

PROGRESS REPORT 01/06/2006

3D Atom Probe Microscopy on Niobium for SRF Cavities

Personnel and Institutions requesting funding

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Project Overview

Introduction

Fermi National Accelerator Laboratory (FNAL) is developing superconducting RF cavities for a future high-energy electron-positron linear collider as the next international, large-scale high energy physics discovery machine. Recently FNAL and the Northwestern University Center for Atom-Probe Tomography (NUCAPT), Evanston, Illinois, have joined forces to investigate the properties of the high purity niobium used for cavity fabrication. NUCAPT is among the world leaders in the field of three-dimensional atom-probe tomography, particularly as result of the recent installation of a local-electrode atom-probe (LEAP) tomograph, manufactured by Imago Scientific Instruments (<http://www.imago.com>). Atomic-probe tomography consists of dissecting a specimen on an atom-by-atom basis, employing pulsed field-evaporation, and determining the chemical identity of each field-evaporated atom by time-of-flight mass spectrometry, with single atom identification capability, using a 2D position sensitive delay line detector, which yields the position of each atom in a specimen with sub-nanoscale resolution. Analysis rates of upwards of 72 million atoms hr^{-1} have been achieved employing a LEAP tomograph at Northwestern. The collected data is used to reconstruct a specimen in three-dimensions, where the chemical identity of each atom is known. The collaboration between FNAL and NUCAPT will produce spectacular results with lasting impact and advance strongly the understanding of the surface chemistry in state-of-the-art high purity niobium for superconducting RF cavities.

Motivation

The study of the surface chemistry of high purity niobium is extremely important for the advancement of the understanding of performance limitations of this material in the high gradient superconducting RF cavities for a future linear collider. During RF operation the high power RF fields penetrate only approximately 50 nm into the surface of the cavity. The interaction of RF photons with the complex electronic system in the surface of the superconductor produces the so-called BCS resistance loss,

heating and ultimately thermal quenching. In niobium this surface resistance contribution is well understood for the “ideal” surface. It is less well understood in the case of “realistic” surfaces. It is known, however, that the presence of metallic oxides and hydrides (e.g. in grain-boundaries) strongly affect the BCS surface resistance because of a weakened superconducting state (reduced gap energy). The BCS resistance measured in state of the art bulk niobium cavities is consistent with a gap energy that is smaller than in the ideal case. This measurement, however, averages over the entire RF penetration layer and thus presumably includes ideal behavior at greater depths and strongly suppressed behavior in the first 10-20 nm of the material. The weakening of the superconducting state also reduces the shielding of magnetic flux associated with the RF electromagnetic fields. It is currently believed that the penetration of only a few magnetic flux quanta will lead to a break-down of the superconducting state as a result of local heating due to the oscillation of the flux lines in the RF fields. Therefore, the assessment of the surface chemistry at the microscopic level is paramount for a better understanding of the surface resistance and magnetic flux penetration into a “real” niobium surface as in high performance RF cavities.

Previously the analysis of the surface chemistry was obtained mostly through x-ray spectroscopy or electron spectroscopy. This research has already yielded a good understanding of the issues at hand. It became clear, for instance, that below the insulating (and therefore inert) penta-oxide layer, a mix of Nb-O compounds with varying stoichiometries exist, which are usually referred to as sub-oxides. The role of these sub-oxides is not completely understood yet, but their mere presence can be a source of gap suppression and flux penetration. The XPS studies were not capable, however, to resolve the surface chemistry layer-by-layer (although new proposals exist to do just that), nor could they clearly resolve the chemistry of grain-boundaries. The atom-probe tomography technique we use is the first to reveal the surface and grain boundary chemistry in state-of-the-art niobium for SRF cavities at the most microscopic level possible, namely atom-by-atom. It needs to be stressed as well that the superior spatial resolution and analytical sensitivity of the atomic probe tomograph makes it possible to investigate how macro-processes, such as chemical polishing, heat treating, welding, exposure to gases, etc, affect the microstructure.

3D Atom Probe Tomography at NUCAPT

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, with FIM being the first universally acknowledged technique capable of seeing individual atoms on a material’s surface. See Figure 1 for a schematic description of an APT.

