

ATOM-PROBE TOMOGRAPHY ANALYSES OF NIOBIUM SUPERCONDUCTING RF CAVITY MATERIALS

J. T. Sebastian, D. N. Seidman, K. E. Yoon[#], Materials Science and Engineering Department, Northwestern University, Evanston, IL 60208-3108, U.S.A.

P. Bauer, T. Reid, C. Boffo, Fermi National Accelerator Laboratory, Batavia, IL, 60510, U.S.A.
J. Norem, Argonne National Laboratory, Argonne, IL, 60439, U.S.A.

Abstract

We present the first atom-probe tomographic (APT) measurements of niobium superconducting RF (SCRf) cavity materials. APT involves the atom-by-atom dissection of sharply pointed niobium tips, along with their niobium oxide coatings, via the application of a high-pulsed electric field and the measurement of each ion's mass-to-charge state ratio (m/n) with time-of-flight (TOF) mass spectrometry. The resulting atomic reconstructions, typically containing at least 10^5 atoms and with typical dimensions of 10^5 nm^3 (or less), show the detailed, nano-scale chemistry of the niobium oxide coatings, and of the underlying high-purity niobium metal. Our initial results show a nano-chemically smooth transition through the oxide layer from near-stoichiometric Nb_2O_5 at the surface to near-stoichiometric Nb_2O as the underlying metal is approached (after $\sim 10 \text{ nm}$ of surface oxide). The underlying metal, in the near-oxide region, contains a significant amount of interstitially dissolved oxygen ($\sim 5\text{-}10 \text{ at.}\%$), as well as a considerable amount of dissolved hydrogen. The experimental results are interpreted in light of current models of oxide and sub-oxide formation in the Nb-O system.

INTRODUCTION

The Nb-O System

The Nb-O system is a complicated system from a materials science point-of-view [1, 2]. Depending on processing conditions (temperature, oxygen concentration or partial pressure), three different equilibrium oxide phases, NbO, NbO_2 , and Nb_2O_5 , can form, see Figure 1 [3], with a number of separate, non-equilibrium phases (e.g., Nb_2O , Nb_2O_3) also reported.

The "simplified" models of niobium RF cavity surfaces typically ignore the complex materials science issues concerning the Nb-O system. In such models, single crystal niobium is assumed to be in contact with Nb_2O_5 , thereby ignoring the fine structure oxide layer(s) that may form on the surface of "real" niobium. These oxide layers, with thicknesses of 10 nm or less, can contribute significantly to the surface resistance, and hence the superconducting behavior, of niobium cavities, and thus it is essential that their chemistry, phase composition, and structure be understood from an atomic-level perspective.

* Supported in part by the USDOE and NSF
megabass@northwestern.edu

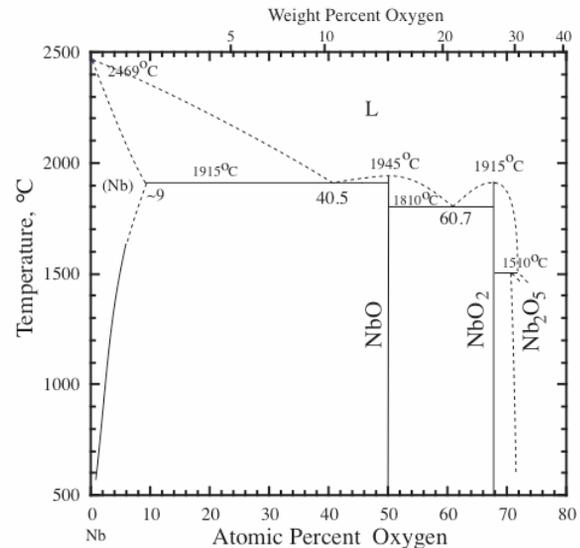


Figure 1. Equilibrium phase diagram of Nb-O system, displaying three different stable oxide phases, NbO, NbO_2 , and Nb_2O_5 [3].

