PROGRESS REPORT 04/16/2007

Local-electrode Atom Probe Tomography on Niobium for SRF Cavities

Personnel and Institutions requesting funding

David N. Seidman, Principal Investigator
Department of Materials Science and Engineering, Northwestern University
Northwestern University Center for Atom-Probe Tomography

Collaborators

Claire Antoine, Chris Boffo, Fermi National Accelerator Laboratory
James Norem, Argonne National Laboratory

Project Leaders

David N. Seidman, Professor of Materials Science and Engineering
d-seidman@northwestern.edu
http://nucapt.northwestern.edu
(847) 491-4391

Kevin E. Yoon, Ph.D.
megabass@northwestern.edu
(847) 491-5883

Project Overview

The 3-D atom-probe tomography (APT) technique [1-3] we utilize is the first to reveal the surface chemistry of niobium for SRF cavities at the most microscopic level possible, namely on an atom-by-atom basis [4]. It is emphasized strongly that the superior spatial resolution and analytical sensitivity of the 3-D APT makes it possible to investigate how macro-processes, such as chemical polishing, heat-treating, welding, exposure to gases, etc., affect the microstructure in the near surface region. It is the tool of choice to study the Q-drop recovery after the baking of niobium SRF cavities [5, 6], which is suspected to be correlated with oxygen diffusion in the first 40 nm of the material.

3-D Atom Probe Tomography at the Northwestern University Center for Atom-Probe Tomography (NUCAPT) with picosecond laser pulsing system

In late April 2006, we acquired a laser-enhanced upgrade for the existing 3-D local-electrode atom-probe (LEAP™) tomograph, with funds provided by an Office of Naval Research DURIP grant, and it has been operational since early May 2006. Fig. 1 shows a picosecond laser pulse (red wave incident from the left-hand side), *in place* of electrical pulses, being used to field-evaporate single ions in a laser-enhanced LEAP™ tomograph (left-hand side); the wave length of the laser light is in the green. The right-

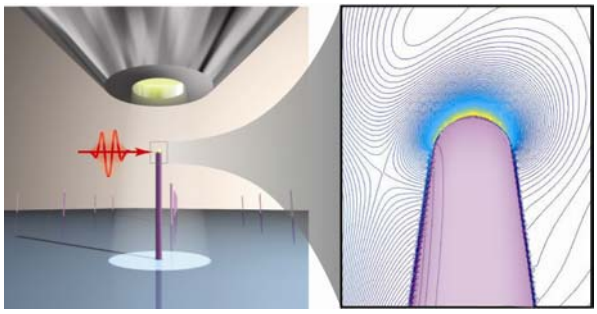

Fig. 1. A pulsed-laser enhanced 3-D *LEAP* tomograph involves replacing electric pulses with picosecond laser pulses, indicated by incident red wave in left-hand figure. Simulation of the electric field (**E**) at a tip caused by the **E**-field of the laser pulse, see right-hand figure. (Prof. Tamar Seideman, Northwestern University)

hand side of Fig. 1 is a simulation of the local **E**-field at a tip due to the **E**-field component of a picosecond laser pulse, with the **E**-field aligned parallel to the long axis of the tip. The exact role played by this **E**-field in the evaporation process is still a matter of scientific debate.
We have found, however, that laser pulsing permits us to obtain significantly larger data sets than electrical pulsing, most likely because the volume being analyzed is not subjected to the elastic Maxwell stresses associated with the electrical pulses; these Maxwell stresses are approximately equal to the values of the elastic constants (GPa) for the material being analyzed and ultimately cause specimens to fail catastrophically. As of April 1, 2007 the NUCAPT record is ca. 300 million properly ranged detected atoms from a single steel specimen, which corresponds to a volume of ca. 3 x 10^7 nm^3.

Progress Report

(1) Employing new sample preparation techniques.

