Atom-Probe Tomographic Analyses of Hydrogen Interstitial Atoms in Ultrahigh Purity Niobium

Yoon-Jun Kim1 and David N. Seidman1,2,*

1Department of Materials Science and Engineering, Northwestern University, 2220 Campus Dr., Evanston, IL 60208, USA
2Northwestern University Center for Atom-Probe Tomography (NUCAPT), 2220 Campus Dr., Evanston, IL 60208, USA

Abstract: Atomic-scale characterization of hydrogen and formation of niobium hydrides, using ultraviolet (wavelength = 355 nm) picosecond laser-assisted local-electrode atom-probe tomography, was performed for ultrahigh purity niobium utilizing different laser pulse energies, 10 or 50 pJ/pulse or voltage pulsing. At 50 pJ/pulse, hydrogen atoms migrate onto the 110 and 111 poles as a result of stimulated surface diffusion, whereas they are immobile for <10 pJ/pulse or for voltage pulsing. Accordingly, the highest concentrations of H and NbH were obtained at 50 pJ/pulse. This is attributed to the thermal energy of the laser pulses being transferred to pure niobium specimens. Therefore, we examined the effects of the laser pulse energy being increased systematically from 1 to 20 pJ/pulse and then decreasing it from 20 to 1 pJ/pulse. The concentrations of H, H2, and NbH and the atomic concentration ratios H2/H and NbH/Nb are greater when decreasing laser pulse energy increases the mobility of H atoms by supplying sufficient thermal energy to form H2 or NbH.

Key words: atom-probe tomography, hydrogen interstitial atoms, hydrides, niobium, metallic superconductors

INTRODUCTION

Niobium is a type-II superconducting metal possessing a critical temperature (Tc) of 9.8 K. The high-energy physics community is developing superconducting radio-frequency (SRF) cavities using ultrahigh purity (ASTM B 393, Type 5 Grade) niobium to enable the exploration of energy and intensity frontiers employing linear accelerators (Phinney et al., 2007). The central issue concerning niobium SRF cavities is their lack of reproducible performance for large-scale production, which means their yield is low and hence their cost for using them for linear accelerators becomes extremely expensive. One of the symptoms of poor performance at the high electric-field gradients, 35 MV/m, specified by the International Linear Collider project and a next-generation accelerator project, Project X, is the appearance of large pits at the edges of the heat-affected zones near the equator welds (Ge et al., 2011). Typical pit dimensions are 0.1–1.0 mm width and 10–100 mm depth (Cooley et al., 2011). In particular, bad cavities exhibit a strong decrease in the quality factor (Q), which is the ratio of stored energy to dissipated power that is diminished by the existence of chemical impurities and/or a rough surface finish (Padamsee, 2009). Therefore, understanding and preventing weld pits have received a great deal of justifiable attention (Champion et al., 2009; Cooley et al., 2011; Singer et al., 2011). Although the exact formation mechanism of weld pits is not fully understood, it is believed that niobium hydrides play a significant role.