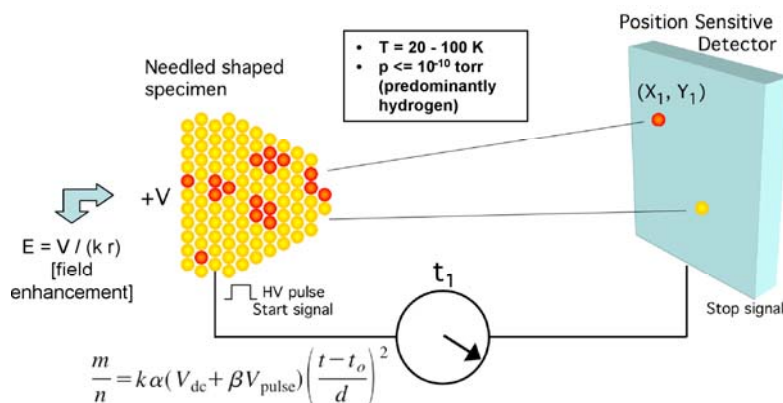


Figure 1 Schematic diagram showing the principle of atom-probe tomography (APT). The equation relating an ion’s mass-to-charge state ratio (m/n) to its total time-of-flight (t) is included in the lower left of the figure; t_0 is the delay time in the electronics, and α and β are constants that can be determined from a simple calibration procedure; this equation is obtained by equating the kinetic energy of an ion to its potential energy.

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. For 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. Atom probe tomography has extremely good analytical sensitivity, statistics and spatial resolution. The field is developing rapidly as the capabilities of the local electrode atom-probe (LEAP) tomograph are fully exploited, with a variety of new ways of sample preparation, and even fundamental changes in atomic ionization (pulsed laser-induced ionization). It promises significant improvements in understanding the surface of RF superconductors.

Project Goals

These investigations aim:

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 increase significantly cavity performance by removing Q-drop,
4. Understanding the interactions between high electric fields and materials (electron field emission, field evaporation of ions, surface stability, field induced stresses, fracture, etc.).

Strong material scientific tools such as APT are needed to generate the intellectual understanding of phenomena such as for instance Q-drop in order to achieve reproducibly 35 MV/m or better in SRF cavities for the ILC.

Broader Impact

The NUCAPT previously has not been part of the High Energy Physics community. One of the primary goals of this work will be to introduce the high level material science expertise as concentrated in NUCAPT to the field of superconducting cavities for HEP accelerators. The arrival of this new expertise will boost superconducting technology in both industry and laboratories.

Progress Report

Of the sample sets indicated above the initial work, started in 9/01/05 concentrated on:

- 1) Developing the sample preparation technology;
- 2) First measurements of high purity niobium samples;

Prior Work

The APT mass spectra obtained on first high purity niobium samples during spring and early summer of 2005 showed 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^+ , NbO^{3+} , NbO^{2+} , NbO_2^{3+} , NbO^{1+} , and NbO_2^{1+} – were also observed. Figure 2 shows an atomic scale reconstruction of the oxide layer on the surface of a niobium RF cavity material sharp tip.

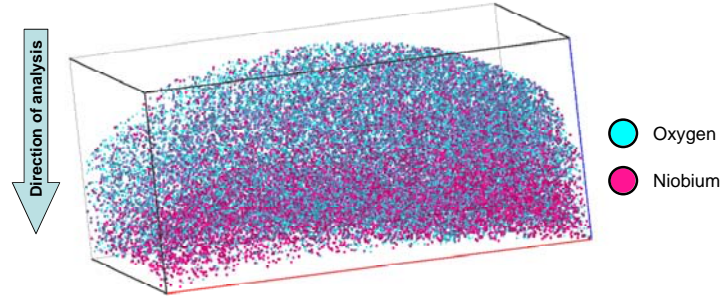


Figure 2: Atomic reconstruction of the oxide layer on the surface of a niobium RF cavity material sharp tip. The overall reconstruction dimensions are 23 nm x 21 nm x 11 nm; the volume contains ~112,000 atoms.

The resulting profile, re-normalized to only display niobium and oxygen concentrations, is shown in Figure 3. We see a clear, smooth transition from near-stoichiometric Nb_2O_5 to near-stoichiometric $NbO_{0.5}$ (equivalent to Nb_2O). 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 $NbO_{0.5}$).

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.

