

INVESTIGATION OF NITROGEN ABSORPTION AND NITRIDE GROWTH ON SRF CAVITY GRADE RRR NIOBIUM AS A FUNCTION OF FURNACE TEMPERATURE*

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Abstract

The current state of the art processing of niobium superconducting radio frequency cavities with nitrogen diffusion is performed at 800°C in a furnace with a partial pressure of approximately ~20 mTorr of nitrogen. Multiple studies have shown the bulk of the nitrogen absorbed by the niobium forms a thick (1-3 microns) non-superconducting nitride layer which must be removed to produce optimal RF results. The depth profiling of interstitial nitrogen and surface nitrides has already been probed using SIMS measurements for this recipe. These measurements have been successfully modelled by extrapolating data from nitride growth studies performed at atmospheric pressure and temperatures above 1000°C [1]. One open question is whether there is a diffusion-only zone at lower temperature in the ~20 mTorr range in which the niobium will absorb nitrogen but not create a non-superconducting nitride layer; or is the absorption of nitrogen only possible by first forming a nitride buffer layer which then frees up nitrogen for absorption which is what has been shown down to 600°C at atmospheric pressures on long time scales. A systematic study of absorption vs. temperature and correlated SIMS measurements is required to answer this question. We report on measurements of the parabolic rate constant vs. temperature from 400°C to 900°C of cavity grade niobium with metallurgically flat witness samples. Depth profiles of witness samples using SIMS are presented together with SEM imaging for nitride crystals and correlated with N absorption.

INTRODUCTION

In 2012 and 2013 the first two results of surface “doping” on SRF cavities were presented using titanium and nitrogen, showing an unprecedented high Q₀, rising with field [2,3]. First theoretical predictions of such low surface resistance, R_s(B), appeared with distinctly decreasing dependence on surface magnetic field [4,5]. The LCLS-II project embarked on a research program 2014-2015 at FNAL, JLab and Cornell University to take advantage of this new phenomenon.

One of the open questions at the time of this study was whether effective doping of niobium without the need for post-heat-treatment chemistry to remove non-

superconducting nitrides can be obtained. Multiple studies at 800°C and above show non-superconducting nitrides form in the pressure range ~20 mTorr [6,7], and nitride formation at 1 atm can be produced down to 600°C [8].

In this study we performed nitrogen doping of SRF grade RRR niobium from 400°C to 900°C at ~20 mTorr to model the total absorption and compare with previous studies to 600°C to 1000°C at 1atm pressure N₂. Along with the absorption data, secondary ion mass spectrometry (SIMS) depth profiles of nitrogen and scanning electron microscope (SEM) data analysis of the surface for witness samples are shown. The absorption parabolic rate constant calculations, SIMS profiles and SEM images all show nitride growth dominates over the entire temperature range. Ignoring bulk diffusion, our data at 20 mTorr and short time scales matches the approximate slope of Clenney and Rosa’s data, but also shows an order of magnitude lower absorption attributed to the lower pressure in our process [8].

DOPING NB SETUP

Doping was performed on two cavity grade niobium half-cell plates from the Spallation Neutron Source (SNS) stock material manufactured by Tokoyo Denka with a RRR=250. The original stock material measured 3.99 mm thick × 381 mm diameter. The two plates were as manufactured with no additional heat treatment, chemistry or forming before this study.

Before each doping the plates were chemically etched by HF(48%) : HNO₃(60%) : H₃PO₄(85%) = 1:1:1 buffered chemical polishing to remove the doping from the previous run and remove the damage layer before the first run. The amount of removal before each annealing step is shown in Table 1. The runs were performed in the following order: 400°C, 500°C, 600°C, 700°C, 800°C, 900°C, and then a retest at 600°C. The re-run at 600°C was for sample verification and the plate absorption rate did not change for the two runs at 600°C. For each run, the two plates along with a nano-polish fine grain and large grain 10 mm × 10 mm sample were loaded into the furnace. The furnace was pumped down to 2×10⁻⁷ Torr before the heaters were turned on. For all runs except 800°C, the furnace was ramped to 800°C at a rate of 5° C/min and held for 2 hours before ramping down/up at a rate of 5C°/min, held for 10 minutes to stabilize the temperature; then doping was performed. For 800°C, the doping proceeded immediately after the 2-hour run.

