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Investigation of Nitrogen Absorption Rate and Nitride Growth on SRF Cavity Grade RRR Niobium as a Function of Furnace Temperature

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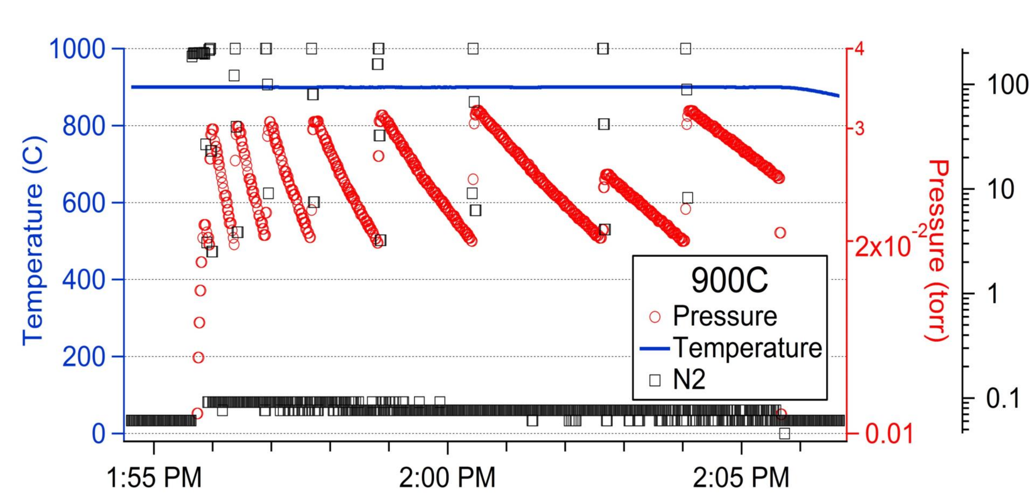
The current state of the art processing of niobium superconducting radio frequency cavities with nitrogen diffusion is performed at 800°C in a furnace with a partial pressure of approximately ~20 mTorr of nitrogen. Multiple studies have shown the bulk of the nitrogen absorbed by the niobium forms a thick (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. 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.

Plate and sample doping history

Temperature during doping (°C)	Doping time (min)	Pressure during doping (mTorr)	Chemical removal before doping	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	20-26	100	U71 UB9

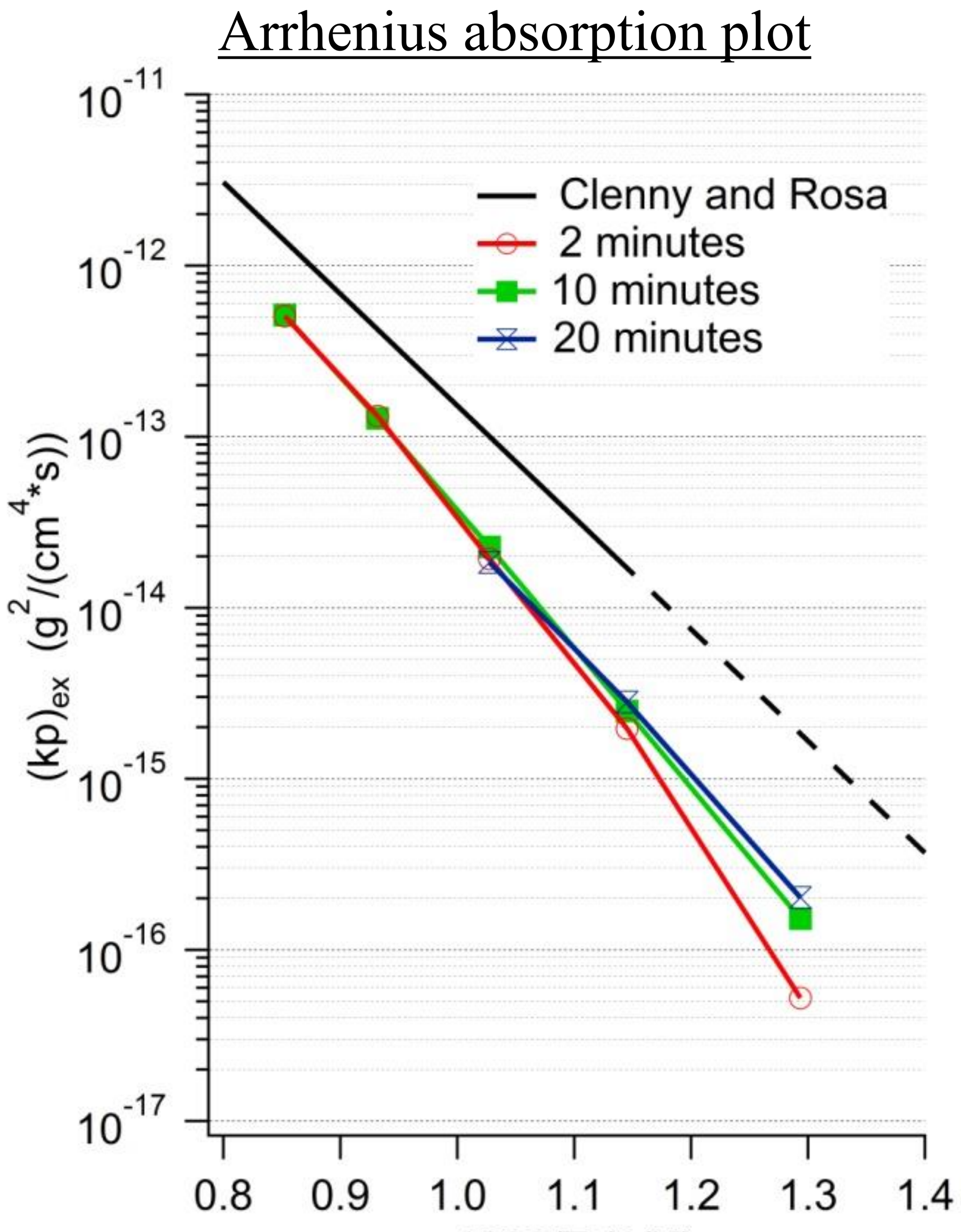
Doping history of plates, the doping is in chronological order from top to bottom.

