3 keV H_2^+ Irradiation to Li/Pd/Cu Trilaminar Neutron Production Target for BNCT

Shintaro Ishiyama^{1,*}, Ryo Fujii², Masaru Nakamura² and Yoshio Imahori²

¹Quantum Beam Science Directorate, Japan Atomic Energy Agency, Naka-gun, Ibaraki 319-1195, Japan

²Cancer Intelligence Care Systems, Inc., Tokyo 135-0063, Japan

For the purpose of avoiding the radiation blistering of the lithium target for neutron production in BNCT (Boron Neutron Capture Therapy) device, trilaminar Li target, of which palladium thin layer was inserted between copper substrate and Li layer, was newly designed. The Li/Pd/Cu trilaminar structures of the synthesized target were characterized under 3 keV H_2^+ irradiation by XPS and XAFS technique, which provides structural/electronic properties of solids, and information about the local structure, such as the nature and number of surrounding atoms and inter-atomic distances. The following conclusions were derived; Pd–Cu physical bonding was produced between the Pd and Cu interface by electro-less plating Pd deposition on a high purity Cu plate. From the XAFS observation of white line of Pd, the Pd L_3 edge jump was found after H_2^+ irradiation, this fact indicates increase of hole density in Pd 4d-band. 0.9 eV chemical shift was also observed in Pd L_3 white line for monolayer and 1 μ m Pd/Cu samples, which will affect the quality of the Li/Pd/Cu target due to the formation of PdH_x in palladium insert layer. [doi:10.2320/matertrans.M2013403]

(Received October 31, 2013; Accepted January 15, 2014; Published February 28, 2014)

Keywords: boron neutron capture therapy, neutron source, lithium target, palladium, copper, X-ray photoelectron spectroscopy, X-ray absorption fine structure, H_2^+

1. Introduction

Many types of pilot innovative accelerator-based neutron source for neutron capture therapy were proposed^{1–3)} and lithium target models of the deposited on molybdenum (Li/Mo), the lithium deposited on titanium (Li/Ti) and the lithium deposited on copper have been developed and the performance of these thick lithium targets on the surface of cooled disk was demonstrated.^{1–7)} At these design models, Bayanov *et al.* pointed out the radiation damages on these lithium target models¹⁾ and a few of reports concerning about the delamination of lithium layer from the substrate during operation in a number of the reported cases including irradiation damage.¹⁾

This problem are very important to be resolved for the maintenance of lithium target on service, therefore material research against reduction of these irradiation damages and the development of *in-situ* repairing and maintenance techniques are required.

We consider that the radiation damages can be effectively avoided by lithium(Li)/palladium(Pd)/copper(Cu) trilaminar structure target. Because Pb is found to be one of good inserted material between lithium and copper, and exhibited the excellent agglutination between them.^{5–7)} Also Pb layer prevents implanted proton atoms from diffusion into lithium and copper interface, which induces hydrogen embrittlement of copper substrate and the interface between Li/Cu.

For this purpose, the development of *in-situ* vacuum deposition technique to create a new target with Li/Pd/Cu trilaminar structure in vacuum is indispensable.^{4–7)} Up to now, no reports were found concerning detailed characterization of the Li/Pd/Cu trilaminar structure under proton irradiation during neutron production.

Present paper demonstrates multi-layered structures and chemical states of the Li/Pd/Cu trilaminar lithium target and

Li/Pd, Pd/Cu interfaces are characterized after H_2^+ irradiation by *in-situ* X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) using X-rays from synchrotron light source.

2. Experimental Method

2.1 Specimens

Copper (Cu) plates (10 mm × 10 mm × 1 mm) coated by metallic palladium (Pd) was used as substrates. Pd was deposited on a high purity Cu plate by electro-less plating. The thickness of the Pd layer was monolayer (sample (b)), 0.1, 0.3, 0.5, 0.8 and 1 μ m (sample (a)). Figure 1 shows the photograph of the Pd/Cu sample (a) and (b) before Li deposition. Metallic lithium rod (4 mm ϕ × 5 mm) purchased from Kojundo Chemical Laboratory Co. Ltd. was used as a source material for deposition. Purity of the lithium was higher than 99%.⁴⁾ For the Li/Pd/Cu sample (sample (c)), Li layer with fairly larger than 1.8 nm thickness was deposited on the Pd/Cu sample by *in-situ* vacuum deposition technique (sample (c)).^{4–7)}

Fig. 1 Pd/Cu samples: (a) monolayer Pd and (b) 1 μ m Pd deposition on Cu substrate.

