Direct Synthesis of Li$_3$N Thin Layer on Lithium Target Surface for BNCT in N$_2$ Gaseous Conditions

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To prevent vaporization damage of BNCT (Boron Neutron Capture Therapy) lithium target during operation, direct synthesis of Li$_3$N thin layer on lithium target surface was demonstrated in 0.1 MPa N$_2$ gas at temperature below 548 K and the following conclusions were derived; (1) Synthesis of Li$_3$N thin layer on lithium surface was confirmed after nitridation at 276–548 K with surface contamination by oxygen and carbon. (2) Rapid nitridation over 1–5 mass% /min was observed above Li melting temperature, whereas slow reaction under 0.02–0.5 mass% /min below melting temperature. (3) During nitridation, removal of oxygen contamination on Li$_3$N thin layer is taken place by nitrogen below Li melting temperature. [doi:10.2320/matertrans.M2013212]

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1. Introduction

Implemented deployment of accelerator-driven neutron source for boron neutron capture therapy (BNCT) is scheduled in 2014 in National Cancer Center, Japan. This BNCT system was designed with the production of neutrons via threshold $^7$Li (p, n)$^7$Be reaction at 25 kW proton beam and reaction control conditions for this conversion was investigated. The surface condition of the Li$_3$N/Li was characterized by X-ray photoelectron spectroscopy (XPS) using X-rays from synchrotron light source.

2. Experimental Method

2.1 Specimens

Metallic lithium pellet (φ5 mm × 8 mm L) purchased from Honjo Chemical Co. Ltd. was used. Purity of the lithium was higher than 99.98% and Na(0.004%), Ca(0.006%), K(0.001%), Fe(0.001%), Si(0.001%), N(0.006%) and Cl(0.001%) were contained in this pellet. Lithium specimens (5 mm × 8 mm × 1 mm) were cut-out from the pellets to ensure smooth nitridation reaction on active Li surface.

2.2 Apparatus

2.2.1 Globe box and bag

Globe box (GB-JV065; W650 × D500 × H450 mm, SUS304 and reinforced glass, Globe-box, Japan) and globe bag (S-20-20; W500 × D500 × H300, polyethylene, Gas-Col Co.) were used for nitridation of the Li specimens above and below 435 K, respectively.

2.2.2 Nitridation procedure

Globe box and bag were evacuated to −0.1 MPa and displaced by argon gas up to 0.1 MPa before nitridation. Li specimens were installed in Petri-dish filled with N$_2$ gas to avoid rapid nitridation reaction during operation, and remove to globe box and bag to heated up to 548 K in 0.1 MPa N$_2$ gas (>99.9%) by digital hot staler (DP-1S, As-one, Co.). P$_2$O$_5$ power was also installed inside these box and bag for water removal.

2.2.3 XPS measurement

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 energy resolution of the monochromator was 0.9 eV 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 $1 \times 10^{-8}$ Pa. The analysis chamber was connected to the load-lock chamber. After the nitridation, the sample was put into the load-lock chamber, and the sample was transferred into the analysis chamber without exposing to air.

XPS spectra 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.

### 2.2.4 Argon sputtering

Argon sputtering to Li specimen surface after nitridation, was done using a cold cathode ion gun. High-purity argon gas (>99.9%) was used as an ion source. The energy of the Ar$^+$ ions was first set at 0 eV. In this condition, the average kinetic energy of the ions was about 30 eV due to the discharge voltage. For second sputtering, the energy of the Ar$^+$ ions was 3 keV. The typical ion flux was $1.4 \times 10^{14}$ atom·cm$^{-2}$·s$^{-1}$, and the pressure during the argon sputtering was $1.2 \times 10^{-3}$ Pa. The time of each sputtering was 10 min. The direction of the ion beam was 45 degree.

### 3. Results and Discussion

#### 3.1 Nitridation of lithium surface

Figures 2(a), 2(b), 2(c) and 2(d) shows the photographs of the Li samples before (Fig. 1(a)) and after nitridation at 423 K for 1 min (Fig. 1(b)), 75 min (Fig. 1(c)) and 548 K (Fig. 2(d)) for 3 (right) and 15 min (left) in N$_2$ gas, respectively. The photograph of the Li sample after nitridation was also taken after exposing to air in a few minutes and shown in Fig. 2(d). The colour of the specimen surface changed after nitridation from metal silver (Fig. 2(a)) to blue (Fig. 2(b)) and a slightly shining, and turned into dark after 75 min (Fig. 2(c)) at 423 K. At 548 K for 3 and 15 min, the specimens were melted to lose original shape with a variety of colours, as shown in Fig. 1(d).

