

A SIMS APPROACH FOR THE ANALYSIS OF FURNACE CONTAMINATION *

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Abstract

Detection of surface contamination for SRF material is difficult due to the minuscule quantities and near atomic resolution needed. Visual inspection of samples known to have experienced surface contamination indicated inconsistent nitride coverage after nitrogen doping. EBSD analysis suggested that nitride suppression tends to be most prevalent when deviating from the [111] and [001] zone axes. XPS suggested that tin was present as a contaminant on the surface with SIMS mass spectra also confirming its presence. SIMS depth profiles show a depletion of nitrogen content as well as an increase in carbon content for contaminated samples.

INTRODUCTION

Superconducting radiofrequency (SRF) cavities are critical components of particle accelerators and responsible for propelling charged particles to relativistic energies which are essential to probe the most fundamental laws of physics. Historically, niobium cavities cooled to 2°K have been used for these applications. Next generation machines, like SLAC's LCLS-II HE will use niobium cavities "doped" with low levels of nitrogen which allows for the instrument to operate more efficiently [1].

Nitrogen "doping", a process discovered at Fermilab in 2013, has yielded highly efficient ($Q_0 = 3.5 \times 10^{10}$ at 16 MV/m) SRF cavities [2]. N-doping is the process in which a small concentration of nitrogen is thermally diffused into interstitial sites of the niobium cavities (properly termed "surface alloying"). During this process, niobium's surface also becomes decorated with lossy nitrides which subsequently must be removed by electropolishing [3, 4].

These N-doped niobium cavities are fabricated with meticulous attention to detail to avoid a premature reduction in efficiency with increasing power (quenching) [5]. Avoiding contamination throughout the fabrication process is critical. It is suspected that metallic contamination can occur during the furnace heat treatment of the cavities. To guard against this, cavities are capped to prevent metallics from depositing on the interior cavity surface which may limit the performance of the cavities [6].

Mitigation of furnace contamination by capping the cavities prophylactically solves the contamination issue, rather than seeks to understand it. Characterization of the contaminated cavities may lead to further understanding of the

doping process and additionally act as a quality assurance check to prevent costly loss of materials. Here we use SEM, SIMS and XPS to investigate the cause of contamination.

Furnace Cap Design and Procedure

The furnace caps are designed not to be gas tight, as the cavity must be allowed to absorb significant gas quantity during the doping process (Fig. 1). RRR grade niobium was machined to include small pores to allow for gas transfer. Two holes on the edge of the caps are also included to attach the caps to the cavities with molybdenum bolts. Prior to assembly, all hardware associated with the caps is precleaned by buffer chemical polishing (BCP). The etch rate for molybdenum is significantly higher than niobium. The molybdenum components are rapid dipped in the BCP solution for ~2 seconds and then rinsed with deionized water. Ultrasonication in detergent and subsequent rinsed with deionized water are repeated and then blown dry with nitrogen. The caps are attached to the cavity in a clean room by tightening the molybdenum bolts finger tight. Over-tightening will lead to cold welding during the high-temperature run.

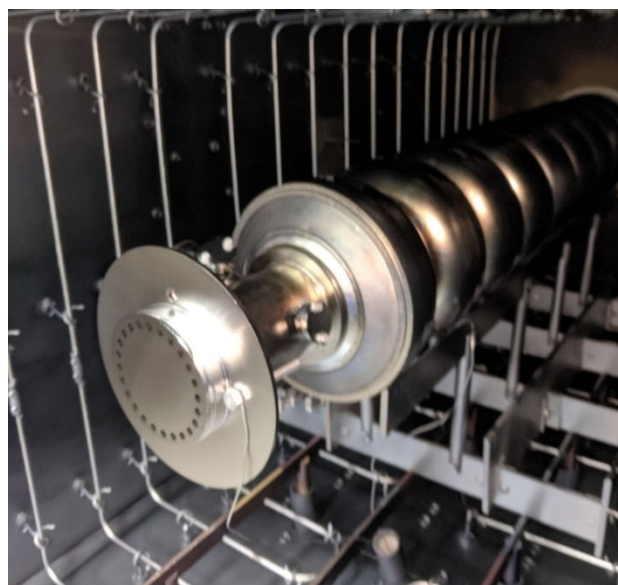


Figure 1: Depiction of a 9-cell cavity with furnace caps attached, loaded in N-doping furnace.

