UPDATE ON NITROGEN INFUSION SAMPLE R&D AT DESY

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Abstract

Many accelerator projects, such as the European XFEL cw upgrade or the ILC, would benefit from cavities with reduced surface resistance (high Q-values) while maintaining a high accelerating gradient. A possible way to meet the requirements is the so-called nitrogen-infusion procedure on Niobium cavities. However, a fundamental understanding and a theoretical model of this method are still missing. The approach shown here is based on R&D using small samples, with the goal of identifying all key parameters of the process and establishing a stable, reproducible recipe. To understand the underlying processes of the surface evolution that give improved cavity performance, advanced surface-analysis techniques (e.g. SEM/EDX, TEM, XPS, TOF-SIMS) are utilized and several kinds of samples are analyzed. Furthermore, parameters such as RRR and the surface critical magnetic field denoted as H_{c3} have been investigated. For this purpose, a small furnace dedicated to sample treatment was set up to change and explore the parameter space of the infusion recipe. Results of these analyses and their implications for the R&D on cavities are presented.

NITROGEN INFUSION IN A DEDICATED SAMPLE FURNACE

The so-called "Nitrogen Infusion" [1] process applied to 1.3 GHz TESLA-type cavities was reported to achieve higher Q-values compared to the standard surface treatments as shown in Fig. 1. The recipe consists of a heat treatment at 800°C for 3 h under vacuum conditions typically ~10^{-7} mbar followed by a ramping down to 120°C. During the hold time of 48 h at 120°C a partial pressure ($3.3 \cdot 10^{-2}$ mbar) of nitrogen is applied. The reproducibility among other laboratories has proven difficult so far since it is very sensitive to furnace cleanliness. It is our goal to find the key parameter for a stable and reproducible recipe. An extensive sample study with a dedicated sample furnace as shown in Fig. 2 is carried out and the results are presented here. The furnace has a ceramic tube with a diameter of 80 mm. A Residual Gas Analyzer (RGA) and a mass-flow controller for nitrogen inlet are installed. The maximum achievable, stable temperature is 1350°C. The pump system saturates at an end pressure of $p < 5 \cdot 10^{-8}$ mbar at room temperature. The furnace has been setup for explicit nitrogen-infusion studies on niobium samples. Data from the RGA during a nitrogen infusion is shown in Fig. 3.

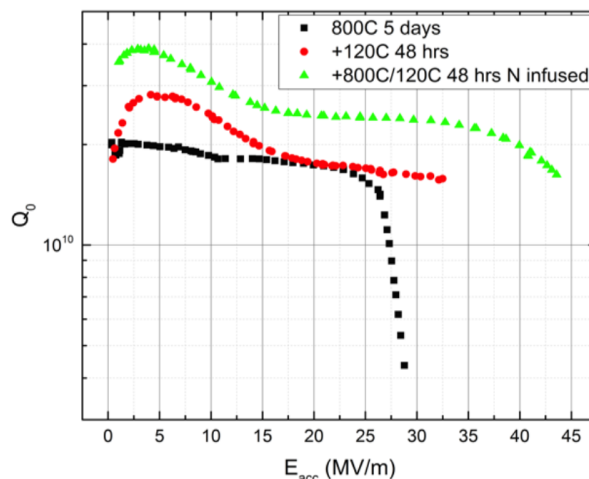---

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Figure 1: Q vs. E comparison between nitrogen infusion and standard EP-treated cavities [1].
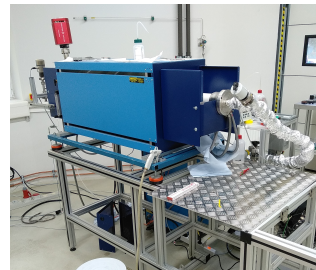

Figure 2: Image of the small sample furnace.