*Corresponding author, E-mail: Ishiyama.shintaro@jaea.go.jp

2.2 Apparatus^{4,5)}

Experiments were performed at the BL-27A station of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF). The X-rays were emitted from the bending magnet, and the photon energy was tuned by an InSb(111) double crystal monochromator. The photon energy of the beam line covers from 1.8 to 4.2 keV, and the typical photon flux was $\sim 10^{10}$ photons $cm^{-2} \cdot s^{-1}$. The energy resolution of the monochromator was 0.9 at 2000 eV.

The analysis chamber consisted of a manipulator, an electron energy analyzer, and a cold cathode ion gun. The base pressure of the analysis chamber was 1×10^{-8} Pa. The sample was horizontally located, and it can be rotated around the vertical axis. The preparation chamber consisted of a vacuum evaporator and a sample transfer system. The base pressure of the preparation chamber was 5×10^{-6} Pa. The sample can be transferred between two chambers without exposing the sample to air.

X-ray photoelectron spectra (XPS) were measured with hemispherical electron energy analyzer (VSW Co. Class-100). The X-rays were irradiated at 55 degree from surface normal and a take-off direction of photoelectrons was surface normal. Typical photon energy used was 2000 eV. The binding energy was normalized by C 1s of adventitious organic carbons adsorbed on the samples at 284.8 eV.

The X-ray absorption fine structure (XAFS) spectra were measured by plotting a sample drain current as a function of photon energy. The sample current was normalized by the photon flux measured by the drain current of aluminum foil located in front of the sample.

2.3 H_2^+ irradiation

The targeted sample surface was bombarded with hydrogen ions in the analysis chamber using a cold-cathode ion gun (OMEGATRON Co. OMI-0045CK). High-purity hydrogen gas (>99.99%) was used as an ion source. The most of the produced ions were molecular ions, H_2^+ . The energy of the H_2^+ ions was 3.0 keV. The typical ion flux was 1.4×10^{14} atoms $cm^{-2} \cdot s^{-1}$, and the pressure during the ion bombardment was 1.2×10^{-3} Pa. The direction of the ion beam was surface normal.

3. Results

3.1 XPS results

3.1.1 Pd/Cu samples

Figure 2 shows the XPS wide-scan spectra for the samples (a) Pd(1 μm)/Cu and (b) Pd(mono)/Cu with different thickness of Pd layers. For comparison, clean surface of the sample (a) before lithium deposition is displayed as a topmost spectrum. The Pd 2p, 3d and 3d peaks were clearly observed in sample (a), whereas the Pd 2p peak completely disappeared for the sample (b), and Cu 2p peaks are seen. This means that the surface of copper is covered with thick film of palladium for the sample (a).

Figure 3 displays the XPS narrow-scans in the Pd 3p region for the sample (a) and (b) (solid lines). Both peaks of Pd 3p_{3/2} and 3p_{5/2} are seen in this region. For the spectrum of the sample (a) and (b), the single peak (marked A) observed for the sample (a) is due to the Pd 3p_{3/2} peak. The binding

Fig. 2 XPS wide scan spectra of the Pd/Cu samples: Thickness of Pd layer are (a) 1 μm and (b) mono size, respectively. Cu 2p peaks were observed in sample (b).

Fig. 3 XPS narrow-scan spectra in Pd 3p region of the Pd/Cu sample (a) and (b): (a') and (b') are (a) and (b) samples after H_2^+ irradiation.

energy of the peak A is 532.1 eV⁴⁾ and virtually corresponding to the Pd 3p_{3/2} from the metallic palladium, because the thickness of the lithium overlayer for the sample (a) is appreciably thinner than the IMFP of the Pd 3p_{3/2} photoelectrons and the Pd 3d peak is also clearly observed in wide-scan spectrum (see Fig. 2).

