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Unprecedented quality factors at accelerating gradients up to $45 \text{ MVm}^{-1}$ in niobium superconducting resonators via low temperature nitrogen infusion

A Grassellino, A Romanenko, Y Trenikhina, M Checchin, M Martinello, O S Melnychuk, S Chandrasekaran, D A Sergatskov, S Posen, A C Crawford, S Aderhold and D Bice

Fermi National Accelerator Laboratory, Batavia, IL, 60510, United States of America

E-mail: annag@fnal.gov

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Abstract

We report the finding of new surface treatments that permits one to manipulate the niobium resonator nitrogen content in the first few nanometers in a controlled way, and the resonator fundamental Mattis–Bardeen surface resistance and residual resistance accordingly. In particular, we find surface ‘infusion’ conditions that systematically (a) increase the quality factor of these 1.3 GHz superconducting radio frequency (SRF) bulk niobium resonators, up to very high gradients; (b) increase the achievable accelerating gradient of the cavity compared to its own baseline with state-of-the-art surface processing. Cavities subject to the new surface process have more than two times the state-of-the-art $Q$ at 2 K for accelerating fields $>35 \text{ MVm}^{-1}$. Moreover, very high accelerating gradients $\sim45 \text{ MVm}^{-1}$ are repeatedly reached, which correspond to peak magnetic surface fields of 190 mT, among the highest measured for bulk niobium cavities. These findings open the opportunity to tailor the surface impurity content distribution to maximize performance in $Q$ and gradients, and have therefore very important implications on future performance and cost of SRF based accelerators. They also help deepen the understanding of the physics of the RF niobium cavity surface.

Keywords: SRF, nitrogen doping, nitrogen infusion, high $Q$, high accelerating gradient, radio frequency surface resistance

(Some figures may appear in colour only in the online journal)

Introduction

Superconducting radio frequency (SRF) cavities [1, 2] are essential instruments for modern efficient particle accelerators and detectors, enabling progress and discoveries in different fields broadly ranging from particle physics, solid-state physics, material science, quantum computing, biology, medicine, industry and society. As the technology progresses towards enabling higher accelerating fields and/or higher efficiency at different RF fields amplitudes, new and unprecedented machines and detectors are enabled, allowing new scientific discoveries [3, 4]. Progress in achievable accelerating gradients and quality factors of niobium cavities has been driven by intense feedback work between empirical finds and the understanding of the physics of the first tens of nanometers of the niobium cavity surface, where low levels of impurity and defect content are known to play a dramatic role in quench fields, Mattis–Bardeen surface resistance [5].
intrinsic residual resistance and even trapped flux induced residual resistance [6–8].

In this paper we present the first set of measurements that demonstrate how to manipulate RF surface resistance and quench fields in a robustly controlled way via low-temperature doping with nitrogen of the Nb cavity surface.

Cavity surface preparation

Several single cell Tesla-type [9] bulk niobium cavities were used to conduct these studies; these cavities were fabricated out of RRR > 300 ATI Wah Chang and Ningxia 3 mm thick niobium material by different cavity manufacturers as PAVAC Industries (identified as TE1PAV) and Advanced Energy Systems (identified as TE1AES). Only one cavity was made out of large grain material, while the fine grain cavities ranged in grain size from 50 to 500 μm, as some of the material showed significant grain growth as the cavities were treated at high temperature. The treatment history of the bulk niobium of these cavities involves barrel chemical polishing (BCP) and/or electropolishing (EP) as final surface finish. Previous studies [10] had proven that good RF performance and contamination free surfaces could be obtained if cavities are heat treated in a high vacuum (HV) high temperature furnace by taking the precaution of using protective niobium caps and niobium foil on the cavity flanges, as illustrated in figure 1. This is a crucial step for the successful surface preparation, as contaminants such as titanium or carbon (or even nitrogen at high temperature) can reach the cavity surface and cause formation of precipitates and unwanted RF losses if caps are not used. Foil and caps will be successful at shielding only if partial pressure of contaminants in the furnace is low, and an accurate comparison should be done between mean free path of background species and size of the gaps in the caps/foils system.

