IN-SITU EXAFS INVESTIGATIONS OF Nb-TREATMENTS IN N_2 AT ELEVATED TEMPERATURES

P. Rothweiler*, B, Bornmann, J. Klaes, S. von Polheim, R. Wagner, D. Lützenkirchen-Hecht
Fk. 4 – Physics, University of Wuppertal, Germany

Abstract

Polycrystalline niobium metal foils of different thickness were exposed to dilute nitrogen atmospheres at elevated temperatures of up to 900 °C, and the resulting changes of the atomic short range order structure were in-situ studied by transmission mode X-ray absorption spectroscopy (EXAFS) experiments. High quality EXAFS data were collected prior to any heat treatment as well as during the different process steps at elevated temperature, and finally after cooling to room temperature. Due to the low solubility of N_2 in niobium, only very small changes of the EXAFS data could be detected after the processing in N_2-atmospheres, and the present experiments gave no evidence for bulk formation of Nb-nitrides such as NbN or Nb_2N. Thus, one major purpose of this contribution is to identify the positions of nitrogen within the bcc-lattice of the Nb host. A quantitative EXAFS data evaluation is possible using only slightly distorted metallic Nb-Nb coordinations, and the obtained results suggest that N-atoms are increasingly incorporated on octahedral interstitial sites in the host lattice with increasing N_2-exposure.

INTRODUCTION

The preparation of superconducting Nb-cavities for particle accelerators comprises several treatments, in particular e.g. buffered chemical polishing (BCP), electropolishing (EP), high pressure rinsing and dry-ice cleaning (DIC) (see e.g. [1]). Recent experiments have shown that the RF-superconducting properties of Nb-cavities can substan-tially be improved, if heat treatments under dilute nitrogen or argon atmospheres are included in the conditioning procedures of the cavities, yielding a significant reduction of the electrical resistivity and an increased quality factor in medium acceleration fields [2-4]. The formation of niobium nitride (NbN) with an increased critical temperature was discussed to explain the observed phenomena [5], however, a full understanding of the structural changes which lead to these improvements is still incomplete. Recent surface analytical experiments have indicated that Nb_2N, Nb_2O_5 and NbN_yO_y oxynitride phases may occur at the surfaces of the nitrogen-treated materials, while however no major alterations of the bulk material seem to occur as probed by X-ray diffraction [6]. In this context, X-ray absorption fine structure spectroscopy (EXAFS) is a valuable alternative and supplemental method to investigate the structure of Nb-samples treated with nitrogen at high temperatures. Due to its inherent sensitivity to probe the atomic short range order structure around the X-ray absorbing atom, it may reveal subtle differences in the coordination environment of the Nb that may not be detectable using other techniques.

The protocol for the Nb-cavities currently comprises the following steps (see e.g. [2, 4]), i.e. a substantial electropolishing of up to 200 µm material removal, a short high pressure rinse with ultra-pure deionized water, a buffered chemical polish and ethanol rinse prior to the introduction of the Nb into a vacuum system with a base pressure of better than 10^{-7} mbar. The heat treatment starts with a slow heating to 800 °C, eventually even more, and a dwell time of three hours to outgas any H_2 dissolved in the Nb primarily from the previous EP. The doping is subsequently performed by introducing N_2 at a level of ca. 25 mbar in the process chamber for 2 minutes, followed by an additional annealing at 800 °C for six minutes under ultrahigh vacuum conditions. Thereafter, the samples are cooled down to room temperature, and a light EP (few µm removal) is applied to remove possible niobium nitrides on the surfaces.

Due to the limited penetration of X-rays through matter in the order of some 10 µm, the structure of real Nb cavities can hardly be investigated by transmission mode EXAFS spectroscopy. Thus, in order to learn about the structural changes in niobium induced by N-doping at elevated temperatures, we have substantially simplified the preparation processes, i.e. we have exposed polycrystalline, smooth thin Nb foils of suited thickness to a nitrogen atmosphere (pressure between $3x10^{-3}$ and $5x10^{+1}$ mbar) in a temperature range from 25 °C to ca. 900 °C, and probed the induced structural modifications in-situ in a newly developed high temperature cell.