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Witness Sample Preparation

Cavity grade niobium sheets 2.8 mm thick were heated to 900 °C for 3 hours in a vacuum oven. Small specimens were electro-discharge machined (EDM) to 6 mm × 10 mm for secondary ion mass spectrometry XPS, SEM and SIMS investigation. A 50 μm removal was performed via buffered chemical polishing and subsequently “nano-polished” to yield a surface finish smoother than 200 nm R_a (Fig. 2). These specimens were then “N-doped” with a niobium cavity to witness the doping procedure, which acts as a pathway to perform representative cost-effective characterization of the cavities.

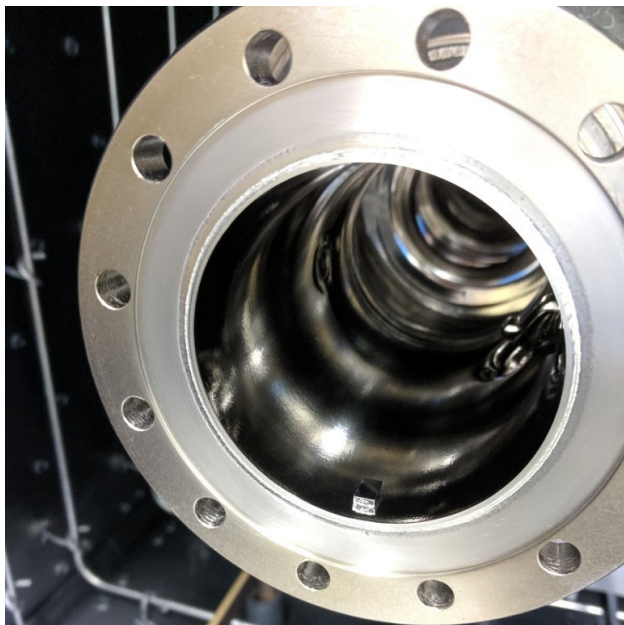


Figure 2: The image above shows a witness sample placed just inside of a cavity prior to nitrogen doping.

Cavity Preparation

High purity RRR grade niobium sheets are placed into dome shaped dies to press and form half cells in a process called deep drawing. Several series of these half cells are electron beam (EB) welded to generate the 9-cell cavity shape used for the LCLS II HE cavity design. The weld iris formed during processing is removed by grinding. Potential defects and contaminants generated during fabrication are removed by annealing and buffered chemical polishing (BCP) respectively. Prior to cavity insertion into the doping furnace, the witness samples were placed just inside the cavity and furnace caps were applied.

Nitrogen doping was performed in three different furnaces to determine the extent of contamination of each. Each furnace followed the 3N60 doping procedure detailed below. The materials (the cavities and witness samples) were loaded into a vacuum furnace and heated to 800 °C for 3 hours under ultra-high vacuum (UHV) conditions. Nitrogen gas was bled into the furnace to sustain 25 mTorr for 3 min, re-evacuated, and held for 60 min. Following the heat treatment, the materials were removed from the fur-

nace. Where noted, electropolishing was performed to remove the surface layer containing nitrides. The cavities were then treated with a high-pressure rinse (HPR) and the rf properties were tested. Witness samples were sent to Virginia Tech for characterization

RESULTS AND DISCUSSION

Following N-doping, SEM was performed using a Tescan SEM at JLab. The 6 mm × 10 mm coupons were mounted onto aluminum SEM pin stubs using carbon conductive tape. A cotton swab soaked in ethanol was used to gently clean the surface of the coupons. Imaging was performed at 5 kV accelerating voltage and 6 nA beam current at a working distance of roughly 10 mm. Examination of the surfaces showed differences between witness samples doped inside the cavity vs. samples exposed to the furnace. The exposed samples showed a reduction of niobium nitrides formed on the surface (Fig. 3A). The extent of this “nitride suppression” varies from sample to sample. Electron backscatter diffraction was also performed on samples with nitride suppression observed. Nitride suppressed grains from the SEM images were cross-referenced to determine if nitride suppression correlated with specific grain orientations. The grains nearest to the [111] or the [001] zone axes appeared to be the most resistant to nitride suppression but were not impervious (Fig. 3B). More statistics in a latter study are needed to determine if a correlation exists.

To understand the nitride suppression in more detail and to identify potential contaminants of the surface of these samples XPS was performed on a Phi Quantera SXM. The XPS was chosen as a screening tool due to it being non-destructive and its near atomic resolution (~10 nm). Spectra were acquired using an aluminum source utilizing a 280 eV pass energy and a 45° take-off angle. The scan range was swept from 0–1100 eV utilizing a 0.5 eV step size. In an effort to enhance the signal-to-noise ratio to detect low concentration contaminants, 100 sweeps were acquired on each sample.

