

3D Atom-Probe Microscopy on Niobium for SRF Cavities

Proposal for LCRD/UCLC 2005

Classification (subsystem)

Material science on niobium for superconducting cavities of main linac

Personnel and Institutions requesting funding

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Project Overview

Introduction

Fermilab (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 [1]. In this context FNAL has been steadily developing its SRF cavity expertise, infrastructure and technology base. 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 in the cavity fabrication. The NUCAPT is among the world leaders in the field of three-dimensional atom-probe microscopy, particularly as result of the recent installation of a local-electrode atom-probe (LEAP) microscope, manufactured by Imago Scientific Instruments (<http://www.imago.com>) Currently only three other LEAP microscopes, with a comparable performance, exist throughout the world. Atomic-probe microscopy 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 microscope at NU. 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 strongly advance 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 to better understanding the surface resistance of 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 [2, 3] or electron spectroscopy [4]. 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) Nb₂O₅ 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 3D atom-probe technique we propose to use, would be the first attempt 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 microscope also makes it possible to investigate how macro-processes, such as chemical polishing, heat treating, welding, exposure to gases,..etc, affect the micro-structure. Furthermore the high spatial resolution of the technique promises to allow the detection of field emitters, another performance limitation encountered in high gradient SRF cavities.

Project Goals

Northwestern University (NU) and Fermilab (FNAL) have agreed to collaborate on the study of the surface chemistry of bulk niobium for SRF cavities using the Imago LEAP microscope in NUCAPT. According to the agreement, FNAL will be responsible to provide samples for the 3DAP studies conducted at NU. Both parties will share the efforts related to analysis and publication.

The following project goals have been defined:

- 1) to improve the understanding of the chemical composition of the surface of state of the art high purity niobium for SRF cavities, including e-beam weld regions;
- 2) to improve the understanding of the chemical composition of the grain boundaries in state of the art high purity niobium for SRF cavities, including e-beam weld regions;
- 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;

To achieve the above-defined goals a series of samples need to be provided to the NU, which are optimized for the use of 3DAP without compromising the chemical condition of the surface. Therefore the initial phase of the project will be devoted to the test of different samples preparation techniques and sample shapes. Different possible techniques are wire erosion cutting of individual specimens from a bulk specimen combined with chemical etching. Alternatively, focused ion beam (FIB) milling of posts, to a diameter in the range 100 to 200 microns, in an initially flat surface, followed by sharpening of the tops of the posts to a radius of less than 50 nm. The samples will undergo the same surface preparation steps as the inner surfaces of cavities, including mechanical deformation, etchings and heat treatments. The weld-samples will be prepared from e-beam welded strips. Following the initial assessment of the best-suited sample preparation technique we will investigate the effect of all major cavity preparation steps on the surface chemistry. Samples prepared with different degrees of completeness (e.g. mechanically deformed and deeply etched versus mechanically deformed, deeply etched and heat treated, etc). The polishing variants, i.e. using chemical etching and electro-polishing, should also be differentiated. Furthermore this series of experiments should include the low temperature bake (~120°C, 50 hrs) that was recently shown to improve cavity performance significantly.

Broader Impact

Toward attracting underrepresented groups and women for careers in science we will provide access to NUCAPT to students and professors at: (1) Harold Washington College, a minority serving institution in downtown Chicago (Profs. Thomas Higgins and Cecilia Lopez); (2) Saint Mary's College, Notre Dame, Indiana, a liberal arts women's college with a strong chemistry major (Prof. Deborah McCarthy); and (3) College of St. Benedict/St. John's University in St Joseph, Minnesota (Prof. Anna McKenna), which is also a liberal arts women's college with a strong undergraduate chemistry program. We will help Professor Higgins in the development of an Undergraduate Research Center (URC). Similarly we will open the doors of NUCAPT to Professors McCarthy and McKenna of Saint Mary's College and College of St. Benedict/St. John's University, respectively, and their students through NSF REU/MRI grants and faculty development awards. Furthermore, we will obtain REU/MRI students through Northwestern's NSF funded Nanoscience and Engineering Center (Prof. M. Hersam) and Material Research Center (Prof. M. Olvera). We will help Dr. Vondracek (Evanston Township High School (ETHS)) construct a field-emission microscope from components we are no longer using. This will allow ETHS students to see molecules on the surfaces of sharply pointed

