

CHALLENGES TO RELIABLE PRODUCTION NITROGEN DOPING OF Nb FOR SRF ACCELERATING CAVITIES*

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Abstract

Over the last several years, alloying of the surface layer of niobium SRF cavities has been demonstrated to beneficially lower the superconducting RF surface resistance. Nitrogen, titanium, and oxygen have all been demonstrated as effective alloying agents, occupying interstitial sites in the niobium lattice within the RF penetration depth and even deeper, when allowed to thermally diffuse into the surface at appropriate temperatures. The use of nitrogen for this function has been often termed “nitrogen doping” and is being applied in the LCLS-II and LCLS-II HE projects. We report characterization studies of the distribution of nitrogen into the exposed niobium surface and how such distribution is affected by the quality of the vacuum furnace environment in which the doping takes place, and the complexity of nitride crystal growth on different grain orientations of surface niobium. Using state-of-the-art quantification methods by dynamic secondary ion mass spectrometry (SIMS) depth profiling in niobium, we identify several phenomena involving furnace-sourced contamination. We also highlight a potential issue with N₂ flow constraints from the flange “caps” used during heat treatments.

INTRODUCTION

The thermal diffusion of interstitial nitrogen into the surface of Nb has been demonstrated to yield reduced rf surface resistance under conditions that are very useful for CW SRF accelerator applications. This alloying of the Nb lattice, commonly called “nitrogen doping”, reduces the electron mean free path within the rf penetration depth and is also strongly suspected of inhibiting the formation of lossy hydrides at low temperatures.

The common process for introducing nitrogen into the niobium surface is via provision of low-pressure N₂ gas at 800 °C into a vacuum furnace at the end of a hydrogen degassing run. Several exposure-time (min)/subsequent anneal-time (min) process combinations have been tried, the most common of which are 2/6, 2/0, and 3/60. The first was chosen for use in LCLS-II [1], the second for LCLS-II HE [2]; the third has seen limited use, but yielded the best performing 9-cell cavities to date (see Fig. 1).

While the basic process has proved stable enough for major project exploitation, variations in performance obtained by different cavity processors motivated research into the sources of process vulnerabilities. We report here the fruit of this research.

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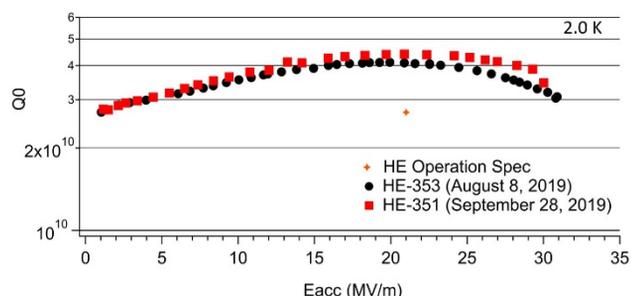


Figure 1: Best-performing N-doped 9-cell cavities to date. Cavities were fabricated by Zanon, with all chemistry, 3/60 doping, 10 μm EP, cleanroom work, and testing performed at Jefferson Lab.

A key feature of this nitrogen doping process is that the desirable interstitial nitrogen is largely mediated by the growth of crystalline nitrides on the niobium surface. The details of the near surface growth dynamics of these nitrides is complex—depending on Nb grain orientation, grain boundary angles, and also surface contamination.

To first order, the standard process removes the nitrides decorating the niobium surface via a shallow electropolish. This presents one of the process optimization challenges: how much material to remove to leave “good” quality surface while still leaving behind sufficient Nb with beneficial interstitial N content. The projects made empirical choices that meet project requirements. Analysis of comparably treated samples, however, reveals complexities that contribute to performance variabilities.

Another open question has been the source of performance differences when nominally the same process is applied at different institutions. We would like to understand the source of performance variability that results from use of different vacuum furnaces. The designs of furnaces in use vary considerably. We examined differences in residual surface contamination found on samples and correlated that with resultant nitrogen concentration profiles. The results highlight the need for minimized carbon sources and well-designed “caps” to intercept evaporative metals, particularly those that derive from prior use of the furnace with other materials.

This research has been enabled by two parallel developments, the establishment of high-quality standard samples with appropriate grain size and surface flatness to enable high-quality dynamic SIMS measurements including implant standards, and the refinement of state-of-the-art dynamic SIMS characterization techniques via the PhD work of Jonathan Angle at Virginia Tech [3].

COMPLEXITY OF NITRIDE FORMATION

Initial characterizations of the nitrogen content into the surface of “N-doped” niobium was simply one dimensional. Surface uniformity was assumed. Close examination reveals complexity, however, that may bear on eventual rf cavity performance consistency and limitations.

Nitride structures, principally Nb₂N, on the surface are highly correlated with the host Nb grain orientation. SEM examination correlated with electron backscatter diffraction (EBSD) characterization illustrates that the precipitating nitrides have a preferred orientation with respect to the host niobium grain. As we reported in 2019, we also found that the chemical reactivity of the surface after exposure to nitrogen at high temperature is dramatically different than that of familiar niobium [4], such that exposure to HF removes >1 micron, leaving the nitride crystals exposed on the surface.