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Table 1: Absorption Plate and Sample Doping History

Doping (°C) Temperature	Doping time (min)	Pressure (mTorr)	BCP (µm)	Witness samples
400	20	22	100	UB4 U48
500	20	20-22	60	UB5 U49
600	20	20-25	60	UB6 U50
700	20	20-28	80	UB7 U51
800	10	20-34	100	NA
900	10	20-32	100	UB8 U56
600	20	20-25	100	U71 UB9

ABSORPTION RATE MODELLING

For each furnace run, the pressure profile of nitrogen during the gas injection/absorption was monitored. The outline of the gas injection and how the absorption rate and total gas absorbed from the mass flow controller as well as furnace pressure drop was shown in previous studies at 800C [9,10]. In order to understand if the absorption of the nitrogen is dominated by the nitride growth at lower temperature as it is at 900°C and 800°C at 20 mTorr, we calculated the parabolic rate constant for each temperature and compared it to previous studies done at atmosphere down to 600 C.

We plot the total absorption in a mass balance equation as a function of time to get a parabolic rate constant of the entire system for each temperature. This assumes the nitride desorption and diffusion are very small compared to nitride growth.

$$(k_p)_{total} = \left(\frac{Mass_{N_2}}{Area} \right)^2 \frac{1}{t}$$

Plotting $(k_p)_{total}$ on an Arrhenius plot for different temperature allows a direct comparison to previous studies on nitride growth at atmospheric pressure [8]. Figure 1 shows $(k_p)_{total}$ for three different times; 2, 10, and 20 minutes and the fitted data curve from Clenney and Roses 1980 [8]. To first order, our data at 20 mTorr scales similarly to data taken at atmospheric pressure, but there is a presumably pressure dependence on the data. This suggests that absorption is dominated by nitride growth from 500°C to 900°C at these pressures as well, so nitrides should be found at all temperatures (See SEM below). There is a small slope change which is also present that would suggest another term missing in this simple model besides pressure. For short time scales and lower temperatures the divergence of the three curves is likely due to the resolution of the setup as the absorption is very small.

SEM NITRIDE GROWTH

The furnace absorption data above showed that nitride should be found on all samples from 500°C to 900°C. For this study all polycrystalline witness samples

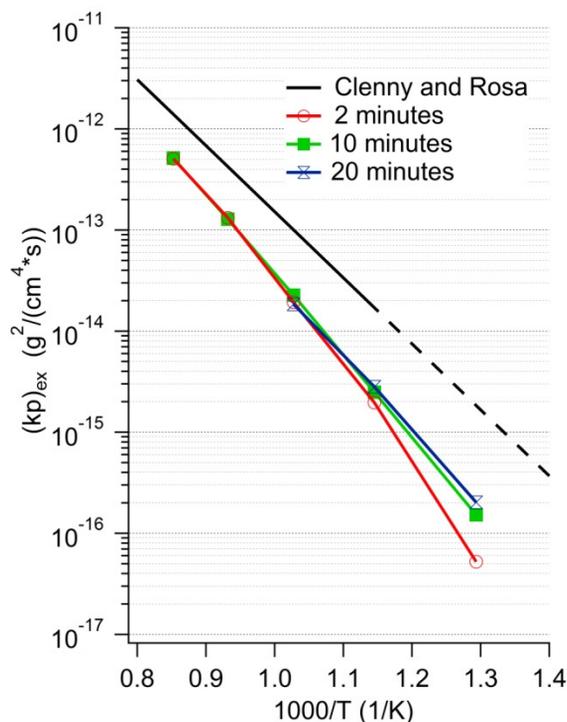


Figure 1: Arrhenius plot of the total parabolic rate constant from the furnace pressure drop data calculated for three different times 2 minutes (red open circles), 10 minutes (green solid squares) and 20 minutes for 500-700°C (dark blue open double triangles). The black line is the 1000°C to 600°C fit data for Clenney and Roses 1980 for 6 hour run at 1 atm parabolic rate constant for nitride kinetics only, the dashed line is the extension of the fit to lower temperature [8].

showed nitride crystal growth on at least one grain orientation after doping, while the all bi-crystal samples at or above 500°C showed nitride growth (not shown). From the bi-crystal as well as single crystals within polycrystalline data there appears to be a correlation between the crystal orientation and the growth of nitrides. The nitride growth and absorption vs. niobium grain orientation will not be addressed here. SEM image examples from the 400°C and 900°C polycrystalline samples are shown in Figures 2 and 3, respectively. The size and spacing of the nitrides change dramatically between the 400°C and 900°C samples. At 400°C the nitrides are very sparse and submicron in size, while the 900°C image has complete surface coverage and microns sized crystals. The 900°C data is consistent with a previous study showing microns sized nitrides at 800°C for a 20 minute doping [7].

SIMS DATA

For each doping, secondary ion mass spectrometry (SIMS) was performed on witness samples examining nitrogen concentration as a function of depth. For the full analysis and experimental details used to create Figure 4 see Tuggle et al. in these proceeding [11].