RESIDUAL RESISTIVITY RATIO (RRR)

RRR is the ratio of electrical resistance $\rho(T)$ at room temperature to the residual one at 4.2 K: RRR $= \frac{\rho(295\,\text{K})}{\rho(4.2\,\text{K})}$. However, since for niobium $T_c = 9.2$ K the RRR at nearly 9.2 K is used or extrapolated down to 4.2 K. As the phonon-electron interaction can be neglected for very low temperatures (but above 4 K), the electrical resistivity then starts to depend only on impurities and lattice defects. The higher the RRR, the fewer defects and interstitials in the material. Thus the RRR characterizes the purity of a metal and is sensitive to changes in impurities due to diffusion during treatments such as heat treatments in vacuum or under certain gas atmospheres and after chemical surface treatments. Therefore, this parameter is particularly interesting for niobium cavities and especially treatments such as nitrogen infusion, which will be discussed in more detail in the following chapters.
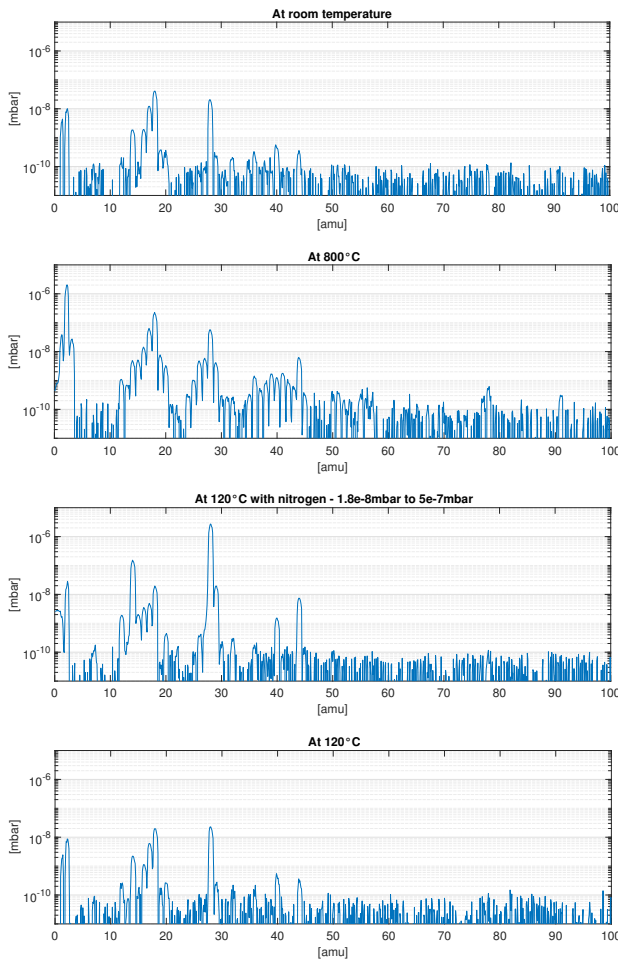
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Figure 3: Residual Gas Analysis (RGA) spectrum at different steps during a 120°C nitrogen infusion run. To protect the RGA the measurement was done at $5 \cdot 10^{-7}$ mbar with nitrogen.

A 4-pt-contact method was selected to investigate the influence of nitrogen infusion on the RRR value of samples. A total of 10 fine grain (50 μm grain size) niobium samples were used, 5 of which were subjected to a nitrogen infusion in a temperature range between 120°C and 400°C. This means that there is a temperature cycle with a ramping up to 800°C for 3 hours under vacuum, subsequently brought down to the desired temperature (120°C – 400°C) for 48 hourss, during which nitrogen is introduced ($3.3 \cdot 10^{-2}$ mbar). The remaining 5 samples are subjected to the same temperature treatment, but without nitrogen, i.e. under permanent vacuum.

The samples are fine grain samples made of niobium from the manufacturer Tokyo Denkai which were cut to a size of (2.88 x 3 x 42) mm. The first step in this process was to BCP the samples for 20 minutes to remove the damage layer on the surface and clean it from any remaining residue. They were then cleaned in an ultrasonic bath and rinsed with deionized water. Two of the samples were measured at this point to find out how much the RRR value changes when baking at 800°C.

The next step was to bake at 800°C in a vacuum ($<10^{-7}$ mbar) for 3 hours in the sample furnace. The two samples that were measured before baking were now measured again and the results are shown in Table 1. The RRR value before and after the 800°C treatment remained unchanged within the measurement uncertainty. Furthermore, the RRR for the remaining samples were also measured at this point. To clean the surface, the samples were then treated again with a short BCP of about 2 minutes and cleaned in an ultrasonic bath and rinsed with deionized water. The samples were then treated with the baking cycle described above, 5 samples each in vacuum and 5 with a nitrogen atmosphere ($3.3 \cdot 10^{-2}$ mbar) at the infusion temperature after the hold at 800°C. The

Table 1: RRR(at 9.2 K) values from two fine grain samples measured by the 4 pt method. Errors are 68% confidence level.