Atom-Probe Tomography

The materials science technique of atom-probe tomography (APT), though relatively new, is a direct descendent of the techniques of field-ion microscopy (FIM) and atom-probe microscopy (APM). The latter two techniques were invented by the late Professor Erwin W. Müller [4-6], with FIM being the first universally acknowledged technique capable of seeing individual atoms on a material's surface. See Figure 2 for a schematic description of an APT.

APT (as well as FIM and APM) relies upon the principle of an enhanced electric field at the surface of a sharply pointed tip held at high positive voltage:

$$E = \frac{V}{kr},$$

where E is the electric field, V is the applied dc voltage, r is the average tip radius, and k is a geometric form factor. For both sufficiently large applied voltages and sharp tips, the electric field at a tip's surface can reach levels on the order of several GV m^{-1} (for example, an applied voltage of 10 kV , an average tip radius of 100 nm , and a form factor of 5, a typical value, yields an electric field of 20 GV m^{-1}). With electric fields this high, atoms on the surface of the tip may be field-evaporated (sublimation with the aid of an electric field), whereby they lose one (or more) of their outermost electrons, become ionized,

and are accelerated away from the tip's surface along trajectories normal to the equipotentials.

After being field evaporated, the TOF of each field-evaporated ion is recorded utilizing a position-sensitive detector. By combining the TOF and positional information from all the atoms in an analyzed volume, using sophisticated data analysis software, a three-dimensional, atom-by-atom reconstruction of a small volume of a material can be obtained. APT reconstructions are determined in real space (the impact positions of the individual atoms themselves are recorded), without recourse to standards and with minimal data deconvolution, and thus represents the ultimate in nanoscale materials science chemical analysis. Therefore, it is ideally suited for atomic-level studies of the surfaces of niobium RF cavities.

The local-electrode atom-probe (LEAP) tomograph [7, 8] recently acquired by Northwestern University, represents the state-of-the-art in APT instruments. With typical analysis volumes of at least 50 nm x 50 nm x 200 nm (500,000 nm³) and data collection rates up to 72 million ions hour⁻¹, an analysis which just two years ago took many, many days now takes on the order of hours.

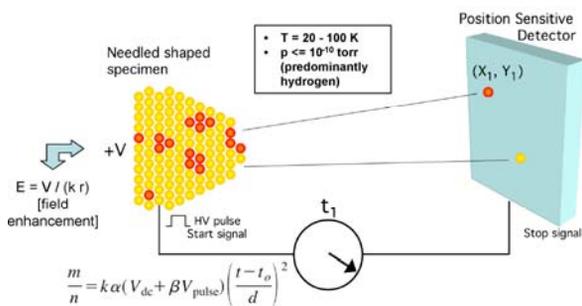


Figure 2: Schematic diagram showing the principle of atom-probe tomography (APT). The equation relating an ion's mass-to-charge state ratio (m/n) to its total time-of-flight (t) is included in the lower left of the figure; t_0 is the delay time in the electronics, and α and β are constants that can be determined from a simple calibration procedure.

Our goal is to investigate the atomic scale chemical composition of the surface and bulk of Nb cavities, and understand the relationship between the elemental distribution and the performance of the cavities. In addition, we will study the change of chemical composition in surface and grain boundaries after various heat treatments.

EXPERIMENTAL PROCEDURE

Specimen Preparation

Niobium RF cavity material (3 mm sheet, RRR 450, polycrystalline) was cut into small, rectangular specimen blanks (0.5 mm x 0.5 mm x 10 mm) at Fermilab (FNAL) using electrical discharge machining (EDM). Blanks were then polished into sharp tips via Electropolishing (EP).

For EP specimens, a solution of 10% HF (49% initial concentration) in 90% HNO₃ (68% initial concentration) was used. A polishing setup that employed a stereomicroscope and a rectangular cuvette (to hold the polishing solution) permitted for close observation of the tip during polishing. DC voltages of ~10-40 V were employed. The “drop off” technique of atom-probe tip preparation was employed [9].