The cavities are first ultrasonically cleaned and caps are installed in class 100 clean rooms. These protective caps and foils are buffered chemically polished and ultrasonically rinsed prior to every use. The cavities are then transported to the furnace through a class 10,000 area, with caps already installed. The installation sequence of the caps and foils to protect the inner surface from titanium is shown in figure 1. The key point for these studies is that the surface preparation procedure will not involve any electropolishing post furnace treatment, so that we can study the effect of manipulation of impurity content on a nanometric level. Therefore, it is important to ensure surface cleanliness prior to the bake, to avoid ‘baking in’ any potential field emitters or unwanted impurities. The heat treatment is performed in a high temperature HV furnace and involves several steps. The first step is always a hold at 800 °C for 3 h in HV (typical vacuum level base pressure is ~1 × 10⁻⁸ Torr and at high T is ~1 × 10⁻¹⁰ Torr dominated by hydrogen). This step is used for hydrogen degassing, but also for ensuring to break the native Nb₂O₅ oxide and disperse any oxygen coming from it in the bulk. At that point, the surface is naked and clean, and impurities can be introduced at low temperature for studying the effect of nanometer sized impurity layers on the surface resistance. The 800 °C step can also serve more in general as a surface reset [10, 12] for the same cavity treated multiple times, since 800 °C for 3 h will disperse also any nitrogen or other surface defects generated during the previous low temperature bake. This surface reset strategy brings the advantage of avoiding having to electropolish the cavity in between heat treatments, allowing for a true comparison of RF performance as a function of heat treatment and independent of surface morphology. No differences were found if the cavity was reset via EP or 800 °C 3 h in between infusion runs.

After the 3 h at 800 °C, the temperature is lowered to a range of 120–200 °C at which point the cryopumps are shut down and BIP Technology nitrogen from Airgas (99.9999% pure) is injected in the furnace at a pressure of ~25 mTorr. Pressure is maintained via roughing pumps. For some of the treatments we did not inject nitrogen during the second step, for others we included a third step of hold at the same low T but without nitrogen, as it will be explained more in detail in the following paragraphs. Four different examples of furnace treatments are shown in figure 2. Following the heat treatment, the cavity is transported to class 10 clean rooms, high pressure water rinsed and assembled with RF hardware, evacuated and sealed ready for RF vertical test.

Experimental results

Nitrogen versus no nitrogen at 120 °C: a cure for the high field Q-slope (HFQS)

The studies began with a comparison of cavities treated with 800 °C for 3 h in HV, followed by 120 °C for 48 h without nitrogen versus 120 °C for 48 h with 25 mTorr of nitrogen, as shown in figures 2(a) and (b). The treatment with 120 °C with no nitrogen was already studied by Ciovati [11] to attempt to
better understand the role of oxygen in the elimination of the HFQS typically obtained with the standard 120 °C bake (starting from regular oxidized Nb surface) [12]. The idea behind the Ciovati experiment is that if oxygen (or presence of the oxide on the surface) does play a role in the cure of the HFQS, then baking at 120 °C for 48 h in vacuum—after 800 °C breaks up the oxide and fully disperses the oxygen in the bulk—should generate a surface with HFQS. If HFQS

Figure 2. Temperature and pressure data for four different low temperature heat treatments.

Figure 3. Left: effect of nitrogen injection versus HV bake at 120 °C post 800 °C 3 h bake. Nitrogen injection helps to fully eliminate the HFQS. Right: large grain versus fine grain treated with 800 °C 3 h in HV, followed by 120 °C for 48 h without nitrogen, both showing the same onset of HFQS.
would not appear, then the experiment would unequivocally rule out the role of oxygen in the HFQS cure. In the Ciovati experiment the conclusion was that oxygen plays no role, as the results post HV 120 °C bake had shown no HFQS up to quench, which was reached at ∼30 MVm⁻¹ (∼120 mT in tesla shape), while HFQS onset in electropolished cavities systematically manifests at ∼25 MVm⁻¹ (∼100 mT).