wire tips. The members of my research group will provide Dr. Vondracek the necessary help to maintain these microscopes. In addition to supervising the research projects of women and underrepresented groups we will conduct a short course for all REU/MRI students each summer to explain to them how the LEAP™ microscope works and how it is employed for diverse research projects being performed throughout the world.

Results of Prior Research

Although not previously been funded by LCRD, NUCAPT has a long been involved in 3DAP. The following presents an example of results that employ three-dimensional atom-probe (3DAP) microscopy, [5],[6], which is the successor to so-called 1DAP microscopy [7]. The example we now focus on is that of an Al-2.2 at.% Mg-0.12 at.% Sc alloy, which is relevant for aerospace applications, where segregation during aging adversely affects the high-temperature creep properties, and as a model system for its microstructural properties. This alloy was prepared employing solidification and

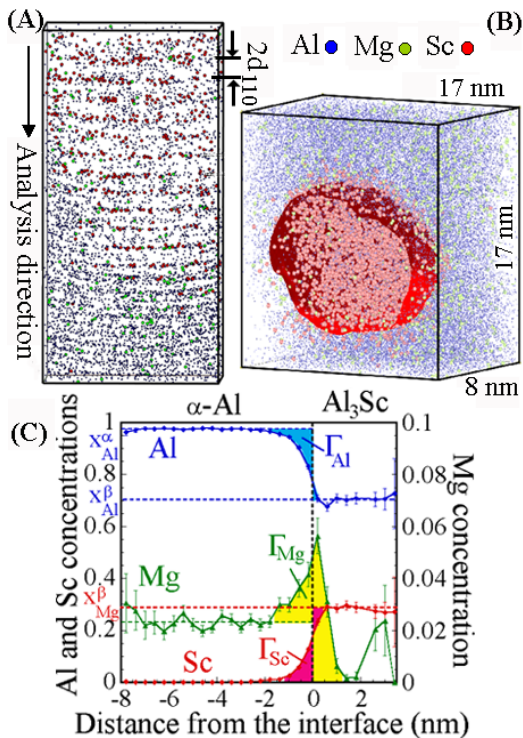


Fig. 1: (A) 3D reconstruction of an Al_3Sc precipitate with a slice taken through it showing the (110) planes. (B) 3D reconstruction of an analyzed volume from a specimen aged at 300°C for 1040 hours, showing the isoconcentration surface used to delineate the Al/Al_3Sc interface. Sc (Mg) atoms are in pink-red (light green), and Al is in blue. (C) Proximity histogram showing Al, Mg, and Sc concentrations with respect to distance from the interface, which is an average for many precipitates.

50% Al are visible, consistent with the L_{12} structure and stoichiometry of the Al_3Sc phase. A proximity histogram calculates average compositions in shells of 0.4 nm

homogenization procedures. During aging at 300°C, the supersaturated solid-solution decomposes into an $\alpha-Al$ matrix and $4 \pm 2 \times 10^{22}$ precipitates m^{-3} of nanoscale Al_3Sc precipitates with radii < 4.5 nm. HREM observations demonstrate that the $\alpha-Al/Al_3Sc$ interface remains coherent, that is, dislocation free, in both the binary Al-0.18 at.% Sc and ternary Al-Mg-Sc alloy, even for precipitates with radii of 4.5 nm. Without Mg, the precipitate shows pronounced facets on the {100}, {110}, and {111} planes, which tend to shrink with the addition of Mg. To investigate the behavior of Mg, we performed 3DAP microscopy resulting in solute composition profiles suitable to determine the Gibbsian interfacial excesses [8]. This demonstrates that segregation decreases the interfacial free energies, which concomitantly decreases the coarsening rate, thereby stabilizing the microstructure at elevated temperatures.

