Hydrogen Depth-profiles in Nb Hydrides Formed in Supercritical Water

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The hydrogen content $x$ of Nb hydrides,NbH$_x$ and/or NbD$_x$, formed in supercritical water under extremely high pressures and temperatures were studied as a function of the depth from the hydride surface via ion-beam analyses (elastic recoil detection analysis with Rutherford backscattering spectrometry, ERDA/RBS). The hydrogen-rich $\alpha'$-NbH ($x \approx 0.9$) formed a surface layer approximately 200-nm thick with a 4–25 nm Nb oxide overlayer, which was invisible or only barely visible in the X-ray diffraction (XRD) analysis, whereas the hydrogen-poor $\alpha$-NbH ($x < 0.2$) was visible to a depth of 1 μm in the bulk. The oxide overlayer thickened with further hydrogenation. The exchange of D with H was suggested in the surface region for the hydride specimen formed with D$_2$O. The chemical states of the studied specimens were also analyzed via the angle-dependent hard X-ray photoelectron spectroscopy, HAXPES. The formation mechanism of Nb hydrides is discussed based on the depth profiles of the hydrogen content $x$ and the chemical states, as well as XRD results of the Nb hydrides.

Keywords Nb hydrides; High-pressure supercritical water; Hydrogen contents; Elastic recoil detection analysis; Depth profile

I. INTRODUCTION

Metal hydrides have been attracting attention as energy-related materials for hydrogen storage, fuel cells and batteries, hydrogen-semipermeable membranes, catalysts for splitting water and hydrogen-containing molecules, and nuclear fusion reactors [1–3]. New metal hydrides have been also searched in particular as a safe and environment-friendly hydrogen solid container for next-generation automobiles. Synthesis under extremely high pressure is one of promising techniques to produce noble materials with contents and structures different from those formed under usual conditions [4, 5]. Furthermore, a direct reaction of Nb with supercritical water might provide a safe technique for hydride synthesis without using flammable hydrogen gas.

Recently, Nb hydride formation with little oxide production was achieved via the infra-red laser heating of Nb in supercritical water (the thermodynamic critical point of water is at 647.3 K and 22.12 MPa) under extremely high pressures (~10 GPa) and temperatures (~2000–3000 K) in a
laser-heated diamond anvil cell (LH-DAC) [5, 6]. In situ X-ray diffraction (XRD) studies of the direct reaction between Nb and supercritical water in LH-DAC [6] revealed that the body-centered cubic (bcc) Nb lattice expanded gradually with the laser heating cycles, in each of which the heating laser spot was scanned over the specimen surface in the LH-DAC. Upon further heating cycles, the lattice expansion of the bcc Nb was saturated and then the face-centered cubic (fcc) XRD pattern appeared with a little oxide. These facts suggest the formation of Nb hydrides NbH$_x$; $\alpha$- and $\alpha'$-NbH as disordered solutions of hydrogen in the interstitial sites of the host-bcc Nb lattice for a hydrogen content $x < 0.2$ and $x = 0.6$–0.9, respectively, and ordered hydrogen solid solutions of the CaF$_2$-type $\delta$-NbH with an fcc Nb sub-lattice for $x = 2$ [1–3].

This is very interesting because the supercritical water possesses the high oxidation ability. Indeed, stable oxide Nb$_2$O$_5$ was formed as the final product of the hydrothermal reactions between Nb and water in an open system under 0.1 GPa below ~1100 K, in which the Nb hydrides were formed as intermediate products [7]. Yoshimura et al. also suggested that observed incomplete oxidization of Nb may be caused by lack of water in the reaction area [7]. Furthermore, preliminary experiment [8] showed that almost all the examined transition metals except for Nb and Pd, which are known as metals with a high hydrogen solubility and a high hydrogen permeability [1–3], formed the oxides or hydroxides by the direct reaction with the supercritical water under 10 GPa in the LH-DAC in view of ex situ XRD structural analysis.