Absence of nitrides near many grain boundaries suggests enhanced N migration into the surface which would result in non-uniform N distribution near the surface (Fig. 2). Samples given controlled 5 μm EP reveal apparent nitrides on some subsurface grain faces, raising the prospect of occasional “deep” nitride features remaining if EP removal depth is inadequate. Perhaps this is a contributor to occasional cavity field limitations.

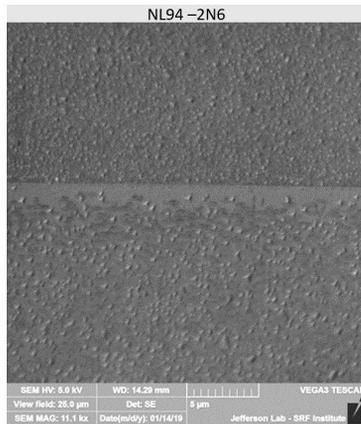


Figure 2: An as-doped Nb grain boundary showing an absence of nitride crystals near one side of the boundary.

VACUUM FURNACE QUALITY EFFECTS ON DOPED SURFACES

The vacuum quality of furnaces used for N-doping can affect cavity surface contamination and also impact nitrogen absorption and effective doping of the eventual rf surface. Controlled samples were co-treated with cavities in several different furnaces, providing one sample “exposed” to the furnace and one “protected” inside the cavity. These samples were then surveyed for residual contamination using a Cameca 7f dynamic SIMS in mass spectrum mode. Exposed Nb surfaces get contaminated with foreign species during 800 °C bake. See example in Fig. 3. (A detailed report is in preparation.) “Caps” used to

cover open cavity ports work well to inhibit evaporative metal accumulation on interior “protected” surfaces.

Significant residual pressure of carbon species at high temperature has the effect of blocking nitrogen absorption, reducing the occurrence of surface nitrides and reducing the resulting interstitial nitrogen concentration. One vendor’s furnace demonstrated the very strong impact that contamination can have on nitride growth and subsurface nitrogen concentration level, as illustrated by the nitrogen and carbon depth profile measurements in Fig. 4.

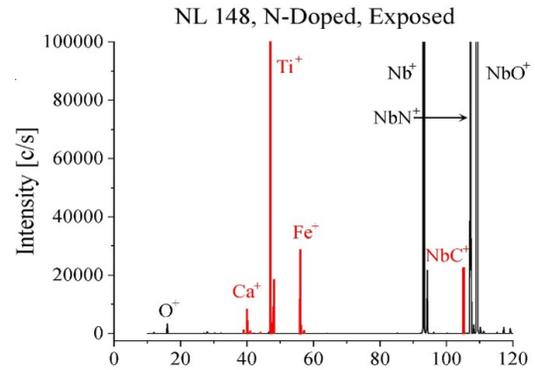


Figure 3: Example SIMS spectra showing Ti and Fe on an exposed sample treated in the JLab furnace.

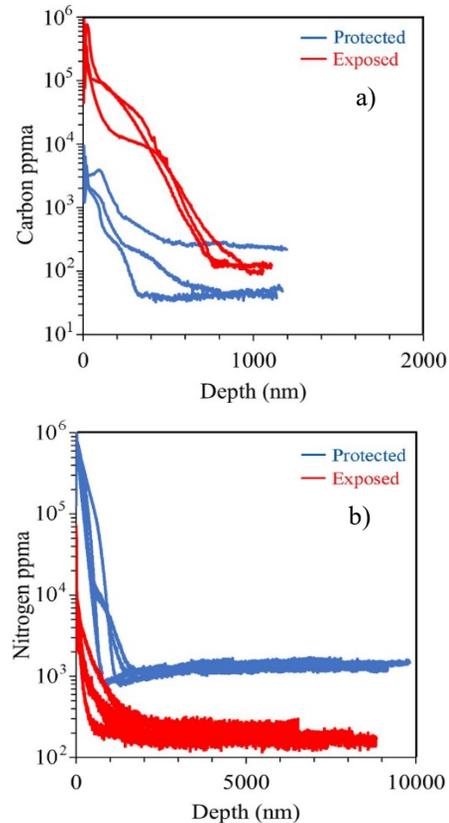


Figure 4: Effect of unusually high furnace contamination on exposed and protected samples. SIMS depth profiles of a) carbon, and b) nitrogen, during a 3/60 N-doping run.

Although not yet quantified, varying furnace quality translates into varying finished N-doping concentrations, so this is a process vulnerability to be carefully addressed.