The spatial resolution of the 3DAP is illustrated in Fig. 1(A), where an analysis reveals the {220} atomic planes perpendicular to the analysis direction. The curvature of the planes comes from the projection of the hemispherical tip onto a planar detector. In the Al_3Sc precipitate, alternating planes containing 100% Al and

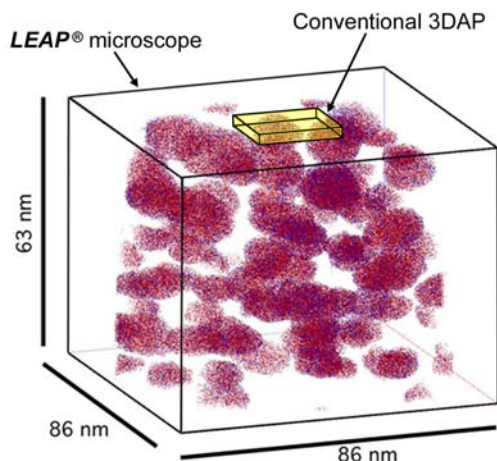


Fig. 2: Analysis volume containing 25 million atoms collected in approximately one hour on a Ni-5.2 Al-14.2 Cr at. % specimen aged for 256 h at 600°C using the LEAP microscope. The highlighted volume in yellow contains 50,000 atoms and marks the volume that would be collected in the same amount of time on a conventional 3DAP microscope. Only Al (red) and Cr (blue) atoms within gamma-prime precipitates are shown for clarity.

thickness at different distances from the α -Al/Al₃Sc interface; the interface is defined by an isoconcentration surface corresponding to 18 at.% Sc [Fig. 1(B)]. Interfacial Mg segregation was observed for all analyzed aging times, and the particular example of Fig. 1(C) exhibits a Mg concentration enhancement of 180%. First-principles calculations were conducted to investigate the energetics of Mg solute atoms in the vicinity of planar coherent α -Al/Al₃Sc interfaces. The agreement between the experimental and theoretical values of the relative Gibbsian interfacial Mg excess establishes that the measured interfacial Mg enhancement reflects pronounced segregation of Mg to coherent α -Al/Al₃Sc heterophase interfaces.

The analytical sensitivity and spatial resolution of 3DAP microscopy are well

documented in the following example. Figure 2 displays a data set for a Ni-Al-Cr alloy recorded with a LEAP microscope; the nanoscale precipitates is the γ' -phase (L1₂ structure). The yellow parallelepiped indicates a typical data set recorded with a conventional 3DAP microscope. The LEAP microscope is capable of recording data a rate that can be a factor of 667 faster than a conventional 3DAP microscope and the volumes analyzed are concomitantly significantly larger.

Facilities, Equipment and other Resources

A. Atom-probe tomographic facility – Northwestern University Center for Atom-Probe Tomography (NUCAPT)

- A high mass resolution 1D-atom-probe field-ion microscope system: It utilizes a single-stage reflectron lens to determine the time-of-flight of the field evaporated ions, and it has a mass resolution of 800, full-width at half-maximum (FWHM) employing electrical pulses to field evaporate ions. The time-of-flight electronics allow for the measurement of up to 128 ions per field evaporation pulse. It also can be used as a pulsed laser atom probe (PLAP), which has a mass resolution of 900, FWHM. It is equipped with a pre-chamber that permits us to deposit controlled amounts of different metallic evaporants. This instrument is also completely computer controlled.
- An Imago Scientific Instruments local-electrode atom-probe (LEAP) microscope, which is a state-of-the-art tomographic atom-probe microscope. This instrument allows us to collect data at a rate of up to 20,000 ions sec⁻¹ (72x10⁶ ions hr⁻¹) from a volume that can be 100 nm² x several microns. This instrument has a variable tip-to-detector distance (80 to 170 nm), which implies

that we can obtain wide-angle field-of-views, as well as analyzing smaller pre-selected areas. This instrument can also examine microposts on a wafer, which implies that we can sample sequentially different areas of the same region with atomic resolution

