

Characterization of Nb Hydrides Synthesized in High-Pressure Supercritical Water by Micro-beam Hard X-ray Photoelectron Spectroscopy

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Abstract

We have characterized Nb hydrides synthesized in high pressure supercritical water by hard X-ray photoelectron spectroscopy. Comparison is made, in particular, of the Nb 2p core level spectra and valence band ones for the Nb hydride specimens in different stages of hydrogenation with those for Nb oxide and metallic references. The Nb 2p core level spectra of the Nb hydride specimens synthesized at relatively low temperature show an intense Nb₂O₅ component and a shoulder structure, which is attributed to Nb hydrides, at the high binding energy side of a metallic component of the Nb metal. The valence band spectra of the Nb hydride specimens also show a broad band at the binding energy E_B between 5 and 9 eV, which is ascribed mainly to Nb oxides. The present results indicate that the surface of the synthesized Nb hydrides is covered with several 10 nm thick Nb oxides and suggest that the Nb hydrides are formed deep inside the specimens. The Nb 2p chemical shift implies the Nb valence of +1.4 for the synthesized hydride NbH_x.

Keywords: hard X-ray photoelectron spectroscopy; Nb hydrides; Nb2p spectra; valence-band spectra; chemical shifts

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1. Introduction

Metal-hydrogen system has been extensively investigated in relation to hydrogen embrittlement, fission and fusion reactor applications, hydrogen storage, batteries and fuel cells, and catalysts for such as water splitting [1,2]. Body-centered cubic (bcc) structured Nb is well-known as one of metals with high hydrogen permeability and solubility. Nb hydrides, NbH_x , are formed up to the considerably large hydrogen concentration x [3,4]; phases α and α' (hereafter denoted by $\alpha\text{-NbH}$ and $\alpha'\text{-NbH}$, respectively) are disordered solutions of hydrogen at the interstitial sites in bcc Nb with the low ($x \sim 0.1$) and high ($x \sim 0.8$) hydrogen concentrations, respectively, while NbH_2 (phase δ) has the CaF_2 -type structure, where Nb is arranged in a face-centered cubic lattice. As for the electronic band structure, hydrogen is considered to show an electronegative character or anion-like behavior in metal hydrides [2]. For the transition metal hydrides, the hybridization of H 1s states with transition metal d states splits their bonding states off from the main d valence bands [5,6].

Recently it has been found that Nb hydrides are formed by infra-red laser-beam heating in high pressure (10 GPa) supercritical water with little oxides [7]. This seems unusual because supercritical water (the thermodynamic critical point of 647.3 K and 22.12 MPa) is believed to have great ability of oxidation. Indeed, for hydrothermal reactions of Nb with water below ~ 1100 K under a pressure less than 0.1 GPa, it has been reported that stable Nb_2O_5 is finally formed, while NbH_x is produced as intermediates, depending on a partial pressure of hydrogen [8]. However, reactions under pressure higher than 1 GPa are still unclear. High hydrogen permeability of Nb as well as gas-like effusive properties of supercritical water may play an important role in the hydride formation. Remarkable increase in hydrogen solubility of Pd [9] and the formation of new metal hydrides [10,11] have been also found under such a high pressure hydrogen condition.

In this report, we have characterized the Nb hydride synthesized in high pressure supercritical water by using micro-beam hard X-ray photoelectron spectroscopy; the hydrides reveal associated chemical shifts of Nb core-levels [12] as well as the above mentioned split-off of the Nb-H bonding bands. Because of the very small size of the synthesized specimens, the Nb hydrides have been neither confirmed nor characterized by other techniques than X-ray diffraction (XRD) measurement yet. Although the hydrogen concentration of the synthesized specimens can be analyzed with ion beam techniques such as the elastic recoil detection analysis [13,14], their chemical states are difficult to clarify by using the ion beam techniques. The high bulk-sensitivity of the hard X-ray photoelectron spectroscopy [15,16] is effective to investigate the chemical

states of the synthesized hydride specimens, which are too small, typical size of 0.1 mm x 0.1 mm x 0.02 mm, to prepare contamination-free surfaces for low excitation photon energy photoelectron spectroscopy. This is the first spectroscopic report of tiny specimens synthesized with use of a diamond anvil cell.