However, the Nb hydrides formed in a closed LH-DAC system have not yet been well characterized, since they are typically smaller than 0.1 mm. A remarkable increase in the hydrogen solubility [9, 10] and the formation of new metal hydrides [11, 12] were also reported for hydrogen pressures of Nb in excess of 1 GPa at high temperatures. For clarifying the hydride formation, it is thus important to further characterize the hydride specimens. Besides the XRD structural analysis, we therefore investigated the chemical and electronic states and hydrogen contents of the Nb hydride specimens in different hydrogenation stages via microbeam hard X-ray photoelectron spectroscopy, HAXPES, and ion-beam analyses (elastic recoil detection analysis, ERDA, and Rutherford backscattering spectrometry, RBS), respectively. The HAXPES results were already reported in detail [13, 14]: the formation of bulk metallic hydrides and the existence and evolution of surface insulating oxides were concluded in view of the electronic states from the observed emission-angle dependence of the Nb 3d core-level and valence-band spectra. Since the HAXPES was a rather surface-sensitive electronic probe and insensitive to hydrogen itself, it is important to characterize the chemical composition, i.e., the hydrogen content, which was postulated in the XRD and HAXPES analyses.

In this article we will report mainly on the hydrogen content $x$ of the synthesized specimens via the ERDA-RBS analyses, which is one of unique techniques to profile the depth distribution of hydrogen in materials [15–17], to confirm the hydride formation via the direct reaction between Nb metal and supercritical water from the view point of chemical composition. A part of the ERDA-RBS results was presented at the 11th International Symposium on Atomic Level Characterization for New Materials and Devises 2017 [18].

II. EXPERIMENT

NbH$_x$ and NbD$_x$ hydride specimens in different hydrogenation stages were prepared via high-pressure synthesis under a pressure of 10 GPa at a temperature of 1000–2000 K using an LH-DAC, where a starting Nb foil measuring typically 0.1 mm $\times$ 0.1 mm $\times$ 0.02 mm was directly reacted with supercritical H$_2$O and D$_2$O, respectively, by 1.09-μm infrared continuous-oscillation fiber-laser heating [14]. Since the diameter of the laser-heated spot was about 10 μm, the spot was scanned over the specimen surface in ~10 min. The use of deuterium D, or heavy water D$_2$O, was intended to distinguish the hydrogen in the present products from H in the surroundings for characterizing the hydride formation. In this study, no isotope effects were found and dealt with. Ex situ XRD patterns for the transmission geometry were obtained for the starting Nb foil and hydride specimens, recovered to the ambient pressure, using a Rigaku R-AXIS7 laboratory diffractometer to estimate the total amounts (fractions) of hydride species from their XRD intensities from a crystallographic viewpoint. For the HAXPES measurement and ion-beam analysis (ERDA and RBS measurements), specimens were attached to a copper pin of the sample carrier using adhesive carbon tape [14]. HAXPES measurements were carried out prior to ERDA measurements for the same starting specimen (referred to as “specimen #5”) and recovered hydride specimens (referred to as “specimens #1” and “specimen #2”). Specimen #1 was synthesized with H$_2$O at relatively low temperatures (<1000 K), whereas specimen #2 was synthesized with D$_2$O at relatively high temperatures (>1500 K). The temperature during the laser heating was estimated by optically observing the brightness of the thermal radiation at the laser-irradiated spots; dark-red radiation induced by our laser output power of 3 W and brilliant-white radiation by the power of 10 W for the heating at the relatively low and high temperatures, respectively. Any significant change in the XRD patterns was not found for those specimens kept in a vacuum of HAXPES and ion-beam analyses [13].