- A three-dimensional (3D) atom-probe microscope: This instrument has an ultrahigh vacuum system, with a specimen exchange system that holds ten specimens, which allows us to change specimens within approximately 20 minutes. It employs an optical detection system fabricated by Kindbrisk Limited and the capability of the detection system is 110,000 ions per hour with a 90% positioning efficiency (defined as the fraction of the detected ions that can be associated uniquely with a given x-y position and simultaneously a given mass-to-charge state ratio). This implies that data sets exceeding one million atoms can be collected in less than a day. The main chamber is equipped with a single-stage reflectron lens, which has a mass resolution ($m/\Delta m$) exceeding 300. This instrument can also be adapted for use as a pulsed laser atom probe (PLAP). This is a completely computer-controlled instrument.
- A versatile system for highly controlled electroetching or electropolishing of field-ion microscope specimens has been developed. This system is particularly useful for backpolishing an atom probe specimen to place a preselected Al/Al₃Sc interface in the field-of-view of a field-ion microscope image. The preselection is performed by TEM in a specially fabricated double tilt stage for an Hitachi transmission electron microscope; this stage can hold a wire specimen about 1 cm long and about 125 to 200 μm in diameter.

B. High-resolution, scanning transmission, and analytical electron microscopes

- At Northwestern University, there is an Hitachi 2000 analytical electron microscope that is equipped with both a parallel electron energy loss spectrometer and an energy dispersive x-ray spectrometer; that latter has a thin window that makes possible the detection of oxygen. This microscope has a cold field-emission gun that produces an electron beam with a spot diameter of 1 nm under best operating conditions. It also has a recently installed GIF.
- At Northwestern University, there is also an Analytical Scanning Transmission Atomic Resolution (A STAR) electron microscope (JEOL JEM-2100F FAST TEM) with the following features: High brightness Schottky emitter operated at 200kV; BF/ADF STEM detectors, EDS system and EMISPEC system for atomic resolution Z-contrast imaging, sub-nanoscale resolution EDS and PEELS point analysis, and automated line scans and maps; UTW x-ray detector; Gatan TV-rate CCD camera; Top-hat aperture to eliminate hard x-ray; Several side-entry specimen holders; Standard single and double-tilt holder; Low-Z(Be) holder for analytical x-ray microanalysis
- At Argonne National Laboratory, there is a JEOL 4000EX, a 400 kV high-resolution microscope available for this project; this instrument has a point-to-point resolution of 0.165 nm and a line resolution of approximately 0.11 nm.
- At Argonne National Laboratory, there is a Vacuum Generators, VG 6032 advanced analytical electron microscope, operated in UHV with a field emission gun (FEG) at voltages up to 300 keV with a 0.28 nm point-to-point resolution. This instrument is equipped with EELS, XEDS, AES, SIMS, LEED and will be available for our use.

- In addition to the HREM instruments at Argonne, a number of conventional tools for structural and analytical observation are available. A listing of the instruments available is as follows: Philips CM 30-300 kV TEM, Energy dispersive x-ray analysis (EDX), PEELS, Philips 420, 120 kV TEM, EDX, EELSJEOL 100 CX 100 kV TEM, EDX.
- At Argonne National Laboratory there is also a dual beam FIB instrument, which is useful for preparing atom-probe microscope specimens from bulk specimens.

