ISBN: 978-3-95450-233-2 ISSN: 2673-5504 doi:10.18429/JACoW-SRF2021-WEPFDV010

STRUCTURAL INVESTIGATION OF NITROGEN-DOPED NIOBIUM FOR SRF CAVITIES

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Abstract

Niobium is the standard material for superconducting RF (SRF) cavities for particle acceleration. Superconducting materials with higher critical temperature or higher critical magnetic field allow cavities to work at higher operating temperatures or higher accelerating fields, respectively. Enhancing the surface properties of the superconducting material in the range of the penetration depth is also beneficial. One direction of search for new materials with better properties is the modification of bulk niobium by nitrogen doping. In the Nb-N phase diagram, the cubic δ-phase of NbN has the highest critical temperature.

In this study niobium samples were annealed and N-doped in the high-temperature furnace at TU Darmstadt and investigated at its Materials Research Department with respect to structural modifications. Secondary ion mass spectrometry showed at which conditions N-diffusion takes place. X-ray diffraction (XRD) confirmed the appearance of γ-Nb_4N_3 and β-Nb_2N phases for the optimized doping process. XRD pole figures also showed grain growth during sample annealing. A single-cell cavity was nitrogen-doped using the parameters of the optimized recipe.

INTRODUCTION

After several decades of continuous research and technological innovation the performance of niobium cavities is very close to the theoretical limit. Today industrialised cavity production with fields up to 45 MV/m and a Q-factors exceeding 10^{10} at 2 K operation is possible [1, 2], in exceptional cases reaching beyond 50 MV/m [3, 4].

Surface modification of niobium, mostly nitrogen doping [5] can increase the Q-factor at 2K operation. Another approach is to use copper as bulk material, coated by Nb, as it is foreseen by the Conceptual Design Report of the Future Circular Collider. The application of both niobium coated copper and bulk niobium cavities is proposed for the accelerator structure of FCC-ee [6]. It builds on the long tradition of coated copper superconducting cavities at CERN. The high heat conductivity of copper would permit 4.5 K operation.

The research on new materials (non-bulk Nb [7]) could lead to more compact and energy efficient accelerators. Nb has the highest critical temperature amongst the elements, but already niobium containing compounds, like NbN and Nb_3Sn [8, 9] have higher critical temperature.

In this contribution the results on NbN phase forming by annealing in nitrogen atmosphere are presented. Here we are not focusing on the α-Nb phase modified by nitrogen doping [10] or nitrogen infusion [11]. In contrast to the previously mentioned cases, where the nitride formation could be detrimental and the surface NbN layer should be removed [12], our goal was to form a thick enough superconducting δ-NbN phase [13] on bulk niobium. In accordance with previous results on Nb cavities with similar annealing procedures [14], we managed to reach a γ-Nb_4N_3 surface phase.

METHODS

High quality niobium sheets [2.8 mm thick with residual-resistivity ratio (RRR) of 300] were treated by buffered chemical polishing (BCP), then cut to 5x5 mm^2 and 10x10 mm^2 squares by high pressure water at Research Instruments (RI). The cut samples were baked out and nitrogen-doped in the high-temperature UHV furnace located at IKP, TU Darmstadt ("Wuppertal oven") [15, 16]. The virgin and treated samples were characterized by x-ray diffraction (XRD), electron microscopy and secondary ion mass spectrometry (SIMS) at the ATFT group of TU Darmstadt. Finally a single cell cavity, purchased from RI, was treated according the optimized recipe.

The XRD measurements were done on a θ-θ geometry Rigaku SmartLab diffractometer with rotating copper anode (λ=1.54 Å), line focus and parallel beam set-up. 2θ-ω scans and pole figures at different Bragg reflections (constant 2θ detector angle) were taken.

The SIMS measurements were done on a Cameca ims5f spectrometer with O^{2+} ions.

RESULTS

The process parameters were optimized on the Nb samples. On Fig. 1 the XRD patterns of a test series are shown. The annealing temperature, nitrogen partial pressure and annealing time was increased from 1450 °C, 50 mbar, 30 min in four steps to 1578 °C, 100 mbar and 60 min, respectively. For the first run (with the lowest temperature, partial pressure and annealing time) we got β-Nb_2N phase, after the final optimization step, phase pure γ-Nb_4N_3.With those optimized conditions a single cell cavity was treated with witness samples at different positions. On Fig. 2 the XRD pattern of witness samples, located at positions "top" and "bottom" are shown. From the fit it can be seen, that the two samples have different ratios of NbN phases, the film on the top sample was almost phase pure: 98% γ-Nb_4N_3, while the bottom one contained still 13% β-Nb_2N phase.

