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Analysis By Time-Of-Flight Secondary Ion Mass Spectroscopy or Nuclear Products In Hydrogen Penetration Through Palladium

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Elemental analysis was performed for the palladium foil through which the hydrogen gas penetrated. We analyzed sample surface by Time-of-Flight secondary ion mass spectroscopy and searched for newly produced elements during the gas permeation process. Significant increase of the counts for Cr, Fe, Cu and Ag were found after the permeation. These elements could have been produced by nuclear transmutation.

1 Introduction

The possibility of inducing nuclear reactions at low temperature in solid-state has been widely investigated for these years. Among several experimental methods for the reaction, the controlled gas out-diffusion with palladium (Pd) deuteride or hydride in the evacuated chamber is one of the unique methods [1,2]. It was developed by Yamaguchi *et al.* and called “in vacuo” method. They observed the excess heat and helium production, which was thought to be a possible result of a nuclear reaction. The gas penetration method is another unique one. Iwamura *et al.* has studied using this method with Pd film complexes, which consist of a thin Pd layer, a CaO and a bulk Pd [3,4]. They have reported observation of elements production in deuterium permeation experiment and recently have found a certain rule of nuclear transmutation, that is, 8 mass number and 4 atomic number increase in the process. The phenomenon was observed with good reproducibility. These results suggest that there is a key to understand the reaction in the mobility of D (or H) atoms in Pd lattice.

In this present study, we have performed the similar penetration experiment using hydrogen with Pd foil without any additional layer, and have searched for nuclear products as a result of low energy reaction. This method has an advantage of involving less contamination of the palladium sample in contrast to other method; the method is preferably used in investigating small amount of elements. This study would provide us information to understand transmutation process systematically. In addition, we would consider the possibility of nuclear transmutation in not only deuterium but also hydrogen system as some researchers have claimed in various experiments [5,6].

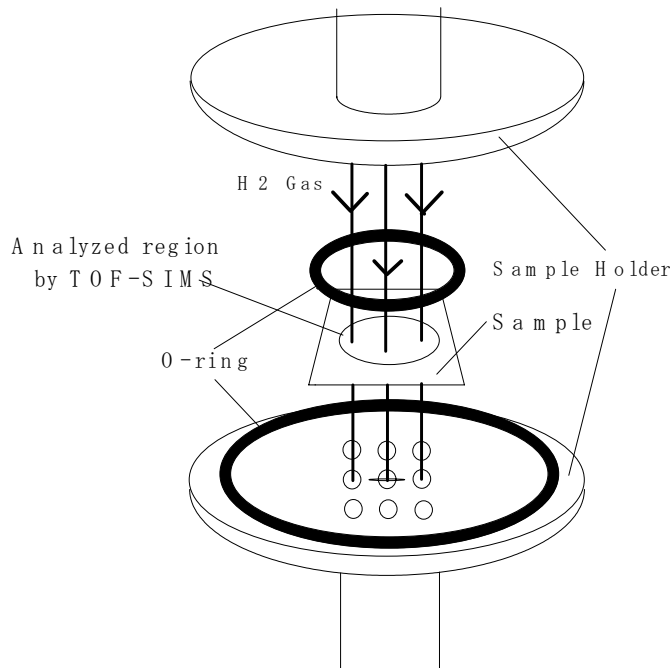


Fig. 1 Sample holder: Hydrogen flows from upper chamber to lower chamber by penetrating the Pd sample.

