

Atomic-scale chemical analyses of niobium oxide/niobium interfaces via atom-probe tomography

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Niobium is the metal of choice for superconducting radio-frequency cavities for the future International Linear Collider. We present the results of atomic-scale characterization of the oxidation of niobium utilizing local-electrode atom-probe tomography employing picosecond laser pulsing. Laser pulsing is utilized to prevent a tip from fracturing as a buried niobium oxide/niobium interface is dissected on an atom-by-atom basis. The thickness of niobium oxide is about 15 nm, the root-mean-square chemical roughness is 0.4 nm, and the composition is close to Nb₂O₅, which is an insulator, with an interstitial oxygen concentration profile in Nb extending to a depth of 12 nm. © 2008 American Institute of Physics. [DOI: 10.1063/1.2987483]

Niobium has the highest critical temperature ($T_c = 9.2$ K) of any element in the periodic table and can be plastically deformed into complex geometries.¹ These properties make Nb the element of choice for superconducting radio-frequency (SRF) cavities for the future International Linear Collider and x-ray free electron laser.^{2,3} The thickness and chemical composition of the surface oxide on Nb SRF cavities and the interfacial chemistry between niobium oxide and bulk Nb are believed to be the determining factors for the performance of SRF cavities. Additionally, recent studies have revealed that baking Nb SRF cavities between 100 to 150 °C in ultrahigh vacuum for 24 h improves the performance of a cavity by recovering the high-field Q (quality factor) drop.^{4,5} Changes, however, in the microstructure and surface chemical composition after baking and the correlation between these quantities and improved performance are not fully understood.

X-ray photoelectron spectroscopy⁶ was used to investigate the surface chemistry of Nb cavities. Also, Delheusy *et al.*⁷ investigated the dissolution of a 20.3 Å thick native oxide layer on a Nb(110) surface upon heating, by combining x-ray reflectivity, grazing incidence diffuse scattering, and core-level spectroscopy. Recently, Local-Electrode Atom-Probe (LEAPTM) tomography with electrical pulsing has been employed to analyze Nb for SRF cavities on an atomic scale.^{8,9} The superior spatial resolution and analytical sensitivity of a LEAP tomograph permit determining the surface composition on an atom-by-atom and atomic layer-by-layer basis.¹⁰⁻¹² Due, however, to the low electric conductivity of the surface niobium oxide and an abrupt change in its value between it and bulk Nb, premature tip fracture occurs when field evaporation is occurring at the surface niobium oxide and/or on passing through the surface niobium oxide/Nb interface.

For this study, we employed picosecond laser (green light) pulsing,^{13,14} instead of electrical pulsing, to ensure continuous and smooth field evaporation of the surface niobium oxide and through the surface niobium oxide/Nb interface. Since laser pulsing evaporates atoms thermally from the surface of a tip, it reduces the periodically varying Maxwell elastic stresses associated with pulsed electric-field evaporation, thereby avoiding or reducing the susceptibility of a tip to fracture.

Niobium wire, 99.9% purity, was utilized for the LEAP tomographic experiments. Wires were electropolished: HF (49% initial concentration) in H₂SO₄ (68% initial concentration) with a 1:10 ratio. The polishing process commenced at 30 V_{dc} and the voltage was decreased to ~20 V_{dc} as the tip sharpened. The process ended at around 15 V_{dc}. This processing produces sharp needlelike tips with a radius of curvature of <50 nm.¹⁵ Each sharpened tip was dipped in HF for 1 min and then rinsed with high-purity de-ionized water. For the LEAP tomographic analyses, the background pressure in the ultrahigh vacuum was <10⁻¹⁰ torr (mainly hydrogen). Two different specimen temperatures and pulse energies for picosecond laser pulsing were utilized, using a pulse repetition rate of 100 kHz: (a) 100 K and 1.5 nJ pulse⁻¹ or (b) start at a specimen at 120 K and then reduce the temperature to 90 K and use 0.5 nJ pulse⁻¹.

A three-dimensional (3D) reconstruction of LEAP tomographic data of a Nb specimen, utilizing a tip temperature of 100 K and a pulse energy of 1.5 nJ, is displayed in Fig. 1. The Nb atoms are pink and the O atoms are in sky blue. The mushroom shape of the tip, which is unusual, can be explained by employing the corresponding steady-state voltage versus number of ions (depth) analysis profile, Fig. 2. It is easier to field evaporate bulk Nb atoms than the atoms in the surface niobium oxide employing the same experimental conditions since the former is a pure metal and the latter is a metal oxide. Due to the difference in the requisite electric fields for evaporation between the surface oxide and bulk Nb, the voltage drops rapidly to maintain a constant field-evaporation rate (ions pulse⁻¹), when arriving at the niobium

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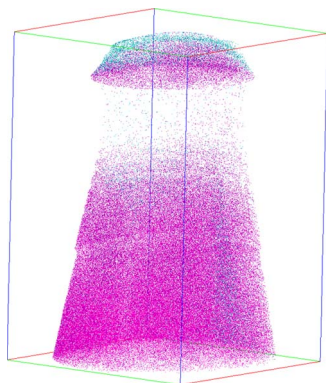