In Fig. 4, the XPS narrow-scans in Pd 3d region are shown. For comparison, the spectrum for Pd(mono)/Cu is also displayed as sample (b). The spectrum for the sample (a) and (b) before lithium deposition virtually exhibits the metallic palladium. The binding energy of the Pd 3d_{5/2} peak for the sample (a) (marked B) is 335 eV for metallic palladium.^{4,5)} The peak shift of the Pd 3d_{5/2} peak was not observed for the sample (b).

3.1.2 H_2^+ irradiation

The XPS narrow-scans in Pd 3p and 3d regions are also shown in Figs. 3 and 4 with broken lines for the sample (a) and (b). In these cases, H_2^+ irradiation (2 h) was conducted for both samples. The binding energy of the Pd 3p and 3d peaks did not shift from that for the sample (a) and (b) before H_2^+ irradiation.

The results suggested that core potential of inner orbit electron of Pd 3p and 3d was not shift from the original values in metallic palladium and no chemical reactions occurred after H_2^+ irradiation for both Pd/Cu samples.

Fig. 4 XPS narrow-scan spectra in Pd 3d region of the Pd/Cu sample (a) and (b); (a') and (b') are (a) and (b) samples after H_2^+ irradiation.

Fig. 5 Pd L_3 -edge XAFS spectra for the sample (a) and (b) before H_2^+ irradiation.

3.2 XAFS results

3.2.1 White-line for Pd/Cu samples

Figure 5 shows the normalized Pd L_3 -edge XAFS spectra for the sample (a) and (b). A sharp peak is observed at 3176.7 eV (marked C) for metallic palladium before H_2^+ irradiation. This peak is so-called "white-line" corresponding to the dipole transition from the Pd $2p_{3/2}$ to the valence unoccupied $4d$ orbitals just above the Fermi level.⁸⁾ The intensity and the energy of this peak scarcely changed between the sample (a) and (b).

There are many peak points (broken ellipsoidal circle) observed in higher energy more than that of point C, this fact indicated that EXAFS data provides information about the local structure, such as the nature and number of surrounding atoms and inter-atomic distance surrounding palladium atoms in these energy regions.

3.2.2 White-line for Pd/Cu samples after 3 keV H_2^+ irradiation

The normalized Pd L_3 -edge XAFS spectra for the sample (a) and (b) before and after H_2^+ irradiation are shown in Figs. 6 and 7. It is clear that the intensity of the absorption edge has increased with respect to that before H_2^+ irradiation

Fig. 6 Pd L_3 -edge XAFS spectra for the sample (a) after H_2^+ irradiation.

Fig. 7 Pd L_3 -edge XAFS spectra for the sample (b) after H_2^+ irradiation.

(edge jump). This edge jump can be directly related to an increase in the number of holes in the d band.⁹⁾

Edge shift to higher energy is also clearly observed in these figures and this shift implied that positively charged palladium atom and the energy shift is corresponding to that of metallic gadolinium 0.9 eV.¹⁰⁾

Many peak points observed in higher energy regions gradually disappeared with increasing of irradiation time. This suggests the dominant presence of a low Z scatterer, (i.e., hydrogen),¹⁰⁾ which are interstitial solute atoms in fcc palladium structure.

4. Discussions

The Li/Pd/Cu trilaminar lithium target consisted with Li/Pd, Pd/Cu interfaces and Pd interlayer are irradiated by high energy and flux protons during neutron production for BNCT, thus irradiation effects on these regions are discussed here.

Fig. 8 The Pd L_3 edge jump in white-band of Pd during H_2^+ irradiation for the sample (a) and (b).

