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STRUCTURAL INVESTIGATIONS OF NITROGEN-DOPED NIOBIUM FOR SUPERCONDUCTING RF CAVITIES*

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Abstract

Niobium is the standard material for superconducting radio frequency (SRF) cavities. 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 (16 K). Already slight nitrogen doping of the α-Nb phase results in higher quality factors. To explore the α-Nb(N) and δ-NbN phases, Nb samples were doped at different temperatures and nitrogen partial pressures. The first results on the structural investigations of the processed Nb samples at the Materials Research Department of TU Darmstadt are presented.

INTRODUCTION

Superconducting radio frequency (SRF) accelerator cavities are becoming the standard for particle energies beyond 1 GeV. The state-of-the art cavities are made of high quality bulk niobium. The cavities undergo multiple processing steps, including chemical etching, high pressure rinsing with ultrapure water and baking to reach their designed quality factor and accelerating gradient.

Grassellino *et al.* managed to increase the quality factor of Nb cavities by introducing an additional N-doping step to the then standard recipe [1]. Recently a new, milder way of nitrogen diffusion was introduced, the nitrogen infusion process [2]. In contrast to the short time, high temperature N-doping the introduction of nitrogen in the infusion is done at low temperature and for long time. The increase in quality factor is achieved without further electro-polishing, a necessary treatment after N-doping to remove the surface nitrides. Koufalis *et al.* emphasized the beneficial role of carbon and oxygen trace elements present in the nitrogen atmosphere [3], possibly causing the same effect in the long time annealing as the short N-doping at the end of the high temperature bake-out.

A different way of improving the performance for SRF cavities could be the enhancement of the critical temperature by transforming the surface region (in the depth of the penetration length) of the Nb-cavity to the cubic δ-phase of NbN [4]. To reach the NbN phase, higher temperatures and partial nitrogen pressures are necessary. The cubic phase of δ-NbN forms above 1300 °C [5].

In this contribution our first results of the N-doping in both directions (α-Nb(N) and δ-NbN) are shown.

METHODS

Niobium samples (Fig. 1) were baked out in the high-temperature UHV furnace located at IKP, TU Darmstadt (the "Wuppertal oven") [6-8]. For comparison, samples were vacuum annealed and N-doped in the Advanced Oxide Molecular Beam Epitaxy (ADOMBE) chamber at ATFT, TU Darmstadt. In this system, a RF-source directed nitrogen atoms to the sample surface. The Nb samples were characterized by X-ray diffraction (XRD), electron microscopy and secondary ion mass spectroscopy (SIMS).

High quality Nb sheets (RRR 300) were treated by buffered chemical polishing (BCP), then cut to 5x5 mm^2 squares by high pressure water at Research Instruments. The XRD measurements were done on a Rigaku SmartLab diffractometer with rotating anode (λ=1.54 Å), line focus and parallel beam set-up. Specular scans were taken in θ-θ geometry and pole figures at different Bragg-peak positions (constant detector angle). For electron microscopy a Philips XL30 FEG high-resolution scanning electron microscope (HR-SEM) was used. The SIMS measurements were done on a Cameca ims5f spectrometer with O^{2+} ions.

Figure 1: Niobium test samples cut from high quality Nb sheet. Typical sample size was 5x5x2.7 mm^3. Distance between two marks is 1 mm.

RESULTS DISCUSSION

The niobium samples (Fig. 1) showed in the as-received state relatively large roughness, as seen by HR-SEM (Fig. 2). The samples were annealed in vacuum in the Wuppertal oven at different temperatures. Next, the N-doping experiments started in the oven [8]. Parallel to those experiments, Nb samples were N-doped in the ADOMBE chamber. The SIMS measurements on those samples showed nitrogen diffusion (Fig. 3).

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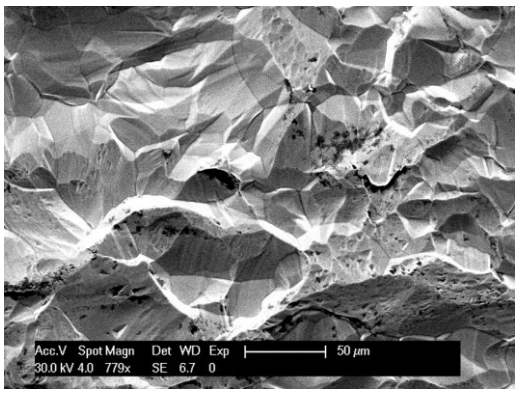

Figure 2: High resolution scanning electron microscope image of a typical virgin niobium sample.