EXPERIMENTAL DETAILS

For the in-situ preparation, a dedicated vacuum chamber (base pressure < 10^{-7} mbar) featuring a small, oil-free turbomolecular pump and a ceramic heating plate suited for temperatures of up to 1200 °C was realized (see Fig. 1). Heating rates of more than 500 °C/minute are possible, while cooling takes much more time. The preparation chamber is entirely remote-controlled, lightweight and sufficiently small to fit on a standard EXAFS beamline, enabling transmission as well as fluorescence mode EXAFS experiments at elevated temperatures. High-purity (5.0) N_2-gas was fed in by a needle valve, and the gas pressure was measured using a standard ultrahigh vacuum gauge. Temperature measurements were performed using a thermocouple placed on the sample holder, resulting in a slightly larger temperature readouts compared to the sample. More details of this chamber will be published elsewhere [7].

---

* patrick.rothweiler@uni-wuppertal.de

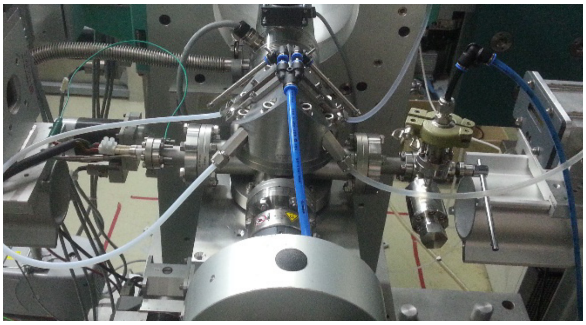

Figure 1: Photography of the high-temperature cell mounted on the diffractometer at DELTA beamline 8. The entrance and exit windows of the samples are cooled by pressurized air.

Processing, i.e. N doping of the Nb samples (foils of 6, 12 and 25 μm thickness) included an annealing treatment in vacuum for 1 h at 900 °C, and a subsequent exposure to high-purity (5.0) N_2-gas under a pressure range from $3x10^{-3}$ to $5x10^{+1}$ mbar for varying times. EXAFS data at the Nb K-edge (18986 eV) were collected prior to any heat treatment as well as during the different process steps at elevated temperature, and during and after cooling to room temperature under high vacuum.

The experiments presented here were performed at the wiggler beamline 8 of the DELTA storage ring (Dortmund, Germany) [8] and the SuperXAS beamline at the Swiss Light Source (Villigen, Switzerland) [9], employing Si(311)-monochromators and using gas-filled ionization chambers for the intensity measurements in the incident and transmitted beams. The energy scans covered a range from ca. 220 eV below the edge up to 1600 eV above the edge, resulting in a k-range of up to 20 $Å^{-1}$. Up to now, about 30 samples have been prepared and analyzed.

The EXAFS data analysis was performed using the Demeter software [10]. The energy scale for each spectrum was calibrated using the absorption edge of a Nb reference foil measured simultaneously with each of the specimen. While a k-range of $2.6\ Å^{-1} \leq k \leq 15.0\ Å^{-1}$ was used for the Fourier-transform (FT), the radial distribution from $1.8\ Å \leq R \leq 3.2\ Å$ was back-transformed into k-space and fitted with phases and amplitude functions calculated in FEFF 8 [11] using the bcc Nb lattice (space group Im-3m, no 229) with a lattice parameter of 3.3004 Å as a starting parameter. While the amplitude reduction factor S_0^2 and the inner potential shift ΔE_0 were treated as global fit parameters, the distances R_1 and R_2 of the first two Nb-Nb shells as well as the related mean squared displacement σ_1^2 and σ_2^2 of those shells were fitted separately. Fits were optimized using k^1-, k^2- and k^3-weighted fine structure data $\chi(k)$ simultaneously. Polycrystalline NbN and Nb_2N reference samples were measured for comparison.

RESULTS AND DISCUSSION

The EXAFS of pristine Nb foils already alter with annealing in a vacuum of about 10^{-7} mbar, as can be seen in Fig. 2(a), with a slight decrease in the magnitude of the Fourier-transform related to the first nearest neighbor. It is important to distinguish such an effect from the N-doping under investigation, and thus the samples were carefully investigated prior to any N_2-exposure.