2. Experimental

Nb hydride specimens were prepared by irradiating an infra-red laser beam onto Nb foils (Nilaco, 99.9 %) of 0.1 mm x 0.1 mm x 0.025 mm in size under 7 ~ 11 GPa in a diamond anvil cell filled with water. XRD patterns were measured in transmission geometry (Rigaku, R-Axis7) for recovered specimens, which were set on the diffractometer by attaching one of their edges on polyimide films with a little silicone grease. Typical XRD patterns of the synthesized Nb hydrides are shown in Fig.1 for different stages of hydrogenation; the specimen #1 obtained by heating at relatively low temperatures (below 1500 K) reveals clear metallic Nb patterns (open squares), the specimens #2 ~ #4 with hydrogenation proceeding show the interstitial hydride NbH_x patterns (open circles) together with the metallic ones (showing small increase in the lattice constant and hence containing a little interstitial hydrogen, $x \sim 0.08$, which implies $\alpha\text{-NbH}$, but referred as metallic Nb in this paper), and the specimen #5 synthesized at relatively high temperature (~ 3000 K) and more hydrogenated does the hydrides NbH_2 (closed circles) and NbH_x patterns without the metallic ones. Here, the growth temperatures are estimated by observing color of light emitted during the infrared laser irradiation. The hydrogen concentration x in the NbH_x hydride of the specimens #2 ~ #5 was estimated as 0.72 ~ 0.94 ($\alpha'\text{-NbH}$) under an assumption of a linear relation between the hydrogen concentration and the lattice expansion [17]. The specimens #4 and #5 with typical low and high hydrogen concentrations were prepared only for investigating the change in the hydrogen concentration or crystal structure due to the possible hydrogen release from the recovered specimens on keeping them in vacuum for photoelectron measurement. Trace of Nb oxides is recognized in the XRD patterns, in particular, for the specimen #5 (high-pressure phase Z- Nb_2O_5 by open arrowheads and low-pressure phase B- Nb_2O_5 by closed triangles). From the comparison of the XRD intensities, a ratio of the Nb oxides to NbH_x is roughly estimated as 0.1 at most for the specimen #3. For the specimens #1 and #2, further comparison of these XRD profiles with that of the specimen #3 shows that the relative amount of the Nb oxides to Nb ($\alpha\text{-NbH}$) and NbH_x ($\alpha'\text{-NbH}$) is about one order less than the specimen #3. No significant change in the XRD patterns is observed on keeping the specimens four days long in vacuum of $\sim 5 \times 10^{-7}$ Pa. Reference oxides of Nb_2O_5 and NbO_2 were

prepared by pressing their commercially available powders (Sigma Aldrich Co., 99.99 % and unknown, respectively) into pellets in the diamond anvil cell. Each of prepared Nb hydride and oxide specimens, as well as Nb foils as a metallic reference, was attached onto a copper pin of a sample holder for photoelectron measurement with adhesive carbon tape.