Several studies were performed on the sub-surface chemistry of SRF cavities, especially on the behavior of H and the formation of NbH in Nb coupons, on an atomic scale, using an ultraviolet (UV) laser-assisted local-electrode atom-probe (LEAP) tomograph in conjunction with aberration-corrected high-resolution transmission electron microscopy (Kim et al., 2013). In addition, secondary ion mass spectrometry (Ciovati et al., 2010; Maheshwari et al., 2011) and elastic recoil detection (Romanenko & Goncharova, 2011) techniques were utilized to obtain quantitative depth profiles of H and NbH in Nb-SRF cavity specimens. Oxygen and oxide formation on pure Nb surfaces were studied utilizing X-ray diffraction techniques (Ma & Rosenberg, 2003; Delheusy et al., 2008). Earlier, LEAP tomographic studies were successfully employed for studying the formation of niobium oxides on Nb surfaces (Sebastian et al., 2006; Yoon et al., 2007, 2008). The behavior of hydrogen interstitial atoms is of paramount importance because niobium has a body-centered cubic (b.c.c.) structure containing octahedral and tetrahedral interstitial sites, and hydrogen atoms can migrate randomly on them and form different hydrides (NbHx) (Schober, 1975a, 1975b). According to the Nb–H phase diagram (Fig. 1; Ricker & Myneni, 2010), hydrogen dissolves exothermically in niobium producing solid solutions of hydrogen in Nb denoted as α- or α'-phases. It is emphasized that the α'-phase contains H in pure Nb up to ~70 at% above ~180°C and the α-phase co-exists with the β-NbH phase and ε-NbH phase at a H concentration of up to ~43 at% at room temperature and 30 K, respectively. The interactions among Nb and H atoms involve short-range ordering, thereby creating a hydrogen superlattice (Makenas & Birnbaum, 1982).
Above room temperature, the $\beta$-NbH phase (face-centered orthorhombic, f.c.o.) can be formed from $\alpha$- and/or $\alpha'$-solid solutions by the ordering of H atoms in the tetrahedral positions in an f.c.o. structure. Employing conventional transmission electron microscopy and selected-area diffraction patterns indicate that hydrogen ordering involves the tetrahedral sites in $\beta$-NbH (f.c.o.), which had precipitated from the $\alpha'$-solid solution (Schober et al., 1973, 1974; Birnbaum et al., 1976; Schober & Wenzl, 1976; Grossbeck & Birnbaum, 1977; Gabriel et al., 2011). The $\beta$-NbH phase is the most common one observed in Nb, and its H/Nb atomic ratio (ratio of the atomic concentrations of hydrogen and niobium) ranges from 0.7 to 1.1 (Gabriel et al., 2011). At temperatures $<230$ K, different ordered hydrides, $\varepsilon$ (orthorhombic) $\zeta$ (orthorhombic), $\gamma$ (pseudo cubic), and $\lambda$ (unconfirmed), can be formed from the $\beta$-phase (Makenas & Birnbaum, 1982; Ricker & Myneni, 2010). The formation of ordered $\beta$-NbH is accelerated by plastic deformation. The interactions among hydrogen atoms and dislocations increase the binding enthalpy of an H–H dimer from $1.265$ (0.05485 eV) to $7,300$ cal/mol ($0.3166$ eV) (Baker & Birnbaum, 1972). The net result is that the diffusivity of an H–H dimer decreases from $10^{-14}$ cm$^2$/s in Nb (Baker & Birnbaum, 1973) to $10^{-32}$ cm$^2$/s at 60 K. Thereby, effectively immobilizing hydrogen atoms via their interactions with dislocations results in $\beta$-NbH precipitates at 60 K.

In this article, we present hydrogen and niobium hydride formation behavior using a picosecond UV laser-assisted LEAP tomograph for different UV laser pulse energies ranging from 1 to 50 pJ/pulse. Hydrogen concentration profiles and three-dimensional (3D) mapping of H and NbH in pure Nb are determined for different laser pulse energies and voltage pulsing. In addition, the following quantities were determined and discussed: (1) mass-resolving power ($m/\Delta m$); (2) the ratio of charge states of Nb ions ($\text{Nb}^{3+}/\text{Nb}^{2+}$); and (3) the ratios of different hydrogen compounds ($\text{H}_2$/H and NbH/Nb) in mole percent.
times an enhancement factor, owing to the polarizability of H₂, that determines the total flux of hydrogen atoms to the surface of a nanotip (Brandon, 1968; Southon, 1968), as expressed by the following equation:

\[ F = F_0 \times \frac{3}{2} \left( \frac{\alpha E^2}{2k_BT} \right) \]

where \( \alpha \) is the polarizability of H₂, \( E \) the electric field, \( k_B \) the Boltzmann’s constant, \( T \) the temperature (in Kelvin), and \( F_0 \) the number of hydrogen molecules/m²/s impinging on a nanotip in the absence of \( E \). The classic gas kinetic factor for the flux of H₂ molecules that arrive at the surface of the nanotip is given by:

\[ F_0 = \frac{p\eta}{\sqrt{2\pi m k_B T}} \]

where \( p \) is the partial pressure of H₂, \( \eta \) the sticking coefficient describing the fraction of incident gas molecules that adsorb on the surface of a nanotip, and \( m \) the molecular mass of H₂. The quantity inside of parenthesis in equation (1) is called an enhancement factor owing to the polarizability of specific gas species. The following values apply to our experiments:

\( a_{H_2} = 5.314 \) a.u. (Olney et al., 1997), \( E = 35 \) V/nm for Nb (Tsong, 1978, 1990), \( P_{H_2} = 2.7 \times 10^{-13} \) Torr, \( T = 30 \) K, and \( \eta = 1 \) [this yields an upper bound value for equation (2)]. These values yield \( F = 2.09 \times 10^{14} \) molecules/m²/s for the H₂ molecule flux to a surface for \( \eta = 1 \). Consequently, the time for monolayer coverage is \( \approx 47.816 \) s (\( \approx 1.328 \) h), which is significantly longer than our APT runs, which are typically <5 h. The above calculation demonstrates that the effects we report in this article cannot be because of the residual H₂ gas in the UHV chamber. In addition, when hydrogen promotion is utilized the nanotip is continuously evaporating (Ast & Seidman, 1968, 1971; Averback & Seidman, 1973), which is not the case for our studies of Nb, where the nanotips are stable when they are not being pulsed with UV light or a voltage.

Quantitative concentration profile of each element was obtained from a 3D reconstruction (Fig. 3). Nb, H, and NbH were the predominant species detected, but oxygen and niobium oxides (NbO and/or Nb₂O₅) were also detected at a maximum concentration of \( \approx 45 \) mol% Nb₂O₅ for the UV laser pulsing mode using 50 (Fig. 3a) and 10 pJ/pulse (Fig. 3b) and \( \approx 5 \) mol% NbO for the voltage pulsing mode (Fig. 3c) within 5 nm from the surface. The behavior of H and NbH depended on the UV laser pulse energies used. At a depth of \( \approx 5 \) nm in the oxide layer, the concentration of H increased continuously with increasing UV laser pulse energy. For 10 pJ/pulse (Fig. 3b) and voltage pulsing (Fig. 3c), the
concentration profiles of Nb and H stabilized at average concentrations of 44.6 mol% Nb, 26.4 mol% H, and 36.5 mol% Nb, 61.4 mol% H, respectively. In addition, the amount of NbH detected using 50 pJ/pulse was ~43 mol%, but it is reduced significantly to ~3 mol% for voltage pulsing and to ~25 mol% for 10 pJ/pulse.

The behavior of Nb, H, and NbH are best understood by constructing 2D cross-sectional views of the 3D reconstructions. The field-desorption image of Nb atoms contains crystallographic information, poles, and zone lines (Fig. 4a). This contrast is attributed to local electric-field variations on the surface of a nanotip (Waugh et al., 1976; Gault et al., 2009). Assuming a stereographic projection, the poles are identified from the symmetry of the image and are accordingly indexed (Fig. 4j; Drechsler & Wolf, 1960; Brandon, 1964).

When the UV laser pulse energy is increased to 50 pJ/pulse, the poles disappear in the Nb-desorption image (Fig. 4c) and concomitantly H decorates the zone lines of Nb (Fig. 4f). This implies that there are high binding energy sites and fast surface diffusion pathways, which are dependent on the crystallographic facets along these zone lines at the highest UV laser pulse energy; this was similar for results obtained using laser-assisted LEAP tomography to analyze pure Al (Gault et al., 2010) and field ion microscopy (FIM) of W using voltage pulsing (Brandon, 1962; Moore & Spink, 1974). The H-enriched zone lines displayed in Figure 4f almost disappear at 10 pJ/pulse (Fig. 4e), and when using voltage pulsing (Fig. 4d), owing to a reduction of the number density of H atoms. Figure 4f displays clearly the threefold zone line decoration with H at the T11 pole toward the 110-type poles, such as the 101 and T10 poles, and sixfold symmetry at the T10 pole toward 111-type poles, such as the T11 and 111 poles. The migration of H atoms implies an interaction with its former nearest-neighbor (NN) Nb atoms at the edge of a plane as a result of different lattice binding energies, and therefore the migration energy of H atoms is a function of the number of NN atoms: see ball model (Waugh et al., 1976). This ball model suggests that the majority of atoms (atoms on {110} planes, except for kink-site atoms) can be evaporated from a nanotip by migrating toward {110}-type planes, while maintaining two first NN atoms. However, kink-site atoms on <111> zone lines have only one NN atom, which are resistant to field evaporation of W atoms, as determined by FIM observations. The larger the picosecond laser pulse energy the higher is the nanotip’s temperature, which results in atomic rearrangements on different crystallographic facets, as
determined by FIM (Brandon, 1962). A field-emission microscope (Gomer, 1961) study of H on W nanotips demonstrated that H atoms migrate from the closest-packed plane, [110], to an atomically rough surrounding surface consisting of terraces, for example, on the 110–211 zones. This indicates that low-impedance pathways, with small activation energies for the diffusion of H atoms, provide the maximum mobility of H atoms and the smallest binding energies.