The Q-factor of the single cell cavity was investigated. First the virgin cavity was measured [15]. After the treatment the 2K temperature range could not be reached due to a cold leak [16]. The most probable cause of the cold leak is the hard NbN film grown on the flange (see Fig. 3).

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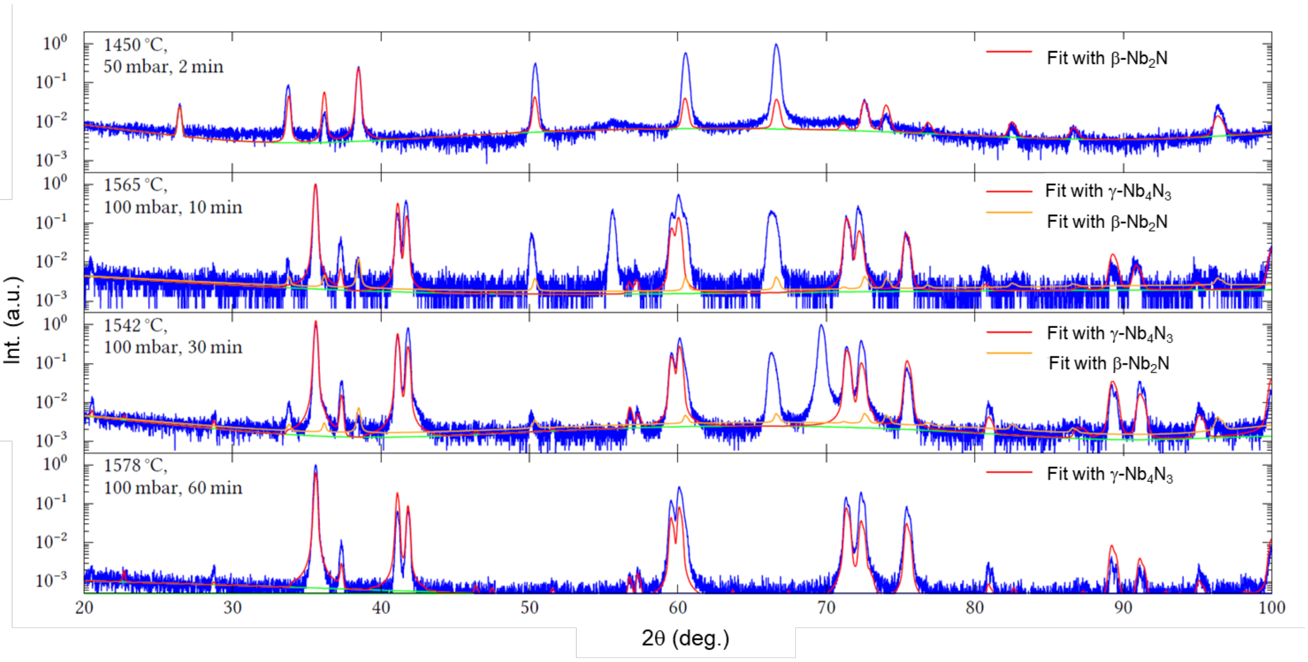

Figure 1: XRD patterns of the niobium square samples of the optimization series. From top to bottom the annealing temperature, nitrogen partial pressure and annealing time was increased. The possible fits with the different NbN phases are shown. The Brag peaks of the first pattern could be fitted with the β-Nb_2N phase, then a mixture of phases appeared, and finally a phase pure γ-Nb_4N_3 was found [16].