Hard X-ray photoelectron measurements were carried out at room temperature at BL47XU of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI) by using an X-ray micro-beam of 0.035 mm x 0.040 mm (FWHM) in cross-sectional size and of 7940 eV in photon energy as an excitation source [18]. Photoelectrons were analyzed with a hemispherical energy analyzer (VG SCIENTA, R4000) in the angle-integrated mode, set perpendicular to the incident X-ray. The acceptance angle of the input lens was 30 degrees in the present measurement. The angle θ between the lens axis of the photoelectron analyzer and the surface normal was set from 2 ~ 5 degrees for bulk-sensitive measurement to 60 degrees for surface-sensitive measurement by rotating the specimen. The inelastic mean free path is estimated to be 8 ~ 10 nm for 6 ~ 8 keV electrons in Nb [19]. The photon energy was calibrated by measuring the Fermi edge of an Au plate and the total energy resolution including the thermal broadening was also estimated to be 0.25 eV from the measured edge. The origin of the binding energy E_B was set to the Fermi energy E_F of the Au plate. Energy shifts due to the recoil effect [16] were estimated to be at most 0.05 and 0.02 eV for Nb and Au, respectively. Since charging effects were recognized for the oxide specimens, a flood gun was used for charge compensation. For the detailed comparison, however, the Nb₂O₅ components of the Nb core levels were aligned to those of the metallic specimens, as shown later.

3. Results and Discussion

Figure 2 summarizes the Nb 2p_{3/2} core level spectra of the Nb hydride specimens #1 ~ #3 together with those of references: metallic Nb foils (Nb (a) as prepared and Nb (b) after polishing in the atmosphere) and Nb oxides (NbO₂ and Nb₂O₅). These spectra are normalized with the integrated intensities, and the spectrum of Nb₂O₅ is shifted so as to be aligned with the high binding energy component observed at $\theta = 60$ degrees for the foil (b).

In the Nb foil (a), a large metallic Nb component and a small Nb oxide one due to the passivation layer are observed at $E_B = 2368.3$ and ~ 2373.6 eV, respectively. In comparison to the oxide component, the band at 2368.3 eV has an asymmetric line shape with tailing towards the high binding energy side of the peak, which indicates its metallic character, *i.e.* the energy loss due to shielding of the photocreated core hole by

the free conduction electrons (the Doniac-Sunjic effects) [20], rather than the recoil effects [15]. As seen in Fig. 2, polishing the Nb foil with lapping films (3M, #4000 (Al_2O_3 particle size of 3 μm) to #15000 (particle size of 0.3 μm)) leads to the surface oxidation by forming Nb_2O_5 ; the component at $E_B = 2373.9$ eV is increased by polishing and enhanced as the surface sensitivity increases from $\theta = 4$ to 60 degrees, while the metallic one is decreased. This is ascribed to the high oxidation activity of polished rough and fresh Nb surfaces under the atmosphere. The Nb $2p_{3/2}$ spectrum of NbO_2 also shows the Nb_2O_5 component at $E_B = 2373.9$ eV besides NbO_2 one at $E_B = 2372.4$ eV. The existence of Nb_2O_5 in all the investigated specimens indicates its high stability. Similar chemical shifts are observed in the Nb 3d core level spectrum, which is also consistent with so far reported results for the Nb oxides [21].

In the Nb hydride specimen #1, hydrogen may be absorbed as an interstitial but almost no Nb hydride is formed; the metallic and oxide components are seen at $E_B = 2368.3$ and 2373.9 eV, respectively. In the Nb hydride specimens #2 and #3, where the hydrogenation proceeds to form NbH_x ($x \sim 0.7$; α' -NbH), their Nb $2p_{3/2}$ spectra show an intense Nb_2O_5 component growing. In the specimen #2, a shoulder structure is also observed at $E_B \sim 2369.7$ eV, slightly deeper than the metallic component of the Nb foils, as indicated by a triangle in the figure. Comparison with reference materials suggests that the shoulder structure can be attributed to the hydride NbH_x (α' -NbH). The Nb valence for NbH_x can be estimated as +1.4 from the present data for the chemical shifts of the Nb $2p_{3/2}$ core level in the Nb oxides. Similar chemical shifts have been reported on the Nb 3d core levels of the hydrogen implanted Nb surface and the hydride $\text{NbH}_{0.86}$ [12].