For the specimen preparation techniques, the goal was to create a sharp tip with an end radius of <100 nm, which is needed for the establishment of a large electric field at the surface of the tip with the application of a “modest” high voltage (~10 kV). After a sharp tip was obtained, the specimens were rinsed with high-purity deionized water and stored in a desiccator before introduction into the Northwestern University LEAP tomograph. Figure 3 shows a picture of a typical niobium tip.

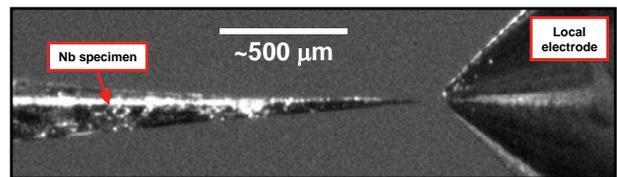


Figure 3: Typical niobium tip in the Northwestern LEAP tomograph. The tip end radius is ~100 nm.

APT Analyses

For the analyses of niobium cavity materials, the typical background pressure in the LEAP tomograph was <= 10⁻¹⁰ torr (predominantly hydrogen). A specimen temperature of 50 K was used, along with a high voltage pulse fraction (ratio of evaporation pulse voltage to steady-state dc voltage) of 15%. The specimen-to-detector flight path distance was 128 mm, allowing for maximum mass resolution in the LEAP.

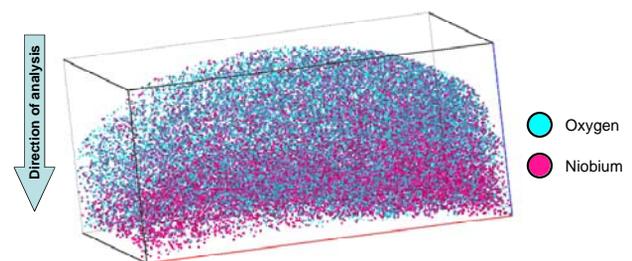


Figure 4: Atomic reconstruction of the oxide layer on the surface of a niobium RF cavity material sharp tip. The overall reconstruction dimensions are 23 nm x 21 nm x 11 nm; the volume contains ~112,000 atoms.

RESULTS AND DISCUSSION

The mass spectra associated with the APT analyses of (oxidized) niobium RF cavity materials show a number of characteristics particular to the field evaporation of oxides. Specifically, in addition to the peaks associated with niobium metal, a number of peaks associated with the field evaporation of the oxide – O⁺, NbO³⁺, NbO²⁺, NbO₂³⁺, NbO¹⁺, and NbO₂¹⁺ – also are typically observed.

Special attention must be paid to these latter “complex ions” – though they result from the detection of a single ion in the APT, they must be represented by the software as several individual and distinct atoms (e.g., one Nb atom and two O atoms in the case of NbO_2^{1+}) in the three-dimensional atomic reconstructions.

Figure 4 shows an atomic reconstruction of the oxide layer on the surface of a niobium RF cavity material sharp tip. Qualitatively, we see a clear transition from oxygen to niobium as we move along the analysis direction. To obtain a quantitative representation of this transition, we employ the proxigram technique [10]. Use of the proxigram technique allows for the determination of a quantitative, one-dimensional composition profile relative to the position of any topologically complex interface. In the case of Figure 4, the irregularly-shaped “interface” is taken as a surface of constant niobium concentration (a niobium “isoconcentration surface”).

The resulting profile, re-normalized to only display niobium and oxygen concentrations, is shown in Figure 5. We see a clear, smooth transition from near-stoichiometric Nb_2O_5 to near-stoichiometric $\text{NbO}_{0.5}$ ($= \text{Nb}_2\text{O}$). The transition is continuous, with no evidence for extended “layers” of a sub-oxide within the overall composition profile (e.g., of an NbO oxide “interlayer” between Nb_2O_5 and $\text{NbO}_{0.5}$).

