Atomic-Scale Chemical-Analyses of Niobium for Superconducting Radio-Frequency Cavities

Kevin E. Yoon, David N. Seidman, Pierre Bauer, Christian Boffo, and Claire Antoine

Abstract—The key technology for the linear collider is the high gradient superconducting radio-frequency (SRF) cavity, approximately 20,000 of which will make up the accelerator. The preferred technology is to make the cavities from high-purity niobium-sheet. From the RF superconductivity point-of-view, the interface between the native niobium oxide on the surface of the cavity and near sub-surface region is the most important one. Superconducting properties of cavities depend on the chemistry and microstructure of the surface oxide and the concentration and location of impurity elements. Little is known, however, about this information and the effect of low-temperature baking on the surface region. Atom-probe tomography (APT) provides chemical information of the analysed materials on an atomic scale utilizing time-of-flight (TOF) mass spectrometry, with the field evaporation of materials permitting atom-by-atom dissection. We employ a 3-D local-electrode atom-probe (LEAP) tomography to analyse the chemistry of niobium tips, from the surface niobium oxide to underlying bulk niobium.

Index Terms—Atom-probe tomography (APT), niobium, oxygen, superconducting accelerator cavities.

I. INTRODUCTION

The study of the surface chemistry of high-purity niobium is extremely important for the advancement of understanding its performance limitations in high-gradient superconducting radio-frequency (SRF) cavities for the next linear collider [1], [2]. During radio frequency (RF) operation the high-power RF fields penetrate approximately 50 nm into the surface of the cavity. The interaction of RF photons with the complex electronic system in the surface of superconducting niobium produces the Bardeen-Cooper-Schrieffer (BCS) resistance loss, heating and ultimately thermal quenching. It is expected that the presence of metallic oxides and hydrides (e.g., in grain-boundaries) and interstitial impurities affect strongly the BCS surface resistance because of a weakened superconducting state (reduced gap energy). Therefore, the assessment of the surface chemistry, such as impurities, sub-oxides, or hydrides, at the microscopic level is of paramount importance 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 mainly using x-ray photoelectron spectroscopy (XPS) [3]. This research has already yielded some understanding of the issues at hand. It is clear, for instance, that below the insulating (and therefore inert) pentoxide, a mixture of Nb-O compounds with varying stoichiometries exists, which is usually referred to as a mixture of sub-oxides. XPS has also shown that there is a non-negligible layer of interstitial oxygen at the metal-oxide interface [4]. The roles of these sub-oxides are incompletely understood, but their mere presence can be a source of gap suppression and flux penetration. The XPS studies, with a sensitivity about 0.1 at% at best, were not capable, however, of resolving the surface chemistry on an atomic layer-by-layer basis (although new proposals exist to do just that), nor could they resolve clearly the chemistry of grain-boundaries. The 3-D atom-probe tomography (APT) technique we utilize is the first to reveal the surface chemistry in state-of-the-art niobium for SRF cavities at the most microscopic level possible, namely on an atom-by-atom basis [5]. 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 [6], [7], which is suspected to be correlated with oxygen diffusion in the first 40 nm of the material.

II. EXPERIMENTAL PROCEDURE

A. Atom-Probe Tomography

3-D APT is a point-projection microscope, which relies upon the principle of an enhanced electric field at the surface of a sharply pointed tip held at high positive voltage [8]–[11]. See Fig. 1 for a schematic description of an APT [5]. For sufficiently large applied voltages and a sharp tip, the electric field at a tip’s surface can reach values of many GV m−1. With electric fields this high, atoms on the surface of the tip can be field-evaporated atom-by-atom and atomic layer-by-layer, and individual ions are then accelerated away from the positively charged tip’s...
surface along trajectories that are orthogonal to the equipotentials. After being field evaporated, the time-of-flight (TOF) of each field-evaporated ion, which provides the chemical identity of an atom, is recorded with an electronic clock and positional information is determined utilizing a 2-D position-sensitive detector based on a multi-channel plate and a delay line detector, which are in series. By combining the TOF and positional information from all the atoms in an analysed volume, a three-dimensional atom-by-atom reconstruction of a volume of material is obtained. 3-D APT reconstructions are determined in real space, with minimal data deconvolution, and thus represent the ultimate in nanoscale materials science chemical analysis. This field is developing rapidly as the capabilities of the 3-D local-electrode atom-probe (LEAP) tomograph [12], [13] are being fully exploited, with a variety of new ways of sample preparation, and even fundamental changes in atomic ionization (pulsed picosecond laser-induced ionization versus pulsed electric-field ionization).

