CHARACTERIZATION OF NITROGEN DOPING RECIPES FOR THE Nb SRF CAVITIES

Y. Trenikhina, A. Grassellino, O. Melnychuk, A. Romanenko, FNAL, Fermilab, USA

Abstract

Nitrogen doping enabled a new state-of-the-art performance standard for Nb SRF cavities. For the future development of this technology, it's vital to understand the mechanisms behind the performance benefits of N-doped cavities as well as the performance limitations, such as quench field. Following various doping recipes, cavity cutouts and flat niobium samples have been evaluated with XRD, SEM, SIMS and TEM in order to relate structural and compositional changes in the niobium near-surface to the quality of SRF performance. Annealing with nitrogen for various durations and at various temperatures, the Nb cavities demonstrated non-superconducting Nb nitride phases, followed by unreacted Nb with elevated N-interstitials concentration. We found that EP of the annealed cavities removes the unwanted niobium nitride phases, confirming that performance benefits are originating from the elevated concentration of N interstitials. The role of low temperature Nb hydride precipitants in the performance limitation of N-doped cavities was evaluated by TEM temperature dependent studies. Finally, characterization of the original cavity cutouts from the N-doped RF tested cavity sheds some light on quenching mechanisms.

INTRODUCTION

Fermilab's search for an optimal solution to the medium field performance degradation, led to the discovery of "nitrogen doping" of Nb cavities. Nitrogen doping of Nb cavities enabled new higher standards for Nb SRF cavity performance. This recipe yields reproducible improvement of the quality factor in addition to the reversal of the Medium Field Q-Slope [1] . Reported values of Q_0 are up to 3 times higher than for electropolished (EP) standardly prepared cavities, and up to 2 times higher than for EP cavities which had mild bake at 120°C. Cavities with non-typical, reversed MFQS show low values of microwave surface resistance.

N-doping of single- and nine-cells Nb 1.3 GHz cavities has a great potential to be adopted for a number of future particle accelerators. However, problems like limited quench field, remain unexplained as well as the origin of the performance benefits. Our characterization work was initiated to reveal the mechanisms leading to the unique SRF performance after N-doping. Our investigations consist of tracking material features of the Nb near-surface induced by the nitrogen doping and relating them to the results of RF cavity testing.

N-doping of Nb cavities includes two major processing steps: annealing of the cavity in the presence of nitrogen gas, and material removal through EP. Annealing of Nb cavities at 800°C in a UHV furnace with nitrogen partial pressure of $\approx 2{*}10^2$ Torr for different time durations is followed by EP and high pressure water rinsing (HPR). The amount of material that has to be removed depends on the duration of the 800°C annealing with nitrogen. Figure [need recent Q vs. E curve(s)] shows the results of RF characterization of the N-doped Nb cavities, which were subject to the described sequence with various experimental parameters.

X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) at room and cryogenic temperatures were performed on Nb samples as well as on the cutouts taken directly from N-doped Nb cavities. A combination of those characterization techniques provides complete insight into the chemical and structural details of the near-surface on different length scales.

EXPERIMENTAL METHODS

Description of Nb Samples and Cavity Cutouts

Square samples were cut from the niobium sheets used for cavity fabrication. All Nb samples were electropolished (EP) prior to treatment with nitrogen. In order to reproduce the effect of the first step of nitrogen doping, Nb samples had been annealed in a UHV furnace at 800°C for time durations of 2 min and 20 min. After characterization of the effects of the first step of nitrogen doping, some Nb samples had been EP and characterized again.

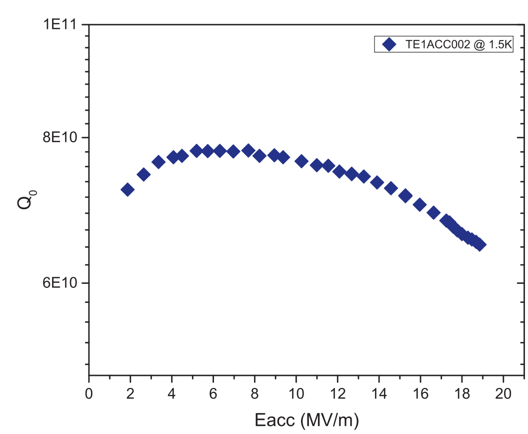

Figure 1: Performance of the Cavity 2 which was baked at 800°C for 20 min in nitrogen atmosphere and 5 μm were removed via EP.

