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NITROGEN INFUSION SAMPLE R&D AT DESY

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Abstract

Many accelerator projects such as 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. One important parameter is the residual resistance ratio (RRR) which is related to the impurity content of the material. We report the investigated RRR on samples in a wide temperature range in a vacuum and under a nitrogen atmosphere. This comparison made it possible to make statements about the differences in the concentration of nitrogen by varying the temperature. The samples are pure cavity-grade niobium and treated in the same manner as cavities. For this purpose, a small furnace dedicated to sample treatment was set up to change and explore the parameter space of the infusion recipe. Care was taken to achieve the highest level of purity possible in the furnace and in a pressure range of $1 \cdot 10^{-8}$ mbar in order to meet the high requirements of nitrogen infusion.

NITROGEN INFUSION ON SAMPLES

In [1] a recipe was reported that drastically improved the performance in quality factor and accelerating gradient of superconducting 1.3 GHz TESLA-type cavities. The formula calls for a three-hour heat treatment at 800°C under vacuum, followed by a ramp down to and hold at 120°C. A partial pressure of nitrogen ($3.3 \cdot 10^{-2}$ mbar) is provided during the 48-hour hold at 120°C. The latest cavity treatment recipes ([1–4]) have shown that we are far away from the possible theoretical limit of achievable SRF performance, many areas of the possible parameter space of cavity treatments are still unexplored. Therefore, excessive sample studies were performed in a dedicated vacuum oven also allowing for nitrogen-infusion investigations. At room temperature, the pump system saturates at an end pressure of $p < 5 \cdot 10^{-8}$ mbar. The RRR value is an interesting parameter that should be examined in more detail for correlation with the cavity performance, since it is also directly related to the mean free path [5]. In this study, the RRR value is examined when the temperature of the nitrogen infusion is varied.

RESIDUAL RESISTIVITY RATIO - RRR

The electrical resistivity following from the Mathiessen rule [6] for metals at low temperatures can be written as the sum of

$$\rho = \rho_{res} + \rho_{ph}(T), \tag{1}$$

where ρ_{res} describes the residual resistivity at $T = 0$ K that is predominantly evoked due to electron-impurity scattering and scattering on lattice defects while ρ_{ph} is caused by the temperature dependent electron-phonon scattering. The residual resistivity scales linearly with the impurity concentration C_i as $\rho_{res} = \sum \frac{\Delta\rho_i}{\Delta C_i} C_i$ and hence Eq. (1) can be written as

$$\rho = \sum \frac{\Delta\rho_i}{\Delta C_i} C_i + \rho_{ph}(T), \tag{2}$$

with $\frac{\Delta\rho_i}{\Delta C_i}$ being the resistance coefficients. The coefficients for some important impurities are given in Table 1. The RRR is defined as the ratio of the electrical resistance at room temperature to the residual one at 4.2 K

$$\mathrm{RRR} = \frac{\rho(295\,\mathrm{K})}{\rho(4.2\,\mathrm{K})}. \tag{3}$$

However, since the critical temperature of niobium is with $T_c = 9.2$ K, above the temperature of liquid helium, the value of $\rho(T_c = 9.2\,\mathrm{K})$ is used or extrapolated down to $\rho(4.2\,\mathrm{K})$. The RRR value is sensitive to changes in surface impurities due to diffusion during heat treatments in vacuum conditions or under certain gas atmospheres and after chemical surface treatments. The extent to which the nitrogen treatment changes the RRR value was therefore investigated on niobium samples.

Table 1: Resistance Coefficients for Different Elements [7] Determined by Resistance Measurements on Niobium Intentionally Contaminated by Impurities

Element	O	N	C	Ta	Zr
$\frac{\Delta\rho_i}{\Delta C_i}\left(10^{-11}\,\frac{\Omega\mathrm{m}}{wt.ppm}\right)$	2.64	3.49	3.33	0.12	0.6

RRR 4-PT CONTACT METHOD

Small fine grain (50 μm grain size on average) niobium samples cut from cavity material, to a size of (2.88 x 3 x 42) mm, were used. To evaluate the effect of nitrogen infusion on sample RRR values, a 4-point-contact approach was chosen. The sample holder is shown in Fig. 1. The sample is immersed in liquid helium for the warm-up and cool-down procedures. Since $\rho = U/I$ it follows by Eq. (3) that the RRR at T_c is determined by

$$RRR_{9.2\,\mathrm{K}} = \frac{U(295\,\mathrm{K})}{U(T_c \approx 9.2\,\mathrm{K})}. \tag{4}$$