The survey scans showed slight differences between samples. The samples protected by the furnace caps appeared to be free of metallic contamination whereas the samples exposed to the furnace environment were observed to have Sn present (Fig. 4). However, the Sn observed in these scans were found to be in very low quantities with the concentration nearing the limit of detection (0.1 at.%) for this technique. For this reason, XPS can be used strictly as a qualitative screening technique for contamination. Once it was discovered that contamination could be detected, a more sensitive technique was needed to confirm the presence of Sn as well as to search for any additional contaminants.

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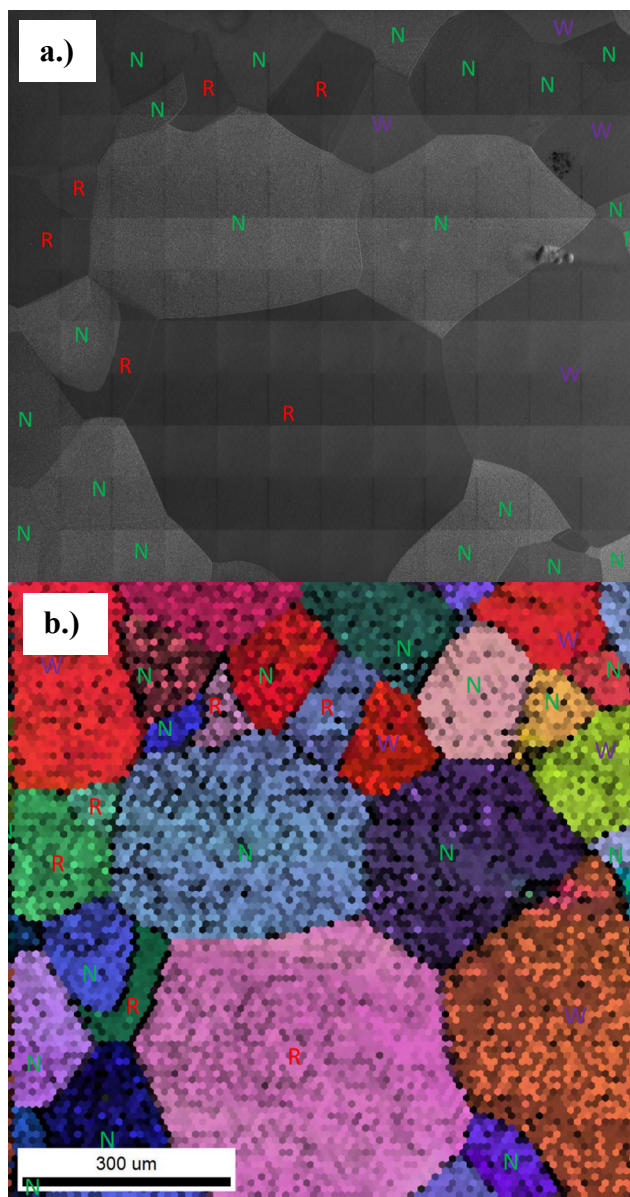


Figure 3: A.) Image shows an SEM image of a contaminated sample with varying degrees of nitride coverage. B.) EBSD was performed. It was found that nitride suppression tends to be most prevalent when deviating from the [111] and [001] zone axes.

Secondary ion mass spectrometry (SIMS) was performed on these samples to further investigate the furnace contamination. Due to its superior depth resolution, Time-of-Flight (ToF) SIMS would normally be the ideal type of SIMS instrument for this work. However, in the interest of better detection limits, the dynamic SIMS, the magnetic sector SIMS was preferred [7].

The protected and the exposed samples were analyzed using a Cameca 7f Geo. A Cs^+ primary ion beam with an impact energy of 8 keV (5 kV_{source}/ -3 kV_{sample}) and a beam current of 25 nA was rastered with an area of $150 \mu\text{m} \times 150 \mu\text{m}$ utilizing an analysis window of $63 \mu\text{m} \times 63 \mu\text{m}$. The entrance and exit slits, which control the mass resolution, were set to obtain a mass resolution of