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VARIABILITY OF N₂ GAS LOAD DURING DOPING

During the doping process, a mass flow controller is used to supply high-purity N₂ gas into the furnace, attempting to sustain a regulated pressure of ~20 mTorr in the furnace chamber during the typically 2 min of gas exposure. Subsequently, the gas supply is terminated and the gas is pumped out. Using careful mass increase measurements, Ari Palczewski quantified the mass of nitrogen absorbed per unit area of niobium during such a 2-minute exposure at 800 °C [5]. The analysis characterized the parabolic growth rate, k_p , of surface nitrides, assuming that only a small fraction of the nitrogen diffuses into the surface.

$$k_p = (\text{mass}_N/\text{area})^2/t = 1.1 \times 10^{-5} \text{ g}^2/(\text{m}^4 \cdot \text{s}) \quad (1)$$

The interior surface area of the ILC/XFEL/LCLS-II 9-cell 1.3 GHz cavities is 0.902 m². With exposure t of 120 s, one finds the expected interior N₂ absorption is 32.8 mg, 1.17×10^{-3} mol, or 7.05×10^{20} N₂ molecules. It is interesting to note that, assuming ideal gas behavior, at 20 mTorr at 800 °C, the cavity volume (0.0243 m³) holds 7.3×10^{-6} mol, so 161 “fillings” of each cavity are required to satisfy the nitrogen absorption target.

To prevent evaporative transmission of furnace materials onto the sensitive interior surfaces, it is standard practice to “cap” the ports of the niobium cavities during their furnace heat treatments. Each production site has its own particular practice for implementing these “caps”, typically involving a combination of bent niobium sheets and niobium foils. For cleanliness, these capping materials receive chemical etching prior to each use. This results in their gradual thinning and eventual need for replacement. If every port is wrapped tightly with foil, the result may be too low conductance for sufficient N₂ gas to enter the cavity to satisfy the intended absorption. The following simplified analysis attempts to set the scale at which process reproducibility will be a concern.

The gas net effusion rate, Φ_N , through an orifice with area A may be characterized by

$$\Phi_N = \Delta P A N_a / \sqrt{2\pi MRT}. \quad (2)$$

Here, ΔP is the pressure differential across the orifice, A is the opening cross-section area, M is the gas molar mass, T is the gas temperature, N_a is Avogadro’s number, and R is the Ideal Gas constant. Initially at least, ΔP is 20 mTorr = 2.67 Pa. $M = 0.028$ kg/mole; $T = 1073$ K. As the pressure in the cavity approaches equilibrium, the mass flow decreases toward zero. If the equivalent orifice size is too small, the cavity will not receive the intended N₂ exposure. The result is a throttling effect on the gas available for absorption by the cavity interior surface.

Figure 5 depicts the maximum N₂ available to the 9-cell cavity interior surface as a function of net effective effusion hole size through the “capped” ports relative to the amount of N₂ that would be absorbed at in 2 minutes at 20 mTorr were there no throttling effect. The blue curve bounds the maximum nitrogen available through this orifice as if the interior were to never develop any pressure,

i.e. instant thorough N absorption. The dashed curve depicts an estimate of the maximum interior surface absorbed N compared with the target intended amount. When this curve is less than one, insufficient N absorption is guaranteed. In this regime, small changes in “capping tightness” result in significant variability of N absorption, which in turn would yield inconsistencies in eventual cavity performance.

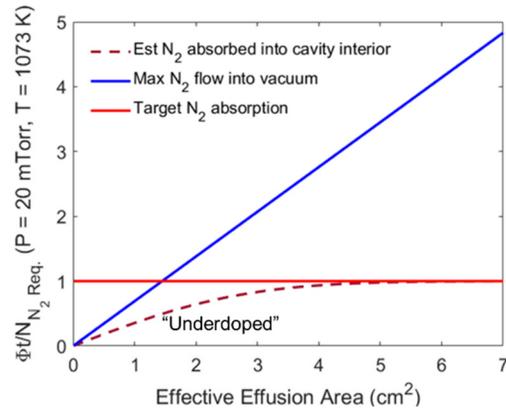


Figure 5: Estimated N₂ absorption reduction with “tight” caps during N-doping.

This simplified analysis is adequate basis for caution against “tight” foil wrap “caps” and suggests confident provision of >4 cm² reproducible effective opening size to the interior of the typical 9-cell cavity in order to avoid having uncontrolled process variability in the nitrogen doping of production cavities. Engineered solid caps with indirect open holes and well-defined generous conductance is recommended. Such were used for the cavities in Fig. 1.

CONCLUSION

The use of nitrogen as an interstitial dopant in surface niobium of SRF cavities is beneficial for reduction of surface resistance. The production processes used to obtain the beneficial surfaces have three challenging aspects addressed here. (1) Surface nitrides grown in complex ways in the near surface, sometimes extend farther into the surface than anticipated. (2) Variability of furnace vacuum quality must be quantified and controlled to realize reproducible doped surfaces. (3) Practical designs for “capping” of cavity ports during “doping” operations must not significantly restrict N₂ gas flow into the cavity as it is absorbed. We note that these challenges are not at issue when the native surface oxygen is used as the interstitial dopant for the same beneficial SRF effect [6-10].

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