RRR(before 800°C)	RRR(after 800°C)	ΔRRR
275 ± 6	281 ± 5	5 ± 7
288 ± 6	293 ± 6	5 ± 8

results from the RRR measurements for different infusion temperatures are summarized in Table 2. The change in RRR from before to after the infusion heat treatment is denoted as $\Delta RRR = RRR_{before} - RRR_{after}$.

Table 2: RRR(at 9.2 K) values from fine grain samples measured by the 4-pt method. Errors are 68% confidence level.

Inf T	RRR(before)	RRR(after)	ΔRRR
400°C w N	295 ± 4	252 ± 4	−43 ± 5
330°C w N	296 ± 4	247.4 ± 2.6	−48 ± 5
260°C w N	289 ± 5	238.6 ± 2.9	−50 ± 6
160°C w N	296 ± 8	259 ± 5	−37 ± 9
120°C w N	293 ± 6	265.7 ± 1.9	−28 ± 6
400°C w/o N	304 ± 6	274 ± 5	−30 ± 8
330°C w/o N	288 ± 5	253 ± 6	−34 ± 8
260°C w/o N	293 ± 7	256 ± 5	−37 ± 9
160°C w/o N	292 ± 6	256 ± 5	−36 ± 7
120°C w/o N	281 ± 5	248 ± 4	−32 ± 6

We will make the assumption that with the "Infusion" treatment without Nitrogen (i.e. the same temperature cycle as with the nitrogen infusion but in a vacuum), the change in the RRR value mainly takes place through processes of contamination within the sample. Furthermore, we make the assumption that these same processes take place with the "actual" infusion with nitrogen in addition to the penetration of nitrogen into the surface. It should be possible to make statements about the pure nitrogen process by comparing these two RRR changes. In Fig. 4 we show the change in ΔRRR between before and after the treatment without nitrogen compared to the samples treated with nitrogen.
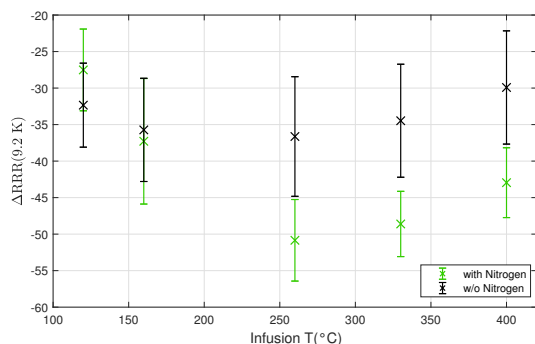
Figure 4: Difference $\Delta RRR(9.2\,\text{K}) = RRR_{\text{treated}} - RRR_{\text{untreated}}$ between before and after infusion treatment of the samples. Errorbars are 68% confidence interval. The infusion treatment was done with Nitrogen (green points) and under Vacuum (black points) respectively with the on the x-axis shown infusion temperature.

If we assume an ideal vacuum and an absolutely pure nitrogen atmosphere, then it would be expected that the change between treatment with nitrogen and treatment without nitrogen in the ΔRRR would be reduced as the infusion temperature is reduced, as less and less nitrogen would diffuse into it. However, we note that the change is maximal at 260°C. This suggests that other processes take place in addition to the nitrogen diffusion.

SURFACE COMPOSITION FOR 400°C N INFUSION

To detect a nitrogen signal with Secondary ion mass spectrometry (SIMS) in niobium samples after a N infusion could help to understand to what extent the nitrogen content plays a role. Measurements on three samples are shown in Fig. 5.

The fine grain sample 3 received electropolishing (EP) for 4 h as a pre-treatment. The fine grain sample 36 received a cavity like pre-treatment consisting of EP for 4 h, 800°C annealing in vacuum for 3 h, a second EP for 1 h and 120°C annealing in vacuum for 48 h. The large grain sample 95 received a BCP. A small niobium box that received BCP and was pre-fired to 1000°C in vacuum, was used (except for sample 3) to cover the sample to protect the sample surface against particle contamination from the oven surface in the line of sight (LOS) [2]. This helped to prevent carbide precipitation observed on samples that were 800°C baked in a hydro-carbon contaminated furnace. Since we are interested in purely interstitial dissolved nitrogen in niobium, we decided on a maximum temperature of 400°C to avoid any Nitrogen precipitation.