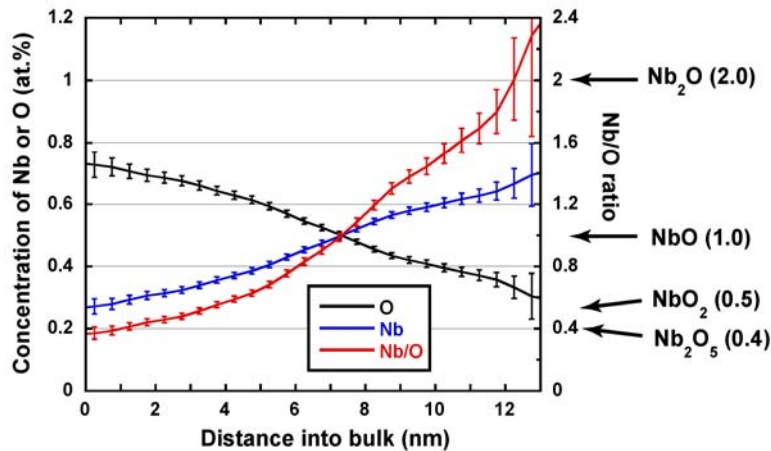


Figure 3: Proxigram analysis showing the quantitative concentration profiles corresponding to the atomic reconstruction shown in Figure 3. The profiles have been renormalized to only include Nb and O concentrations.

Work under this contract

- 1.) To date we have successfully collected data from samples that were prepared with the electro-polishing technique used in the processing of SRF cavities. The development of the sample preparation procedure requires an intensive effort that is not yet completed.

Atom-probe tomography specimens were cut from the niobium sheet into $\sim 0.2 \times 0.2 \times 1 \text{ mm}^3$ blanks using electrical discharge machining (EDM). The specimen blanks were then subjected to standard electropolishing techniques at room temperature. The electrolyte is hydrofluoric acid in sulfuric acid (1:10 volume ratio). The polishing commences at 26 Vdc and the voltage is lowered to $< 15 \text{ Vdc}$ as the tip sharpens to a point. A neck formed at ca. 10 Vdc and electrolytic cutting of the neck was performed at $< 5 \text{ Vdc}$. We prepared 68 samples with a 10% success rate during the LEAP tomography experiments. The main reason for this success rate is that the tips are not yet sharp enough. The blanks we are provided with are rectangular in cross-section rather than square, so the final tip shape is asymmetrical because each tip retains the rectangular shape of the blanks. We need to improve the EDM (electrodischarge machining) procedure, so we can start the electropolishing using square-shaped blanks. Additionally, the electrolyte we are using is the same solution that the SRF community utilizes for the surface treatment of the real cavity. This works well for polishing the cavity surface, it is not, however, the best choice for producing a sharp tip. We are therefore aiming at further refining the technique to the particularities of the tip making process.

2.) APT data performed on several samples have given a first insight into the chemical compositions of not only the oxide layer but also the niobium bulk.

Figure 4 displays the third atomic reconstruction of an oxide layer on the surface of a niobium RF cavity material tip. The reconstruction contains 500,000 atoms in a $5 \times 5 \times 48 \text{ nm}^3$ volume, which is currently the largest data set we have collected. From the reconstruction, it is clear that the oxygen atoms are concentrated at the surface. The renormalized profile exhibits the evolution of Nb and oxygen concentration along the direction of analysis, Figure 5. The concentrations of niobium and oxygen in this profile are almost constant in the oxide layer (first 20 nm below the surface). The concentration of niobium is a constant in the bulk niobium region, while the oxygen concentration decreases steadily. This result exhibits clearly that the analysis is going through bulk metallic niobium and the niobium oxide layer has a thickness of ca, 20 nm.