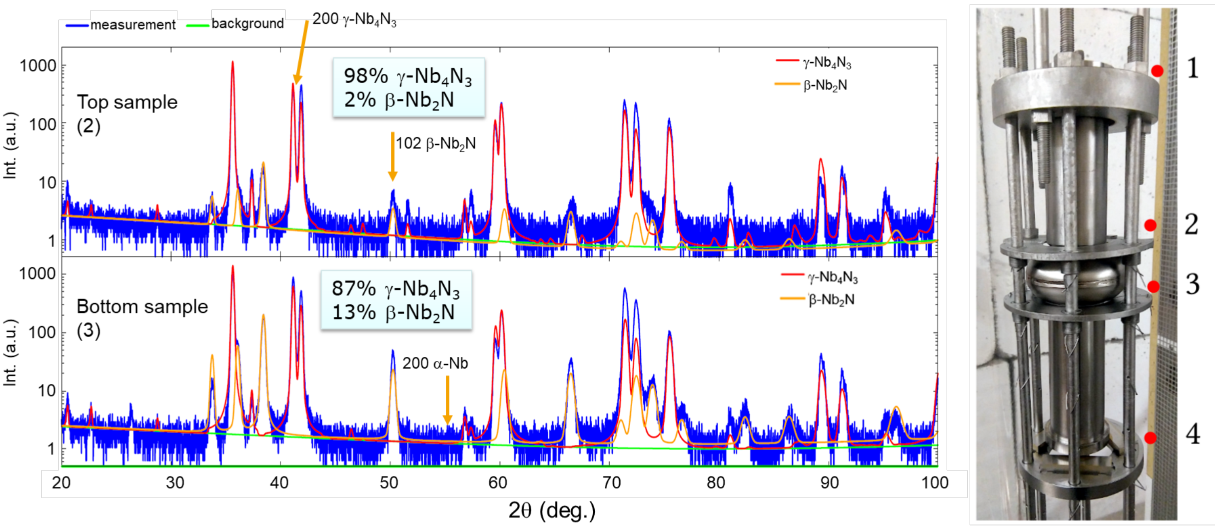

Figure 2: XRD patterns of the two witness samples [16]. The cavity and witness samples were annealed at the optimized conditions of 1573 °C under 100 mbar N_2 for one hour in the Wuppertal oven. On the right the photo of the single cell cavity with the niobium holding structure is shown. The red dots mark the position of the witness samples. The “top sample” (number 2) was almost phase-pure (with only 2% β-Nb_2N contribution), while the “bottom” one (number 3) had 13% of the β-phase. The yellow arrows mark the Bragg peaks used for texture measurements (see Fig. 4).

In order to get a more detailed view of the formed phases, pole figures were taken. We have shown in our previous studies, that the niobium recrystallizes at high temperature annealing [17, 18], sometimes leading to almost single crystalline Nb. We took poled figures at three 2θ detector angles, representative of the three phases. The α-Nb 200, the β-Nb_2N 102 and the γ-Nb_4N_3 reflections were selected, as there is no overlapping Bragg peak of the other phases at those angles. The pole figures are shown in Fig. 4. Interestingly, no x-ray diffraction from the Nb bulk phase is seen in the pole figure. The small intensity blobs around the middle empty square are background scattering from the system (intensity maximum was a mere 150 counts), suggesting film thickness of at least 10 µm on top of the bulk Nb substrate, based on x-ray attenuation. The bottom sample shows a tiny β-phase contribution but for both samples the majority is the γ-phase. The grown films are strongly textured with small domains of both phases.

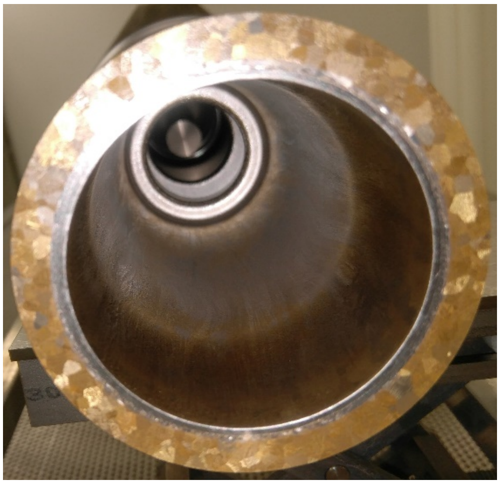

Figure 3: Photo of the single cell cavity from the flange side after the optimized treatment (see Fig. 2 for details). The gold coloured surface is indicative of the formation of the γ-Nb_4N_3 phase [13].