FIG. 1. (Color online) 3D reconstruction of a Nb specimen analyzed by LEAP tomography employing laser pulsing. The rectangular parallelepiped contains 1.5×10^6 atoms in a $62 \times 60 \times 106 \text{ nm}^3$ volume. Niobium atoms are colored in pink and O atoms in sky blue.

oxide/Nb interface and reaching the easily field evaporating bulk Nb. When the voltage decreases in a short time ($\sim 250 \text{ V s}^{-1}$), hydrogen gas atoms inside the chamber are field ionized at a tip's surface since H has the smallest requisite electrical field for field ionization.¹⁶ These H atoms, which are not shown for the sake of clarity, occupy the empty space in Fig. 1.

In the second experiment, the specimen was initially held at 120 K to develop the tip to an end form and then we decreased its temperature to 90 K. A higher electric field is necessary to field evaporate bulk Nb at a lower temperature and this reduces the difference in electric fields for evaporation between the surface niobium oxide and bulk Nb, thereby preventing a voltage drop. Figure 3 displays a 3D reconstruction of a Nb specimen with the second set of parameters. The color coding is the same as in Fig. 1. This figure exhibits clearly the change from an O-rich surface niobium oxide to a Nb-rich bulk metal, along the analysis direction. The combination of 90 K and smaller laser pulse energy ($0.5 \text{ nJ pulse}^{-1}$) avoids the voltage drop at the surface niobium oxide/Nb interface. The use of laser pulsing instead of electrical pulsing does not, however, prevent totally microfractures, indicated by sudden changes in the tip

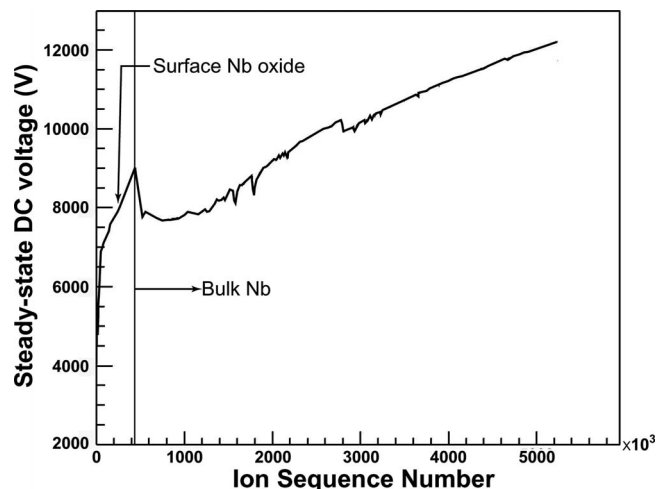


FIG. 2. Steady-state voltage vs number of ions (depth) analysis profile showing a voltage drop at the surface niobium oxide/Nb interface, which explains the mushroom shape of the atomic reconstruction displayed in Fig. 1.

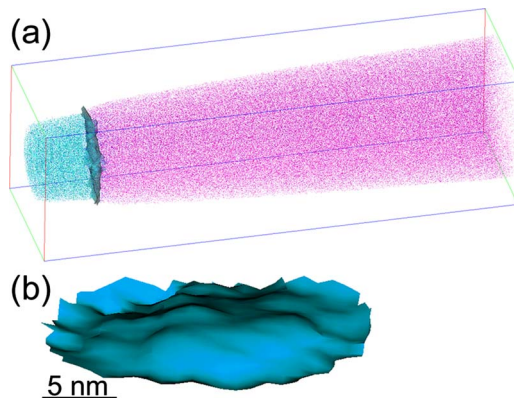


FIG. 3. (Color online) (a) Atomic reconstruction of surface metal oxide layer on bulk Nb. The overall reconstruction dimensions are $33 \times 32 \times 111 \text{ nm}^3$ and the volume contains 2×10^6 million atoms. The surface niobium oxide/Nb interface is identified with a 30 at. % O isoconcentration surface. (b) The surface niobium oxide/Nb interface identified with a 30 at. % O isoconcentration surface. The rms chemical roughness of the interface is 0.4 nm.

radius when the analysis passes through a surface niobium oxide/Nb interface. Nevertheless, the magnitude of microfractures is significantly reduced employing laser pulsing, which is measured by the difference in the radius of curvature between the surface niobium oxide and bulk Nb. The interface between the surface Nb oxide and bulk Nb is identified using an isoconcentration surface with a threshold value of 30 at. % O. The root-mean-square (rms) chemical roughness of this interface is approximately 0.4 nm, Fig. 3(b), which is consistent with the range of values of 0.2–0.4 nm determined by Delheusy *et al.*⁷ Quantitative information from the 3D reconstruction is obtained utilizing the isoconcentration surface to plot a proximity histogram (proxigram for short).¹⁷