The results of our experiment are shown in figure 3. Interestingly, the first finding is that the vacuum 120 °C bake post 800 °C does not fully eliminate the HFQS, as it can be seen in figure 3 for the cavities TE1PAV010, TE1AES011 and TE1AES016 (large grain), but rather shifts its onset up to ∼30 MVm⁻¹ These results can still be in line with the previous findings by Ciovati [11, 12]. One of the two cavities TE1PAV010 plus a different one TE1AES015 were then baked at 800 °C for 3 h, the temperature was then lowered to 120 °C with injection of 25 mTorr of nitrogen for 48 h. As shown in figure 3 (left), the cavities did not exhibit HFQS up to the quench fields of ∼38 and 45 MVm⁻¹ (∼160 and 190 mT). The conclusion from this study is that (a) 120 °C bake post 800 °C (so in absence of oxide) has some effect on HFQS (pushes the onset ∼20% higher), but does not eliminate it completely; (b) 120 °C bake post 800 °C (so in absence of oxide) but in an atmosphere of nitrogen fully eliminates the HFQS. The interpretation of these findings will be discussed in a later section, but they unequivocally reveal that nitrogen does play a role in the elimination of the HFQS. Nitrogen also plays a role in a systematic improvement of Q at mid and high field, as is clear from figures 4 and 5. The origin of the improvement in Q stems from an improvement of both the residual resistance (Rres) and the Mattis–Bardeen surface resistance (RBCS), as a function of field, as it will be shown from the analysis of the surface resistance decomposition as a function of RF field [13], in figure 6.

The 120 °C bake for 48 h in nitrogen pressure was applied to three different cavities. Figure 4 shows clearly the systematic improvement in Q and even accelerating gradients compared to cavities baked with the ‘standard’ 120 °C (post oxidation). This is even more strongly demonstrated in the direct comparison shown in figure 5 where the same cavity is sequentially: (a) treated at 800 °C for 5 d, no EP after furnace treatment (b) standard 120 °C baked (post oxidation) (c) 800 °C baked for 3 h followed by 120 °C in the furnace with 25 mTorr of nitrogen. The sequence for identical morphological surface (no EP in between heat treatments) reveals a clear trend of improvement in Q and accelerating gradients. The 800 °C treatment produces the same results as a regular EP surface—large field independent BCS surface resistance ∼14 nanoOhms (2 K), and presence of HFQS at 25 MVm⁻¹ onset. The standard 120 °C bake cures the HFQS, lowers the BCS surface resistance at low field but makes it highly field dependent, and increases the residual resistance and its field dependence [13]. The 120 °C with nitrogen infusion improves simultaneously the residual resistance and the BCS surface resistance. A comparison of the field dependence of BCS and residual surface resistance for the three different 120 °C bake conditions (standard 120 °C bake, N infused 120 °C bake, oxide free 120 °C bake) are shown in figure 6.

As it can be clearly seen from figure 6 comparison, the improvement in Q with the ‘oxide free’ treatments (120 °C in furnace directly after 800 °C) stems from a reduction of the field dependent residual resistance of about a factor of two. An additional gain is coming from the reduction of the BCS surface resistance especially for the nitrogen infused treatments. It is interesting to note that the field dependent BCS surface resistance increases with field, reaches a maximum and then starts decreasing with field. For the post oxidation 120 °C the peak is reached at ∼20 MVm⁻¹, while interestingly for the nitrogen infused 120 °C bake, the peak moves to the left ∼16 MVm⁻¹.

Summarizing, infusing nitrogen at 120 °C helps (a) to eliminate the HFQS (field dependence of residual resistance in figure 6(b) below), (b) further lowering of the BCS surface

![Figure 4](image1.png)  
**Figure 4.** Effect of nitrogen infusion at 120 °C versus standard 120 °C bake post oxidation.

![Figure 5](image2.png)  
**Figure 5.** Cavity performance results for same cavity subject to different heat treatments. No electropolishing is done in between treatments for direct comparison of effect of surface impurities on same surface topology.
resistance (figure 6(a)), (c) achieving 45 MVm$^{-1}$. As it will be discussed later, the enhancement of the maximum accelerating gradient might be consequence of the nitrogen-enriched layer present in the first tens of nanometers, in agreement with some theoretical models of dirty layer on clean superconductor \[14, 15\].