Cavity cutouts for material characterization were taken from two TESLA shape 1.3 GHz fine grain cavities which underwent nitrogen doping with different parameters. The first cavity (labeled "Cavity 1" for the following) was baked in a UHV furnace at 1000°C with nitrogen gas for 10 min.

ISBN 978-3-95450-178-6

After the bake, 60 μm of the near-surface had been removed via EP.

The second cavity (labeled “Cavity 2” for the following) was baked in nitrogen atmosphere for 20 min at 800°C. 5 μm had been removed via EP. This cavity was RF characterized with the temperature mapping system attached [2]. Dependence of the quality factor on peak applied magnetic field was measured at 1.5K (Fig.1). The cavity quenched at ≈18.5 MV/m and the quench spot had been identified from the temperature map. The quench spot was cut from the cavity for the material characterization.

Characterization of Nb Samples and Cutouts

Cross sectional TEM samples were prepared from Nb samples and cavity cutouts by the Focused Ion Beam (FIB) lift-out technique. A Helios 600 FEI instrument was also used for SEM imaging. Two types of TEMs were used for this work: a field-emission gun (FEG) TEM and a thermionic LaB_6 gun TEM. The JEM 2010F Schottky FEG TEM at the Materials Research Laboratory (MRL) at the University of Illinois at Urbana-Champaign (UIUC), operated at 197kV, was used for the temperature dependent nano-area electron diffraction (NED) and imaging. An approximately 80 nm sized parallel beam was used to record NED patterns onto the Fuji imaging plates. A JEOL JEM 2100 LaB_6 thermionic gun TEM at MRL/UIUC was used for imaging and temperature dependent scanning electron nano-area diffraction (SEND). A description of the instruments and TEM diffraction techniques that were used for the temperature dependent study of niobium hydrides can be found in [3]. A Gatan liquid nitrogen cooled double-tilt stage was used for the low temperature measurements.

XRD was done at MRL/UIUC with Pananalytical/Philips X’pert[2] Material Research Diffractometer equipped with crossed-slit collimator, parallel plates collimator, flat graphite monochromator and proportional detector. Surface composition was explored with Thermo Scientific ESCALAB 250 Xi instrument with Al Kα source at Northwestern University (NU). SIMS measurements were performed by the commercial company.

RESULTS AND DISCUSSION

Annealing of Nb Samples in Nitrogen Atmosphere

Formation of niobium nitride phases in the near-surface of Nb cavities which underwent the first step of nitrogen doping was confirmed by XPS and XRD and reported in [4]. In this work we extend our investigations and explore the effect of different durations of annealing in nitrogen atmosphere. Extended material characterization of the nitrogen doping parameters can help to finally reveal the origins of particular cavity performance.

Characterization of the first step of nitrogen doping is intended to show the depth of the near-surface which is affected by stoichiometric niobium nitrides. The potential presence of a small amount of niobium nitrides in the near-surface of the cavity after the material removal, is a primary concern. If non-superconducting niobium nitride phases were left after EP, the cavity performance will be severely degraded.

We’ll start with comparison of the surface of Nb samples that were baked with nitrogen for 20 min and 2 min (Fig.2a and 2a, respectively). Characteristic surface morphology with star-shaped features on the surface agrees with the results reported in the literature under similar experimental conditions [5], [6]. Nitrogen bulk diffusion reaction with niobium occurs by inward diffusion of nitrogen. The original morphology of the niobium sample affects the directions of niobium nitride preferential growth. The obvious size difference of the star-shaped features is a result of the different amount of time spent at 800°C with nitrogen gas. Star-shaped features in the sample that had been baked for 20 min are about 2 μm in diameter. Similar features on the sample that had been baked for 2 min do not exceed 0.5 μm in size.