A Keithley Digital-Multimeter is used to measure the voltage, which has an accuracy of about 1 nV and a magnitude of about 2 mV thanks to the use of a pre-amplifier and a

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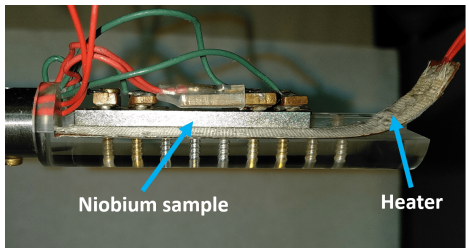

Figure 1: Photograph of a niobium sample clamped in the holder for RRR measurement via 4-pt contact method.

polarity-reversal device. The overall error thus consists of the voltage measurement resolution multiplied by the error estimated from the temperature estimation in quadrature. The whole systematic and absolute accuracy, including that which can be attributable to deviations generated by assembling and disassembling the samples, has been demonstrated decisively in [8] to be in the range of 2-3%.

A total of ten niobium samples were used, with five of them receiving a nitrogen infusion at temperatures ranging from 120 to 400°C. A cycle was performed by raising the temperature to 800°C over 3 hours under vacuum conditions and then to the desired temperature (120°C to 400°C) over 48 hours with the introduction of nitrogen ($3.3 \cdot 10^{-2}$ mbar). The remaining 5 samples were subjected to the same temperature treatment without nitrogen, that is, under vacuum conditions.

Before the actual infusion treatment the samples received a BCP of 20 minutes to remove the damage layer and clean the surface. The samples were then baked at 800°C in vacuum for 3 hours. Two of the samples were measured before and after the 800°C baking and the results are shown in Table 2 which remained unchanged within the measurement accuracy. Large decrease in RRR after baking at 800°C would have indicate contamination in the oven. To clean the surface again after the 800°C baking the samples received another short BCP of 2 minutes. The samples then were treated with the baking cycles (800°C for 3 hours → ramp down to the infusion temperature "Inf T" for 48 hours) and measured. Table 3 summarizes the results of the RRR measurements at

Table 2: RRR(at 9.2 K) Values from Two Fine Grain Samples before and after 800°C Baking in Vacuum for 3 Hours (Errors are 68% Confidence Level)

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

different infusion temperatures with nitrogen and in vacuum. The difference between before and after the treatment is denoted as $\Delta RRR = RRR_{after} - RRR_{initial}$ A decrease of the RRR after baking in a vacuum system indicates that a diffusion process must have taken place due to contamination. Since no decrease was observed for only baking at 800°C (table 2) the afterward combination of the 800°C with the

Table 3: RRR at 9.2 K Values before and after the Infusion Treatment with Nitrogen (w N) and in Permanent Vacuum (w/o N) (Errors are 68% Confidence Level)

Inf T	RRR(initial)	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

additional infusion temperature for 48 hours in one baking cycle is suspected to be the main cause for the observed change in RRR. We assume that these same processes also take place in the presence of nitrogen in addition to the penetration of nitrogen into the surface. Therefore, it should be possible to make statements about the pure nitrogen process by comparing these two RRR changes.

The change in ΔRRR before and after the treatment without nitrogen compared to the samples treated with nitrogen is shown in Fig. 2. No significant changes are observed be-

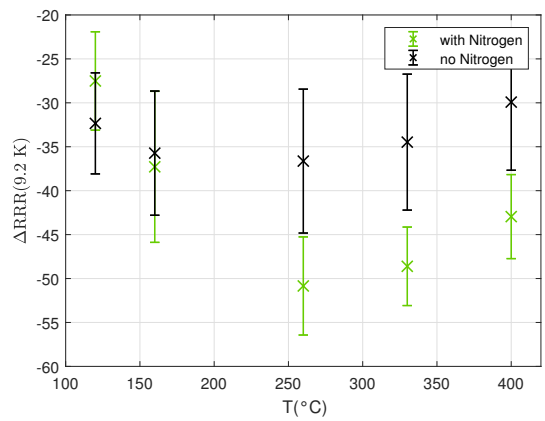

Figure 2: ΔRRR between before and after infusion treatment. The temperature was first heated to 800°C for 3 hours and then ramped down to the on the x-axis shown infusion temperature for 48 hours. Errorbars are 68% confidence level.

tween treatment with and without nitrogen at 120°C and 160°C. 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, although the data is insufficiently precise to establish this, the trend of the data indicates that less interstitial-diffusion into the sample for infusion temperatures above 260°C happened.