Angle-dependent HAXPES measurements were performed at the beamline BL47XU of SPring-8, an 8-GeV electron synchrotron facility in Hyogo, Japan, using a ~1-μm and 8-keV hard X-ray microbeam [19]. Because the inelastic mean free path was estimated to be 10 nm for the 8-keV photoelectrons in Nb (using the TPP2M algorithm [20]), the angle-dependence of the HAXPES spectra provides the depth distributions of the chemical species in the surface region, approximately 20 nm from the specimen surface. Details are described elsewhere [13, 14].
Ion-beam ERDA and RBS analyses were carried out at the Wakasa Wan Energy Research Center, Fukui, Japan. **Figure 1** shows photographs of specimen #1 and the experimental setup for the ion-beam analyses. A 5-MeV \(^{4}\text{He}^{2+}\) microbeam of 10 \(\mu\text{m}\) in diameter, produced by a Tandem ion-beam accelerator, W-MAST, was irradiated onto the specimens at an angle \(\theta\) of 80° (\(\theta\) is referred to the surface normal). Recoiled hydrogen ions, \(\text{H}^{+}\) and/or \(\text{D}^{+}\), were detected using a solid state detector SSD (active area of 50 \(\text{mm}^2\)) at a scattering angle of 140° to obtain the depth profile of Nb in the specimens. Thus, the depth profiles of hydrogen contents \(x\) (H/Nb and D/Nb) up to approximately \(1\ \mu\text{m}\) could be estimated from the recorded ERDA and RBS spectra, \(I_{\text{ERD}}(z)\) and \(I_{\text{RBS}}(z)\), and the corresponding cross-sections, \(\sigma_{\text{ERD}}\) and \(\sigma_{\text{RBS}}\) [17]:

\[
x(z) = \frac{\frac{I_{\text{RBS}}(z)}{\eta_{\text{RBS}}}}{\frac{I_{\text{ERD}}(z)}{\eta_{\text{ERD}}}} \frac{\sigma_{\text{RBS}}}{\sigma_{\text{ERD}}} \left(\frac{E_{R}(z)}{E_{S}(z)}\right)
\]

Here, \(E_{R}\) and \(E_{S}\) stand for the detected energies of the recoiled and scattered ions, respectively. Depths \(z\) from which \(\text{H}^{+}\) and/or \(\text{D}^{+}\) ions were recoiled or \(\text{He}^{2+}\) ions were scattered were estimated from the SRIM code [21] taking account of the energy loss by the Al stopping foil for ERDA, and ion scattering cross-sections [17]. The obtained relationships between the recoiled or scattered ion energy, \(E/\text{MeV}\), and the depth, \(z/\text{nm}\), were represented by the following equations:

\[
z(E) = \begin{cases} 1207.9 - 410.22E - 56.446E^2 & \text{for recoiled H}, \\ 1287.5 - 315.29E - 28.529E^2 & \text{for recoiled D}, \\ 1803.9 - 353.18E - 15.612E^2 & \text{for He scattered by Nb}. \end{cases}
\]

We measured the ERDA and RBS spectra from a polyimide \((\text{C}_{22}\text{H}_{10}\text{N}_{2}\text{O}_{5})_n\) film (Kapton®) to obtain the experimental factors, \(\eta_{\text{RBS}}/\eta_{\text{ERD}}\), \(\sigma_{\text{ERD}}/\sigma_{\text{RBS}}\), \(\sigma_{\text{H}}/\sigma_{\text{D}}\), \(\sigma_{\text{RBS}}/\sigma_{\text{ERD}}\), \(\sigma_{\text{ERD}}\) of the detecting solid angles and efficiencies, \(\Omega\) and \(\eta\), of SSD for estimating the absolute values of the hydrogen content \(x\) under an assumption of \(x/\text{H} = 0.45\). For estimating the D content, we furthermore took account of the difference in the recoil differential scattering cross sections, \(\sigma_{\text{H}}/\sigma_{\text{D}}\), and “effective” stopping powers (including the He-filter), \(S_{\text{H}}\) and \(S_{\text{D}}\), for \(\text{H}^{+}\) and \(\text{D}^{+}\). For the Rutherford scattering, the recoil differential scattering cross section \(\sigma_{\text{ERD}}\) for \(\text{H}^{+}\) (its mass is denoted by \(m_{\text{H}}\)) at an angle \(\phi\) by the incident \(\text{He}^{2+}\) mass \(m_{\text{He}}\) and energy \(E\) may be given by the following equation [17],