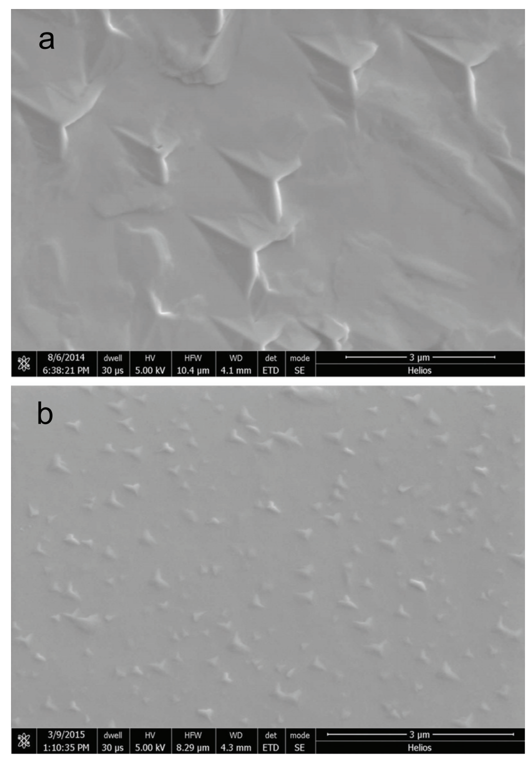

Figure 2: SEM image of sample that had been annealed in nitrogen gas at 800°C for (a) 20 min, (b) 2min.

The structure of the near-surface of the samples baked for 20 min and for 2 min was investigated with TEM. Fig.3 shows a FIB-prepared TEM sample which was cut from the 20 min-baked sample. Patches of darker SEM contrast, which can be noticed under the protective platinum layer, were identified as stoichiometric niobium nitride phases, as is discussed below.

The TEM images in Fig.4a and b show the effects of nitrogen annealing for 2 min and 20 min, respectively. The size of the “shark teeth features" of lighter contrast in the near-surface is proportional to the duration of baking in ni-

ISBN 978-3-95450-178-6

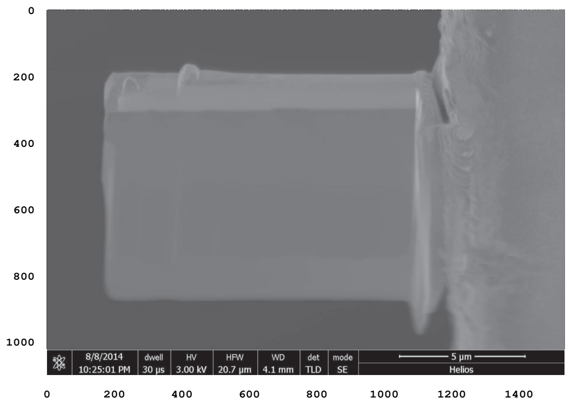

Figure 3: SEM image of FIB sample which was cut out of Nb sample annealed at 800°C for 20 min.

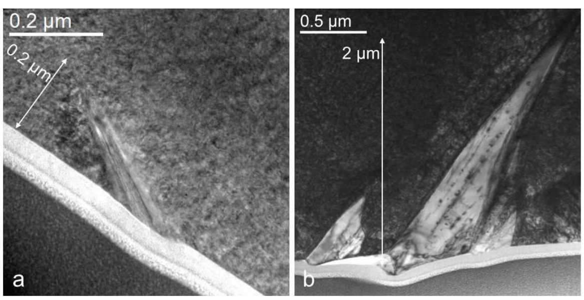

Figure 4: TEM image of Nb sample baked with nitrogen gas at 800°C for (a) 2 min, (b) 20 min

trogen atmosphere. Annealing for 2 min at 800°C produces the features that extend to approximately 0.2 μm deep. Annealing for 20 min produces the features that affect the first 2 μm of the near-surface.

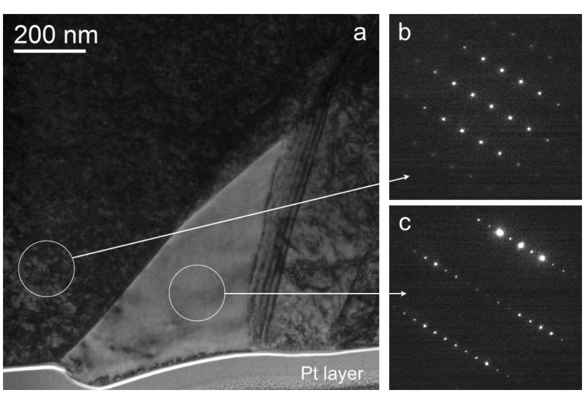

Figure 5: (a)TEM image of Nb sample treated at 800°C for 20 min; (b) NED patterns from Nb, [113] zone axis; (c) NED pattern of Nb_2N close to [310] zone axis.