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NITROGEN CONCENTRATION CALCULATED FROM RRR VALUES

From Eq. (2) follows that the residual resistance can be written as the sum of the contamination resistances depending on the respective concentration C_i. This with Eq. (3) leads to

$$\mathrm{RRR} \approx \frac{\rho_{ph}(295\,\mathrm{K})}{\rho_{res}} = \frac{1.45 \cdot 10^{-7}\ \Omega\mathrm{m}}{\sum_i \frac{\Delta\rho_i}{\Delta C_i} C_i}. \tag{5}$$

The material has an initial contamination, $\Delta\rho_{init}$ defining RRR_{init}. After the treatment in vacuum conditions an additional contamination $\Delta\rho_{new}$ will be present. It can be assumed to be composed of any contamination from the interior of the oven. This leads to

$$\mathrm{RRR}^{noN}_{after} = 1.45 \cdot 10^{-7}\ \Omega\mathrm{m} \cdot \left(\frac{\Delta\rho^{noN}_{init}}{\Delta C^{noN}_{init}} C^{noN}_{init} + \frac{\Delta\rho_{new}}{\Delta C_{new}} C_{new} \right)^{-1}. \tag{6}$$

For the treatment when nitrogen is added the RRR is then given simply by an additional term as

$$\mathrm{RRR}^{wN}_{after} = 1.45 \cdot 10^{-7}\ \Omega\mathrm{m} \cdot \left(\frac{\Delta\rho^{wN}_{init}}{\Delta C^{wN}_{init}} C^{wN}_{init} + \frac{\Delta\rho_{new}}{\Delta C_{new}} C_{new} + \frac{\Delta\rho_N}{\Delta C_N} C_N \right)^{-1}. \tag{7}$$

This transforms to

$$C_N = \frac{\Delta C_N}{\Delta\rho_N} \cdot \left(\frac{1.45 \cdot 10^{-7}\ \Omega\mathrm{m}}{\mathrm{RRR}^{wN}_{after}} - \frac{\Delta\rho^{wN}_{init}}{\Delta C^{wN}_{init}} C^{wN}_{init} - \frac{\Delta\rho_{new}}{\Delta C_{new}} C_{new} \right). \tag{8}$$

The concentration of nitrogen can then be deduced from

$$C_N = \frac{1.45 \cdot 10^{-7}\ \Omega\mathrm{m}}{\frac{\Delta\rho_N}{\Delta C_N}} \cdot \left(\frac{1}{\mathrm{RRR}^{wN}_{after}} - \frac{1}{\mathrm{RRR}^{wN}_{init}} - \frac{1}{\mathrm{RRR}^{noN}_{after}} + \frac{1}{\mathrm{RRR}^{noN}_{init}} \right), \tag{9}$$

where $\frac{\Delta\rho_N}{\Delta C_N} = 3.49 \cdot 10^{-11} \frac{\Omega\mathrm{m}}{wt.ppm}$ is taken from Table 1. The results from Table 3 with Eq. (9) give nitrogen concentrations for the respective infusion temperature shown in Table 4.

Table 4: Nitrogen Concentration in wt.ppm Calculated from RRR Values in Table 3 by Eq. (9)

Inf T	C_N(wt.ppm)
400°C	0.9 ± 0.5
330°C	0.8 ± 0.6
260°C	1.0 ± 0.6
160°C	0.04 ± 0.6
120°C	-0.5 ± 0.5

CONCLUSION

It was possible to establish that a change in impurity concentration in the bulk occurs differently between N infusion at different temperatures and the same heat cycle without nitrogen by measuring the RRR on fine grain samples. At temperatures above 260°C, the deterioration is higher for the treatment with nitrogen injection. The results show evidence that other impurities than nitrogen influence the interaction kinetics and that the vacuum environment is critical. A redistribution and increase of oxygen in the bulk is thought to be involved, and the nitrogen infusion appears to have an impact as well for temperatures above 260°C.

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