\[
\sigma_{\text{ERD}} = e^{4}E^{-2}(1 + m_{\text{He}}/m_{\text{H}})^{2}\cos^{-2}\phi
\]

and then the ratio of the cross sections for \(\text{D}^{+}\) and \(\text{H}^{+}\), \(\sigma_{\text{ERD}}/\sigma_{\text{RBS}} = (1 + m_{\text{He}}/m_{\text{D}})^{2}/(1 + m_{\text{He}}/m_{\text{H}})^{2}\), may become 0.36. The ratio of the stopping powers \(S_{\text{D}}/S_{\text{H}}\) was approximately 1.3, as seen in the depth scales of **Figure 4**. A correction factor for the estimation of the D contents from the ERDA spectra was thus obtained as \(\sigma_{\text{ERD}}S_{\text{D}}/\sigma_{\text{RBS}}S_{\text{H}} = 2.1\). To confirm the formation of a D-rich surface layer, we performed another ion-beam analysis measurement without the HAXPES characterization as quickly as possible after the preparation of NbD\(_3\), specimen (referred to as “specimen #3”) at relatively low temperatures. Since surfaces of the present hydride specimens were rather rough, present results were regarded as the averaged one over the probed area of \(0.01 \times 0.06\ \text{mm}^2\) with some deviation of the scattering condition.

### III. RESULTS AND DISCUSSION

**Figure 2** presents typical XRD patterns expanded around the diffraction index (002) of the bcc Nb (sub-)lattice for the starting Nb foil #S, and hydride specimens #1 and #2 in dif-
different hydrogenation stages. In the figure, the cubic backgrounds were subtracted and the intensities were normalized with the integrated intensities between diffraction angles $\theta_d$ of 52° and 58°. The XRD patterns exhibit lattice expansion due to the formation of the hydrogen-poor $\alpha$- and hydrogen-rich $\alpha'$-hydrides. Irrespective of the difference in the Nb sub-lattice, a linear relationship is observed between the lattice constant $a$ of NbH, and the hydrogen content $x$ [1, 2]: $\Delta a/a = (0.054 \pm 0.003) \Delta x$, where $\Delta a$ and $\Delta x$ are the increments in $a$ and $x$, respectively. Thus, the hydrogen contents $x$ of $\alpha$- and $\alpha'$-NbH (NbD) were estimated to be $x = 0.044$ and 0.67 for specimen #1, and $x = 0.058$ and 0.67 for #2. Specimen #1, synthesized at a relatively low temperature, mainly consists of $\alpha$-NbH with a little $\alpha'$-NbH. Both the $\alpha$- and $\alpha'$-NbH (NbD) with a little Nb oxide were formed in specimen #2, prepared at a relatively high temperature [14]. Fractions $c_1$ and $c_2$ of $\alpha$- and $\alpha'$-NbH (NbD) may be estimated from the ratio of the integrated (002) peak intensities as $c_1 = 97\%$ and $c_2 = 3\%$ for specimen #1, and $c_1 = 74\%$ and $c_2 = 26\%$ for #2, respectively. Thus, the average dissolved hydrogen content is 0.06 and 0.21 for specimens #1 and #2, respectively.