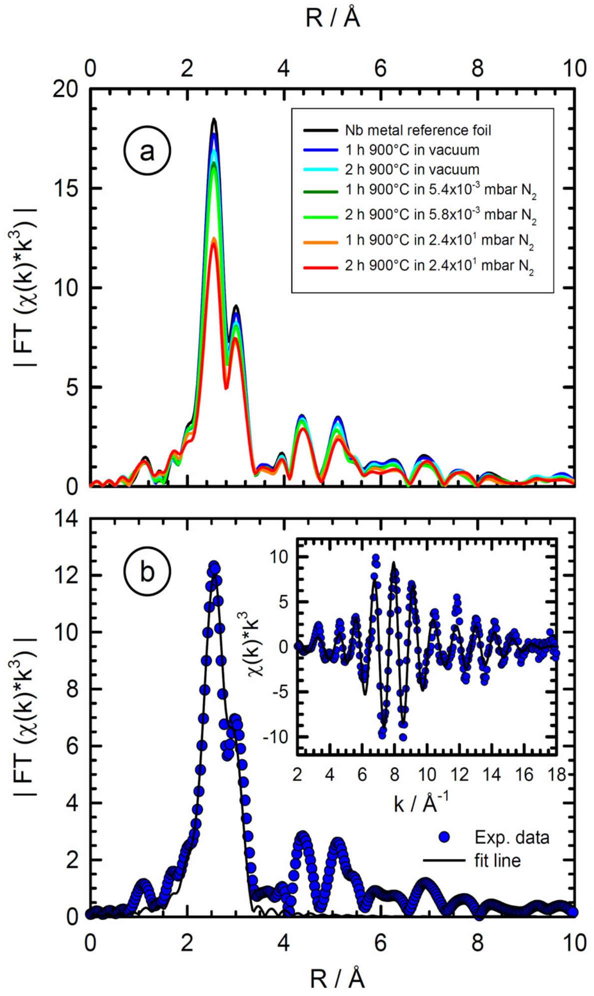

Figure 2: (a) Magnitude of the Fourier-transform of the k^3-weighted EXAFS fine structure $|FT(\chi(k)*k^3)|$ after the treatments as indicated, in comparison to the FT of a Nb metal reference foil. All the presented data were recorded at room temperature after cooling down from the reaction temperature. (b) Exemplary fit to a sample treated by a N_2-exposure at 900°C under a pressure of 22 mbar for 20 minutes, modeled by a least-square fit using the single scattering paths of the first two bcc Nb shells.

In general, after about 15 minutes heat-treatment in vacuum, no additional changes were detectable in the EXAFS data. However, after increasing the N_2 pressure to levels between $5x10^{-3}$ mbar up to 50 mbar, additional distinct reductions of the EXAFS signals were found, that can unambiguously be associated to the influence of the supplied nitrogen gas. In all cases, a reduction of FT-amplitude with no substantial change in shape may be noted, and for all the different thicknesses of the Nb-foils investigated. The quantitative EXAFS data evaluation shows that all the data sets can be well fitted using metallic Nb-Nb coordinations only (see Fig. 2(b)), suggesting that no Nb-containing impurity phases were formed in substantial amounts. From experiments on oxidized Nb-foils performed for comparison, the detection limit can be estimated to less than one atomic %. Therefore, we can give no evidence for the formation of substantial amounts of Nb-nitrides as reported by previous studies in the past (see, e.g. [5]).

By collecting data and fitting parameters for each treated sample at room temperature, within the errors we find no significant structural changes for the annealed samples, i.e. the bcc structure of the pristine Nb-material is entirely preserved after the N_2-exposure at elevated temperature, in agreement with recent diffraction experiments [6]. However, by increasing the N_2 - exposure, the subtle changes detected in the FT of the measured data (see Fig. 2(a)) lead to systematic changes of the derived short range order parameters, as can be seen in Fig. 3, where the evaluated Nb-Nb bond distances (R_1 and R_2) and the related mean squared displacements (σ_1^2 and σ_2^2) are plotted as a function of the nitrogen exposure, i.e. the product of the N_2-pressure and the duration of the treatment at 900°C. It is important to note that this temperature is slightly larger than those of the optimized recipe applied for N-doping niobium at Fermilab (e.g. [3, 4]). However, due to the position of the thermocouple used for temperature measurements here, the temperature of the sample is systematically lower by more than about 50 C compared to the readout of the thermocouple. Thus we are currently improving the temperature measurement by the implementation of an IR-camera allowing also to access the temperature distribution of the sample.