Figure 2(e) shows surface of the specimen after air exposure. Surface colour changed into white after few minutes air exposure, it indicated that LiOH was formed by moisture in the atmosphere, resulting with decomposition of Li$_3$N with H$_2$O in air.

Nitridation of the Li specimens were conducted at 308–548 K for 1–600 min in N$_2$ gas and these conditions are listed in Table 1.

Figures 3 and 4 show the wide-scan XPS spectra for the Li specimen before and after nitridation at 423 K for 75 min. Besides Li 1s, O 1s and C 1s peaks are seen before and after nitridation, and N 1s peak are observed after nitridation (Fig. 4).

From electron kinetic energy at 2000 eV, inelastic mean energy path (IMFP) is calculated and the relationship between electron energy and mean free path with measure attenuation lengths for various materials was given in Ref. 8). For the Li$_3$N/Li target model in present study, IMFP is estimated in the order of 20 Å from the surface of Li$_3$N layer.

The high intensity of the O 1s and C 1s peaks compared with that of the Li 1s and N 1s are due to the high photoionization cross section of O 1s $(1.75 \times 10^4$ barn) and C 1s $(5.73 \times 10^3$ barn) by 2000 eV photons compared with that of Li 1s $(3.04 \times 10^2$ barn) and N 1s $(1.05 \times 10^4$ barn),

### Table 1 Nitridation conditions of temperature and time at present experiment.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature (K)</th>
<th>Reaction time (min)</th>
<th>Weight change $\Delta W$ (mass%)</th>
<th>Binding energy $E_{Li1s}$ (eV)</th>
<th>$\delta_{Li1s}/Li1s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>548</td>
<td>3</td>
<td>45.1</td>
<td>54.9</td>
<td>0.127</td>
</tr>
<tr>
<td>#2</td>
<td>548</td>
<td>15</td>
<td>78.2</td>
<td>54.9</td>
<td>0.085</td>
</tr>
<tr>
<td>#3</td>
<td>435</td>
<td>60</td>
<td>63.1</td>
<td>—</td>
<td>0.301</td>
</tr>
<tr>
<td>#4</td>
<td>435</td>
<td>60</td>
<td>64.0</td>
<td>54.5</td>
<td>0.297</td>
</tr>
<tr>
<td>#5</td>
<td>423</td>
<td>1</td>
<td>2.4</td>
<td>53.8</td>
<td>0.080</td>
</tr>
<tr>
<td>#6</td>
<td>423</td>
<td>75</td>
<td>42.2</td>
<td>54.5</td>
<td>0.271</td>
</tr>
<tr>
<td>#7</td>
<td>353</td>
<td>60</td>
<td>25.3</td>
<td>58.2</td>
<td>0.171</td>
</tr>
<tr>
<td>#8</td>
<td>320</td>
<td>180</td>
<td>54.7</td>
<td>—</td>
<td>0.635</td>
</tr>
<tr>
<td>#9</td>
<td>308</td>
<td>600</td>
<td>10.1</td>
<td>54.6</td>
<td>0.535</td>
</tr>
<tr>
<td>Mean (SD)</td>
<td></td>
<td></td>
<td>55.1 (±1.33)</td>
<td>0.283 (±0.18)</td>
<td></td>
</tr>
</tbody>
</table>
and the O 1s peak observed in the spectrum for the Li specimen seems to come from adsorbed water in the top surface region of metallic Li. It is suggested that the top surface region of lithium was covered with lithium oxides.

The XPS spectrum in the nitrogen region is shown as small inset of Fig. 3. The binding energy of the peak of N 1s is 391.3 eV, and binding energy of Li 1s is also identified as 54.5 eV and the values of binding energy observed in present experiment are listed in Table 1.

There have been no reliable data about Li 1s and N 1s binding energy for stoichiometric lithium nitride (Li3N). In previous paper, we measured the XPS spectra for N2+ ion implanted lithium layer that was deposited in vacuum. In that work, it was shown that before the N2+ bombardment, the binding energy of the Li 1s peak is 52.8 eV due to the metallic Li, and after nitridation, the binding energy shifted to 55.1 eV, so the chemical shift is 2.3 eV. From Table 1, Li 1s binding energies obtained in present study are located at 55.1 ± 1.33 eV, and it seems that Li–N compounds are formed with ionic bonds due to the high positive nature of lithium compared with nitrogen. So, we assigned that the Li 1s peak observed in Fig. 3 originated from lithium nitride.