**N infusion for longer time and higher temperatures: the $R_{BCS}$ field dependence reversal**

The effect of the low temperature nitrogen treatment becomes even more pronounced as time duration at 120 °C is increased or as temperature is increased to 160 °C and above, showing the typical anti-$Q$-slope behavior of nitrogen doped cavities \[6, 16\]. This is consistent with nitrogen diffusing deeper in the surface and will be discussed in a later section. In figure 7 we show a comparison for four different 120 °C conditions: (a) for 48 h in HV post 800 °C 3 h in HV; (b) for 48 h with 25 mTorr of nitrogen, post 800 °C 3 h in HV; (c) for 96 h with 25 mTorr of nitrogen, post 800 °C 3 h in HV (d) standard 120 °C bake post oxidation. It is interesting to see how the $Q$ curve (figure 7) and the BCS surface resistance (figure 8) change dramatically with only doubling the exposure time to nitrogen at 120 °C.

120 °C bake post oxidation. It is interesting to see how the $Q$ curve (figure 7) and the BCS surface resistance (figure 8) change dramatically with only doubling the exposure time to nitrogen at 120 °C, which would seem to indicate that the impurity that causes the antislope behavior is diffusing on the order of tens of nanometers. A premature $Q$-slope starting at 13 MVm$^{-1}$ is also found, reminiscent of HFQS behavior, or of the behavior of overdoped cavities.

Figure 9 shows another interesting comparison: for exact same cavity, identical surface topology, but only different surface impurity content as dictated by the sequence of heat treatments (where the 800 °C 3 h in HV each time resets the surface state), we can see that 160 °C for 48 h with nitrogen
causes the reversal of the medium field $Q$-slope. This is confirmed by the surface resistance decomposition (figure 11) showing the typical reversal of the BCS resistance. Its value appears to be the one of a typical doped cavity (close to somewhat underdoped as it decreases only from 7 to $\sim$6 nanoOhms, while typical ideally doped values show a decrease from 7 to $\sim$4.5 nanoOhms). However, a $Q$-slope appears at higher fields. In appearance it seems similar to HFQS with a higher onset, however from the decomposition analysis shown in figures 11 and 12, we notice something very interesting and new: the high field slope appears in the BCS surface resistance, rather than in the residual. The standard HFQS of regular EP cavities typically appears in the residual resistance [13]. Further studies will be done in the future with T-map to understand the pattern and therefore originate of these high field losses.

The same cavity was then baked at 160 °C for 48 h with nitrogen but then followed by 96 h with no nitrogen, with the idea to create a deeper and less steep nitrogen impurity profile. As it can be seen from figures 10 and 11, the BCS surface resistance now approaches fully that of ideally N doped cavities (decreasing from 7 to 4.5 nanoOhms), but the $Q$-slope with 30 MV/m onset is again present and actually steeper than in the 160 °C for 48 h case. Another cavity, shown in figure 10, TE1AES011 was baked in an intermediate way—at 160 °C for 48 h with nitrogen followed by 48 h with no nitrogen—and this cavity reached the highest fields without steep $Q$-slope, reaching $Q$ values $>3 \times 10^{10}$ at 2 K up to 32 MV/m, and above $2 \times 10^{10}$ up to 38 MV/m (quench limited in presence of x-rays). Then, when the same cavity was baked just 10 °C higher—at 170 °C for 48 h with nitrogen followed by 48 h with no nitrogen—the obtained quench field degraded significantly from 38 to $\sim$28 MV/m (with no field emission present at 28 MV/m quench). In both cases impressive $Q$ values were reached at mid field approaching $5 \times 10^{10}$ at 2 K, 20 MV/m. A difference can be found in BCS surface resistance: for the 160 °C case, the BCS surface resistance approaches unprecedented values of $<2$ nanoOhms for 1.3 GHz, 2 K, $>20$ MV/m accelerating fields.