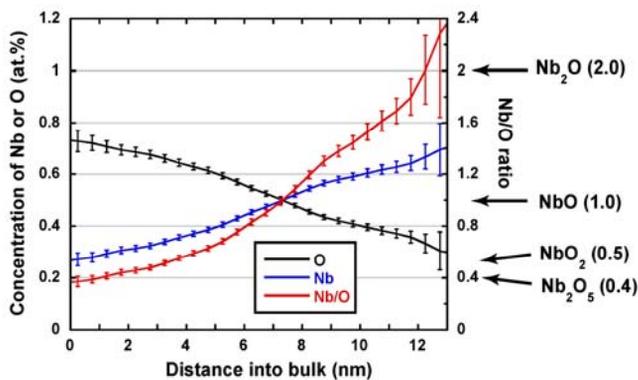


Figure 5: Proxigram analysis showing the quantitative concentration profiles corresponding to the atomic reconstruction shown in Figure 4. The profiles have been re-normalized to only include Nb and O concentrations.

Re-normalization of the concentration profile to include only niobium and oxygen concentrations is required due to the presence of a number of additional peaks in the mass spectrum of the analysis. In particular, APT tomographic analyses of niobium cavity materials typically exhibit a large hydrogen peak (hydrogen is the dominant impurity gas in stainless steel UHV chambers), peaks related to residual nitrogen in the APT chamber, and some small peaks related to fluorine atoms (HF is used during the tip preparation process). For example, raw analyses of the APT data show a concentration of hydrogen in the near-surface region of the reconstruction shown in Figure 4 of nearly 30 at.%, decreasing to ~10 at.% after a distance of ~13 nm into the bulk. Though a

fraction of this detected hydrogen is, no doubt, dissolved hydrogen in the cavity material, much of it is probably related to residual hydrogen in the APT chamber that becomes ionized in the high-field region of the specimen tip. As a result, in the absence of detailed investigations of the “dissolved hydrogen vs. residual gas hydrogen” issue, and of the issues associated with other residual atoms, concentration profiles such as that shown in Figure 5 have been re-normalized to only display niobium and oxygen concentrations.

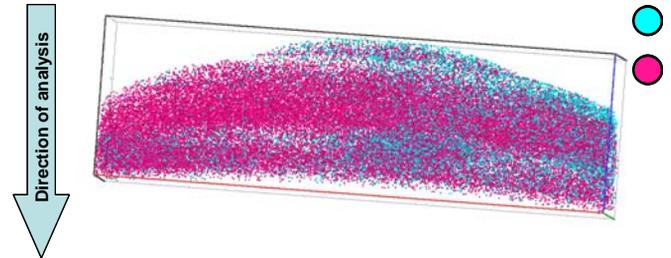


Figure 6: Atomic reconstruction of the oxide layer on the surface of a niobium RF cavity material sharp tip. The overall reconstruction dimensions are 25 nm x 25 nm x 6 nm (3750 nm^3); the volume contains ~75,000 atoms.

Figure 6 displays another atomic reconstruction of the oxide layer on the surface of a niobium RF cavity material tip. Using the same proxigram technique, the re-normalized profile exhibits the transition of niobium and oxygen concentration along the direction of analysis in Figure 7. Unlike the gradual increase of the Nb/O ratio in Figure 4, the Nb/O ratio in this figure increases rapidly after 5 nm below the surface. This may be an indication that the analysis is going through bulk metallic niobium. In addition, the oxygen profile shows that the dissolved oxygen in bulk Nb is approximately 5 to 10 at.% depending on the distance from the surface.

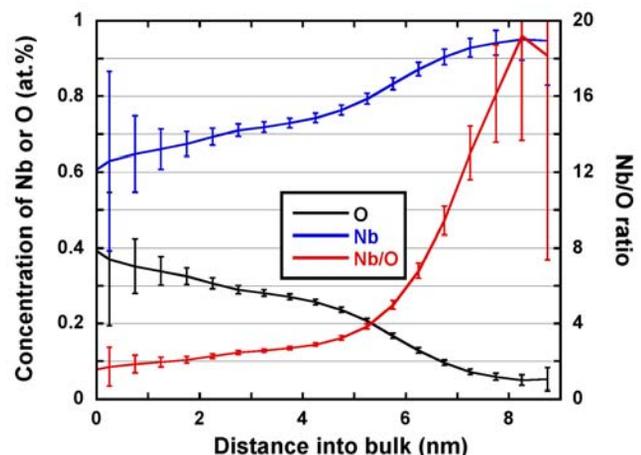


Figure 7: Re-normalized proxigram showing the quantitative concentration profiles corresponding to the atomic reconstruction shown in Figure 6. The transition from oxide to metal is marked by a rapid increase in the ratio of Nb and O concentrations.