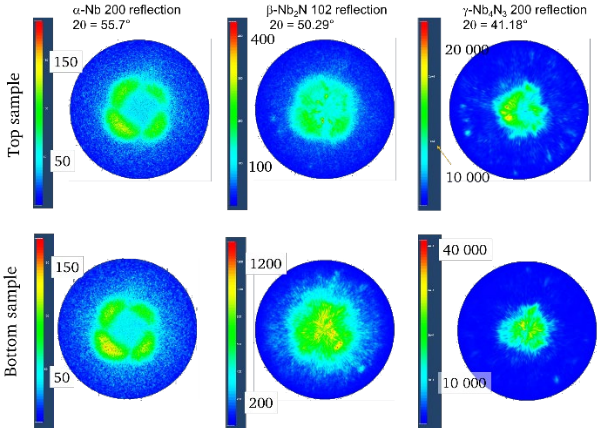

Figure 4: Pole figures taken at three representative Bragg peak positions of the witness samples “top” and “bottom”.

DISCUSSION

The main goal of our project was to grow and investigate NbN coatings on bulk niobium to be used as improvement for superconducting cavities. Our first result was the growth of a thick enough (detectable by x-rays) surface NbN film. On this way we learned by SIMS, that the vacuum annealing in itself can be beneficial as it reduces the hydrogen trace concentration [19].

The next intriguing effect was the strong recrystallization of niobium with increasing temperature, and the importance of clean annealing environment. Mainly the detrimental side effects of oxygen impurities in our lab furnace on the phases were found [17]. Based on those studies the annealing parameters were optimized in the Wuppertal oven, allowing of the formation of the first “x-ray visible” NbN phases [18]. This important result was achieved by a modified annealing protocol, where the nitrogen gas was flowing continuously through a regulated valve to keep the partial pressure constant [15], in comparison to previous attempts, where the nitrogen pressure was periodically fed to the hot-pot [20]. This continuous nitrogen-flow is better, as the whole hot-pot is made of niobium which acts as a strong nitrogen absorber at high temperatures. The annealing time was also increased up to one hour from the starting 10 minutes.

In a previous work [18] we related the Bragg peaks to the high-temperature δ-NbN phase, which is cubic. A better match could be achieved with the tetragonal γ-phase, which is the equilibrium phase at room temperature [21].

In this study we were able to grow phase-pure γ-NbN films on Nb when annealing small samples in the Wuppertal oven (see Fig. 2.). This result is in accordance with literature [14]. When the single cell cavity was inserted to the hot-pot for annealing, the different witness samples and the cavity’s inner surface showed a non-homogenous nitride formation (see Fig. 3.). This could partially be due to the strong nitrogen absorption of the large virgin Nb surface of the cavity itself, and the partial blocking and thus depletion of the nitrogen at the irises of the cavity during the annealing. A solution to this could be the modification of the bake-out parameters (higher temperature, pressure, time). A second approach could be the redesign of the cavity geometry, by omitting the narrow iris (shown as the bright ring on Fig. 3) to allow a more homogenous nitrogen diffusion through the whole structure.

The practically missing intensity for the Nb pole figure (Fig. 4) is a strong indication on the formation of thick coating layer of NbN. Based on x-ray attenuation we estimate the film thickness to be at least 10 µm. The witness samples show mostly γ-phase in accordance with literature [14]. From the result of previous runs we also conclude the recrystallization of the bulk Nb below the film [17, 18]. A fast cooldown (quench) is impossible for the Wuppertal oven, due to its complex structure and huge mass.

CONCLUSION

Niobium samples were annealed and nitrogen-doped in a high-temperature UHV oven (the Wuppertal oven). With continuous nitrogen flow protocol NbN phase formation was observed. After optimizing the bake-out temperature, nitrogen pressure and annealing time, a minimum 10 µm thick surface NbN film formed. The film was phase-pure γ-Nb_4N_3 in accordance with literature [14].

First cavity treatment was done under the optimized conditions. Here inhomogeneous phase formation was found and no quality factor measurement at 2K was possible due to a cold vacuum leak.

In conclusion, growth of the δ-phase with the present method and setup is not possible as the Wuppertal oven cannot be quenched, thus the formed cubic δ-phase will always convert to the tetragonal γ-phase on cooldown. This γ-phase could also be a potential candidate for performance enhancement, as its critical temperature is superior to niobium. To achieve a more homogenous surface coating the modification of the cell geometry could be beneficial.

ACKNOWLEDGEMENTS

This work is supported by BMBF through the project 05H18RDRB2 (part of "Key technologies for SRF accelerators") and the AccelencE Research Training Group (GRK 2128).

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