Typical Nb 3d core-level HAXPES spectra are summarized in Figure 3, where the background due to the secondary electrons was subtracted from the recorded spectra by an iteration procedure [23] and the spectral intensities were normalized with the intensity integrated from 200 to 213 eV. The starting Nb foil #S shows an asymmetric and sharp Nb metal component and a symmetrical and broad Nb$_2$O$_5$ oxide component in the passivation layer. Their spin-orbit pair features are indicated by linked bars. From their dependence on the emission angle $\theta_e$ (referred to the surface normal) [13], the thickness of the passivation layer in the present #S specimen was estimated to be 3.5 nm. In the spectra for specimen #1, a slightly chemically shifted component was found, which was attributed to $\alpha$-NbH, and a 0.8-eV shifted one of $\alpha'$-NbH and an oxide Nb$_2$O$_5$ component were also observed. In the surface sensitive spectrum recorded at $\theta_e = 45\°$, the oxide component increased, whereas the hydride ones decreased, relative to the bulk-sensitive spectrum recorded at $\theta_e = 5\°$. According to the analysis of their $\theta_e$-dependences, the oxide layer in specimen #1 is 8.7-nm thick and the $\alpha$- and $\alpha'$-NbH components are almost constant in the probed depth region. Oxide components are not discernible in the XRD patterns of specimens #S and #1 but observable in the photoelectron spectroscopy due to it having a higher surface sensitivity than the XRD measurement [13]. The Nb 3d spectrum of specimen #2 exhibits only oxide components, Nb$_2$O$_5$ and NbO$_2$ [13, 14]. This indicates that the oxide layer grew by at least 20 nm as a result of the synthesis at relatively high temperatures or further hydrogenation, and that the Nb hydrides observed in the XRD pattern were formed deeper than the oxide surface layer. Here we should also note that the Nb 3d core-level chemical shift of the hydrides seems linearly dependent on the hydrogen content $x$. This relation suggests that the hydrogen may act as a negative H$^-$ ion in Nb.

Figures 4 and 5 show typical ERDA and RBS spectra of the starting Nb #S, and hydride specimens #1 and #2, respectively. In the upper abscissa of Figures 4 and 5, the estimated depths $z$ are indicated where H$^+$ and/or D$^+$ ions are recoiled or $^4$He$^{2+}$ ions are scattered, respectively. The surface positions are also shown by the solid and broken vertical lines for the H and D ERDA spectra, respectively. As can be seen in the ERDA spectra, hydrogen-rich regions are formed within an approximately 200-nm depth for H in specimens #1 and #2 and a D depletion region up to a depth of 200 nm in specimen #2. As shown later, the hydrogen-rich regions are attributed to the $\alpha$'-NbH (NbD) formation. The existence of the D-poor and H-rich regions in specimen #2 may sug-
Figure 5: RBS spectra of starting Nb #S, hydride specimens #1 and #2 at different hydrogenation stages. Estimated depths from which $^4\text{He}^+$ ions are scattered are shown in the upper abscissa. The downward- and upward-pointing arrows indicate boundaries between surface oxides and bulk hydrides, and between the $\alpha'$- and $\alpha$-hydrides, respectively.

gest the D–H exchange in the period from the preparation of deuteride specimens to the last ion-beam analysis measurements, because the present ex situ measurements could not prevent from the exposure to H origins such as H$_2$O in the surroundings. The formation of both H- and D-rich layers was found in the ERDA spectrum, measured as quickly as possible after the preparation without the HAXPES analysis for specimen #3, shown in Figure 4. In comparison with specimen #3, the shift of the leading edge of the H-rich region to about 50 nm in the depth scale and the reduction in the maximum recoiled ion energy of D were observed for specimen #2, which is ascribed to the formation of an approximately 50-nm thick oxide surface layer in specimen #2. The hydrogen signals were also observed for specimen #S. This may be attributed to the hydrogen dissolution in the starting Nb foil #S, although this point requires further study.

In the RBS spectra, Nb depletion surface layers are observed. This is attributed to the Nb oxides of the passivation layer, since the Nb atomic density in Nb$_2$O$_5$ is approximately half of that of Nb metal [13]. A measure of the boundary is indicated by the downward-pointing arrows, being approximately 25 nm for specimens #S and #1, and 50 nm for #2. These values are larger than, but consistent with, the above-mentioned HAXPES results, and in agreement with the observation in the ERDA spectrum for specimen #2. In the RBS spectrum of the specimen #2, a small step, indicated by the upward-pointing arrow, is also found at around 175 nm. The intensity change at the step is approximately 10%. This corresponds well to the observation of the hydrogen-rich region in the ERDA measurement, and agrees well with the lattice-constant expansion $\Delta a/a$ of 3.3%, observed in the XRD pattern of specimen #2, and hence the 10% unit volume expansion from $\alpha$-NbH to $\alpha'$-NbH.