- Sample 3: No nitrogen Signal; High oxygen signal → Vacuum leak suspected during this treatment; No LOS protection was used;
- Sample 95: Some parts of a underlying niobium sheet went blue during the infusion → Oxygen residues in nitrogen line are suspected; However, oxygen signal no-

ticeably smaller and for positive ions only → again no nitrogen signal; no visible precipitates on SEM images;
- Sample 36: Best vacuum conditions of the sample furnace so far for this treatment; A nitrogen signal is present;

Two reasons are the main suspects why no nitrogen was measured for sample 95: On the one hand the oxygen residues which passivated the surface for the infusion process; on the other hand the fact that the diffusion in niobium is dominated by diffusion along grain boundaries. Sample 95 is a large grain sample which had no grain boundary on the whole sample. Sample 36 is a fine grain sample, providing a better diffusion potential for nitrogen.
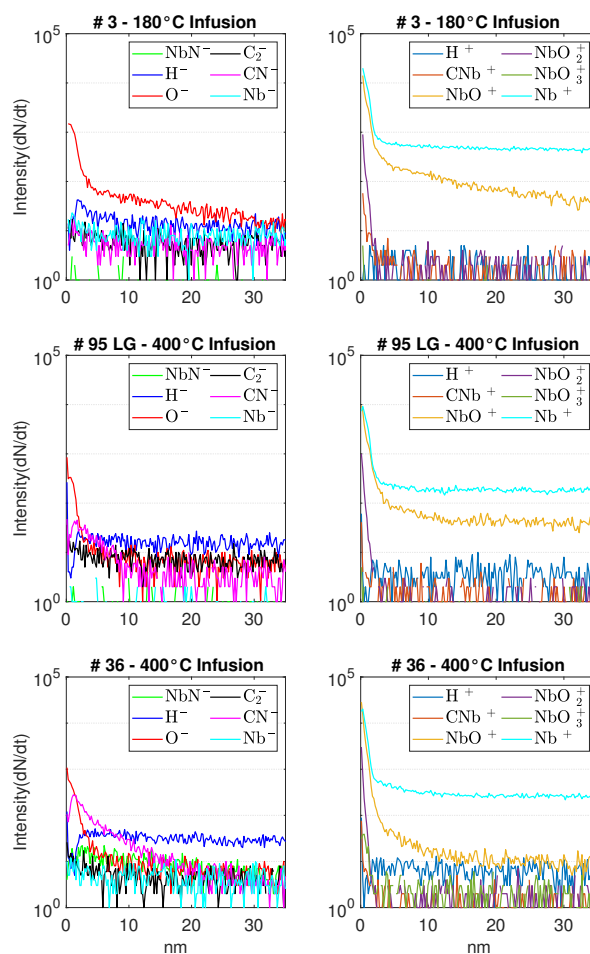

Figure 5: SIMS data of niobium samples that have been nitrogen infused in the sample furnace. Counts per second vs. depth are shown. Sample 3 and 36 are from fine grain (∼50 m grain size, RRR 300) and 95 from large grain (grain size several cm, RRR 500) material. Sample 95 was cut from of a single grain.

SURFACE CRITICAL MAGNETIC FIELD H_{c3} BY SQUID

It was shown that superconductivity nucleates at a metal-insulator interface in a parallel field H_{c3} which is higher

than H_{c2} by a factor r where $r_{GL} = 1.695$, according to the Ginzburg-Landau theory [3]. AC-susceptibility measurements of niobium samples with a superconducting quantum interference device (SQUID) were carried out to observe the dependence of surface treatments on H_{c3}. With the help

Table 3: Provided samples(all fine grain with RRR~ 300) for SQUID measurements. Sample U is a raw untreated sample.