In Figure 4 the XRD pattern of a Nb sample is shown before and after N-doping in the ADOMBE chamber. This sample was annealed at 1200 °C for 1 h in $2 \cdot 10^{-6}$ mbar N-atmosphere. The XRD pattern changed drastically. Slight changes in the pattern were already observed for lower doping temperatures [9], but now no Bragg peaks left, only a background with a broad hump. To investigate the possible origin of this change, pole figures were taken at the 200 peak position of Nb to determine the texture of the surface. As seen in Fig. 5, the reason of the missing peaks in Fig. 4 is the strong texture change of the sample. The virgin Nb is already textured, but the relatively small peaks are distributed to broad regions, thus there is always a peak for the specular geometry (the middle of the disc in Fig. 5). After annealing, the number of peaks reduces drastically, and the intensity of those peaks increases, transforming the sample into a "few crystal" state.

With the up to now described low nitrogen partial pressure range the surface showed no formation of the NbN phase, a different approach was taken.

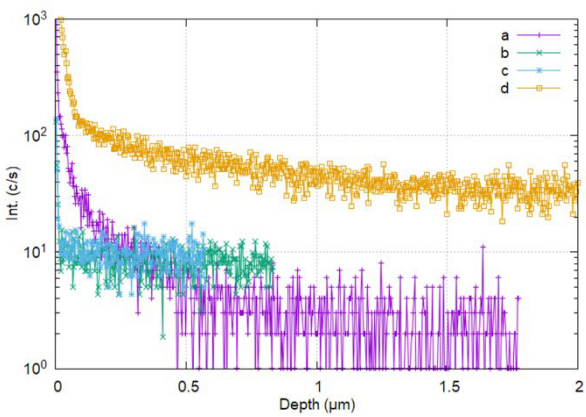

Fig 3: SIMS data for ^{14}N of the Nb samples. The series starts with the virgin Nb *a*), then the vacuum annealed (in the Wuppertal oven) at 850 *b*) and 1027 °C *c*) results are shown. Finally, the data of the sample nitrogen doped in the ADOMBE chamber *d*) at 965 °C for 80 min in $1.9 \cdot 10^{-6}$ mbar partial nitrogen pressure is presented. The curves were normalised to the $^{93}Nb_2$ signal. The sputtering was ended when no further intensity change was observed.

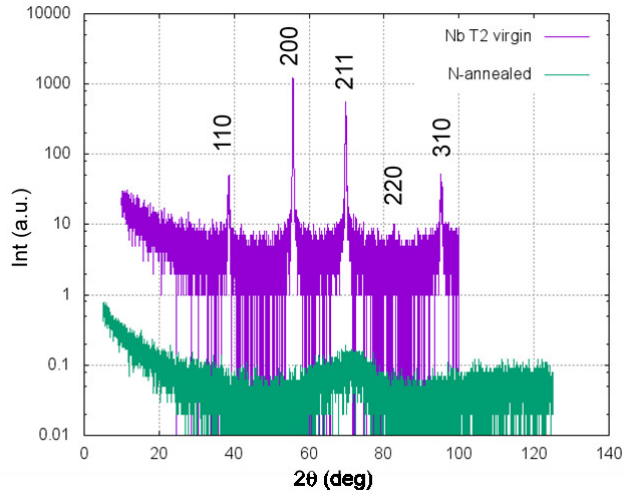

Figure 4: Specular X-ray diffraction pattern of a Nb sample *before* (pink, top) and *after* (green, bottom) N-doping in the ADOMBE chamber at 1200 °C. The curves are shifted vertically for clarity.

Nb-samples were annealed in 1 bar N_2 atmosphere in an alumina tube furnace at different temperatures (1400-1700 °C) [10]. The temperature was optimized to get the maximal possible δ-phase ratio of NbN.

As seen in Fig. 6, the NbN_x phase is formed, but not phase-pure and NbO_2 and Nb_2N_2 phases with other minority peaks corresponding to unresolved phases.

DISCUSSION

For the low pressure N-doping series in the Wuppertal oven, the SIMS measurements showed the decrease of hydrogen and carbon levels, both for the vacuum annealed and N-doped samples [9]. Up to 1400 °C sample temperature no nitrogen diffusion was seen by SIMS [8] for those doping trials, in contrast to the samples doped in the ADOMBE chamber. For the latter ones the atomic N-flux resulted in nitrogen doping already at 965 °C as shown in Fig. 3.

