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SIMS INVESTIGATION OF FURNACE-BAKED Nb

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Abstract

Impurity-alloying SRF cavities via thermal diffusion has yielded highly efficient Nb resonators. Recently, SRF cavities vacuum heat treated at 300 – 400 °C for a few hours have exhibited high quality factors and behavior typical of alloyed cavities. Using secondary ion mass spectrometry, we investigated the interstitial concentration of carbon, nitrogen, and oxygen in niobium prepared by this method. Our investigation shows that oxygen is likely the primary diffusant in such recipes and is well-described by Ciovati's model for native niobium oxide dissolution and oxygen diffusion.

INTRODUCTION

Recently, Ito [1] explored vacuum heat treating Nb SRF cavities between 200 °C and 800 °C. After vacuum heat treating the cavities for 3 hours in the temperature range of 300 °C to 400 °C, their RF tests showed a pronounced "anti-Q-slope" (decreasing surface resistance with increasing field), extremely high quality factors, and reduced quench fields, which are all typical qualities previously associated with nitrogen-alloyed Nb cavities. In Ito's work, oxygen diffusion from the native Nb oxide was assumed to be the alloying mechanism. Recent works performed at Fermi National Accelerator Laboratory (FNAL) are extremely similar to the vacuum heat treatments of Ito where cavities were first vacuum heat-treated, in some cases exposed to nitrogen, and RF tested without exposure to atmosphere [2, 3]. FNAL's time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements observed Nb_2O_5 dissolution and a qualitative increase in nitrogen concentration near the surface ~10 nm deep. From these observations it was assumed that nitrogen was the primary alloying diffusant. In both works, the cavities did not require the injection of gases or post heat treatment chemistry to yield the high quality factors.

Our recent SIMS investigation [4] found elevated oxygen content near the surface of samples prepared in the similar way as Ito [1]. RF measurements of a Nb SRF cavity prepared via vacuum heat treatment at 300 °C and subsequently electropolished 180 nm to exclude any ingress of C and N demonstrated that the enhancement in quality factor is mainly due to interstitial oxygen alloying via a thermal diffusion process. The measurements made in [4] found that the thermal diffusion process was consistent with Ciovati's model [5] of Nb_2O_5 dissolution and oxygen diffusion.

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EXPERIMENTAL

Nb samples were prepared following a similar process to Ito [1]. Samples were cut from Tokyo Denkai ASTM 6 Nb stock procured using the XFEL/007 specification. First the stock was vacuum annealed at 900 °C to promote grain growth following the same procedure as the 1.3 GHz single-cell cavity, SC-11 used for RF validation. Samples were first nano-polished (NP) by a vendor to provide sufficiently flat samples for SIMS measurements. After the nano-polish, the samples underwent a 600°C/10hr heat-treatment to remove hydrogen introduced by the mechanical polishing. Subsequently samples underwent a 20 µm cold electropolish with the typical HF/H_2SO_4 solution [6]. During each heat treatment, samples were housed in a double-walled Nb foil container to minimize any furnace contamination [7]. To investigate the parameter space of the diffusion process, samples were baked for various times and temperatures.

A CAMECA 7f Geo magnetic sector SIMS instrument was used to acquire dynamic SIMS measurements. The primary ion beam is comprised of Cs^+ ions with an impact energy of 8 keV. The ion beam is rastered over a 150 ↘m × 150 ↘m area with a data collection area of 63 ↘m × 63 ↘m centered inside the larger raster. Quantitation of the SIMS depth profiles was performed using implant standards [8]. The implant standards used here were dosed with C, N and O at 2×10^{15} atoms/cm^2 at 135 keV, 160 keV and 180 keV, respectively by Leonard Kroko Inc.