Example furnace data



Plot of Furnace profile data during the 10 minute nitrogen injection at 900°C doping of the two test plates and samples UB8 and U56. Blue line- temperature; red circles - pressure from convectron gauge, and black circle - gas flow from 200 ccm/min mass flow controller.

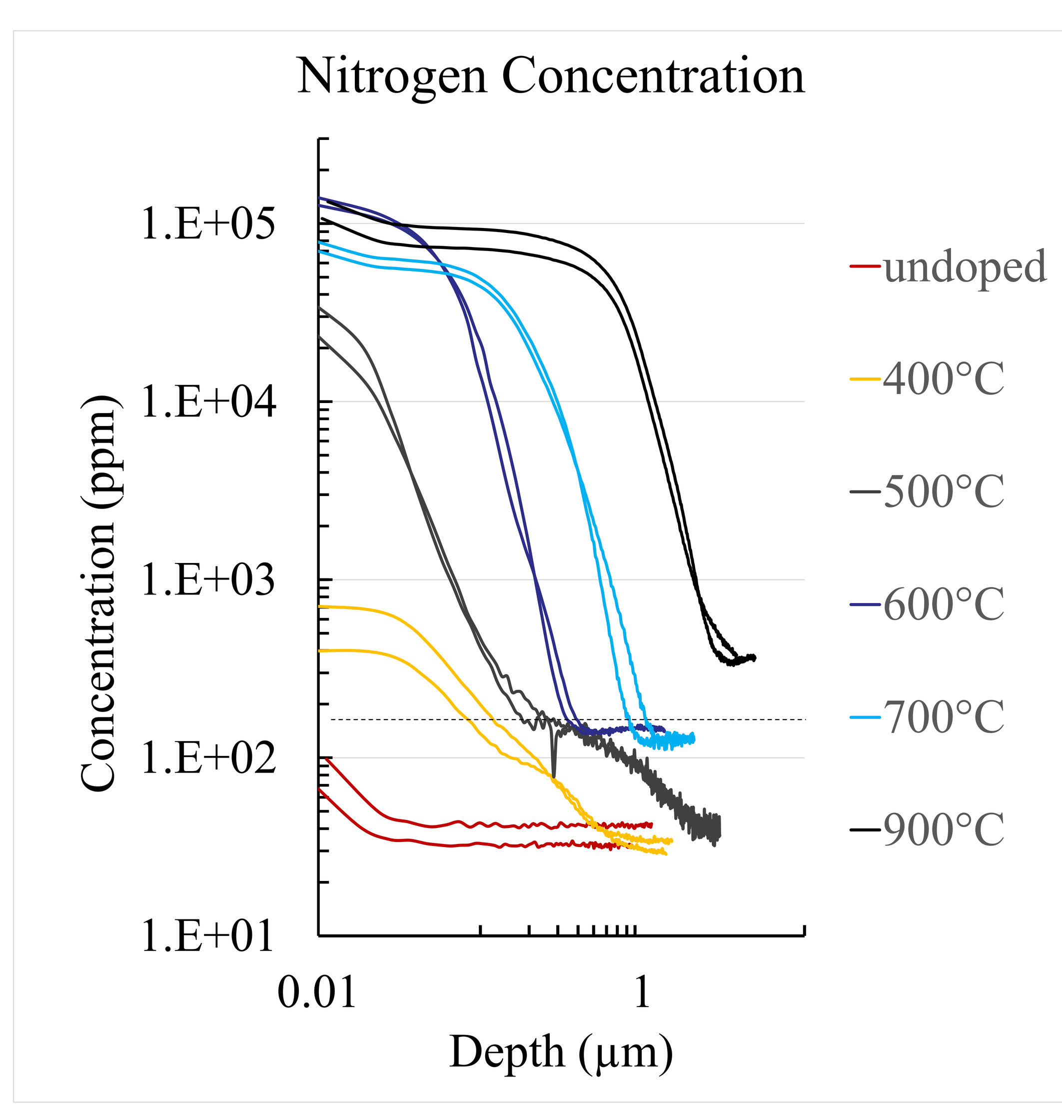
Arrhenius absorption plot



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 .*

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

SIMS measurement



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.