4.1 Chemical state at the Li/Pd interface

Figure 8 shows the Pd L_3 edge jump in white-band of Pd after H_2^+ irradiation for the sample (a) and (b). Within shot time irradiation less than 30 min, the L_3 edge peaks for the sample (a) and (b) immediately increased up to about 3 times before irradiation and then saturated. The intensity change of the white line feature is based on the change of the d -occupancy of Pd sites and the L_3 absorption spectra in Figs. 6 and 7 indicate an increase in the number of unoccupied states of Pd d -character upon increasing the Pd thickness. Therefore, the charge transfer to increasing d -states of Pd and contribution to the filling of the empty d -states of Pd affects the formation of local chemical bonds between Li and Pd after H_2^+ irradiation, and is expected to enforce these chemical bonding.

Therefore, design of the BNCT target must take notice upon disturbance of fill-up in unoccupied d -band of Pd white-band, avoiding degradation of Li–Pd jointing condition.

In previous studies,⁴⁾ we reported that the electronic structure at the Pd–Li interface changed after Li deposition with decrease of the white line area when the thickness of lithium deposition layer on Pd surface increased. This implied that the unoccupied d -band of Pd is filling upon alloying with lithium because the L -edge white line is very sensitive to the unoccupied d states according to selection rules.¹⁰⁾

From Fig. 9, the spectrum feature of the sample (c) is fairly different from that of metallic Pd. Palladium is one of the noble metals. Thus, we consider that the spectral change is due to the formation of Pd–Li alloy at the interface on the basis of the following speculation.

Within the single particle approximation, the oscillator strength of the white line of the L_3 edge of the d transition metals would be proportional to the hole population in the d -band.¹⁰⁾ Actually, in the case of Ag (next to Pd in the periodic table), the d bands are essentially full and no white line is observed at the L -edge. Thus, the intensity of the L_3 white line is sensitive to the variation of the density of the empty states above the Fermi level. The Pd L_3 -edge XAFS spectra in Fig. 9 indicate a decrease in the number of unoccupied states of Pd d -character at the Pd–Li interface. Thus the charges are transferred from lithium to the Pd d -band and

Fig. 9 Pd L_3 -edge XAFS spectra for the sample (a) and (c) before H_2^+ irradiation and sample (c') after irradiation.

Fig. 10 Pd L_3 edge shift after H_2^+ irradiation for the sample (a) and (b).

contribute to the filling of the empty d -states of Pd. The decrease in the intensity of white line in Pd L_3 -edge XAFS spectra were also observed in Pd–Ag alloys and Pd–Cu alloys.^{10–13)} Similarly, we can conclude that Pd “ d -band” is being filled upon alloying with lithium. It is considered that the broad peak appeared around 3182 eV is due to the delocalized nature of the sp continuum states. It is expected that the formation of Pd–Li alloy would contribute to the stability of the Li layer.

After H_2^+ irradiation, the spectrum feature for the sample (c') is fairly different in its intensity level from that of the sample (c). This is due to increase of holes population in d -band after H_2^+ irradiation to the sample (c).

4.2 Pd interlayer

Figure 10 shows Pd L_3 edge shift after H_2^+ irradiation for the sample (a) and (b). The edge shift increased with irradiation time and saturated within about 100 min for both samples.

The difference between the energy at half of maximum of the two absorption edge spectra in Figs. 6 and 7 is found to

be 0.9 eV. This edge shift implied that a positively charged palladium atoms, and we assumed that the three conduction electrons is transferred to hydrogen atoms implanted in Pd metallic.¹⁰⁾ This fact suggests that charge transfer from the palladium atom to the hydrogen atoms may be responsible for the formation of palladium hydrides, and induces lattice expansion. About 10% volume expansion is expected at the formation of PdH₃ (β -phase) and recently lattice expansion of Pd β -phase (H/Pd = 0.58) was observed from 0.275 to 0.285 nm by *in-situ* XRD and XAFS techniques.¹⁴⁾