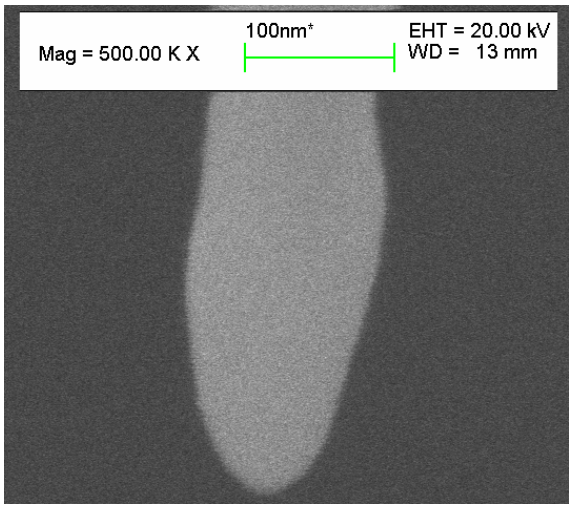

Fig 2.SEM micrograph of a niobium tip, with a radius of curvature less than 100 nm

We are now using Nb wires to create sharp tips for the LEAP™ tomographic experiments, instead of Nb blanks. It has been a great challenge to cut square blanks from the Nb sheets. When we electropolished rectangular blanks, we ended up with a wedged shape tip. This resulted in unsuccessful experiments. By using Nb wires, we are able to produce symmetrical and conical tips; Fig. 2 displays a SEM micrograph of a tip.
Additionally, the oxide thicknesses measured were quite variable. We think that the thickness is highly dependent on the electropolishing technique, at which voltage we end the polishing, how fast we take out the tips from the electrolyte, etc. We are now cleaning the tips with HF after the electropolishing, to obtain a constant oxide thickness.

(2) 3-D APT results for before and after a heat treatment

An atomic reconstruction of the oxide layer on the surface of a niobium RF cavity material is displayed in Fig. 3. Qualitatively, we see a clear transition from an oxygen-rich surface oxide to the niobium-rich bulk as we march along the analysis direction, which we denote the z-direction. To obtain a quantitative representation of this transition, we employ the proximity histogram (proxigram) technique [7]. This analysis technique integrates the chemical and three-dimensional positional information and then generates a histogram of the atomic fractions of all alloying elements versus distance to an interface. This is accomplished for all the interfaces in a specimen in parallel, delineated by an isoconcentration surface. Furthermore, it does not require choosing an arbitrary axis or geometric subvolume. In this study, an isoconcentration surface with a threshold value of 30 at.%

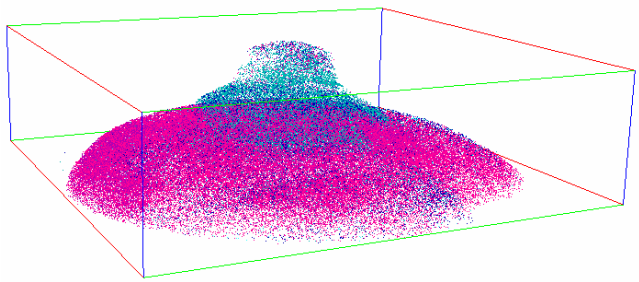

Fig. 3. 3-D atomic reconstruction of an oxide layer on the surface of a niobium tip. The overall reconstruction dimensions are 53 nm x 53 nm x 14 nm; this volume contains approximately 300,000 atoms. Niobium atoms are in magenta and oxygen atoms are in cyan.

oxygen is used to define the location of the oxide/metal interface.

The resulting profile is displayed in Fig. 4. Contrary to previous observations [4], which display a continuous transition from near-stoichiometric Nb_2O_5 to near-stoichiometric Nb_2O, we do not observe a sharp transition in the oxide layer. Our newest result indicates that the composition of the surface oxide layer is almost constant with a thickness of 10 nm. Fig. 5 displays the O/Nb ratio (ratio of the atomic concentration of oxygen divided by that of niobium) of the 3D reconstruction along the analysis direction. From this result, we investigate the stoichiometry of the oxide and this indicates that the oxide may be a mixture of NbO and NbO_2. This type of microstructural characterization should, however, also be performed employing transmission electron microscopy (TEM), since the positioned atoms in a 3D reconstruction of APT results are not on an absolutely perfectly rigid-lattice structure.