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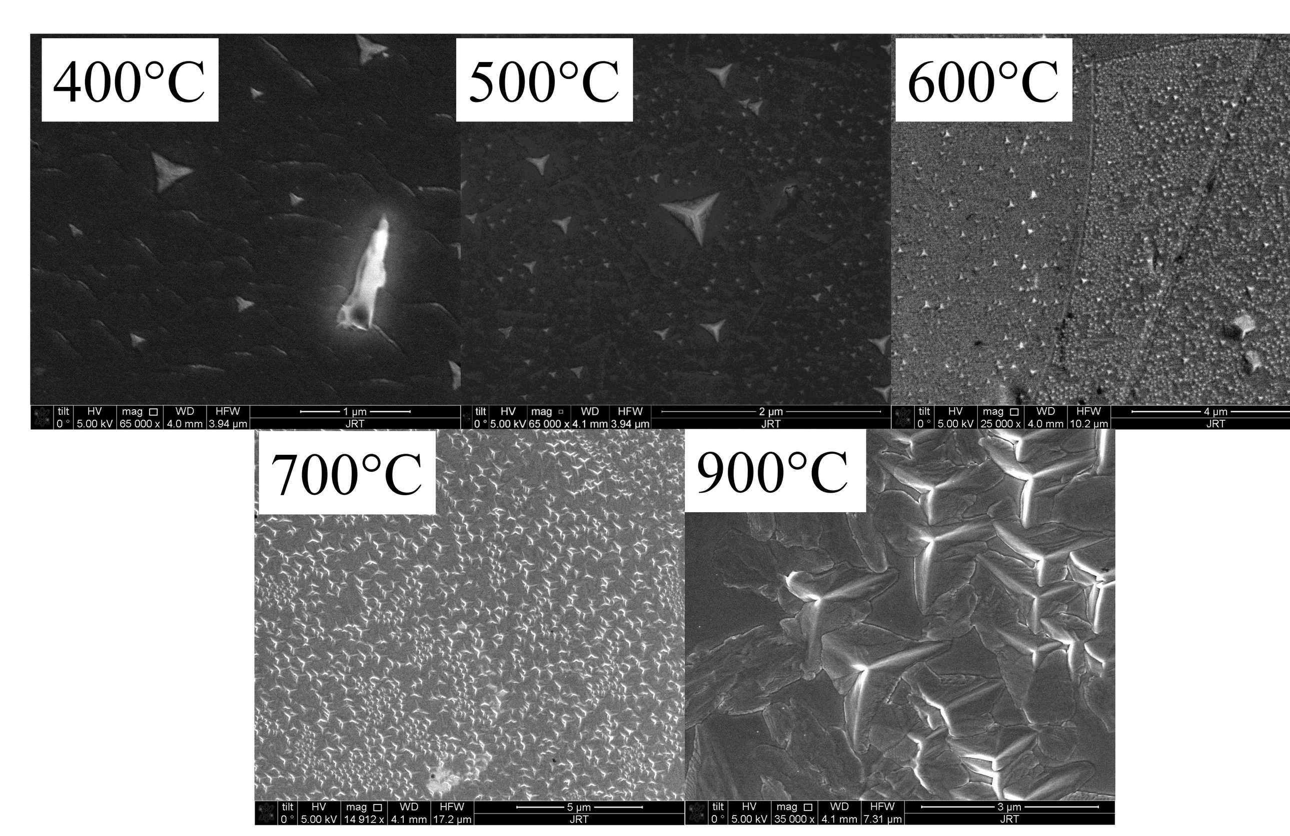
Doping Nb setup

Doping was performed on two cavity grade niobium half-cell plates from the Spallation Neutron Source (SNS) stock material manufactured by Tokoyo Denkai 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.

SEM nitride growth images - polycrystalline



SEM surface images of polycrystalline samples from 400 to 900°C. All samples show nitride growth with the 700°C and 900°C showing nitrides cover the entire surface. - note - not all scales are the same..

Summary

- 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 with these recipes as long as the post heat treatment chemistry is done correctly.
- SIMS at 400°C showing good doping at the surface is most likely due to nitrides than to interstitial nitrogen.
- The absorption data matches the approximate slope of Clenney and Rosa's data but also show an order of magnitude lower absorption rate attributed to the lower pressure in our setup.
- 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.

*J. T. Clenny and C. J. Rosa, "Nitridation kinetics of niobium in the temperature range of 873 to 1273 K", Metallurgical Transactions A **11**, 1575 (1980).