In Fig.3, typical valence band spectra are shown for the investigated specimens together with total electronic densities of states calculated for Nb [22], γ -NbH_{tet} [5] and NbH_2 [23]. The spectra were normalized with the integrated intensity up to $E_B = 11$ eV. For reference, the valence band spectrum of Nb_2O_5 is also presented by shifting it so that the valence band bottom is aligned with those of other spectra; because the neutralization by using a flood gun was very sensitive to the intensity of the incident X-rays, the Nb_2O_5 spectra seem to be slightly broadened by the small fluctuation of X-ray intensity during the measurement, and the location of the band is indeed tentative. However, the spectral shape is in agreement with so far reported one [12], which was also measured with use of a flood gun.

The valence band spectrum of the Nb foil (a) reveals a triple-peaked feature below $E_B \sim 5$ eV, which is in good agreement with the calculated density of states of Nb [22,24]; while two higher-lying bands mainly consist of the Nb 4d states, the lowest

band has large s-like character and hence relatively enhanced contribution in the present photoelectron spectra due to the photoionization cross section in the hard X-ray region [16]. In line with the Nb core level spectra, a broad band around $E_B = 5 \sim 9$ eV is enhanced on polishing and is attributed to the Nb oxide in the surface layer of Nb foils. Although there is a very small C 1s signal due to the surface contamination observed for the reference Nb foil (a), it appears that the present Nb valence band spectra are little affected by the contamination.

The valence band spectrum of the hydride specimen #1 consists of Nb metal and oxide components, which is consistent with the above-mentioned core level results. In the valence band spectra of the hydride specimens #2 and #3, an intense and broad band is observed in the binding energy region from 5 and 9 eV, which is mainly ascribed to the Nb oxide. It resembles the oxides layer of the Nb foils and the valence band of NbO₂, where peaks are located at $E_B \sim 6$ and 8 eV, as well as the Nb₂O₅ valence band showing a peak with a shoulder structure separated by ~ 2 eV from the peak and a comparable width to the bands in the hydride specimens #2 and #3, although the exact location of the Nb₂O₅ valence band is not clear. According to the calculated results [5,23], the split-off bands appear in the same region. In contrast to the oxides layer of the Nb foils and NbO₂, a small hump is recognized at $E_B \sim 7.4$ eV in the hydride specimens #2 and #3. This might reveal the hydride formation. Weak structures observed below $E_B = 4$ eV are also different from the metallic Nb valence band, possibly corresponding to the shoulder structure in the Nb 2p_{3/2} core level spectrum. However, it is still difficult to assign them to the hydride by comparison with calculated densities of states of the hydrides. The valence band spectra below $E_B \sim 4$ eV might be modified by the C-derived band of the adhesive tape, grease or the surface contamination, because large C 1s and Si 2s signals (possible origin of Si is the silicone grease or the glue of the adhesive tape) were observed for the hydride specimen #2 and the intensity of the valence band features seems to correlate with that of the C 1s signal. In NbO₂, another unknown band is found at $E_B \sim 1.3$ eV, which might be also induced by the surface carbon contamination because of a little but relatively large C 1s signal and no Si 2s one for this specimen, or defect states in a gap; at present its origin is not clarified yet.

The present spectroscopic data show that the surfaces of the synthesized hydride specimens are covered with an at least 10 nm thick Nb oxide, Nb₂O₅, even for the specimen with little oxide recognized in the XRD measurement and hence Nb hydrides observed in the XRD measurement turn out to be formed deep inside the specimens; the attenuation length, *i.e.* probing depth, for the Cu K α X-ray used in the XRD