2 Experiment

The Pd plate (99.95% pure) sample ($0.1 \times 12.5 \times 12.5$ mm) was rinsed with acetone and pure water, then washed by aqua regia to remove impurities on the sample surface. No hydrogen gas was loaded to the sample before experiment. Fig. 1 shows the sample holder and flowing path of the hydrogen gas. The Pd plate was set into a stainless steel holder placed between two chambers. The upper chamber is filled with hydrogen gas at a pressure up to 10 atm, and the lower is evacuated by a diaphragm pump (ULVAC: DAM-010) to prevent the Pd sample from being contaminated from the atmosphere. The gas atoms are driven through the Pd sample to the evacuated chamber by the pressure gradient. The lower sample holder has several holes where the gas flows. The gas was kept flowing for about 2 weeks, then the sample (“After sample”) was taken out from the holder. Before the element analysis, the sample was heated to 400°C to purge the hydrogen atoms remaining in. Finally the sample surface of high-pressure side was analyzed by Time-of-Flight secondary mass spectroscopy (TOF-SIMS) (ULVAC-PHI: TFS-2100). TOF-SIMS has a good sensitivity for a small quantity of the elements on the sample with high resolution in mass number although it is difficult to deduce the absolute quantities from its output data alone. The primary ion in TOF-SIMS was Ga^{+} and measured area was 40×40 micron square. In order to take into account the contamination from the environment, we prepared the control sample (“Control sample”), which was set into and removed from the holder without flowing the hydrogen gas, and compared the composition of the elements on the sample between them to specify newly produced elements during the experiments. TOF-SIMS is capable of analyzing all the elements with their isotopes. We also analyzed the isotopic compositions for the elements detected.

3 Results and Discussion

3.1 Possible elements production

In TOF-SIMS analysis, three randomly selected areas ($40 \mu\text{m} \times 40 \mu\text{m}$) of each sample were analyzed. We did not see significant difference in the mass spectrum for every area. In this study, we do not discuss absolute quantities of the elements, since we have difficulties in quantitative analysis with the TOF-SIMS method. Instead, we use a normalized intensity that is defined here as the count of the secondary ions of each element divided by the total count of ions recorded, and multiplied by 10000.

Fig. 2 shows a typical mass spectrum obtained for the Pd surface of the “Control sample” in the mass number range of 42–65. Low intensities corresponding to elements of Ca, Cr, Mn, Fe, Ni and Cu are seen. These elements are considered to be the impurities included in the Pd sample and contaminants introduced from environments during the time between the experiment and the TOF-SIMS analysis.

Fig. 3 shows a typical spectrum of the sample after the gas penetration. Increasing of the intensity for mass numbers 50, 52, 53, 54, 55, 56, 57, 58, 60, 63, 64 and 65 can be seen. These mass numbers correspond to elements of Cr (^{50}Cr , ^{52}Cr , ^{53}Cr , ^{54}Cr), Mn (^{55}Mn), Fe (^{54}Fe , ^{56}Fe , ^{57}Fe), Ni (^{58}Ni , ^{60}Ni , ^{64}Ni), Cu (^{63}Cu , ^{65}Cu) and Zn (^{64}Zn), respectively.

The TOF-SIMS system is capable of removing the surface layers of the sample by Ga sputtering for surface cleaning and measurement of depth distribution. Fig. 4 and Fig. 5 show mass spectrum after 10s sputter cleaning by Ga^+ ion beam for the same area as Fig. 2 and Fig. 3, respectively. Fig. 4 gives similar spectrum to Fig. 2 for the case of “Control sample”.