C. Heat-treatment and metallography facility

- Three resistive-convection furnaces (temperature capability: 1050°C) in the P.I.'s laboratory, allowing precise temperature measurement (within 1°C) for heat-treatment in air or vacuum of samples to be homogenized or aged.
- The Optical Microscopy and Metallography Facility (OMMF) is equipped for the metallographic preparation of specimens by producing strain-free surfaces usually examined by optical microscopy. Equipment includes fourteen optical microscopes bright field and dark field modes, and polarized light and digital image capture, a micro hardness tester (loads from 10 grams to 1000 grams with either Knoop or Vickers indentors), an interference microscope, and a hot stage (300 C maximum) for viewing optically clear specimens are available. A "digital" darkroom with AV Macintosh, scanner and a dye-sublimation printer capable of photographic quality prints and a standard darkroom are available. Metallographic specimens can be cut with diamond-tipped blades on either a slicer/dicer, low-speed, or high-speed cut-off saw. Samples can be encapsulated in either cold-mount acrylics or phenolic resins. Manual abrading with silicon carbide paper or with variable speed 12" diameter SiC platens can be done in the facility. Various 8" diameter platens for polishing are available with diamond paste sizes ranging from 30 to 0.1 micrometer. Alumina slurry polishing is also available with sizes from 1.0 to 0.05 micrometer. A semi-automatic Buehler Ecomet IV Abrasive and Polishing System is capable of preparing up to eight specimens simultaneously with reproducible parameters of platen speed, pressure, and diamond concentrations.

Project Activities and Deliverables

During the first year we plan to complete initial 3DAP measurements of different shape samples of weld and non-weld material, prepared by different methods to assess the general feasibility of the measurements. These initial measurements will not only serve to debug the measurement technique but most likely also deliver first publishable results and possibly also raise questions that will determine the course of the subsequent investigations. The first year deliverables are the technical reports describing how to successfully implement 3DAP measurements with high purity niobium for SRF cavities.

During the second year we plan to complete the experimental program outlined above. The list of samples to be prepared by Fermilab and submitted to tests at NU is outlined in Table 1. The second year deliverables are expected to be high quality 3DAP measurement results that should lead to a new understanding of the surface chemistry of bulk niobium and possibly leading to the suggestion of new or improved cavity surface

treatment procedures. Obviously such results should be published in a journal such as Physical Review.

Table 1: Run-plan for 3DAP microscopy studies on niobium for SRF cavities. The roster of samples includes specimen prepared to different degrees of completeness. Also for each preparation condition there should be samples representative of the two different cavity areas (the weld and non-weld area) and/or the two main polishing techniques: BCP and EP (where BCP refers to “buffered chemical polishing” and EP stands for “electro-polishing”).

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

During the third year we plan to address the issues that arose during the systematic testing of year 2. The effect of new preparation steps suggested as a result of this (or other work) on the surface chemistry should systematically be tested by 3DAP.

Budget Justification

The activities outlined above will involve NU and FNAL staff members, whose salaries are not included in the budget request below. The budget request includes only funding for Dr. Jason Sebastian, who will dedicate four months per year to this effort (including travel to meetings/conferences). Also included is the minimum operating cost of the LEAP microscope (\$250/day), assuming a total of twenty days (listed under “Materials and Supplies”). Although FNAL will generally cover the cost of sample preparation, the budget also includes the projected cost of sample preparation outside of FNAL, should such a need occur. NU, as the general contractor for this proposal will also administer these funds. The following budgetary estimate is in k\$.

Table 2: Budgetary estimate (in k\$) for NU-FNAL collaboration on 3DAP microscopy of high purity niobium for SRF cavities.

Item	FY 2005	FY2006	FY2007
Other professionals	11.7	12.1	12.4
Total Salaries (incl. 24% fringe benefits)	14.3	14.8	15.4
Travel	5.0	5.0	5.0
Materials and Supplies	5.0	5.0	5.0
Sample preparation	5.0	5.0	5.0
Total direct costs	29.3	29.8	30.4
Total indirect costs (incl. 48%)	14.2	14.5	14.7
Total direct and indirect costs	43.5	44.3	45.1

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