The proxigram corresponding to the 3D reconstruction is displayed in Fig. 4. The concentration profile indicates that the thickness of the surface niobium oxide is approximately 15 nm with a constant composition throughout the oxide. Figure 5 displays the O/Nb ratio (ratio of the atomic concentration of oxygen divided by that of niobium) ob-

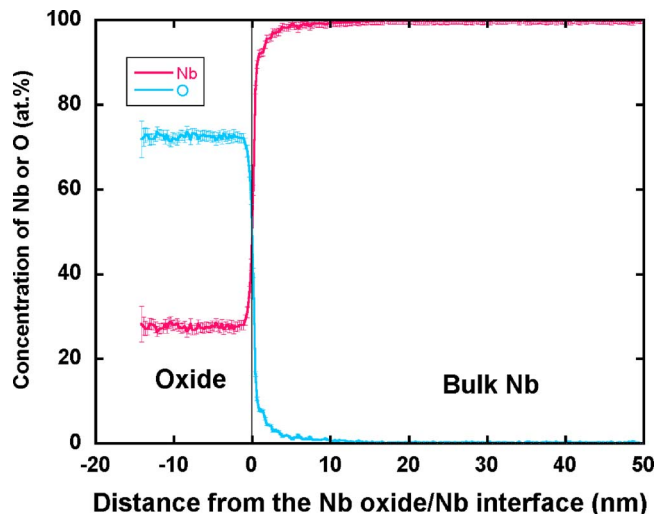


FIG. 4. (Color online) Proxigram showing quantitative Nb and O concentration profiles corresponding to the atomic reconstruction displayed in Fig. 3. The profiles yield a thickness of the surface niobium oxide of 15 nm, with a constant surface Nb oxide composition corresponding to Nb_2O_5 .

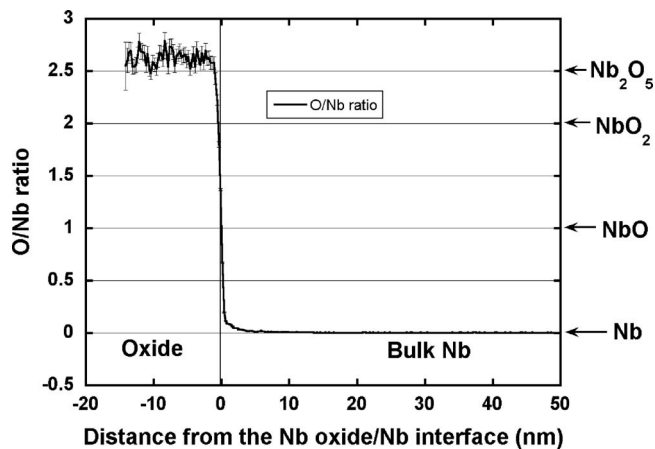


FIG. 5. The O/Nb ratio from the reconstruction of an oxidized Nb specimen plotted as a function of distance from the Nb oxide/Nb interface at zero. The stoichiometry of the surface Nb oxide is deduced from this profile, which indicates that it is close to Nb_2O_5 .

tained from the reconstruction along the analysis direction. This result yields the stoichiometry of the surface niobium oxide, which is close to Nb_2O_5 (electric insulator¹⁸). The O concentration profile, Fig. 4, in bulk Nb decays to essentially zero at approximately 12 nm. By plotting \log_e (concentration of oxygen) versus distance squared, we obtain the value of $1/4D_0t$, where D_0 is the diffusivity of O in Nb and t is time. Since we know our time for electropolishing (20 min), we can calculate D_0 from our data ($1.8 \times 10^{-20} \text{ m}^2 \text{ sec}^{-1}$) and the temperature (325 K). The $D_0(T)$ value at 325 K from Powers' and Doyle's results is $1.69 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$.¹⁹ The two D_0 ($T=325 \text{ K}$) values are consistent, thereby confirming that the observed oxygen decay profile in Nb is the frozen-in concentration profile of interstitially dissolved oxygen. Furthermore, the interstitial oxygen concentration profile in Nb indicates that oxidation of Nb occurs by oxygen diffusion through the oxide to the interface, followed by it dissolving in Nb, where more oxides form and not by diffusion of Nb through niobium oxide to the oxygen/niobium oxide interface. The concentration of interstitially dissolved oxygen in bulk Nb is calculated to be 2.97 at. %.

In summary, we have investigated the surface niobium oxide on Nb for SRF cavities, employing LEAP tomography with picosecond laser (green light) pulsing system. We find that picosecond laser pulsing yields a smoother evaporation of the niobium oxide and niobium oxide/niobium interface

when compared to electrical pulsing. The thickness of the surface Nb oxide is measured to be 15 nm for the preparation conditions employed, with a stoichiometry close to Nb_2O_5 and a rms chemical roughness of the interface that is approximately 0.4 nm, Fig.3(b). Oxidation of Nb occurs by oxygen diffusion through the forming niobium oxide layer where bulk Nb is continuously oxidized.

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