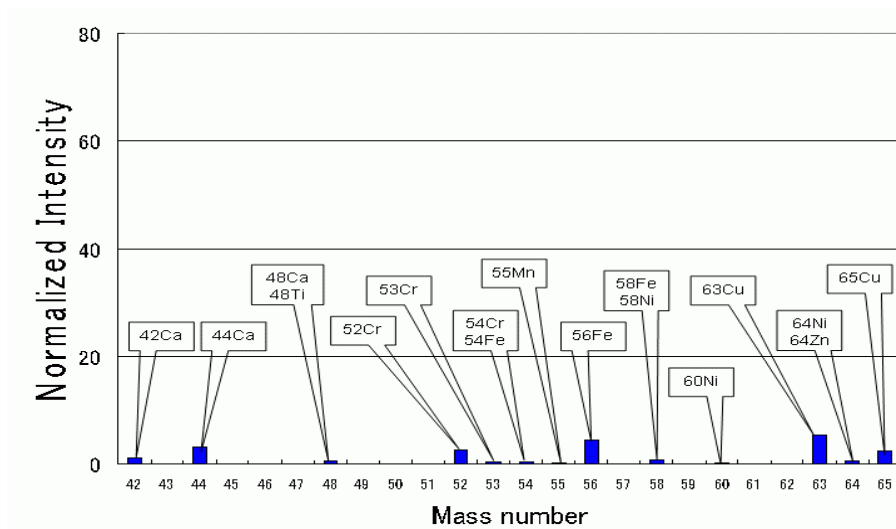


Fig. 2 Normalized count intensity for mass number 42-65 for the control Pd sample.

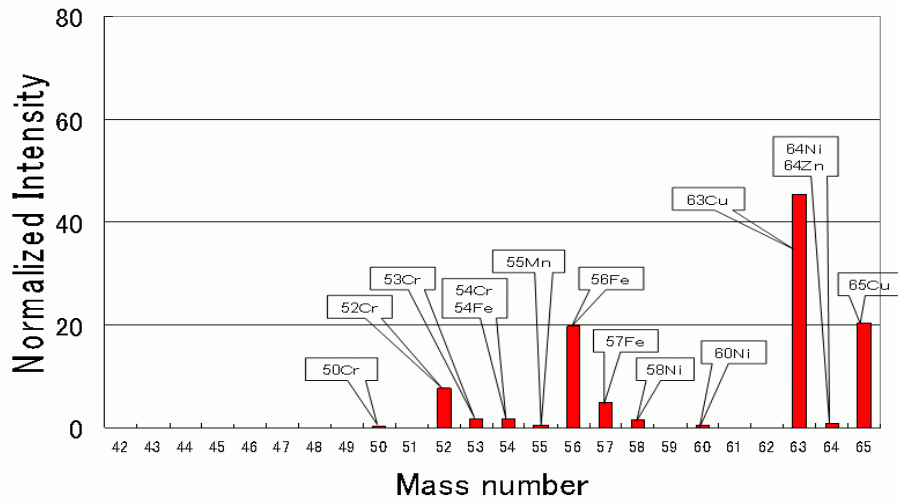


Fig. 3 Normalized count intensity for mass number 42-65 for the Pd sample after experiment.

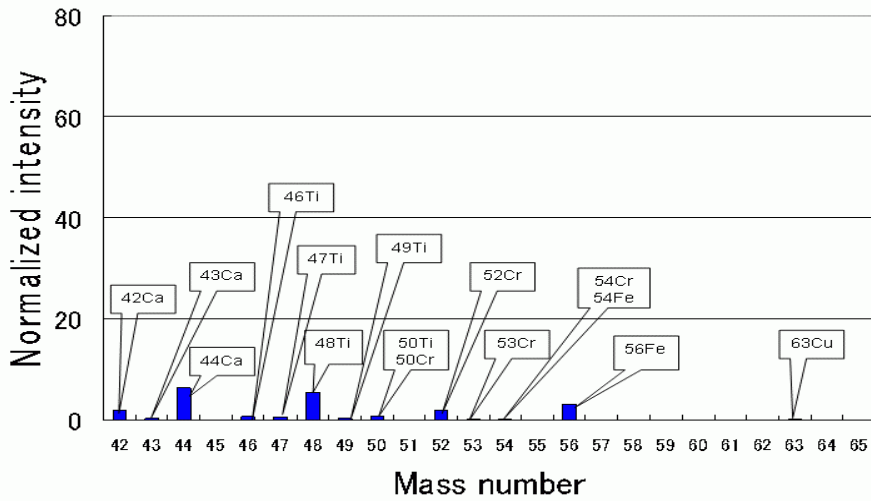


Fig. 4 Normalized count intensity for the control Pd sample with 10s sputtering.