4.3 Chemical state at the Pd/Cu interface

First we estimate the thickness of the Pd deposited layer for the sample (b) using the peak intensities of the Pd 3d_{5/2} (adsorbate) and Cu 2p_{3/2} (substrate) in XPS. The intensity ratio of photoelectrons, $I_{\text{Pd } 3d_{5/2}}/I_{\text{Cu } 2p_{3/2}}$, is expressed as

$$\frac{I_{\text{Pd } 3d_{5/2}}}{I_{\text{Cu } 2p_{3/2}}} = \frac{\sigma_{\text{Pd } 3d} \cdot \lambda_{\text{Pd } 3d} n_{\text{Pd}}}{\sigma_{\text{Cu } 2p_{3/2}} \cdot \lambda_{\text{Cu } 2p_{3/2}} n_{\text{Cu}}} \cdot \frac{1 - \exp(-d/\lambda_{\text{Pd } 3d_{5/2}})}{1 - \exp(-d/\lambda_{\text{Cu } 2p_{3/2}})} \quad (1)$$

Where σ (barn) is the photoionization cross section¹⁵⁾ for the respective photoelectron indicated as a subscript, λ (nm) is the inelastic mean free path (IMFP) of the photoelectrons in the material indicated as a subscript,¹⁶⁾ n is the atomic concentration of an element in the material shown as a subscript, and d is the thickness of the layer in nm. In Fig. 2, the $I_{\text{Pd } 3d_{5/2}}/I_{\text{Cu } 2p_{3/2}}$ ratio calculated by eq. (1) is obtained to be 0.528 for sample (b), and the thickness of the Pd layer is estimated to about 1.397 nm. For the density, d and atomic weight, W of Pd, the precise number of layers of Pd/Cu sample (b) is estimated 5.71 ($= 13.97/\sqrt[3]{(d/W \times 6.02 \times 10^{23})}$).

The thickness of Pd layer for the sample (b) is thin enough to catch photon electron reflected from Pd/Cu interface for the sample (b). This implied that XPS scan spectra in Fig. 1 for the sample (b) includes Pd/Cu interface information, whereas only Pd information for the sample (a).

The results of binding and photon energy obtained in present study were provided in Table 1 with the results after H₂⁺ irradiation (2 h) for both samples. Comparing with the sample (a) and (b) before irradiation, binding energy of Pd 3p_{5/3}, 3p_{3/2} and photon energy of 4d for both samples is very near to the values of metallic palladium. This fact indicates that Pd/Cu interface is consisted by physical

bonding, but not chemical or covalent bonding. In practice use of BNCT, thickness of Pd on copper substrate is designed as thick enough to stop all of accelerated protons within Pd interlayer to avoiding direct impact of proton to the Pd/Cu interface.

5. Conclusions

For the purpose of avoiding the radiation blistering of the lithium target for neutron production in BNCT (Boron Neutron Capture Therapy) device, trilaminar Li target, of which palladium thin layer was inserted between copper substrate and Li layer, was newly designed. The Li/Pd/Cu layered structures of the synthesized target were characterized after 3 keV H₂⁺ irradiation by XPS and XAFS technique, Li/Pd/Cu trilaminar structure of Li target was created in vacuum deposition using metallic lithium as a source material. The structures and chemical states at the surface and interface were characterized by XPS and XAFS measurements, and the following results were derived;

- (1) Pd–Cu physical bonding was produced interface of the Pd/Cu sample fabricated by electro-less plating Pd deposition on a high purity Cu plate.
- (2) H₂⁺ irradiation would contribute enforcement of Li–Pd covalent bonding between Li/Pd interface by sharing of electrons on Pd 4d-band due to increase of hole density.
- (3) The formation of PdH_x in Pd metallic matrix would cause to degradation of Pd insert layer after H₂⁺ irradiation and higher hydrogen concentration results in significant volume change and embrittlement with the change of lattice distance between Pd–Pd.
- (4) Pd/Cu interface dose not experience little direct impact from H₂⁺ irradiation, however, the volume change of Pd due to PdH_x formation induces share stress between Pd/Cu interface.

From these results, it is concluded that the Pd insert layer between Li and Cu substrate in the Li/Pd/Cu trilaminar structure mostly experience direct impact from high energy and flux of proton irradiation, and implement a range of measures to avoid PdH_x formation during BNCT operation.