TEM diffraction was used in order to identify the local composition of the shark teeth features and surrounding area. Fig.5 shows a bright field (BF) image of the shark teeth feature along with NED patterns taken from the sample which had been baked for 20 min in nitrogen atmosphere. The NED pattern in figure 5b was taken from the "featureless" region about 300 nm deep from the surface. It shows Nb BCC reflections close to [113] zone axis. NED pattern in figure 5c was taken from the light-contrast feature, which shows hexagonal Nb_2N phase close to [310] zone axis. The same hexagonal Nb_2N niobium nitride phase was identified by XRD measurements. XRD taken from a Nb sample that had been annealed in nitrogen atmosphere for 10 min was indexed according to the hexagonal P63/mmc Nb_2N [7]. We can conclude that contrast variations in the first $\approx$ 500 nm show the presence of several phases, which include hexagonal Nb_2N phase and pure Nb.

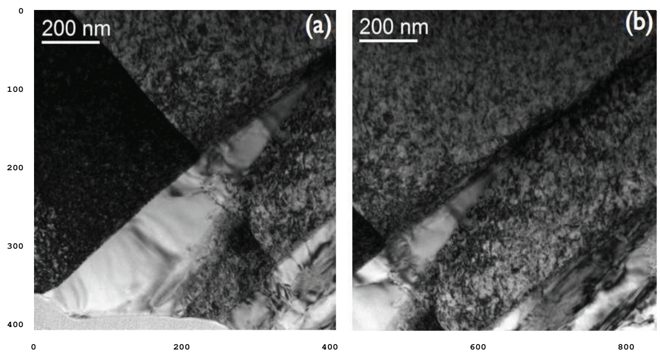

Figure 6: TEM image of grain boundary region in Nb sample baked at 800°C with nitrogen for 20 min: (a) near-surface, (b) deeper into the bulk.

TEM BF images of the grain boundary region in a Nb sample annealed with nitrogen at 800°C for 20 min are shown in Fig.6. Shark teeth features that had been identified as niobium nitride inclusions are present to within approximately 2 μm from the surface of the sample (Fig.6a). No extended propagation of these features along the grain boundary was observed in TEM images (Fig.6b) so far. Additional experiments will be conducted in order to collect more images of the grain boundary regions.

Post Material Removal Characterization

Annealing of Nb cavities in nitrogen atmosphere is followed by the removal of a particular amount of the surface via EP. The amount of the material that has be taken away is dictated by the conditions of the annealing. SRF performance benefits are optimal if the removed material thickness equals to approximately a quarter of the nitrogen diffusion length at annealing temperature.

Nb samples which had been baked in nitrogen atmosphere for 2 and 20 min were EP in order to remove 5 μm of the near-surface surface. Removal of 5 μm was intentionally chosen in order to take away the minimal amount of material which is typically used for the cavities that had been baked in nitrogen atmosphere for only 2 min.

The possibility of the presence of niobium nitride phases in the near-surface of electropolished Nb samples and cavity cutouts has been checked with TEM and XRD. Previous XRD and XPS studies have shown no niobium nitride phases in the near-surface of niobium after the EP. TEM characterization had confirmed the absence of stoichiometric niobium nitride phases in the near-surface of Nb sam-

ISBN 978-3-95450-178-6

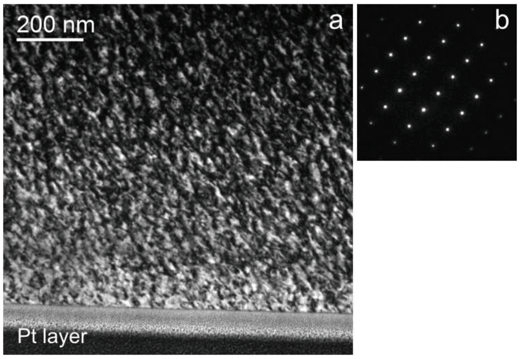

Figure 7: (a) TEM image of the near-surface of the cavity cutout; (b) NED pattern of Nb, [110] zone axis.

ples after the EP, as well as in the nitrogen doped cavity cutouts. Fig.7 shows a TEM image of the near-surface of a sample prepared from the cavity cutout taken from the Cavity 1. Fig.7a shows a relatively uniform near-surface with no obvious inclusions of different contrast. A representative NED pattern in Fig.7b shows only BCC Nb reflections. NED patterns were taken right underneath the oxide as well as a few hundred nm deep into Nb.