Atom probe tomography has extremely good analytical sensitivity, statistics and spatial resolution. The field is developing rapidly as the capabilities of the LEAP tomograph are fully exploited, with a variety of new ways of sample preparation, and even fundamental changes in atomic ionization (laser induced ionization). It promises significant improvements in understanding the surface of rf superconductors. The overall goal of these investigations are: (1) to improve the understanding of the chemical composition of the surface of state of the art high purity niobium for SRF cavities, (2) to improve the understanding of the chemical composition of the grain boundaries in state of the art high purity niobium for SRF cavities, (3) to correlate surface and grain-boundary chemical composition with the various macro-treatment steps used to prepare cavities for RF performance of SRF cavities, such as for instance the low temperature, in situ bake-out, which was recently shown to significantly increase cavity performance by removing Q-drop, and (4) understanding the interactions between high electric fields and materials (electron field emission, field evaporation of ions, surface stability, field induced stresses, fracture, etc.).

Although the capabilities of the APT technique are great, surface analysis using this method is, however, somewhat new, and may require some optimization directed at sample preparation and understanding. The needs of the superconducting rf community are, in principle, quite specific, however complete understanding of the all aspects of the surface chemistry, metallurgy and structure is difficult and may take time.

CONCLUSIONS

Nanochemical, atomic scale analyses of the oxide surface and of the near-surface bulk niobium are being performed employing LEAP tomography.

- A “smooth” transition from surface Nb₂O₅ to Nb₂O (and into the bulk Nb) has been observed.
- The results exhibit the ability of LEAP tomography to detect a small number of contaminant atoms in the oxide surface and in the near-surface bulk niobium.
- The levels of interstitially dissolved oxygen in the near-surface bulk niobium (metal) of 5-10 at.%.

ACKNOWLEDGEMENTS

This research was sponsored by Fermi National Accelerator Laboratory and Argonne National Laboratory. Atom-probe measurements were performed at the Northwestern University Center for Atom Probe Tomography (NUCAPT) and the LEAP microscope was purchased with funding from the NSF-MRI (DMR 0420532) and ONR-DURIP (N00014-0400798) programs.

REFERENCES

- [1] Halbritter J, Kneisel P, Palmieri V, Pekeler M. IEEE Trans. Appl. Supercond, 11, 1864 , (2001).
- [2] Ma Q, Rosenberg RA. Appl. Surf. Sci., 206, 209, (2003).
- [3] Massalski TB, Okamoto H, Subramanian PR. Binary alloy phase diagrams, ASM International, Materials Park, Ohio, (1990).
- [4] Muller EW. Advances in electronics and electron physics, 13, 83, (1960).
- [5] Muller EW. Science, 149, 591 (1965).
- [6] Muller EW, Panitz JA, McLane SB. Review of Scientific Instruments, 39, 83, (1968).
- [7] Kelly TF, Camus PP, Larson DJ, Holzman LM, Bajikar SS. Ultramicroscopy, 62, 29, (1996).
- [8] Kelly TF, Gribb TT, Olson JD, Martens RL, Shepard JD, Wiener SA, Kunicki TC, Ulfing RM, Lenz DR, Strennen EM, Oltman E, Bunton JH, Strait DR. Microscopy and Microanalysis, 10, 373 (2004).
- [9] Krakauer BW, Hu JG, Kuo SM, Mallick RL, Seki A, Seidman DN, Baker JP, Loyd RJ. Review of Scientific Instruments, 61, 3390 (1990).
- [10] Hellman OC, Vandenbroucke JA, Rusing J, Isheim D, Seidman DN. Microsc. Microanal, 6, 437 (2000).