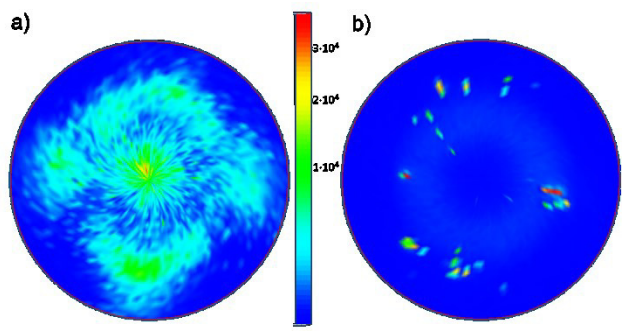

Figure 5: Pole figure of the 200 Bragg-reflection of a Nb sample before *a*) and after *b*) N-doping in the ADOMBE chamber at 1200 °C. The colour bar represents the intensity on a square root scale.

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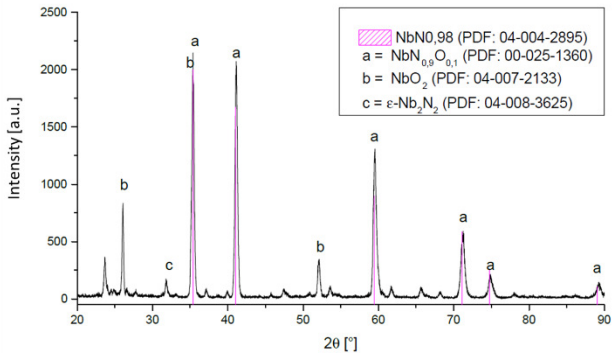

Figure 6: Specular X-ray diffraction pattern of Nb annealed in 1 bar N_2 in the tube furnace. The annealing temperature was 1500 °C. Pink lines are corresponding to the NbN_x (majority) phase. Other phases also present, indicated with their powder diffraction file (PDF) number of the International Centre for Diffraction Data) [10].

We attribute the difference in the results to Nb itself, as it is a very good N-getter material at high temperatures [8], and to the RF-source, as the reactivity of atomic nitrogen is much higher, than of the inert N_2 gas. In those experiments XRD showed no formation of new phases, the sample remained in the α-Nb(N) phase.

The most intriguing change occurred in the specular X-ray diffraction patterns. In Figure 4 it is compared for the 1200 °C annealed sample, but quite similar changes were seen for all high temperature N-doped and vacuum annealed Nb-samples. The pole figures helped to find the seemingly missing peaks.

In case of a polycrystalline material the XRD pattern is a sum of all possible orientations. When the material is highly textured, only crystallites with an appropriate orientation can contribute to the pattern. In the extreme case of a single crystal, the material must be carefully oriented, to find the Bragg peak. A pole figure is taken at a fixed detector angle by rotating and tilting the sample around. It shows the location of the appropriate directions in space. Each maxima corresponds to a crystallite with the correct orientation. Mapping out the Bragg peaks show the texture of the material. In our case the initially broad distribution of peaks changes to a few, extreme sharp Bragg peaks. In other words, only a few huge crystallites are present after the annealing. For the X-ray measurements a source with line focus was used, with slit height of 5 mm, to ensure, that the information is collected from the full surface. The recrystallization of Nb at even lower temperatures is a well-known phenomenon already seen as the softening of cold-rolled Nb-sheets [11]. Here the softening was reported to occur between 590-630 °C.

For the attempt to reach the NbN phase with 1 bar N_2 pressure the appearance of oxide and oxynitride phases was unavoidable with the available setup. This is in line with the recent results of Pandey *et al.* [12]. The conditions of the Nb-annealing, like gas purity, must be determined with high precision and should be strictly controlled.

CONCLUSION

In this contribution we reported on the first results of nitrogen doping of niobium in different N-pressure ranges. In case of low nitrogen pressures and high temperatures no formation of δ-NbN was found. For samples doped in the ADOMBE chamber nitrogen diffused to Nb. The surface of the Nb samples recrystallized, as was shown by XRD pole figure measurements.

At high temperatures and 1 bar N_2 pressure the cubic δ-NbN phase was formed. Despite optimizing the procedure, no phase pure NbN could be obtained. The gas atmosphere and the environment (oven) must be carefully controlled to avoid the formation of niobium oxynitrides and niobium oxides.

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