A large grain cavity was also baked together with TE1AES011 with the 170 °C recipe. As shown in figure 10, this cavity reached the highest $Q$ out of all cavities, a record for 1.3 GHz cavities $Q \sim 6 \times 10^{10}$ at mid field, 2 K. This is an interesting data point, as impurity diffusion could be assisted by grain boundaries and should be therefore different for fine grain and large grain cavities. Interestingly the large grain cavity resembles in RF performance the fine grain cavity baked for 96 h at 120 °C, with a very steep antisolpe and high $Q$ achieved at mid field, but a premature onset of $Q$-slope. The trapped flux sensitivity [8] was also studied for these 170 °C baked cavities and found to match the values of high temperature doped cavities treated with 2/6 min plus EP5 protocol (which produces light doped surfaces in the 100–200 nm mfp range) [8, 16–18].

Another treatment was done at the higher temperature 200 °C for 48 h with nitrogen. As shown in figure 10, the curve at 2 K appeared like a regular EP curve, however from the decomposition in figure 11 one could see that the BCS surface resistance was low, while the residual resistance was very large, origin of which is unknown.

**Nitrogen versus no nitrogen injection at 160 °C**

During the gas injection period the cryopumps are shutoff and therefore the partial pressure of other gases as oxygen, carbon, hydrogen rises significantly. These gases will be also absorbed by the cavities. Therefore, to ensure that the effect of the reversal of the BCS surface resistance arises truly from nitrogen, two cavities were reset and baked with identical procedure, 800 °C first, then 160 °C for 48 h, clean BCP’d caps and foils, with the difference that rather than injecting ultrapure nitrogen, ultrapure argon (25 mTorr, 99.9999% purity) was used. The results are shown in figure 12, showing...
a comparison of same treatment (duration and temperatures) but different gas injected (nitrogen versus argon). The 2 K curves of the argon treated cavities did not show anti-$Q$-slope and actually the performance was somewhat substandard compared to a regular EP cavity. The decomposition in BCS and residual resistance show a very large BCS resistance $\sim 14$ nanoOhms, about three times larger than that of doped cavities. A larger than typical residual resistance was also found, about three times of when the cavity was treated with nitrogen instead of argon. In contrast to the results claimed by the Cornell SRF group in [19], the results unequivocally prove that nitrogen is the key element generating the dramatic improvement in performance, in particular the peculiar reversal of the field dependence of the BCS surface resistance.

**Sample analysis via SIMS, FIB/TEM and discussion**

Samples treated together with the cavities at 120 °C 48 h and 160 °C 48 h versus a reference unbaked samples were analyzed with the TOF-SIMS technique at both IONTOF and FNAL. Two 160 °C samples versus two reference and one 120 °C samples were analyzed. Modern TOF-SIMS with optimized sputtering/analysis conditions has better than ppm level elemental sensitivity, as well as nanometer depth resolution. Results are shown in figure 13, where a relative comparison of non-baked, doped at 120 °C and doped at 160 °C can be seen. The x-axis is sputtering time, and for reference the Nb$_2$O$_5$ layer is plotted in each graph, to give a sense of the magnitude of depths. The RF layer where supercurrents flow is underneath the oxide and concentrations of impurities right under the oxide are of interest for RF performance—in the few to tens of nanometers. Some interesting conclusions can be drawn from these measurements. In figure 13(a) the NbN signal (blue unbaked versus black 120 °C versus red 160 °C) shows that nitrogen concentration is increasing at the surface accordingly to the temperature increase of a factor of 10–20 compared to un-doped background, right underneath the oxide layer.

The factor of 10–20 over nitrogen background is exactly what has been shown to give the doping effect for the high temperature doping treatments [20, 21], so this result agrees with the nitrogen doping effect as it was previously known. The difference stays in the fact that with the low T treatment the nitrogen-enriched layer is just few-tens nanometers deep, versus microns for the high T treatments. The fact that 120 °C 48 h with N$_2$ (which does not lead to anti-$Q$-slope) versus 160 °C samples differ in nitrogen concentration just in the first few nanometers, gives yet again a sense of how important the first nanometers underneath the oxide layer are for RF performance, in agreement with previous HF studies in [7].

