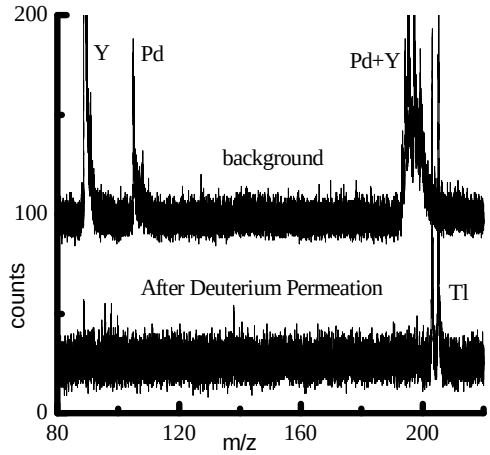

Fig.2 Tl observed in Pd-Y after deuterium permeation

The "counts" in the figure denotes the intensity of the secondary ions. In the background mass spectrograph, the compound ion Pd+Y, the m/z of which was 193,194,195,197,199, respectively were found in addition to Pd and Y, but there was no peak near m/z=203,205. Some other elements, such as Na, Si, K, Ar, Fe, and Zn were found, but they could not form any compound ion whose m/z=203,205. The natural abundance of Tl is Tl-203 29.52%, Tl-205 70.48%, which is different from the distribution in mass spectrograph shown here.

Some points on the surface layer of sample No. 5 were analyzed to study element variation by depth. These points were bombarded continuously (primary ion intensity: 10 mA), and the secondary ion intensity was measured at every minute. The mass spectrograph is shown in Fig. 3.

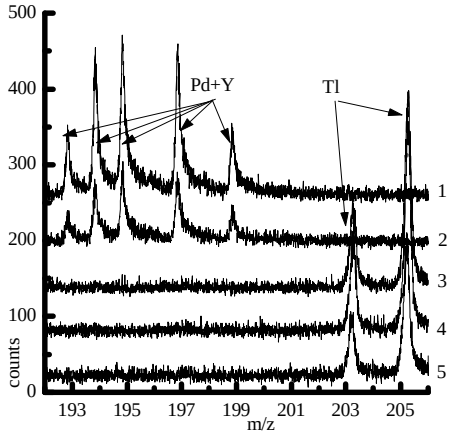

Fig. 3. Element variation at different depths

Curve 1 shows the SIMS analysis for the layer at the first minute on the surface; Curve 5 shows the SIMS analysis for the layer at the 9th minute. The time interval between neighboring curves is 2 minutes. Each curve is shifted upwards by 60 counts in order to show them clearly. In the initial 5 minutes, there was no Tl but there was Pd+Y; while in the following 5 minutes, there was no Pd+Y but there was Tl.

Just after this point was bombarded, another point in the nearby region was bombarded (Fig. 4, showing curves plotted like those in Fig. 3).

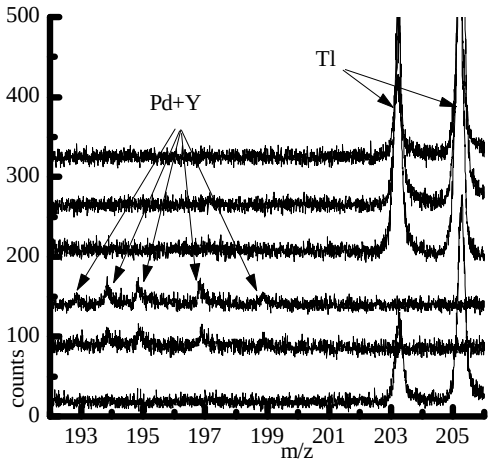

Fig. 4. Element variation at different depths at a nearby point.

In this case, Tl was detected during the initial 5 minutes, but no Tl was found over the next 5 minutes. After 10 minutes Tl appeared again. Probably there was no Tl in the

original surface layers at this location, but the Tl sputtered from the previous nearby location. There was almost no Pd or Y where the Tl appeared. The causation should be studied further in our next experiments.

Tl did not appear at the every point on the surface of the sample. We attempted to use SEM (Scanning Electron Microscope, WSD mode) to confirm this trace of Tl after the samples were taken out from this apparatus; however, SEM analysis (WDS mode) did not show any Tl on the surface. A possible explanation for this is that the Tl appeared only on some points and in the layer under the surface (as confirmed by Fig. 3 and Fig. 4). Tl was not observed in samples No. 3 or 4, so the slow cooling down of sample No. 5 may be essential. The negative results with samples No. 3 and 4 exclude the possibility of contamination in this apparatus.

2. Gadolinium (Gd), Terbium (Tb), Niobium (Nd) observed in Pd after deuterium permeation

The element analysis of No. 1 and 2 samples (Pd) shows peaks from m/z=155 to 160 after deuterium permeation. In Fig. 5, the upper two curves show the SIMS analysis of the background, the lower two curves show the SIMS analysis after deuterium permeation.

There are no peaks in this range of mass numbers in the background analysis. It was determined that the elements in these peaks are Gd (m/z=155, 156, 157, 158, 160) and Tb (m/z=159). There is also peaks of Nd (m/z=142, 143, 144, 145, 146, 148, 150). We observed the Tb in earlier experiments[4] as well.

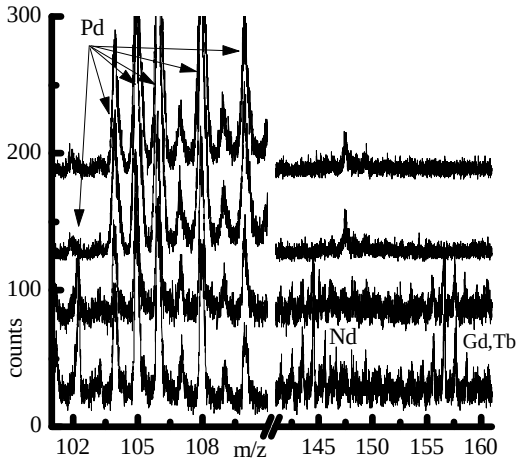

Fig. 5. Gd,Tb,Nd observed in Pd after deuterium permeation

Conclusion and Discussion

Based on this experimental observation we conclude that: Gd, Tb, Nd are observed in Pd after deuterium permeation; and Tl is observed in Pd-Y alloy, and this Tl did not exist on the surface layers of Pd or Pd-Y before deuterium permeation. Contamination and compound ions have been excluded, so the new elements are presumably produced by nuclear reactions. This conclusion should be bolstered in our next set of experiments. We will increase the number of times deuterium permeation is performed, which we believe to be a critical parameter.

This experiment showed that deuterium flux permeating through the palladium surface might introduce not only the heat flow[1], but also the nuclear transmutation[2,4]. This experiment showed also that the multiple layer coating on the surface might be not necessary, and the operation temperature can be higher than that in Mitsubishi's experiment[2].

Acknowledgement

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