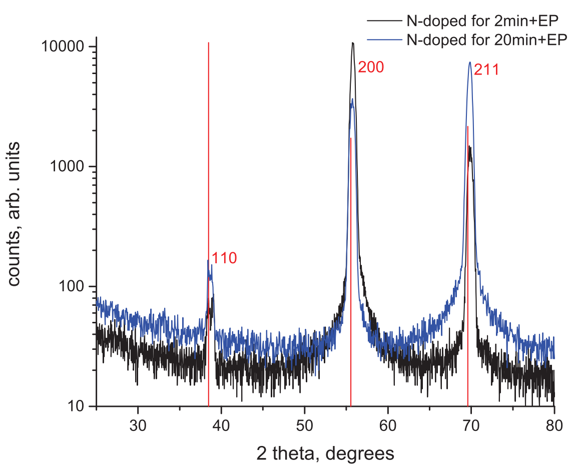

Figure 8: XRD taken from Nb samples after the complete "nitrogen doping".

Post-EP XRD characterization was done on the two Nb samples discussed in the previous section. Fig.8 shows XRD patterns taken after the EP of the samples initially baked for 2 min and 20 min in black and blue curves, correspondingly. No stoichiometric niobium nitride phases were detected with XRD after the EP. Red vertical markers indicate positions of the BCC Nb peaks taken from the reference powder diffraction file (PDF 00-035-0789). Comparing to the reference, Nb peak positions from the both samples which underwent nitrogen doping are slightly shifted. Further XRD experiments are underway in order to determine whether the peak shifts are an indication of the strained Nb as a result of nitrogen doping treatment.

The effect of the nitrogen doping on the Nb near-surface was additionally evaluated by SIMS. While all the techniques discussed in the previous sections were used to confirm the absence of stoichiometric niobium nitrides, SIMS provides ppm-level of nitrogen concentration as a function of depth. Fig.9 shows variations in nitrogen concentration in the niobium near-surface of the samples which were baked in nitrogen atmosphere for different time durations. The black curve corresponds to the reference Nb sample that had been baked with no nitrogen gas. All the samples that had been annealed in nitrogen show elevated N concentration within the first approximately 2 μm, which corresponds to the presence of stoichiometric niobium nitrides. Niobium nitrides are followed by Nb with elevated nitrogen concentration which is about 2 orders of magnitude higher compared to the reference sample that had been baked with no nitrogen. Nb near-surface with elevated N concentration corresponds to the presence of N atoms in Nb interstitials. Nb near-surface with elevated N concentration is of great importance for SRF applications, since only Nb enriched with N interstitials shows medium field performance benefits that are unachievable with other surface treatments.

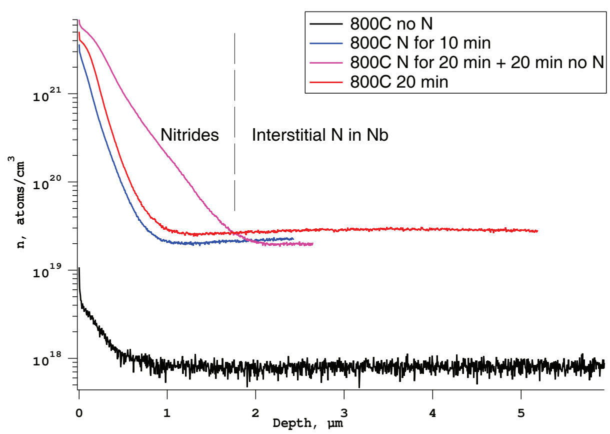

Figure 9: SIMS taken from Nb samples which were baked under different conditions.

Nb Hydrides Precipitation in N Doped Cavities and Samples

In order to overcome quenching problem in nitrogen doped SRF cavities, it is essential to understand how Nb enriched with N interstitials affects the surface superconductivity. It's been recently confirmed that the presence of niobium nano-hydrides in the near-surface can be detrimental for the Nb cavities performance [3]. Since hydrogen intake during the cavity processing is unavoidable, N doped cavities have a great potential to be affected by low temperature niobium hydrides precipitation. TEM temperature-dependent studies of the N doped cavities and samples were performed in order to explore the possibility of niobium hydrides formation at cryogenic temperatures. Identical experimental parameters and instrumentation had been used for the cryogenic TEM measurements of N doped cavities samples and the samples from EP and 120°C-baked EP cavities [3].

As has been shown above, room temperature TEM diffraction on nitrogen doped cavity cutouts and samples shows only Nb reflections, which confirms the absence of stoichiometric Nb hydrides. The same result was obtained for EP and 120°C-baked EP cavities at room temperature.

Fig.10 shows an NED patterns at 94K taken from the near-surface of the EP Nb sample that had been initially baked in nitrogen for 2 min. Low temperature reflections can be clearly noticed along with Nb reflections.