**Figure 11.** Comparison of field dependence of BCS and residual surface resistance for all the different heat treatments in the range 160 °C–200 °C, referenced to standard 120 °C bake post oxidation.

**Figure 12.** Comparison of argon versus nitrogen treated cavities, injected for 48 h at 160 °C. Nitrogen is the key element causing the improvement in performance.
Figure 13. TOF-SIMS profiles for (a) nitrogen, (b) oxygen, (c) Nb$_2$O$_5$ and NbO$_2$ (d) carbon for unbaked, 120 °C and 160 °C doped samples.

Figure 14. TOF-SIMS profiles for samples treated at 160 °C with 25 mTorr of argon versus nitrogen.
From the other SIMS measurements, we notice also some other interesting differences: in figure 13(c) the 160 °C sample shows (systematically for both samples analyzed) a thinner oxide Nb₂O₅ (and also NbO₂ signal) of about half the depth compared to the un-doped and 120 °C case. This is a potentially very interesting finding, as it may be revealing that the improvement in performance via N doping/infusion may stem in part from the growth of a different, better quality oxide thanks to the presence of a certain needed concentration of nitrogen at the surface. This may be similar to what is observed in semiconductors applications, where the growth of wet versus dry oxides plays a crucial role in performance of microelectronic devices. However, there is no difference in oxide 13(c) nor oxygen content 13(b) for the 120 °C versus non-baked sample, eliminating any role of oxygen in the removal of the HFQS and pointing to the cure of HFQS with this new process coming from the presence of interstitial nitrogen underneath the Nb₂O₅ layer. In terms of oxygen and carbon we can observe that both show a stronger signal increasing with the temperature. In particular, oxygen shows no difference between un-doped and 120 °C, but stronger presence in 160 °C as O⁻ ion, however NbO₂ signal shows a lower tail compared to 120 °C and un-doped. Carbon signal does increase accordingly to temperature, leaving some possibility that carbon may play a role in modification of RF performance.

Figure 15. TEM images of samples treated at 800 °C with and without infusion. Precipitates at grain boundaries are found.
We therefore studied additional samples baked with the cavities treated at 160 °C with argon instead of nitrogen, which had shown poor RF performance (figure 12). SIMS results of these samples are shown in figure 14. We can see that large concentration of oxygen and carbon is present also in this case, but no nitrogen, therefore ruling out role of oxygen and carbon in improvement of RF performance. Actually, combined with the cavity results of figure 12, these results point towards interstitial carbon in the absence of protective Nb box.

Further studies of 800 °C baked, 120 °C and 160 °C infused samples with different surface techniques are ongoing, and some results are shown in figure 15, via TEM. As it can be seen, interestingly some precipitates at grain boundaries are found, of the order ∼ hundreds of nanometer size and depth. Even in the case of samples protected by line of sight (bake in protective Nb box), precipitants are found at grain boundaries at some depths from the surface. Further studies will be performed on the origin of these precipitates, but preliminary XRD results indicate they are niobium carbides. The origin of these carbides is currently under investigation, but it is expected to affect negatively cavity performance. So perhaps the presence of nitrogen helps binding carbon and reducing the size and number of carbide precipitates. In absence of nitrogen, carbides could be larger and cause larger residual resistance or lower quench fields. It is possible that if one could really obtain a pure nitrogen diffusion and no other contaminants (e.g. no carbon), then cavity performance could be boosted further.

Conclusions

The presented studies have shown for the first time a method to obtain a controlled layer of nanometric size enriched with nitrogen. The nitrogen infusion treatment at 120 °C has proven to remove the HFQS and give for the first time very high $Q$ at very high gradients up to 45 MVm$^{-1}$. Increasing duration and temperature leads to the reversal of the BCS surface resistance and outstanding values of quality factors at mid to high fields up to $6 \times 10^{10}$ at 2 K for 1.3 GHz cavities. Further studies are ongoing, exploring other temperatures and partial pressures of nitrogen, in feedback with SIMS studies, in search of a better optimum for cavity performance in terms of N enriched surface nano-layer.

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