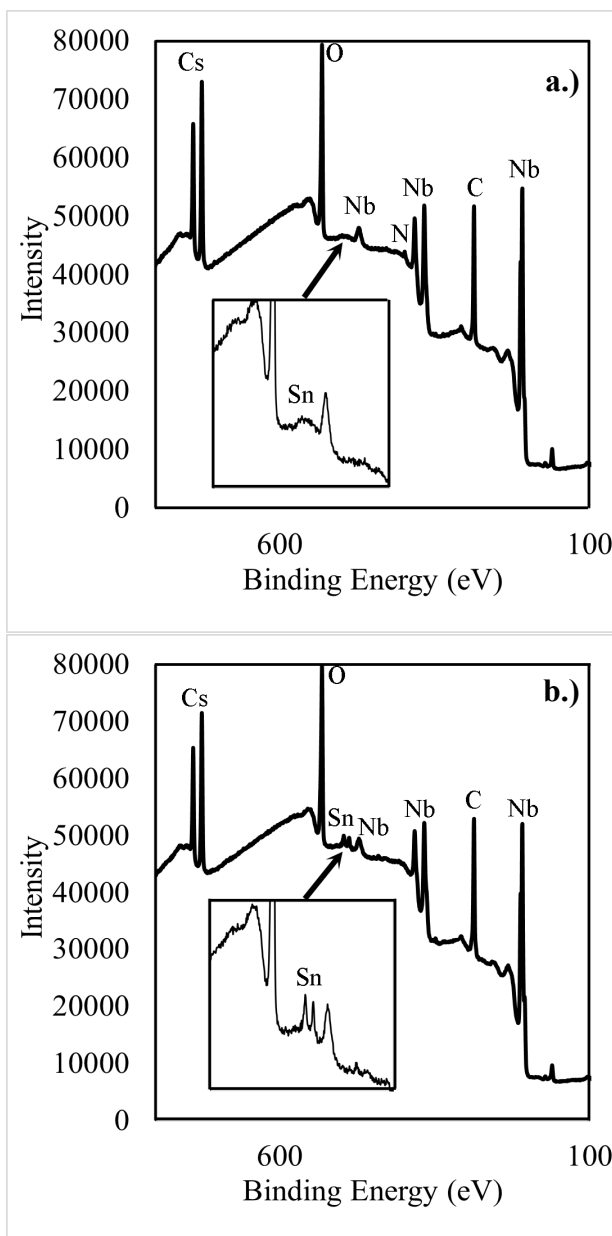


Figure 4: XPS survey scans for niobium witness samples which were a.) protected by furnace caps and b.) exposed to the furnace environment. The main observation for these scans was the presence of Sn found for the exposed sample. This signal was nearing the limit of detection (0.1 at. %) for this technique.

1200 $\text{M}/\Delta\text{M}$. Signal was acquired by scanning a large mass range of 10–200 amu.

The average sputter rate for niobium samples typically ranges from 0.5-0.8 nm/s at 25 nA of beam current. Therefore, a single survey scan could not be performed over the entire 10–200 amu range. To keep the scans from exceeding 100 nm in depth, individual mass spectra were acquired consisting of 10 amu scan ranges and then moved prior to the acquisition of another scan. This method resulted in compiling 20 scan ranges over $1400 \mu\text{m} \times 1750 \mu\text{m}$ area of the sample surface.

The secondary ions generated may include polyatomic compounds (i.e. $^{12}\text{C}^-$ and $^{24}\text{C}_2^-$). These polyatomic species add a degree of complexity when identifying peaks on a mass spectrum. Therefore, mass spectra for suspected contaminants (Ti and Sn) were collected and compared to ensure the accuracy when identifying peaks. The mass spectra revealed much higher intensity for peaks associated with carbon for the sample exposed to the furnace environment (Fig. 5). In this region of the mass spectra, Ti was also observed at 48 amu however it was noted that this signal did not strongly correlate to the pure titanium mass spectrum. Isotopes of Sn were observed around 120 amu for the exposed sample. The comparison mass spectra acquired for the pure Sn sample suggested a very strong match for Sn (Fig. 6).