In Figure 6, the hydrogen contents $x$, H/Nb and D/Nb, are
plotted as a function of the depth $z$. Here, the averaged hydrogen contents are estimated by integrating the original ERDA and RBS data for a depth interval of approximately 80 nm. A constant D signal in the ERDA spectrum for specimen #2 reaches 0.9 in the surface region up to a depth of 200 nm, whereas it becomes 0.18 in the bulk at a depth of 1 µm. These values are larger than, but consistent with those of 0.67 and 0.04–0.06 estimated for $\alpha'$- and $\alpha$-NbH from the XRD results, since the hydrogen content estimated from the XRD measurement is regarded as the increment of the hydrogen content $\Delta x$ from specimen #S. This implies the formation of $\alpha'$- and $\alpha$-NbH with $x \approx 0.9$ and 0.2, respectively. In specimen #1, the H content $x$ is ~0.35 up to a depth of 250 nm and decreases to 0.12 in the bulk. This suggests that a small portion of hydrogen-rich $\alpha'$-NbH ($x > 0.6$) in the hydrogen-poor $\alpha$-NbH ($x < 0.2$) phase was formed near the surface.

The present results show that hydrogen-rich $\alpha'$-NbH is formed mainly near the surface up to a depth of 200 nm, whereas hydrogen-poor $\alpha$-NbH is extended over the whole specimen. The extremely high hydrogen permeability of Nb [2] may induce the formation of this extended $\alpha$-NbH. The gradual decrease in the hydrogen content up to about 500 nm can be explained by the reduction of the portion of $\alpha'$-NbH toward the bulk, as illustrated in Figure 7. A direct reaction of Nb with supercritical water possibly produces Nb oxides and hydrogen molecules: $2\text{Nb} + 5\text{H}_2\text{O} \rightarrow \text{Nb}_2\text{O}_5 + 5\text{H}_2$. Oxide $\text{Nb}_2\text{O}_5$ produced via the direct reaction, or existing initially in the passivation layer, is a well-known catalyst [24] in the decomposition of hydrogen molecules: $5\text{H}_2 \rightarrow 10\text{H}$. Then, hydrogen atoms diffuse rapidly into the bulk, forming, for example, an amount of $\alpha$-NbH that is 100 times larger than $\text{Nb}_2\text{O}_5$ with a hydrogen content $x = 0.1$.

Another possible reaction which creates no oxides, such as $2\text{Nb} + 2\text{H}_2\text{O} \rightarrow 2\text{NbH} + \text{H}_2\text{O}$, produces rapidly migrating hydrogen atoms to form $\alpha$-NbH in the bulk. The amount of oxide in the present hydride specimens is estimated to be less than 1% of the Nb hydrides from the XRD profiles, which may turn out to expect 1–2 µm thick hydride with a hydrogen content $x = 0.2–0.1$, respectively, and ~20 nm thick oxide layer. Since the starting Nb “metallic” phase did not remain in hydride specimens, more oxygen was produced than those forming the Nb oxides. The residual oxygen may be dissolved into the surrounding water. The formation of $\alpha'$-NbH in the near-surface region may be attributed to the relatively slow hydrogen diffusion in the hydrogen-rich region. In the present study, we examined specimens in the relatively early hydrogenation stages.

**IV. CONCLUSIONS**

We successfully and consistently confirmed hydride formation in supercritical water under extremely high pressures and temperatures, not only from the chemical-state viewpoint of HAXPES, but also from the hydrogen content analysis of ERDA/RBS. Hydrogen-poor $\alpha$-NbH is rapidly formed throughout the entire specimen, while hydrogen-rich $\alpha'$-NbH grows gradually from the surface to the bulk. The Nb passivation layer also evolves gradually but is not produced in the closed system as much as in the open system [7].

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