Since the temperature was constant for all measurements, the changes in mean squared displacements σ_1^2 and σ_2^2 can accordingly be directly attributed to an increase in the disorder in the coordination geometry of the X-ray absorbing Nb atoms. For dilute nitrogen atmospheres we find σ_1^2 and σ_2^2 to increase with N_2-exposure. This trend eventually reaches a plateau and starts to decrease for samples treated at large N_2-pressures of 50 mbar and prolonged heating for 1 hour or more. Intriguingly the Nb-Nb bond distances R_1 and R_2 stay almost constant within measurement uncertainty on the full range of more than 5 decades of N_2-exposure, with only a very slight increase of about 10^{-3} Å per decade (see the dashed lines in Fig. 3). Such a linear increase of the bond length with exposure is well compatible with diffusion limited processes, i.e. diffusion of N-atoms in the Nb-matrix in the present case. The increase in disorder combined with slightly increasing bond distances may be explained by a location of nitrogen atoms onto interstitial lattice sites, leading to a small and only local deformation of the niobium bcc structure, which in average leads to the observed dependencies.

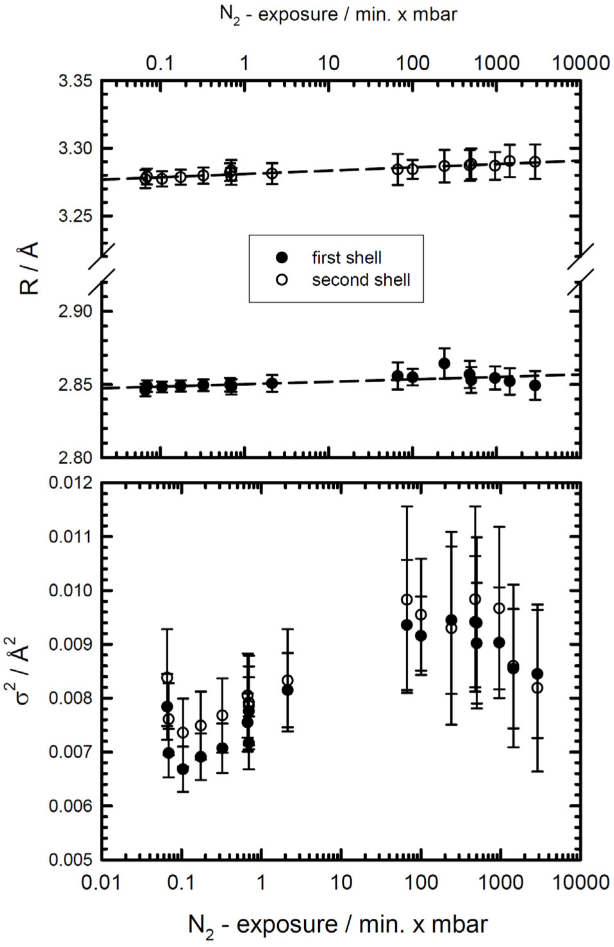

Figure 3: Structure parameters for the first two Nb-Nb shells, derived from least-square fits of the in-situ room temperature EXAFS data from Nb foils treated at 900 °C in N_2, as a function of the N_2-exposure, i.e. N_2-pressure times the duration of the treatment. (top) Bond distances R_1 and R_2. The dashed lines show a slight increase of the bond lengths with exposure. (bottom) mean squared displacements σ_1^2, and σ_2^2.

CONCLUSION

According to the presented EXAFS experiments, a heat treatment of smooth, polycrystalline Nb foils in dilute N_2-atmospheres at elevated temperatures leads to an increasing disorder in the bcc Nb lattice, however with an almost neglectable expansion with increasing exposure time, i.e. the EXAFS method seems to be sensitive enough to detect the small structural changes induced by N-doping. The possible formation of Nb-nitrides, could not be proved on the basis of the EXAFS data measured and analyzed so far, and any star-like features on the Nb-surface, that are characteristic for NbN/Nb_2N formation, could not be detected on the samples prepared here. Similarly, energy dispersive electron spectroscopy gave no evidence for N-signals for samples treated under less than an exposure of 100 mbar minutes.