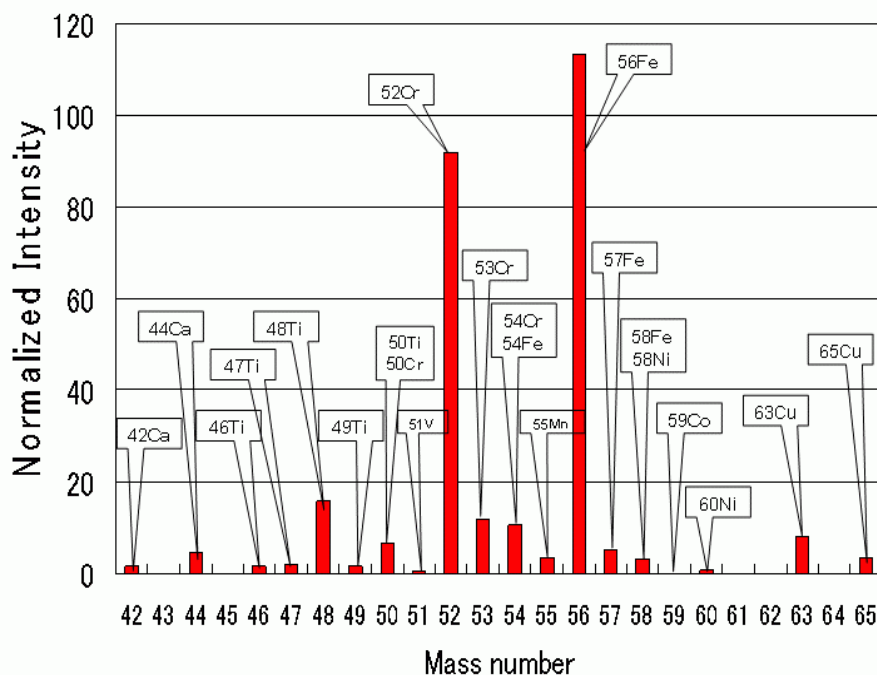


Fig. 5 Normalized count intensity after experiment with 10s sputtering.

Most of the elements with low intensities appearing in Fig. 4 are thought to be impurities included in the Pd foil. After the experiment, increase in the intensity for mass numbers 46, 47, 48, 49, 50, 52, 53, 54, 55, 56 and 63 can be seen in Fig. 5. These correspond to elements of Ti (^{46}Ti , ^{47}Ti , ^{48}Ti , ^{49}Ti , ^{50}Ti), Cr (^{50}Cr , ^{52}Cr , ^{53}Cr , ^{54}Cr), Mn (^{55}Mn), Fe (^{54}Fe , ^{56}Fe) and Cu (^{63}Cu), respectively. In particularly, marked increases in the intensities for Cr, Fe and Cu were observed. We also found elements of mass number 51, 57, 58, 59 and 65 only after experiments, which correspond to elements of ^{51}V , ^{57}Fe , ^{58}Fe , ^{58}Ni , ^{59}Co , and ^{65}Cu , respectively. Furthermore, considerable increase in the intensities for mass number 107 and 108, corresponding to element of Ag (^{107}Ag , ^{109}Ag), was observed.

Fig. 6–9 show the normalized intensity for the isotopes of Cr, Fe, Cu and Ag at three areas on the control samples and those after gas penetration both with sputtering. Note that selected areas for the control sample (a, b, c) are different from those analyzed after experiment (A, B, C). As shown in Fig. 6, very low normalized count intensities for mass numbers corresponding to Cr isotopes was found for the control sample, and significant increase for the intensity was observed at all three areas after experiment. For Fe, Cu and Ag isotopes, the normalized intensities were also increased apparently after experiment, as shown in Fig. 7, 8 and 9, respectively. These results suggested that Cr, Fe, Cu and Ag could have been produced during the gas penetration.