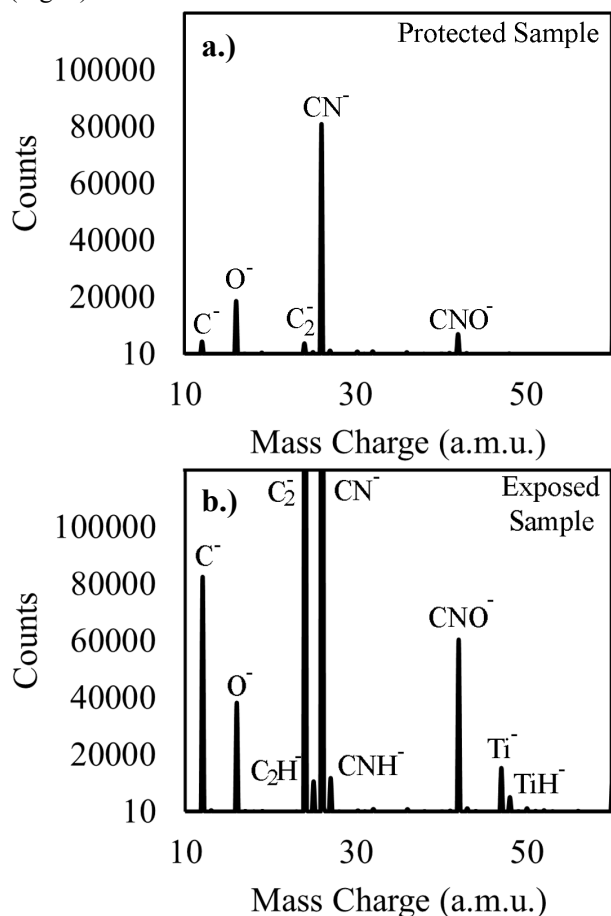


Figure 5: Mass spectra ranging from 10–60 amu for a.) protected sample and the b.) exposed sample. The results showed increased carbon activity with very minor Ti signal noted for the exposed sample.

SIMS depth profiles were obtained to determine if the contamination negatively influenced nitrogen diffusion. The instrument conditions were kept the same as the mass spectrum work. However, specific masses were monitored as a function of depth. $^{12}\text{C}^-$, $^{93}\text{Nb}^-$ and $^{107}\text{Nb}^-$ secondary ions were monitored. Previous works have indicated using the beam centering function available to the CAMECA 7F Geo can increase the accuracy and decrease the uncertainty between measurements [1].

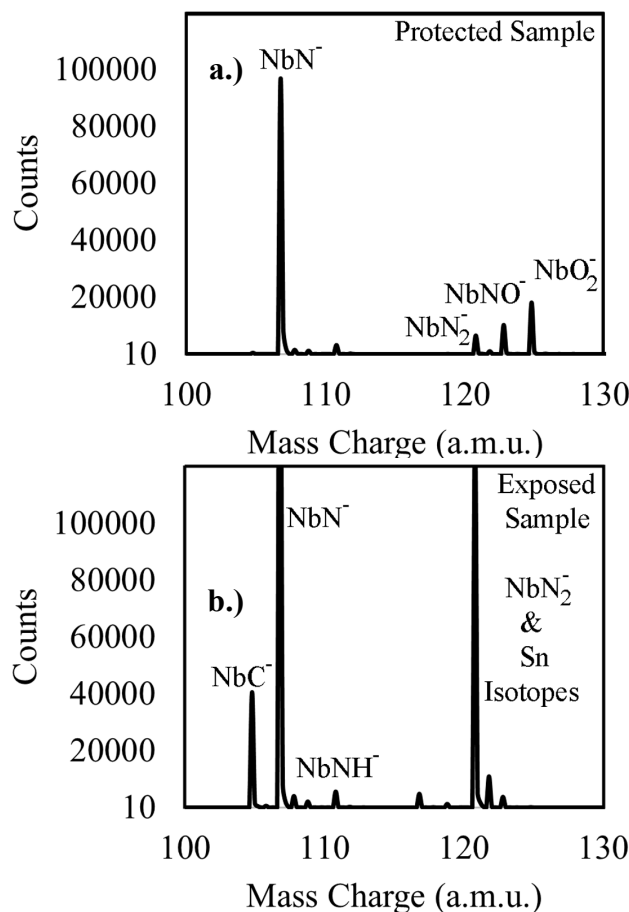


Figure 6: Mass spectra ranging from 100–130 amu for a.) protected sample and the b.) exposed sample. The exposed sample was noted to have Sn present on the surface of the sample.

As a result, the dynamic transfer contrast apertures were adjusted between analyses. The depth must first be determined to convert the x axis of the depth profiles from time to depth. Crater depth determination was performed using a Tencor Alpha Step 500 stylus profilometer using a scan speed of 50 $\mu\text{m/s}$. Scans were performed on both axes of the crater and the average value was used. Conversion from counts to concentration is made possible by using an implantation standard prepared by Leonard Kroko, Inc. The niobium standard, first polished as the experimental samples, was dosed with 2×10^{15} atoms/ cm^2 of oxygen and nitrogen at 180 keV and 160 keV respectively.