Obviously, N_2 is adsorbed and diffuses into the bulk Nb metal, where interstitial sites are randomly occupied in increasing amounts. Since the solubility of N in niobium is only small, with a value below 1 at. % at 900°C [12], it is likely that above a certain concentration impurity phases may appear at grain boundaries with the polycrystalline niobium. Future experiments using larger N_2-exposures are planned to elucidate this effect in more detail. First time resolved experiments have already been conducted to directly study the dynamics of the structural changes at elevated temperatures, and better to compare with the shorter exposure time used during N-doping of cavity materials according to [2, 4]. Furthermore, it is planned to investigate samples prepared by the established process protocol for comparison. Last not least, doping experiments using inert gases such as argon and krypton are currently under way [13].

ACKNOWLEDGEMENTS

We like to thank DELTA, DESY and the Swiss Light Source for the provision of beamtime, and P. Becker, O. von Polheim, J.-C. Gasse and M. Nachtegaal for the technical support at the beamlines. Financial support by the German Federal Ministry of Education and Research (BMBF) under project No. 05H15PXRB1 and 05H18PXRB1 is gratefully acknowledged.

REFERENCES

[1] H. Padamsee, “The science and technology of superconducting cavities for accelerators”, *Supercond. Sci. Technol.*, vol. 14, pp. R28-51, 2001. `doi:10.1088/0953-2048/14/4/202`

[2] A. Grasselino *et al.*, “Nitrogen and argon doping of niobium for superconducting radio frequency cavities: A pathway to highly efficient accelerating structures”, *Supercond. Sci. Technol.*, vol. 26, 102001, 2013. `doi:10.1088/0953-2048/26/10/102001`

[3] A. Grassellino *et al.,* “N doping: progress in development and understanding”, in *Proc. SRF'15*, Whistler, Canada, Sep. 2015, paper MOBA06, pp. 48-54. `doi:10.18429/JACoW-SRF2015-MOBA06`

[4] D. Gonnella *et al.*, “Nitrogen-doped 9-cell cavity performance in a test cryomodule for LCLS-II”, *J. Appl. Phys.*, vol. 117, p. 023908, 2015. `doi:10.1063/1.4905681`

[5] M. Pham Tu, K. Mbaye, L. Wartski, J. Halbritter, “RF characterization of thermally diffused superconducting niobium nitride”, *J. Appl. Phys.*, vol. 63, pp. 4586-4590, 1988. `doi:10.1063/1.340160.`

[6] A. Dangwal Pandey *et al.*, “Surface characterization of nitrogen-doped Nb (100) large-grain superconducting RF cavity material”, *J. Mater. Sci.*, vol. 53, pp. 10411-10422. 2018. `doi:10.1007/s10853-018-2310-8`

[7] J. Klaes, B. Bornmann, D. Lützenkirchen-Hecht, “An in-situ cell for X-ray investigations at elevated temperatures”, unpublished.

[8] D. Lützenkirchen-Hecht *et al.*, “The materials science X-ray beamline BL8 at the DELTA storage ring”, *J. Synchrotron Rad.*, vol. 16, pp. 264-272, 2009. `doi: 10.1107/S0909049509000508`

[9] O. Müller *et al.*, “Quick-EXAFS setup at the SuperXAS beamline for in situ X-ray absorption spectroscopy with 10 ms time resolution”, *J. Synchrotron Rad.*, vol. 23, pp. 260-266, 2016. `doi:10.1107/S1600577515018007`

[10] B. Ravel, M. Newville, “ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT”, *J. Synchrotron Rad.,* vol. 12, pp. 537-541, 2005. `doi:10.1107/S0909049505012719`

[11] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, “Real Space Multiple Scattering Calculation and interpretation of x-ray-absorption near-edge structure*”, Phys. Rev. B*, vol. 58, pp. 7565-7576, 1998. `doi:10.1103/PhysRevB.58.7565`

[12] G. Brauer, R. Esselborn, “Nitridphasen des Niobs”, *Z. Anorg. Allg. Chem.*, vol. 309, pp. 151-170, 1961. `doi:10.1002/zaac.19613090303`

[13] P. *Rothweiler*, Masters thesis, University of Wuppertal, 2019.