3.2 Change in isotopic ratio

Most of observed elements have several isotopes and own natural isotopic abundance. A detailed mass number for one of isotopes of an element is sometimes close to that of another element. Therefore, we could not distinguish the count intensities between element ^{48}Ca and ^{48}Ti also ^{50}Ti and ^{50}Cr by the TOF-SIMS. Thus, We tried to find out the change in ratio of count intensities for isotopes, which mass number have no overlapping with that of other elements. For the case of Ti, the mass numbers for isotopes ^{47}Ti and ^{49}Ti have no overlapping with those of other elements. The natural isotopic ratio of ^{47}Ti to ^{49}Ti is 0.73 and the value fairly agrees with that for “Control sample”. In contrast, one of the isotopic ratios of ^{47}Ti

to ^{49}Ti for “After sample” showed a marked change to be 0.94. These ratios for the other two analyzed areas are 0.87 and 0.91, fairly higher than the natural one.

For the case of Cr, the mass numbers for isotopes ^{52}Cr and ^{53}Cr have no overlapping with those of other elements. The natural isotopic ratio of ^{52}Cr to ^{53}Cr is 1.13. The obtained ratios for the three analyzed areas on “After sample” also gave fairly changes to be 1.25, 1.35 and 1.45, respectively. While, no anomaly of the isotopic ratio was seen for Fe, Cu, Ag and Pd. The ratios both for “Control” and “After” samples are consistent with natural ones. The changes in isotopic ratios for Ti and Cr could be the possible evidence of nuclear transmutation in/on Pd foil.

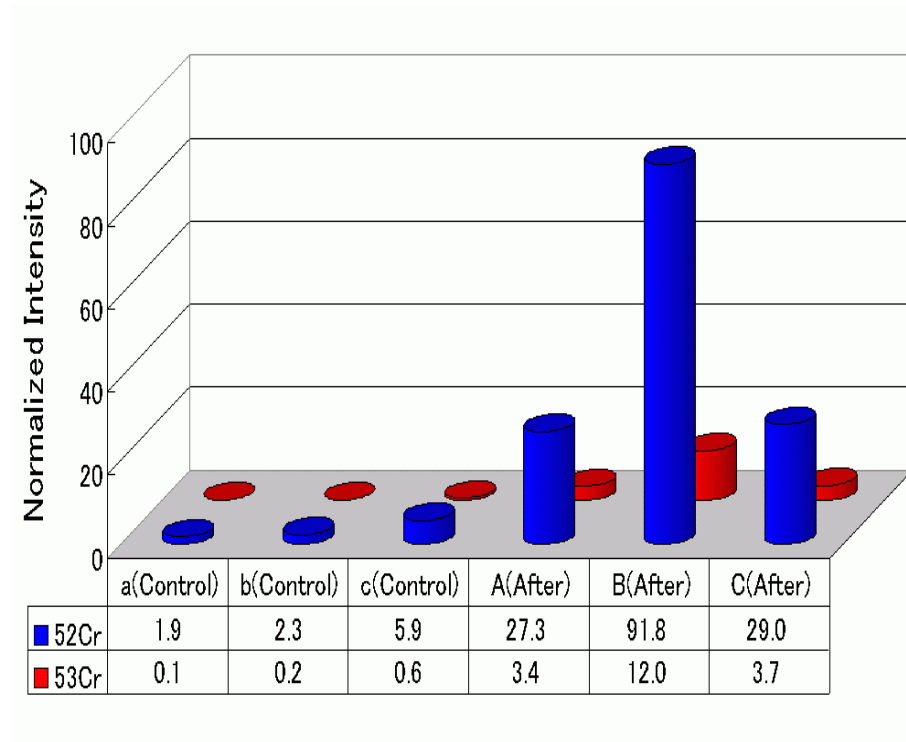


Fig. 6 Normalized count intensity for two isotopes of Cr at three areas with 10s sputtering before and after gas penetration.