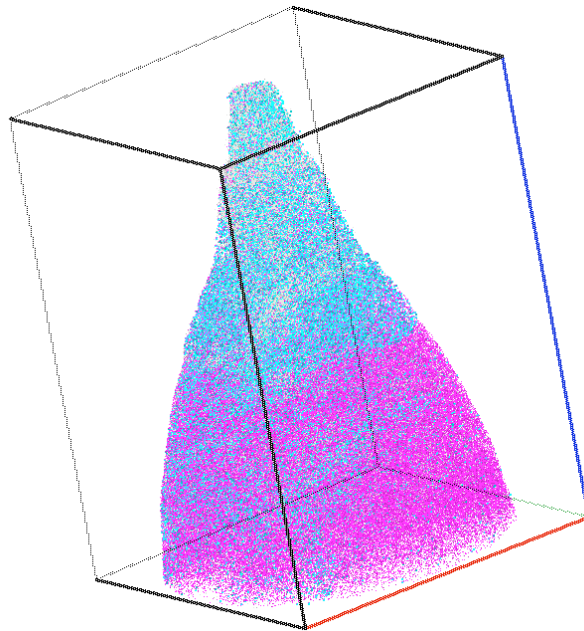


Figure 4: Atomic reconstruction of an oxide layer on the surface of a niobium RF cavity material. The overall reconstruction dimensions are $5 \text{ nm} \times 5 \text{ nm} \times 48 \text{ nm}$; the volume contains $\sim 500,000$ atoms.

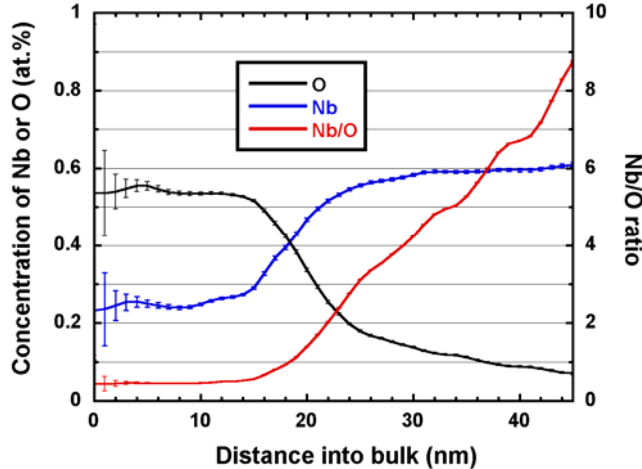


Figure 5: Renormalized proxigram showing the quantitative concentration profiles corresponding to the atomic reconstruction shown in Figure 4. The profiles indicate that the niobium oxide layer is chemically uniform.

3.) A program was started to address the hydrogen background issue.

APT tomographic analyses of niobium cavity materials typically exhibit a large hydrogen peak. For example, raw analyses of the APT data exhibit a hydrogen concentration in the near-surface region of the reconstruction 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 (hydrogen is the dominant impurity gas in a baked stainless steel UHV chamber) that becomes ionized in the high-field region of a specimen's 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 renormalized to display only niobium and oxygen concentrations. With hydrogen being one of the elements that we are most interested in, we have started a program that is intended to address the hydrogen background issue. Titanium reacts instantaneously with hydrogen and forms titanium hydride. We are fabricating a titanium sublimation pump (TSP), which will work as a hydrogen getter pump, and plan to attach it to the LEAP tomograph shortly. This will minimize the residual gas hydrogen, therefore helping us to resolve the origin of the hydrogen in our result.

Publication During Year 1

"Atom Probe Tomography Analyses of Niobium Superconducting RF Cavity Materials", J.T. Sebastian, D.N. Seidman, K.E. Yoon, P. Bauer, T. Reid, C. Boffo, J. Norem, paper TuP06 presented at the 12th International workshop on RF Superconductivity (SRF 2005), Ithaca, NY, USA, July 10-15, 2005 – will be published on the journal, *Physica C*.

Second Year Project Activities and Deliverables

1.) New sample preparation techniques, such as focused ion beam (FIB) milling, will be explored. Also commercial sources for tips will be pursued.

So far, we have employed the electropolishing technique to produce our samples, utilizing the same solution that is developed by SRF community for the surface treatment of the real cavity. The results

are, however, not totally satisfactory. Compared with the usual size of a data set from most metallic materials (steels and superalloys), which is 10 million atoms, the largest data set for niobium is only 500,000 atoms. To collect larger data sets, we have to sharpen our tips as sharp as much as possible, with an end radius of curvature less than 50 nm. To date the shape obtained employing electropolishing is rather blunt. Therefore, we are planning to explore the possibility of manufacturing tips using the dual beam focused ion beam (FIB) milling technique. This method enables us to observe the progress of the tip sharpening process using images obtained with an electron beam, which will also help us to fabricate tips containing a grain boundary. Figure 6 exhibits our first attempt to fabricate a sharp niobium using FIB milling.