Shallow depth profiles found expected background concentrations [9] of C and N, but a large enhancement in oxygen content as shown in Fig. 1. Any ingress of C or N was minor in samples vacuum heat treated at 350 °C for 2.7 hours. In a process of vacuum heat treating Nb without a gaseous oxygen source, the ingress of oxygen is due to oxygen dissolution from the 3-6 nm thick native pentoxide rather than from oxygen pickup from the furnace environment [10-12].An SRF cavity, SC-11, was subjected to a vacuum heat treatment at 320 °C for 1 hour using furnace caps [7] to confirm the effects of O alloying. Afterward, the heat treatment, the cavity underwent a high pressure rinsed before assembly for RF testing. RF measurements for SC-11 are shown in Fig. 2. Prior to O alloying, the cavity was high field Q slope limited. After the O alloying the cavity exhibited a pronounced "anti-Q-slope" with a maximum Q_0 of 4.6×10^{10} at 16 MV/m and

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a quench field of 27 MV/m. This observed "anti-Q-slope" is due primarily to

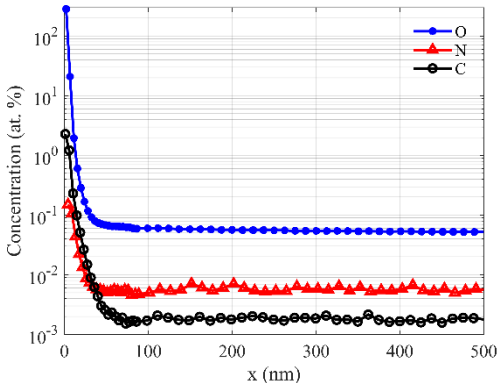

Figure 1: Typical calibrated SIMS depth profile of a sample vacuum heat treated at 350 °C for 2.7 hours presenting a large enhancement in oxygen with minor amounts of C and N.

the interstitial oxygen observed in our SIMS measurements which was confirmed by a cavity that underwent a shallow electropolish to remove any ingress of nitrogen or carbon in [4].

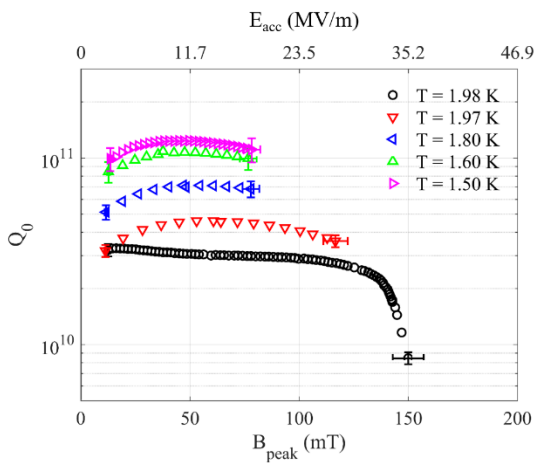

Figure 2: $Q_0(B_{peak})$ measurements for cavity SC-11 after a 40 ↘m electropolish in black and after vacuum furnace heat treatment at 315 °C for 1 hour in blue, magenta, green and red at several temperatures.

PREDICTION OF ALLOYING TIMES AND TEMPERATURES

In [4] we showed that this process is well described by Ciovati's diffusion model for oxide dissolution and diffusion into a semi-infinite slab of Nb. The system is governed by the one-dimensional diffusion equation with a source term of a specific form [5]

$$\frac{\partial c(x,t)}{\partial t} = D(T)\frac{\partial^2 c(x,t)}{\partial x^2} + q(x,t,T). \quad (1)$$