When voltage pulsing is utilized, hydrogen atoms do not diffuse between poles and are desorbed essentially directly from crystallographic poles. Figure 5 displays a 50 at% H isoconcentration surface obtained using voltage pulsing, which demonstrates that the T00, 001, T10, 101, 111, T11, and 121 crystallographic poles of Nb are enriched with hydrogen.

Figures 4g to 4i display the distributions of NbH molecules obtained using the voltage pulse mode and different picosecond UV laser pulse energies, 10 and 50 pJ/pulse, respectively. First, using the voltage pulsing mode (Fig. 4g) NbH is distributed around the T10 pole. Second, picosecond UV laser pulsing produces more NbH molecules throughout the Nb nanotips, as displayed in Figures 4h and 4i for 10 and 50 pJ/pulse, respectively; the desorption images exhibit zone lines from 001 to T11 poles and from 001 to T00 poles. The differences in the NbH concentration profiles (Fig. 3) depend on the picosecond UV laser pulse energy, which determines the nanotip temperature, and electric-field pulsing (voltage pulsing), which clearly does not affect the nanotip temperature.

Several studies indicate that hydride formation is caused by external forces (the so-called Maxwell stresses); specifically, the mechanical stresses generated by the electric field, \( E \), exerted on a nanotip (Panofsky & Phillips, 2005):

\[
\sigma = \frac{\varepsilon_0}{2} E^2, \tag{3}
\]

where \( \sigma \) is the negative hydrostatic stress caused by \( E \), and \( \varepsilon_0 \) the vacuum permittivity of free space. The evaporation field of niobium is 35 V/nm (Tsong, 1978, 1990); therefore, the Maxwell stress, \( \sigma \), is -5.42 GPa; the transverse elastic constant \( (C = 0.5(C_{11} - C_{22})) \) of pure Nb at 30 K is ~59 GPa (Simmons & Wang, 1971). Akaiwa & Wada (1990) demonstrated, using FIM, that the formation of NbH is temperature- and \( E \)-field dependent, thereby showing that hydrogen atoms on 111 poles tend to rearrange themselves, subsequently producing an expansion of the nanotip for a stress >1 GPa. Similar findings exist for the 111 and 001 poles of GaP (Gaussmann et al., 1992) and 111 poles of Si (Sakata & Block, 1982). The presence of hydrogen is, thus, a precursor to the \( E \)-field-induced formation of surface hydrides on specific \( hkl \) poles.

Besides the fact that the distribution of H atoms and formation of NbH molecules are related to the \( hkl \) poles of Nb, the concentrations of H and NbH are highly correlated with the picosecond UV laser pulse energy (Fig. 3). As field evaporation is a thermally activated process governed by the Boltzmann factor, with an activation energy that is a function of the \( E \)-field (Brandon, 1963, 1965; Kellogg, 1983), hydrogen is thermally desorbed with each UV laser pulse. The higher the picosecond pulse energy, the more copious is the thermally activated hydrogen desorption. The desorbed \( ^1H^+ \) and \( ^1H_2^+ \) ions interact with the surface Nb atoms to form NbH. In addition, hydrogen field desorption in
Combination with field-induced hydride formation have been observed using pulsed laser APT studies of Si (Kellogg, 1983) and Mo (Kellogg, 1981).