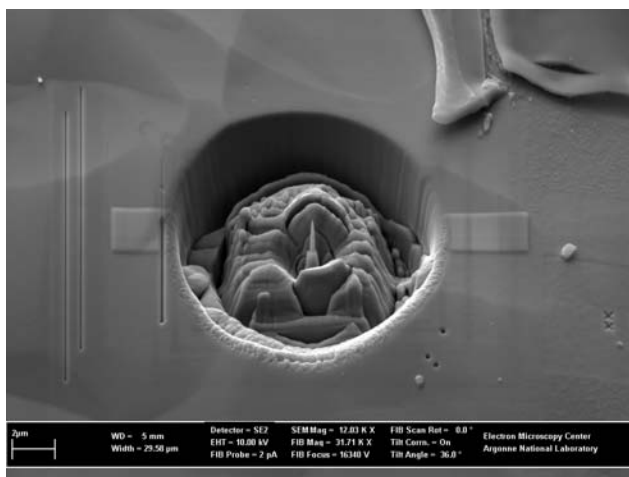


Figure 6: First niobium tip milled with FIB by Jon Hiller at Argonne National Laboratory

2) The LEAP tomograph at Northwestern University employs an electric pulser for field-evaporating the atoms from the tip. Laser pulsing using a femto- or picosecond laser is known to improve the mass resolution and the signal-to-noise ratio of a mass spectrum..

Field desorption (evaporation) is known to produce mass spectra with better mass resolution than with an electric pulser [1]. Additionally, it is less sensitive to the shape of a tip, so it is possible to collect larger data set with a relatively blunt tip. Therefore, we are planning to run the niobium tip on a LEAP tomograph with a laser pulser at Imago Scientific Instruments, Madison, WI -- the manufacturer of our LEAP tomograph.

3.) Whenever the issues related to the development of a sample preparation technique that is simultaneously representative of the SRF cavity processing and which at the same time gives good quality APT samples is resolved, we will return to the core of this program.

At the core of this program is a series of APT studies on samples as listed in Table 1. This list of samples includes specimen surface 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: BCP and EP (where BCP refers to “buffered chemical polishing” and EP stands for “electropolishing”). The samples are to be prepared by Fermilab and tested at NU.

Table 1: Run-plan for 3DAP tomography studies on niobium for SRF cavities.

Sample normal/weld	as received	deep drawn	100 μm etch (BCP/EP)	heat treatment (750°C/5hrs)	20 μm etch (BCP/EP)	Low temp bake (120°C/50hrs)
1	X					
2	X	X	X			
3	X	X	X	X		
4	X	X	X	X	X	
5	X	X	X	X	X	X

We are planning to investigate the heat-treated niobium materials to investigate how the elements in the materials, especially oxygen and hydrogen, redistribute after the heat treatment. These results will clarify the effect of chemistry and microstructure on the performance of the cavity. Although APT has absolute atomic resolution, there is a positional error involved in the three-dimensional reconstructions. We can extract the composition of the niobium oxide layer from the results of APT. However, we need to employ other techniques to confirm the microstructure of it. Transmission electron microscopy (TEM) will be utilized to conduct the microstructural studies of niobium tips.

Budget Justification

Budget justification: Northwestern University

The activities outlined above will involve Fermilab staff members, whose salaries are not included in the budget request below. The budget request only includes salaries for the NUCAPT staff members participating in this study. The quoted amount includes a request for 49% of Dr. Kevin Yoon's annual time to conduct research at Northwestern University.

Two-year budget, in then-year K\$ Institution: Northwestern University

Item	Next year	Subsequent year	Total
Professionals	19.7	19.7	39.4
Total Salaries and Wages	19.7	19.7	39.4
Fringe Benefits (23.4%)	4.6	4.6	9.2
Total Salaries, Wages and Fringe Benefits	24.3	24.3	48.6
Charge for using LEAP tomograph	2.5	2.5	5.0
Travel	1.5	1.5	3.0
Materials and Supplies	1.0	1.0	2.0
Total direct costs	29.3	29.3	58.6
Indirect costs (49.5%)	14.5	14.5	29.0
Total direct and indirect costs	43.8	43.8	87.6

References

[1] 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).