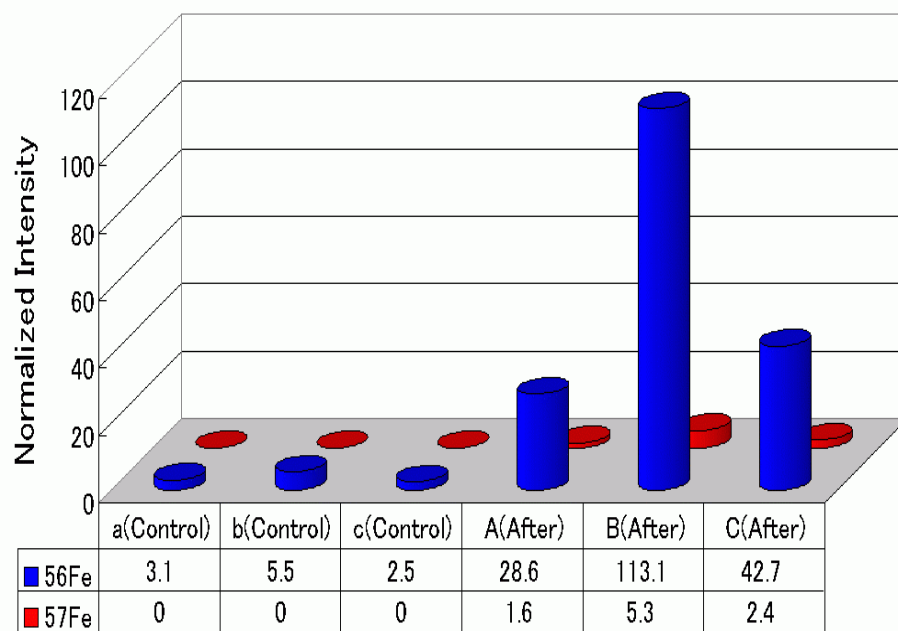


Fig. 7 Normalized count intensity for two isotopes of Fe at three areas with 10s sputtering before and after gas penetration.

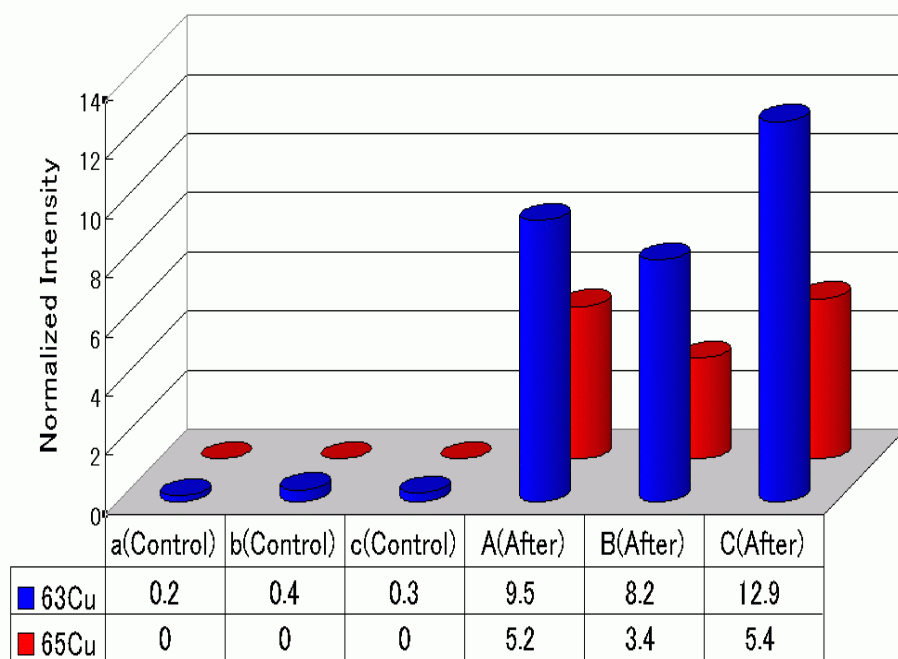


Fig. 8 Normalized count intensity for two isotopes of Cu at three areas with 10s sputtering before and after gas penetration.