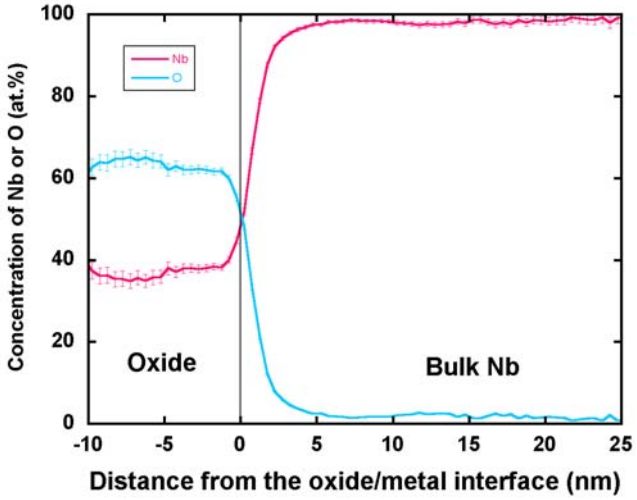

Fig. 4. Proxigram showing the quantitative concentration profiles corresponding to the atomic reconstruction displayed in Figure 3. The profiles are re-normalized to include only the Nb and O concentrations. The profiles show that the composition of surface oxide is almost a constant with a thickness of 10 nm.

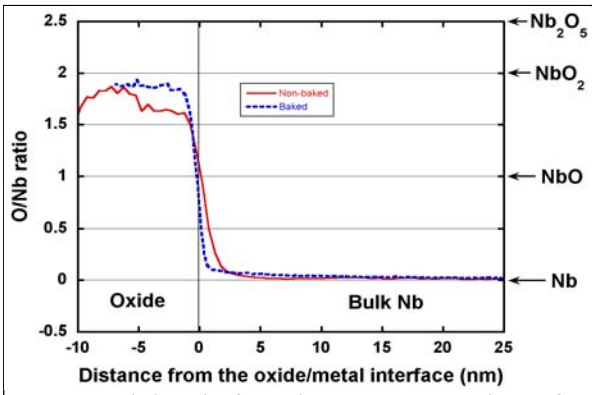

Fig. 5. O/Nb ratio from the 3D reconstructions of unbaked and baked niobium tips. The stoichiometry of the oxide is deduced from the profile. The profile clearly demonstrates that the thickness of the oxide decreases after baking. The chemistry of the oxide, however, does not change.

Renormalization 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 an analysis. Specifically, APT tomographic analyses of niobium cavity materials typically exhibit a large hydrogen concentration, up to 40 at.% (hydrogen is the dominant impurity gas in a baked stainless steel UHV chamber). Though a fraction of this detected hydrogen is, no doubt, dissolved hydrogen in the cavity material, much of it is related to residual hydrogen in the APT chamber that becomes ionized in the high-field region at the tip of a specimen. The concentration of hydrogen is higher in our experiments compared to a previous experiment [4], since our experiments were performed at 100 K, which is a high specimen temperature for APT experiments; this temperature permits the surface diffusion of hydrogen from the shank of the tip to the apex of tip region. As a result, in the absence of a detailed investigation of the "dissolved hydrogen vs. residual gas hydrogen" issue, and of issues associated with other residual species, concentration profiles such as those shown in Fig. 4 have been renormalized to display only niobium and oxygen concentrations.

Fig. 6 displays an atomic reconstruction of the oxide layer on the surface of a niobium RF cavity material tip after baking the tip at 120 °C for two days in air. Qualitatively, the thickness of the surface oxide seems to be thinner than that of an unbaked niobium tip. Once the dissection process passes through a oxide/metal interface, it exhibits smoother field-evaporation behavior since mainly niobium

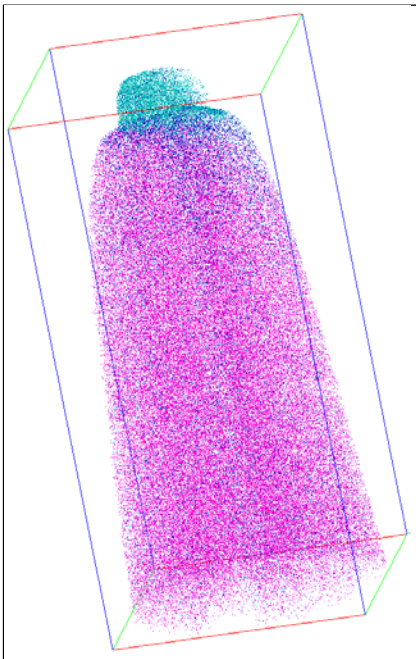

Fig. 6. Atomic reconstruction of a baked niobium tip with an oxide layer on the surface. The overall reconstruction dimensions are 37 nm x 38 nm x 79 nm; this volume contains approximately 1.6 million atoms. Niobium atoms are in magenta, and oxygen atoms are in cyan.