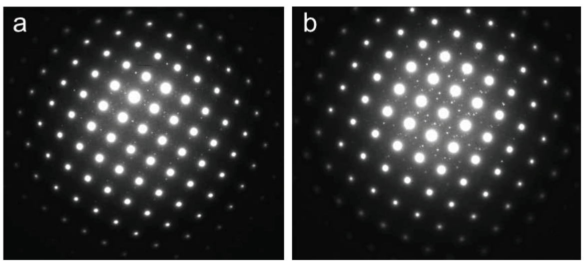

Figure 10: NED patterns taken from EP Nb sample which was initially annealed with nitrogen for 2 min.

Fig.11 shows an NED pattern at 94K taken from the sample prepared from the quench spot of the Cavity 2. Strong niobium hydride reflections can be recognized as ϵ-phase niobium hydride. Large near-surface area was affected by niobium hydride precipitation in the sample prepared from the quench spot. Nearly all spots that had been probed with the NED showed additional low temperature reflections. About 32 spots of a size of ≈80 nm had been probed.

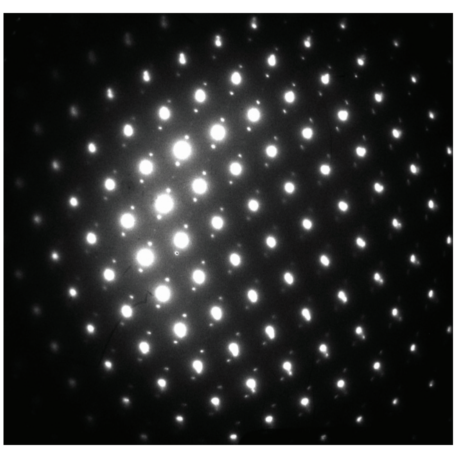

Figure 11: Typical NED pattern taken from the "quench" spot in nitrogen doped cavity.

Another cutout was prepared from the Cavity 2. Location of this cutout was chosen in the area with no significant dissipation. Cryogenic temperature structural characterization of the cutout prepared from non-dissipating area is underway. Comparison of the quench spot and the spot with no dissipations will unambiguously identify the role of niobium hydride precipitation in nitrogen doped cavities.

CONCLUSION

Material characterization of "nitrogen doping" gives insight into the microscopic evolution of the Nb near-surface, which governs superconducting properties. Annealing of Nb cavities in nitrogen atmosphere produces non-superconducting Nb nitride phases in the Nb near-surface, followed by unreacted Nb with elevated N interstitials concentration. We found that electropolishing of annealed cavities removes the unwanted niobium nitride phases, confirming that performance benefits are originating from the elevated concentration of N interstitials.

NED measurements at cryogenic temperature demonstrated precipitation of niobium hydrides in nitrogen doped cavities and samples. Direct observation of low temperature precipitants in nitrogen doped cavities suggests their relevance in the performance limiting mechanisms for the nitrogen doped cavities. Evaluation of the specific role of niobium hydrides in the nitrogen doping recipe is underway.

REFERENCES

[1] A. Grassellino, A. Romanenko, D. Sergatskov, O. Melnychuk, Y. Trenikhina, A. Crawford, A. Rowe, M. Wong, T. Khabiboulline, F. Barkov, Supercond. Sci. Technol. 26 102001 (2013).

[2] M. Checchin et. al., "Origin of premature quench in superconducting nitrogen doped cavities", MOPB022, *These Proceedings*, SRF'15, Whistler, Canada (2015).

[3] Y. Trenikhina, A. Romanenko, J. Kwon, J.-M. Zuo, J.F. Zasadzinski, J. Appl. Phys. 117 (15), 154507 (2015).

[4] Y. Trenikhina, A. Grassellino, A. Romanenko, SRF'13, TUP065, Paris, France (2013).

[5] R. Musenich, P. Fabbricatore, G. Gemme, R. Parodi, M. Viviani, B. Zhang, V. Buscaglia, and C. Bottino, Journal of Alloys and Compounds, 209(1-2), 319 (1994).

[6] Y. Ufuktepe, A.H. Farha, S.-I. Kimura, T. Hajiri, F. Karadag, M.A. Al Mamun, A.A. Elmustafa, G. Myneni, and H.E. Elsayed-Ali, Materials Chemistry and Physics, 141(1), 393 (2013).

[7] Powder Diffraction File 04-003-1490, International center for diffraction data, 2005. PDF-2/Release.

ISBN 978-3-95450-178-6