measurements is $\sim 5 \mu\text{m}$ [25], much larger than the present photoelectron probing depth of $\sim 10 \text{ nm}$. The ratio of the photoelectron probing depth to that of XRD is comparable with the relative amount of the Nb oxides to Nb and NbH_x estimated from XRD profiles for the hydride specimen #2. This also indicates the hydrides formed in the bulk and almost all the oxides in the surface layers. There are suggested possible reactions to form no or little oxides: $2\text{Nb} + 2\text{H}_2\text{O} \rightarrow 2\text{NbH} + \text{H}_2\text{O}_2$ and $12\text{Nb} + 5\text{H}_2\text{O} \rightarrow 10\text{NbH} + \text{Nb}_2\text{O}_5$ for NbH, and $\text{Nb} + 2\text{H}_2\text{O} \rightarrow \text{NbH}_2 + \text{H}_2\text{O}_2$ and $7\text{Nb} + 5\text{H}_2\text{O} \rightarrow 5\text{NbH}_2 + \text{Nb}_2\text{O}_5$ for NbH_2 . The present results may imply that a reaction of Nb with H_2O in the high pressure supercritical water produces hydrogen atoms, which diffuse rapidly into deep bulk Nb to form the Nb hydrides, and forms Nb_2O_5 oxide surface layers. On recovery, the surface oxide layer will play a roll of a barrier to keep the hydrides inside the specimen [26]. On the other hand, the XRD observation of little Nb oxides formation in comparison to the hydrides reveals a large amount of produced oxygen in a form of H_2O_2 or dissolved in the water. Indeed bubbles are observed on recovery to the ambient pressure, although their content remains unknown at present.

For the hydride specimen #2, where the hydrogenation does not proceed so much, we have found the hydride component in the Nb 2p core level spectrum. This would be confirmed by depth profiling of the chemical components and their correlation with oxygen. In the present study, however, because of small signal intensity for the tiny hydride specimens, in particular at large detection angles, it was difficult to investigate the angular dependence of the spectra by rotating the specimens. Angle-resolved measurements are intended with a recently developed input lens of wide angle acceptance (60 degrees) and the smaller X-ray beam of $1 \mu\text{m} \times 1 \mu\text{m}$, and will be reported elsewhere.

4. Conclusions

It is found that the surfaces of the Nb hydrides synthesized in high pressure supercritical water are oxidized at least several 10 nm in depth with forming Nb_2O_5 , even for specimens with little oxides recognized in XRD measurements. The Nb hydrides observed in XRD profiles turn out to be formed deep inside the specimens. The present results also demonstrate that micro-beam hard X-ray photoelectron spectroscopy is a powerful tool for characterizing such a small sample as specimens newly synthesized in the diamond anvil cell. Further confirmation of the hydride formation and the valence band electronic structure of the hydride will be obtained by investigating the depth profiles of the chemical species and decomposing the valence-band spectrum with use of angle-resolved micro-beam hard X-ray

photoelectron spectroscopy.

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Figure captions

Fig.1 X-ray diffraction patterns of Nb hydride specimens synthesized in high pressure supercritical water. For specimens #4 and #5, X-ray diffraction patterns are compared before (thin gray curves) and after (broken curves) keeping these specimens in vacuum during about 4 days. KCl was set as an angular standard. Numbers near symbols stand for identified Miller indices. Diffraction intensity of each specimen is normalized with the integrated intensities of (110) diffraction peaks of Nb (α -NbH) and NbH_x (α' -NbH) underlying bcc lattice.

Fig.2 Nb 2p_{3/2} core level spectra of synthesized Nb hydride specimens #1 ~ #3, and reference NbO₂ and Nb₂O₅ oxides and metallic Nb foils (a) and (b). The detection angle θ measured from the surface normal for each spectrum is indicated in the figure. The spectrum of Nb₂O₅ is shifted so as to be aligned with the high binding energy component observed at $\theta = 60$ degrees for the foil (b).

Fig.3 Valence band spectra of synthesized Nb hydride specimens #1 ~ #3, reference metallic Nb foils (a) and (b), and Nb oxides Nb₂O₅ and NbO₂. The detection angle θ measured from the surface normal for each spectrum is indicated in the figure. The spectrum of Nb₂O₅ is shifted so that its valence band bottom is aligned with those of the other. Total electronic densities of states calculated for Nb, γ -NbH_{tet} and NbH₂ are also shown for comparison.