More systematic APT experiments were performed to verify the effects of picosecond UV laser pulse energy (thermal energy) on H interstitial atoms, utilizing different picosecond UV laser pulse energy steps: 20 → 10 → 5 → 3 → 1 → 3 → 5 → 10 → 20 pJ/pulse to analyze the behavior of H in Nb. The mass spectra collected are displayed in Figure 6 for the mass-to-charge state ratio ranges of 0–3.0 and 30–50 amu: approximately two million ions were collected for each UV laser pulse energy. Note that the range of pulse energies is from 1 to 20 pJ and that the $^1$H$^+$ peak is essentially unaffected by the pulse energy. Although the $^1$H$_2^+$ peak depends on the pulse energy and pulse energies of 10–20 pJ yield the best results, the positions of the peaks of $^{93}$Nb$^{3+}$, $^{93}$Nb$^{2+}$, and $^{93}$NbH$^{2+}$ are unaffected strongly by the UV laser pulse energy in the range 1–20 pJ. The atomic ratios of H$_2$/H, NbH/Nb, and Nb$^{17}$/Nb$^{15}$ at each UV laser pulse energy step and the mass-resolving power, $m/\Delta m$, of H are displayed in Figure 7. A symmetrical behavior between increasing UV laser pulse energy and decreasing UV laser pulse energy is observed (compare Fig. 7a with Fig. 7d and Fig. 7c with Fig. 7f). These figures indicate that the higher $m/\Delta m$ and the higher concentration of Nb$^{2+}$ rather than Nb$^{3+}$ are obtained at higher picosecond UV laser pulse energies. An exception to this symmetric behavior is displayed for H$_2$/H as a function of picosecond UV laser pulse energy (compare Fig. 7b with Fig. 7e). In general, the H$_2$ molecules are detected more frequently for increasing UV laser pulse energies owing to the thermal energy absorbed from the UV laser pulses, with the assumption being that thermal energy absorbed in the apex of the nanotip is proportional to the applied UV laser pulse energy. The higher H$_2$/H ratio is achieved when decreasing the UV laser pulse energy from 20 to 1 pJ/pulse as opposed to increasing the UV laser pulse energy from 1 to 20 pJ/pulse. For example, H$_2$/H is ~0.011 ± 0.00015 at 10 pJ/pulse after decreasing it from 20 pJ/pulse; however, alternatively H$_2$/H is ~0.0017 ± 0.000084 at 10 pJ/pulse after increasing it from 5 pJ/pulse. This difference in H$_2$/H values at the same UV laser pulse energy between increasing and decreasing the UV laser pulse energy steps is mainly due to the residual thermal energy in the apex of the nanotip from a previous higher UV laser pulse energy step, when decreasing the laser pulse energy. The higher residual thermal energy after decreasing the laser pulse energy increases the mobility of H atoms by supplying sufficient thermal energy to form H$_2$ molecules. This is also true for the NbH/Nb ratio because it is obtained when decreasing the UV laser pulse energies as opposed to increasing the UV laser pulse energies.
In summary, the behavior of hydrogen in Nb (b.c.c.) employed for SRF cavities has been investigated utilizing LEAP tomography, employing different UV laser pulse energies utilizing a picosecond UV (wavelength $\lambda = 355$ nm) laser, and additional voltage pulsing. It is strongly emphasized that hydrogen dissolves exothermically in niobium and that the partial pressure of hydrogen in the UHV chamber was $2.7 \times 10^{-13}$ Torr during all the analyses as determined by an RGA. We present evidence for accelerated hydrogen surface diffusion resulting from the thermal energy input of UV laser pulses at 50 pJ/pulse. For a UV laser pulse energy of $<10$ pJ/pulse this effect almost completely disappears. The formation of NbH depends on the surface diffusivity of hydrogen, as NbH is observed around the $\{110\}$ pole. Our analyses include the sub-surface region, where the magnetic field penetrates $\sim 40$ nm from an Nb cavity’s surface during the operation of a linear particle accelerator. Therefore, residual hydrogen interstitial atoms or ordered niobium hydrides formed during a cavity’s processing results in radio-frequency losses.

**Acknowledgments**

This research was supported by the Fermi Research Alliance LLC under contract number DE-AC02-07CH11359 with the US DOE. Atom-probe tomography measurements were performed at the Northwestern University Center for Atom-Probe Tomography (NUCAPT) and the LEAP tomograph was purchased and upgraded with funding from the NSF-MRI (DMR 0420532) and ONR-DURIP (N00014-0400798, N00014-0610539, N00014-0910781) programs. NUCAPT is a Shared Facility of the Materials Research Center of the Northwestern University, supported by the National Science Foundation’s MRSEC program (DMR-1121262). We are also grateful to the Initiative for Sustainability and Energy at Northwestern (ISEN) for grants to upgrade NUCAPT’s capabilities.

**References**