REFERENCES

- 1) B. Bayanov, V. Belov, V. Kindyuk, E. Oparin and S. Taskaev: *Appl. Radiat. Isot.* **61** (2004) 817–821.
- 2) B. F. Bayanov, V. P. Belov, E. D. Bender, M. V. Bokhovko, G. I. Dimov, V. N. Kononov, O. E. Kononov, N. K. Kuksanov, V. E. Palchikov, V. A. Pivovarov, R. A. Salimov, G. I. Silvestrov, A. N. Skrinsky, N. A. Soloviov and S. Yu. Taskaev: *Nucl. Instrum. Meth. Phys. Res. A* **413** (1998) 397–426.
- 3) B. Bayanov, A. Burdakov, V. Chudakov, A. Ivanov, S. Konstantinov and A. Kuznesov: *Appl. Radiat. Isot.* **67** (2009) 285–287.
- 4) S. Ishiyama, Y. Baba, R. Fujii, M. Nakamura and Y. Imahori: *Nucl. Inst. Meth. Phys. Res. B* **288** (2012) 18–22.
- 5) S. Ishiyama, Y. Baba, R. Fujii, M. Nakamura and Y. Imahori: *Nucl. Inst. Meth. Phys. Res. B* **293** (2012) 42–47.
- 6) S. Ishiyama, Y. Baba, R. Fujii, M. Nakamura and Y. Imahori: *Mater. Trans.* **54** (2013) 1760–1764.
- 7) S. Ishiyama, Y. Baba, R. Fujii, M. Nakamura and Y. Imahori: *Mater. Trans.* **54** (2013) 1765–1769.
- 8) M. Brown, R. E. Peierls and E. A. Stem: *Phys. Rev. B* **15** (1977) 738–744.
- 9) M. Di Vece, A. M. J. Van der Eerden, J. A. Van Bokhoven, S. Lemaux,

Table 1 XPS and XAFS results of the Pd/Cu sample after 3 keV H₂⁺ irradiation (2 h).

Sample	E _K , E/eV (Pd 3d _{5/3})	E _B , E/eV (Pd 3d _{5/3})	E _K , E/eV (Pd 3p _{3/2})	E _B , E/eV (Pd 3p _{1/2})	E _K , E/eV (4d)
Sample (a)	2660.8	335.0	2463.5	532.3	3171.1
Sample (a') (H ₂ ⁺)	2661.0	334.8	2463.8	532.0	3171.8
Sample (b)	2661.2	334.6	2464.1	531.7	3171.0
Sample (b') (H ₂ ⁺)	2661.0	334.8	2463.8	532.0	3171.8

- J. J. Kelly and D. C. Koningsberger: [Phys. Rev. B](#) **67** (2003) 035430.
- 10) Y. S. Lee, C. N. Whang, Y. Jeon, B. S. Choi, T. J. Han, J. J. Woo and M. Croft: [Nucl. Instrum. Meth. Phys. Res. B](#) **129** (1997) 387–391.
- 11) K. H. Chae, Y. S. Lee, S. M. Jung, Y. Jean, M. Croft and C. N. Whang: [Nucl. Instrum. Meth. B](#) **106** (1995) 60–64.
- 12) E. Cho, S. Lee, S.-J. Oh, M. Han, Y. S. Lee and C. N. Whang: [Phys. Rev. B](#) **52** (1995) 16443–16450.
- 13) K. H. Chae, S. M. Jung, Y. S. Lee, C. N. Whang, Y. Jeon, M. Croft, D. Sills, P. H. Ansari and K. Mack: [Phys. Rev. B](#) **53** (1996) 10328–10335.
- 14) L. Bollmann, J. L. Ratts, A. M. Joshi, W. D. Williams, J. Pazmino, Y. V. Joshi, J. T. Miller, A. J. Kropf, W. N. Delgass and F. H. Ribeiro: [J. Catal.](#) **257** (2008) 43–54.
- 15) J. H. Scofield: Theoretical Photoionization Cross Section from 1 to 3000 eV, Lawrence Livermore Laboratory, Livermore UCRL-51326, (1973).
- 16) M. P. Seah and W. A. Dench: [Surf. Interf. Anal.](#) **1** (1979) 2–11.