Characterization of Nb hydrides synthesized in high-pressure supercritical water by micro-beam hard X-ray photoelectron spectroscopy

Kazuo Soda [a,*], Hiroki Kondo [a], Masahiko Kato [a], Tatsuhito Shiraki [b], Ken Niwa [c], Keiji Kusaba [c], Masashi Hasegawa [c], Eiji Ikenaga [d]

[a] Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[b] Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[c] Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[d] Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

ARTICLE INFO

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 Nb_2O_5 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.

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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 α-NbH and α'-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 infrared 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 $\sim$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

* Corresponding author. Tel.: +81 52 789 4683; fax: +81 52 789 5155.
E-mail addresses: j45880a@nucc.cc.nagoya-u.ac.jp, k-soda@nucl.nagoya-u.ac.jp (K. Soda).
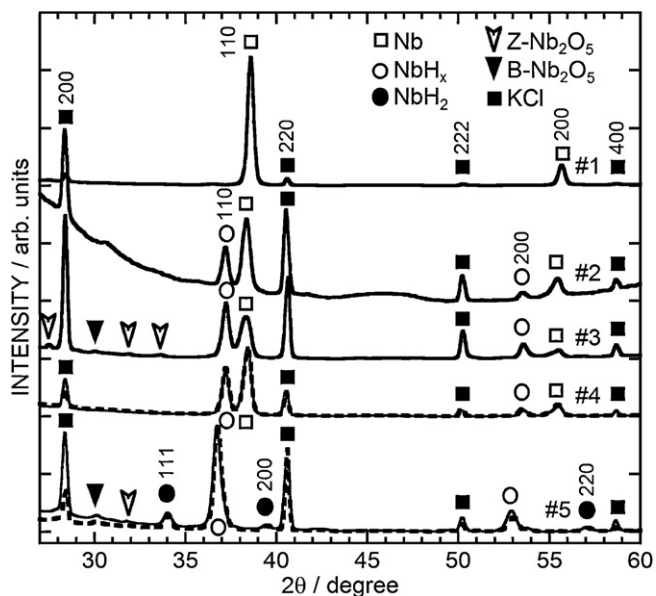
Fig. 1. X-ray diffraction patterns of Nb hydride specimens synthesized in high-pressure supercritical water. For specimens #4 and #5, X-ray diffraction patterns are compared before (thin gray curves) and after (broken curves) keeping these specimens in vacuum during about 4 days. KCl was set as an angular standard. Numbers near symbols stand for identified Miller indices. Diffraction intensity of each specimen is normalized with the integrated intensities of (1 1 0) diffraction peaks of Nb (α-NbH) and NbH$_x$ (α'-NbH) underlying bcc lattice.

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 × 0.1 mm × 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 infrared laser beam onto Nb foils (Nilaco, 99.9%) of 0.1 mm × 0.1 mm × 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 α-NbH, but referred as metallic Nb in this paper), and the specimen #5 synthesized at relatively high temperature ($\sim$3000 K) and more hydrogenated does the hydrides NbH$_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 (α'-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$_2$O$_5$ by open arrowheads and low-pressure phase B-Nb$_2$O$_5$ 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 (α-NbH) and NbH$_x$ (α'-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$5 × 10^{-7} Pa. Reference oxides of Nb$_2$O$_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 cupper 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 × 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 to 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 Nb$_2$O$_5$ components of the Nb core levels were aligned to those of the metallic specimens, as shown later.

3. Results and discussion

Fig. 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 (NbO$_2$ and Nb$_2$O$_5$). These spectra are normalized with the integrated intensities, and the spectrum of Nb$_2$O$_5$ is shifted so as to be aligned with the high binding energy component observed at θ = 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 $\sim$2373.6 eV, respectively. In comparison to the oxide component, the band at 2368.3 eV has an asymmetric line shape with