3.2 Chemical states of the nitridated layer

In order to estimate the stoichiometry of lithium nitride, we also calculated the atomic ration of nitrogen to lithium, \( \frac{n_N}{n_{Li}} \), on the basis of the XPS peak intensities. The value of \( \frac{n_N}{n_{Li}} \) is calculated by\
\[
\frac{n_N}{n_{Li}} = \frac{I_{N1s}/\sigma_{N1s}}{I_{Li1s}/\sigma_{Li1s}}
\]

(1)

Where \( I \) (cps) is the intensity of the photoelectrons and \( \sigma \) (barn) is the photoionization cross sections by 2000 eV photons for the respective core levels and given as \( \sigma_{N1s} = 1.1 \times 10^3 \) and \( \sigma_{Li1s} = 3.0 \times 10^2 \), respectively. The \( \frac{n_N}{n_{Li}} \) ratio obtained by eq. (1) is to be 0.28 ± 0.18 in Table 1.

The value is far from the ratio of lithium azide LiN (\( n_N/n_{Li} = 3.0 \)), but rather close to that of lithium nitride Li3N (\( n_N/n_{Li} = 0.33 \)). The value is also close to that obtained in the previous works for nitrogen-ion implanted lithium. Although the exact composition is not clear only judging from XPS peak intensities, we consider that the nearly stoichiometric Li3N layer is formed at the lithium surface, considering surface observation above-mentioned.

3.3 Formation of Li3N thin layer on the lithium surface in N2 gas

The weight change \( \Delta W \) (mass%) of the Li specimens after nitridation were measured and listed in Table 1, and nitridation reaction rate, \( R \) (mass%/min) was evaluated as the following equation.

\[
\Delta W = Rt
\]

(2)

Where \( t \) is nitridation time (min) and the reaction rate evaluated by eq. (2) are listed in Table 2. We plot the \( \Delta W \) as a function of nitridation temperature, which is displayed in Fig. 5. From the figure, it is found that the reaction rate behaves quite different below and above lithium melting point \( T_{mp} (= 453 \text{ K}) \). The reaction rate increases drastically with reaction temperature in the case above \( T_{mp} \), whereas that increases slowly below \( T_{mp} \) and these behaviours can be expressed as the broken line in the figure. These results indicate that reaction between lithium and N2 gas is enhanced with reaction temperature and facilitated above \( T_{mp} \).

Here, on the assumption of uniform formation of Li3N thin layer on the Li surface specimen, the thickness of the layer is estimated by the following eqs. (3) and (2) and the results are listed in Table 2.
## 3.4 Contamination on the surface of Li$_3$N thin layer

Remarkable contamination by O and C was observed after nitridation in Sec. 3.1. We discuss the contamination level on the nitridation conditions and use the intensity of the photoelectrons, $I$ and intensity ratio, $I_{N1s}/I_{O1s}$ as contamination parameter. The data measured in present study is listed in Table 3, and we plot the $I_{N1s}/I_{O1s}$ ratio as a function of nitridation temperature, which are displayed in Fig. 6. From Fig. 6, it is found that $I_{N1s}/I_{O1s}$ ratio decreases with increase in nitridation temperature and reach to the bottom value above $T_{mp}$. These results mean that the replacement of oxygen on the Li$_3$N layer surface observed in Fig. 5, is taken place by nitrogen during nitridation reaction and enhanced with increasing temperature.

To reduce oxygen contamination on Li$_3$N layer, the Li$_3$N layer formed at 320 K was sputtered by Ar$^+$ ions. The intensity ratio of $I_{N1s}/I_{O1s}$ was 0.03 before sputtering. The ratio increased to 0.07 after the first sputtering ($E_K \sim 30$ eV), and the ratio was not changed after second sputtering ($E_K = 3$ keV). Since the sputtering yield of lithium by 30 eV Ar$^+$ ions is less than $10^{-2}$ atom/ion,$^{15,16}$ it is suggested that the thickness of the surface lithium oxide layer is in the order of nanometer.

### 4. Conclusions

Direct nitridation technique to create lithium target for BNCT apparatus was demonstrated in 0.1 MPa N$_2$ gas. After creation of Li$_3$N thin layer on lithium surface, the layer was sputtered by Ar$^+$ ion. The structures, chemical states of nitridated zone formed on the lithium surface were characterized by XPS, and the following results were derived:

1. Uniform nitridation thin layer was formed on lithium surface by direct nitridation technique.
2. During nitridation process, the colour of nitridation surface changes from silver, blue and dark as nitridation proceeding.
3. The chemical state of the nitridated zone was close to the stoichiometric lithium nitride, Li$_3$N and its surface is contaminated by O and C.
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