The solution to equation (1) is a linear combination of the solution related to the initial interstitial oxygen concentration $v(x,t)$ as and the solution related to oxygen introduced into the surface via oxide dissolution $u(x,t)$ such that $c(x,t) = v(x,t) + u(x,t)$. The solutions to this system are [5]

$$v = \frac{v_0}{\sqrt{\pi D(T)t}} e^{-x^2/(4D(T)t)} + c_\infty \quad (2)$$

$$u = \frac{u_0}{\sqrt{\pi D(T)}} \int_0^t \frac{k e^{-k(T)s}}{\sqrt{t-s}} e^{-x^2/(4D(T)(t-s))} ds. \quad (3)$$

v_0 is the initial interstitial oxygen concentration near the surface and u_0 is related to the oxygen contribution from dissolution of the oxide layer. The rate constant of oxide dissolution and the diffusion coefficient are assumed to exhibit Arrhenius behavior $D(T) = D_0 e^{-E_{aD}/RT}$ and $k(T) = Ae^{-E_{ak}/RT}$. c_∞ is the background bulk concentration of interstitial oxygen. From [4] the parameters that describe this process are v_0 = 3.5 O at. % nm, u_0 = 200 O at. % nm, E_{aD} = 119.9 kJ/mol, D_0 = 0.075 cm^2/s, E_{ak} = 131 kJ/mol which corresponds to Nb_2O_5 dissolution, and the frequency factor, A = 0.9 ×10^9 1/s. Using these values, the landscape of average O concentration in the first 150 nm of Nb can be calculated as a function of vacuum heat treatment temperature and time as shown in Fig. 3. As with nitrogen alloying, the minimization in surface resistance is observed with similar interstitial oxygen concentrations on the order of 1000 ppm [8, 9].

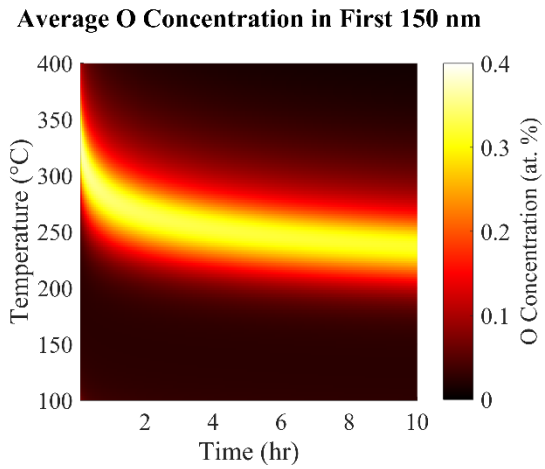

Figure 3: Average oxygen concentration within the first 150 nm colormap using the oxide dissolution and oxygen diffusion values as described in the text.

CONCLUSION

In conclusion, we have shown that the alloying effect observed in the temperature range of 300 – 400 °C for a few hours is primarily assosciated with oxygen impurities in the RF penetration depth. The effects of oxygen impurity alloying has been confirmed in RF measurements. Using the oxide dissolution and oxygen diffusion model of Ciovati we have predicted the sets of times and

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temperatures that should result in an alloying effect using a theory of oxide dissolution and oxygen dissolution.

This oxide dissolution and oxygen diffusion process is an extremely promising development. This process allows for precise tuning of oxygen content by only adjusting the temperature and time the cavity undergoes vacuum heat treatment. Compared to nitrogen alloying (casually known as "doping"), oxygen alloying occurs at temperature where the ingress of other uncontrolled contaminants like C and N is significanty reduced. Furthermore, deleterious phases do not develop upon heat treatment as shown by our RF results after vacuum heat treatment and those in [1, 2]. Unlike cavities subjected to N doping recipes, cavities subjected to O alloying do not require post treatment chemistry. Another benefit is that the oxygen source is already on the cavity. These facts open the possibilitity to alloy cavities of any geometry.

The relatively low temperatures involved for O-alloying also open alloying to structures where 800°C N alloying heat treaments would be prohibitive. Tailored impurity profiles [13] via a complex temperature ramp vacuum heat-treatment, multiple dissolutions, or tuning the oxygen source preanodization [14] may further add to the versatility of this process allowing full tunability of the electron mean free path from clean to dirty limits. This may may be critical for emerging technologies like devices for quantum information systems [15] as well as other applications where the surface interstitials need tuning i.e. thin films [16]. Oxygen alloying related to this work is patent pending under application number 63/189,530.

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