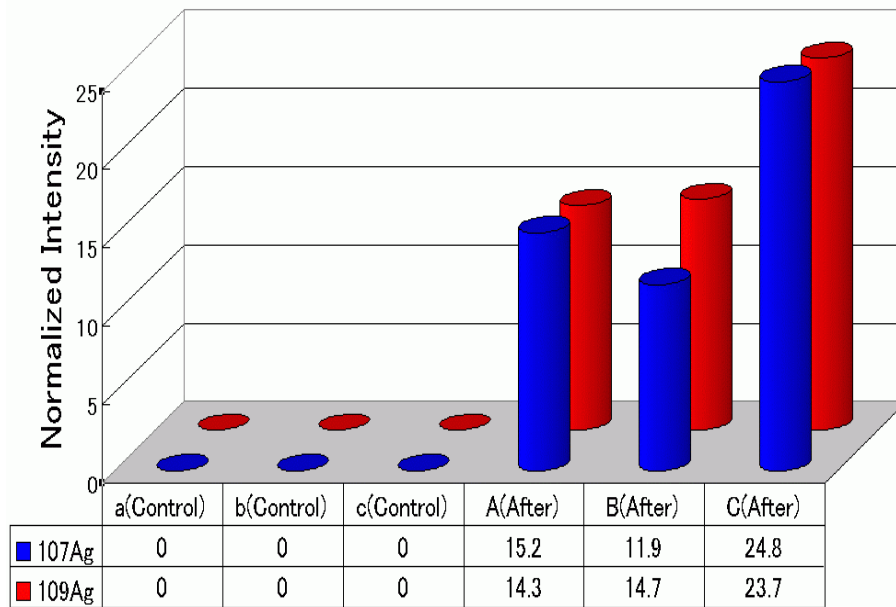


Fig. 9 Normalized count intensity for two isotopes of Ag at three areas with 10s sputtering before and after gas penetration.

4 Conclusion

We performed the hydrogen penetration experiment with Pd sample, and elements on the sample were surveyed for the control sample and that after experiment. Increases in count intensity of TOF-SIMS, corresponding to elements of Ti, Cr, Mn, Fe, Ni, Cu and Ag, have been observed by the hydrogen penetrate through Pd foil. These elements were possibly produced during the gas penetration. V and Co were also detected on deeper regions revealed by the Ga^+ sputtering for 10s. These elements might have been produced by nuclear transmutation.

In the isotopic ratio of Ti and Cr, difference from the natural one was observed in the three analyzed areas of a sample. While, almost no change in isotopic ratio was seen for other elements. The results have strongly suggested that all these elements were produced by a nuclear transmutation and that the reaction could occur in hydrogen system as well as deuterium system.

References

1. E. Yamaguchi, T. Nishioka, *Jpn. J. Appl. Phys.*, **29**, L 666 (1990)
2. E. Yamaguchi, H. Sugiura, *Proceedings of 7-th International Conference on Cold Fusion*, p.420 (1998)
3. Y. Iwamura, T. Itoh and M. Sakano *Proceedings of 8-th International Conference on Cold Fusion*, p.141 (2000).
4. Y. Iwamura, T. Itoh and, M. Sakano, *Jpn. J. Appl. Phys.*, **41**, 4642 (2002).

5. J. Dufour, D. Murat, X. Dufour and J. Foos, *Proceedings of 8-th International Conference on Cold Fusion*, p. 153 (2000).
6. T. Ohmori, H. Yamada, S. Narita and T. Mizuno, *Proceedings of 9-th International Conference on Cold Fusion*, p. 284 (2002)