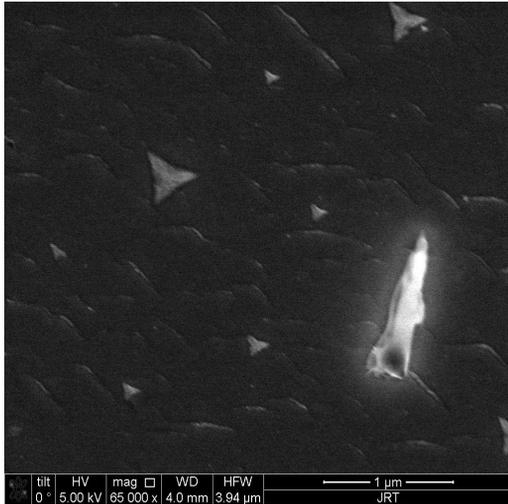


Figure 2: SEM micrograph of surface of 400°C heat treated poly-crystalline witness sample U48, showing sparse and small but visible niobium nitride growth on the surface. The image is within a single grain. The large spike is contamination [11].

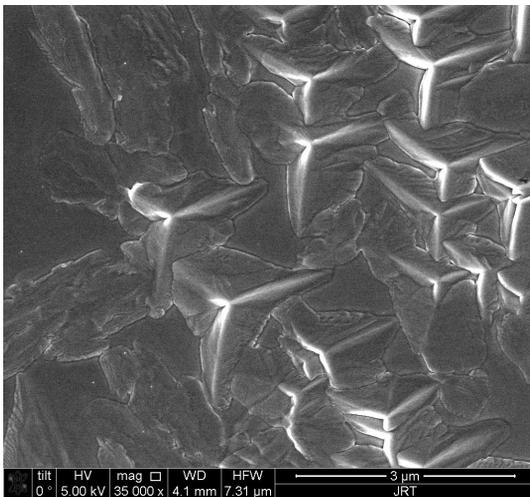


Figure 3: SEM micrograph of 900°C heat treated poly-crystalline witness sample, U56, showing strong nitride growth on the surface.

There are two clear results looking at the SIMS data in the eyes of SEM and absorption modelling:

- Nitride formation and doping are clearly coupled from 400°C to 900°C.
- Good RF results should be able to be obtained down to 600°C as long as the post heat treatment chemistry is done correctly. Below 600°C, the doping appears to be too little with these recipes. The SIMS data are taken over a large area compared to the nitride crystals so the high nitrogen concentration within 1 μm at 400°C, is most likely due to nitrides than to interstitial nitrogen.

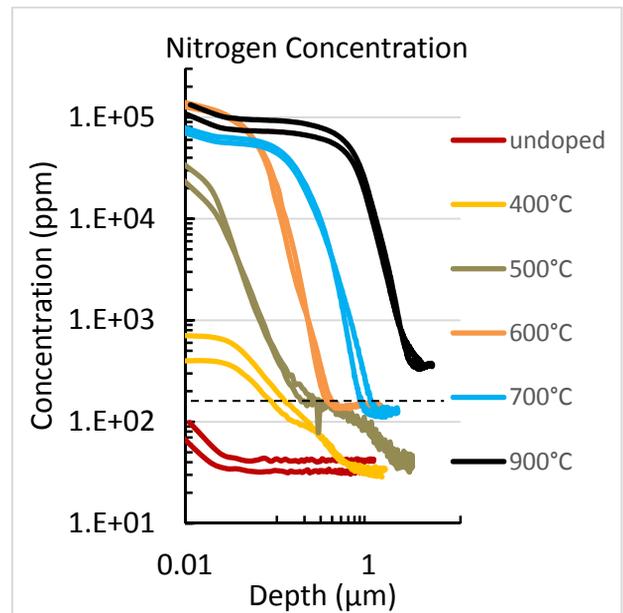


Figure 4: SIMS measurements of polycrystalline samples at 900°C, 700°C, 600°C, 500°C, and 400°C. The approximate LCLS-II doping level after light EP is shown in the dotted line.

SUMMARY

The absorption parabolic rate constant calculations, SIMS profiles and SEM images all show nitride growth dominates over the entire temperature range tested. Ignoring bulk diffusion, our data at 20 mTorr and short time scales matches the approximate slope of Clenny and Rosa's data but also show an order of magnitude lower absorption rate attributed to the lower pressure in our setup [8]. Doping at the target LCLS-II level can be achieved with small modification down to 600°C, but unlikely to be obtained at lower temperatures. Nitride growth appears to be the dominant absorption parameter down to 400°C, so post heat treatment chemistry will always be needed to remove the non-superconducting nitrides to obtain optimal SRF performance.

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