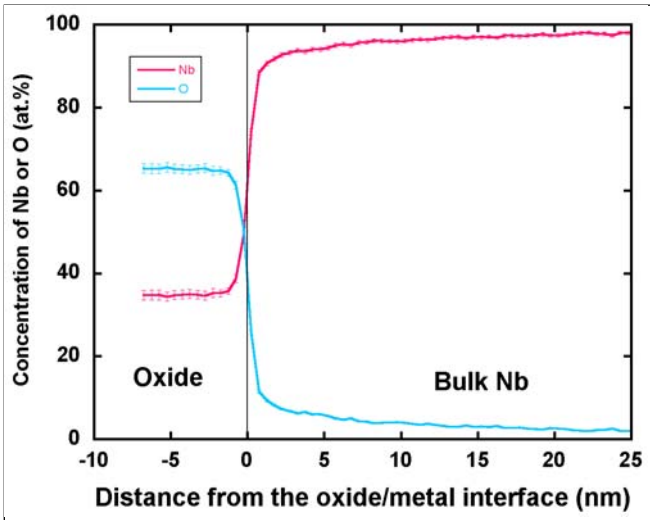

Fig. 7. Proxigram showing quantitative concentration profiles corresponding to the atomic reconstruction shown in Figure 6. The profiles have been renormalized to include only Nb and O concentrations. The profile shows that the composition of the surface oxide is almost a constant, with a decreased thickness of 5 nm, after the baking.

atoms, which are, of course, metallic, field evaporate from the tip. Using the same proxigram technique, the renormalized profile exhibits the transition of niobium and oxygen concentrations along the direction of analysis, Fig. 7. The O/Nb ratio from the 3D reconstruction of the baked niobium tip is superimposed on Fig. 5. This profile indicates that the thickness of the surface oxide is decreased from 10 nm to 5 nm after baking of a niobium tip. Additionally, the concentration of oxygen below the oxide/metal interface is smaller after the baking. The chemistry of the oxide, however, remains the same after the baking, Fig 5, with the same O/Nb ratio before and after the baking procedure.

3) Laser pulsing system with a picosecond laser

Laser pulsing produces mass spectra with better mass resolution than with an electrical pulser because the spread of momenta of the evaporated ions (atoms) is smaller. Additionally, it is less sensitive to the shape of a tip, so it is possible to collect larger data sets with a relatively blunt tip.
The following is the first result of the analysis of a niobium tip using a laser-assisted LEAP™ tomograph. Figure 8 displays an atomic reconstruction of an oxide layer on the surface of a niobium RF cavity specimen, which contains 0.5 x 10^6 atoms. Since we are able to evaporate niobium tips at lower standing dc voltages employing the laser-assisted LEAP™ tomograph, the size of a reconstruction in the x-y plane is smaller than the ones obtained when using voltage pulses..

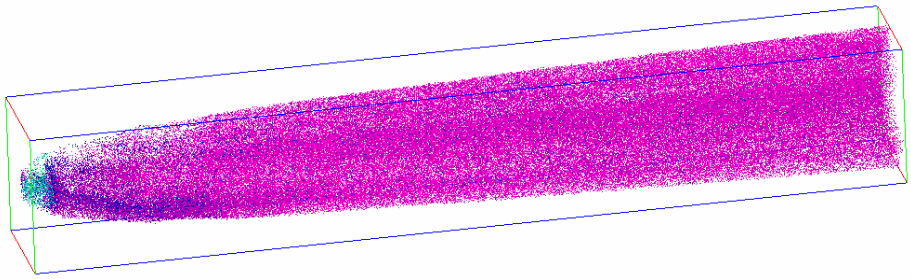

Fig 8. 3-D atomic reconstruction of the oxide layer on the surface of a niobium tip, employing laser pulsing system. The overall reconstruction dimensions are 18 nm x 19 nm x 116 nm; this volume contains approximately 500,000 atoms. Niobium atoms are in magenta and oxygen atoms are in cyan.

Publications During Year 2

J. Norem, P. Bauer, J. Sebastian, D. N. Seidman, "Atom Probe Tomography studies of Radio Frequency Materials," Particle Accelerator Conference, PAC 2005, Knoxville Tennessee, Proceedings of PAC05, in press, 2007.