The depth profiles showed a significant effect on nitrogen and carbon diffusion because of surface contamination. The sample protected by the furnace caps had a baseline nitrogen content of 1320 ± 200 ppm whereas the sample which was exposed was reduced to 200 ± 40 ppm of nitrogen (Fig. 7a). Conversely the carbon content was found to increase from 90 ± 80 ppm to 120 ± 20 ppm for the protected and the exposed samples, respectively. The carbon content was also found to diffuse deeper for the exposed sample, reaching baseline at 870 ± 100 nm compared to 450 ± 120 nm for the protected sample (Fig. 7a).

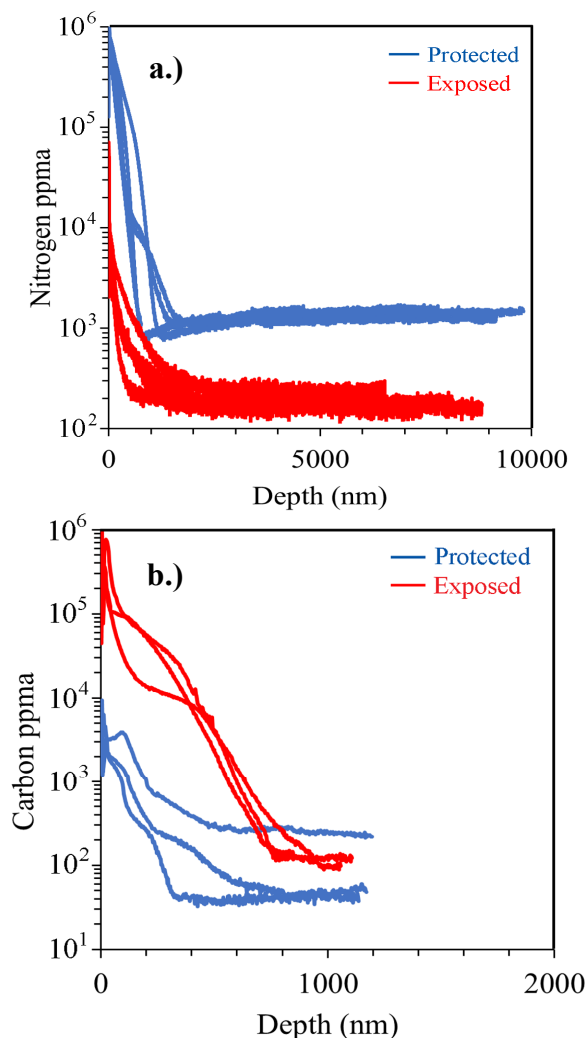


Figure 7: Depth profile of protected and exposed samples. a.) shows a reduction in nitrogen uptake because of exposure to the furnace environment. Additionally, b.) shows that carbon had a higher concentration on the surface which diffused deeper into the bulk as a result of the exposure.

CONCLUSION

Contamination of SRFs has been an ongoing problem for cavity production since the inception of nitrogen doping due to the techniques high processing temperatures. Contamination of niobium surfaces can be immediately observed by visually examining the surface nitrides by SEM. In certain cases, nitride depletion appears to be grain specific. EBSD was performed in conjunction to the SEM analysis. Grains were tabulated and categorized by the extent of nitride suppression with the data superimposed. It was determined that a correlation exists with the [111] and [001] grains closest to the zone axis being most resistant to nitride suppression. Limited statistics are available for this data at the present time and more analysis is desired to increase the robustness of this study.

The identity of the surface contamination is difficult to determine due to the contamination layer existing less than 100 nm thick. Due to its non-destructive nature and surface

sensitivity, XPS was performed to screen for possible contaminants. Sn was observed to be qualitatively present on samples which were exposed to the furnace environment. However, when detected, the signal was marginally above the limit of detection.

To confirm the presence of Sn and to further examine the surface for other possible contaminants SIMS was performed in mass spectrum mode. A survey of the samples indicated that samples exposed to the furnace environment had an increase in carbon signals as well as confirmed the presence of Sn. Ti was potentially observed as well. However, it was determined that the Ti signal only loosely matched a mass spectrum acquired from pure titanium. The effect of contamination was evaluating by performing SIMS depth profiles to examine the diffusion behaviour of carbon and nitrogen. It was found that the baseline nitrogen content significantly decreased for the exposed sample with carbon diffusing deeper and in higher quantities.

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