Sample	Chem.	Pre-Anneal	Last
60	BCP	✗	N-inf.
65	EP	800°C(3 h)	✗
67	EP	800°C(2 h) + 120°C(48 h)	N-inf.
62	EP	✗	✗
U	✗	✗	✗

Table 4: Obtained values for the surface nucleation field H_{c3} from susceptibility measurement. An error of roughly ±50 mT is estimated for the determination of H_{c3}.

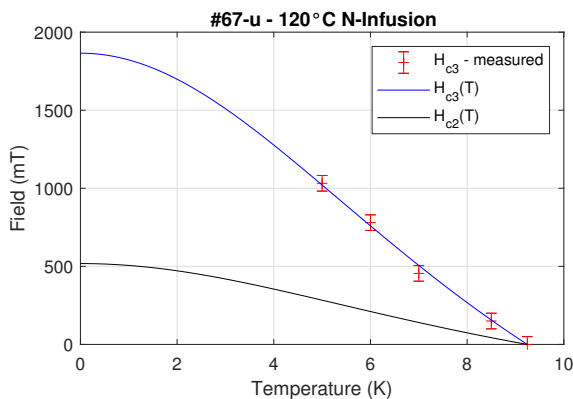| Sample	H_{c3} (T = 5 K) in mT
U	1055
60	1165
65	1175
67	1200
67-l	1077
67-u	1032

Figure 6: Measured H_{c3} of sample 67-u as a function of the temperature. Also shown is $H_{c2}(T)$(black line) and $H_{c3}(T)$(blue line) from the parabolic law equation $H_{c2,3}(T) = H_{c2,3}(0) \cdot \frac{1-(T/T_c)^2}{1+(T/T_c)^2}$ with $H_{c2}(0) = (518 \pm 16)$ mT from resistivity measurements on samples 60 and 62 and $H_{c3}(T)$ was obtained from susceptibility measurements. From $H_{c3} = r \cdot H_{c2}$ we obtain $r = 3.6 \pm 0.18$.

of the alternating-field susceptibility measurement, it can be shown that superconducting effects can be detected even with magnetic fields $H > H_{c2}$ and from this the superconducting properties of a surface layer within a thickness of order of the coherence length can be inferred.

The provided samples for the measurements and their pre treatment are listed in Table 3. Results for the obtained H_{c3} at 5 K are given in Table 4. Sample 67 was cut in half to compare the surface treated upper half 67-u and the untreated lower half 67-l. Comparison of sample U with the differently treated samples shows that the treatment of the samples visibly increases the surface superconductivity critical field H_{c3}. Sample 67-u was measured at more different temperatures as shown in Fig. 6. The proportionality factor obtained for sample 67-u $r = 3.6 \pm 0.18$ is much larger than was predicted by St. James and De Gennes $r_{GL} = 1.695$ and also exceeds the factors obtained from S. Casalbuoni et al. [4] with $r_{BCP} = 1.86 \pm 0.03$ for BCP and $r_{EP} = 2.1 \pm 0.03$ for EP samples.

Our results can also be interpreted in another way: Since the H_{c2} derived by the resistivity measurement is a bulk-measurement, it might underestimate the value at the surface. Hence, the relation $H_{c3} = r_{GL} \cdot H_{c2}$ would then allow to attribute the increase of H_{c3} not to the proportionality factor, but to the H_{c2}^{surf}. Such an increase of H_{c2} is justified by a reduction of the coherence length in the near-surface region due to the nitrogen uptake during the infusion.

CONCLUSION

By measuring the RRR on fine grain samples for different N infusion temperatures it could be shown that an impurity redistribution in the bulk takes places differently compared between N infusion and the same heat cycle without nitrogen. A maximum in the deterioration of RRR occurs at 260°C regardless if nitrogen is introduced or not. The deterioration is higher for the nitrogen infused samples except at 120°C. It is assumed that a redistribution of the oxygen in the bulk plays a role here and the nitrogen infusion apparently also has an influence on it.

SIMS measurements showed an NbN signal on a fine grain sample nitrogen infused at 400°C. No such signal is observed on a large grain sample and another fine grain sample that was nitrogen infused at 180°C. However, oxygen contamination were present on those.

Superconducting effects can be detected even with magnetic fields $H > H_{c2}$ and from this the superconducting properties of a surface layer within a thickness of order the coherence length can be inferred. The currently used niobium material shows extremely high H_{c3} values compared to [4].

ACKNOWLEDGMENTS

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