J. Norem, A. Hassanein, Z. Insepov, A. Moretti, Z. Qian, A. Bross, Y. Torun, R. Rimmer, D. Li, M. Zisman, D. N. Seidman, K. E. Yoon, "The Interactions of Surface Damage and RF Cavity Operation," to appear in European Accelerator Physics Conference, June 24, 2006.

J. T. Sebastian, D. N. Seidman, K. E. Yoon, P. Bauer, T. Reid, C. Boffo, and J. Norem, "Atom-Probe Tomography Analyses of Niobium Superconducting RF Cavity Materials," *Physica C* **441**, 70-74 (2006).

A. Hassanein, Z. Insepov, J. Norem, A. Moretti, Z. Qian, A. Bross, Y. Torun, R. Rimmer, D. Li, M. Zisman, D. N. Seidman, and K. E. Yoon, "The Effects of Surface Damage in RF Breakdown," *Physical Review Special Topics - Accelerators and Beams* **9**, 062001-1 to 062001-16 (2006).

" Atomic-Scale Chemical-Analyses of Niobium for Superconducting Radio-Frequency Cavities ", K.E. Yoon, D.N. Seidman, P. Bauer, C. Boffo, C. Antoine, poster presented at the Applied Superconductivity Conference (ASC 2006), Seattle, WA, USA - will be published in the journal, IEEE Transactions on Applied Superconductivity.

Final Year Project Activities and Deliverables

We start investigating the heat-treated niobium materials employing voltage pulsing system, to study how the elements in the materials, especially oxygen and hydrogen, redistribute after the heat treatment and baking. We will utilize the laser pulsing system to collect larger data sets to increase statistical significance. These results will clarify the effect of chemistry and microstructure on the performance of the cavity.

We are planning to perform a series of 3-D APT studies on different samples, including specimen surfaces processed as cavities, but to different degrees of completeness. This allows the investigation of the effect of the various processing steps, such as etching and baking, on surface chemistry. Also for each preparation condition, there should be samples representative of two different cavity areas, the weld and non-weld areas and the two main polishing techniques: buffered chemical polishing (BCP) and electropolishing (EP).

References

[1] T. F. Kelly, T. T. Gribb, J. D. Olson, R. L. Martens, J. D. Shepard, S. A. Wiener, T. C. Kunicki, R. M. Ulfig, D. R. Lenz, E. M. Strennen, E. Oltman, J. H. Bunton, and D. R. Strait, "First data from a commercial local electrode atom probe (LEAP)," *Microscopy and Microanalysis*, vol. 10, pp. 373-383, 2004.

[2] A. Cerezo, T. J. Godfrey, S. J. Sijbrandij, G. D. W. Smith, and P. J. Warren, "Performance of an energy-compensated three-dimensional atom probe," *Review of Scientific Instruments*, vol. 69, pp. 49-58, 1998.

[3] D. Blavette, B. Deconihout, S. Chambreland, and A. Bostel, "Three-dimensional imaging of chemical order with the tomographic atom-probe," *Ultramicroscopy*, vol. 70, pp. 115-124, 1998.

[4] J. T. Sebastian, D. N. Seidman, K. E. Yoon, P. Bauer, T. Reid, C. Boffo, and J. Norem, "Atom-probe tomography analyses of niobium superconducting RF cavity materials," *Physica C-Superconductivity and Its Applications*, vol. 441, pp. 70-74, 2006.

[5] G. Ciovati, "Effect of low-temperature baking on the radio-frequency properties of niobium superconducting cavities for particle accelerators," *Journal of Applied Physics*, vol. 96, pp. 1591-1600, 2004.

[6] J. Halbritter, P. Kneisel, V. Palmieri, and M. Pekeler, "Electric surface resistance R-E(T, f, E-perpendicular to) of Nb/Nb2O5-y-interfaces and Q-drop of superconducting Nb cavities," *Ieee Transactions on Applied Superconductivity*, vol. 11, pp. 1864-1868, 2001.

[7] O. C. Hellman, J. A. Vandenbroucke, J. Rusing, D. Isheim, and D. N. Seidman, "Analysis of Three-Dimensional Atom-Probe Data by the Proximity Histogram," *Microscopy and Microanalysis*, vol. 6, pp. 437-444, 2000.