B. Specimen Preparation

Niobium wire, which was commercially available with 99.9% purity, was utilized for the 3-D LEAP tomograph experiments. The baking of a niobium tip was performed at 120 °C for 2 days in air, to investigate the change in surface oxide after this baking procedure. It was shown that the HF rinsing does not affect the performances of cavities (baked or unbaked) [14]. Wires were polished into sharp tips with electropolishing (EP).

For EP specimens, a solution of HF acid (49% initial concentration) in H2SO4 acid (68% initial concentration) was used with a 1:10 ratio. The polishing commenced at 30 Vdc and the voltage was gradually lowered as the tip sharpened and formed a neck. The electrolytic cutting of the neck [15] was performed at ca. 10 Vdc. This method produces sharp needle-like tips with an end radius of curvature of <50 nm.

After a sharp tip was obtained, the specimen was dipped in HF acid (68% initial concentration) was used for one minute and then rinsed with high-purity deionized water. The purpose of this HF rinsing is to minimize the variation of surface oxide thickness. As it is very difficult to apply the same voltage on each tip, we had observed previously a large variation in the oxide thickness. HF rinsing is known to dissolve the oxide layer, while a fresh (reproducible) one should build up on the niobium upon water rinsing.

Fig. 2 shows a photograph of a typical niobium tip.

C. Atom-Probe Tomographic Analyses

For the analyses of niobium cavity materials, the typical background pressure in the 3-D LEAP tomograph was <10^-10 torr (predominantly hydrogen). A specimen temperature of 100 K was used to ensure continuous and smooth field evaporation through the oxide/metal interface, along with a high-voltage pulse-fraction (ratio of evaporation pulse voltage to steady-state dc voltage) of 15%.

III. RESULTS AND DISCUSSIONS

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 is the z-direction. To obtain a quantitative representation of this transition, we employ the proximity histogram (proxigram) technique [16]. This analysis technique integrates the chemical and three-dimensional positional information and then generates a histogram of the atomic factions of all alloying elements versus distance to an interface. This is accomplished for all the interfaces in a specimen in parallel, delineated by an iso-concentration surface. Furthermore, it does not require choosing an arbitrary axis or geometric subvolume. In this study, an iso-concentration surface with a threshold value of 30 at.% oxygen is used to define the location of the oxide/metal interface.

The resulting profile is shown in Fig. 4. Contrary to previous observations [5], which display a continuous transition from near-stoichiometric Nb2O5 to near-stoichiometric Nb2O,
we see no 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 shows 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 can investigate the stoichiometry of the oxide and this indicates that the oxide can be a mixture of NbO and Nb₂O₅. 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.

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 baked stainless steel UHV chambers). 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 [5], 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 detailed investigations 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 experiment passes through an oxide/metal interface, it exhibits smoother field-evaporation behavior since mainly niobium atoms, which are, of course, metal, 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 lower after
the baking. The chemistry of the oxide, however, remains the same after the baking, which is shown in Fig. 5, with the same O/Nb ratio before and after the baking.

As we have already mentioned this variation of oxide thickness was also observed before an HF rinse. Some variation is to be expected: a recent TEM study on monocrystals show that the oxide thickness varies with crystalllographic orientation, with a high interface roughness [17]. Previous work by Halbritter also indicates that the oxide is serrated on the surface [18]. We need to understand better if the variability of our results arises from the intrinsic properties of the Nb or from other experimental issues, such as premature fracture of the oxide due to fatigue induced failure associated with the stresses generated by the high electric field on a Nb tip.

Nevertheless, the results that we obtain show clearly that HF rinsing modifies deeply the oxide layer in comparison to what is observed without HF rinsing. In contact with water, the oxide layer should grow until its equilibrium thickness (~5 nm, mainly Nb2O5) is achieved. On pure niobium, delayed growth, taking as long as one week has been observed [19].

IV. CONCLUSIONS

Atomic scale chemical analyses of surface niobium oxide and of the bulk niobium, before and after the baking of niobium tips, are performed employing 3-D LEAP tomography.

- The surface oxide after HF rinsing may be a mixture of NbO and Nb2O5, which is very different from the usual pentoxide found on Nb. If this result is confirmed then high field dissipation observed in the RF cavities (Q-drop) may not be related to the surface oxide composition.
- The surface niobium oxide thickness decreases from 10 nm to 5 nm after baking a niobium tip at 120 °C for two days in air, and the level of oxygen concentration below the oxide/metal interface also decreases.
- The chemistry of the surface oxide remains the same, with the same O/Nb ratio of 1.8, after baking.
- We still need to determine if the variability of the oxide thickness is related to some experimental issues or if it is related to a natural variability of the oxide properties.

REFERENCES