

# SURFACE CHARACTERIZATION OF NITRIDED NIOBIUM SURFACES\*

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## Abstract

Thermal treatment of niobium radio frequency cavities in nitrogen atmosphere is employed in ILCLS-II Project in order to improve the quality factor of Nb cavities. A so called "N-infusion" thermal treatment is applied without any post processing [1, 2], whereas "N-doping" requires the removal of the upper layer of 5-30  $\mu\text{m}$ . For better understanding the mechanism of such an improvement, a detailed characterization of the nitrided surface is necessary. Our studies are focused on characterization of the niobium surface subjected to such treatments (surface morphology, nitrogen concentration profile, hardness, phase composition). The sample preparation technique for studying the hydride precipitation in N-Nb system is presented, and current activities on studying of N-infused Nb samples by SQUID and PPMS are briefly discussed.

## INTRODUCTION

The SRF niobium cavities, a key component of current and future efficient particle accelerator, are made from high-purity niobium and undergo a complex multi-step production process to achieve a high accelerating gradient,  $E_{acc}$ , and a high quality factor,  $Q_0$ . These quantities, together with the manufacturing yield, drive cost and performance factors such as cryogenics plant size, beam energy, machine length etc. Recently new processing procedures including thermal treatments in nitrogen atmosphere demonstrated  $Q_0$  values two times above the previous record [1, 2]. The possible mechanism of such improvement is the decrease of the superconducting surface resistance of niobium by lowering mean free path of "normal" electrons caused by interstitial nitrogen [3] as well as possible suppression of small hydride precipitates due to the trapping effect [4]. In order to contribute to understanding of the improved cavity performance we perform similar treatments of samples to gain knowledge about the surface state. Here we demonstrate a technique for sample preparation in order to study the N-H interaction in Nb with varied nitrogen content at the surface, as well as characterisation of such surface with X-ray Photoelectron Spectroscopy (XPS) and laser profilometry. We also present some data on our current studies of the samples subjected to same treatments as TESLA cavities (EXFEL, N-doping, N-infusion): magnetisation curves and complex magnetic susceptibility.

## EXPERIMENTAL DETAILS

The experimental work was carried on at DESY site,

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ILC-HiGrade Lab within a common R&D Project. Investigations were carried out both on fine-grained (FG, Tokyo Denkai) and large-grained (LG, Heraeus) Nb samples cut by electro erosion from 2.8 mm-thick sheets followed by a few  $\mu\text{m}$  BCP. The sample heat treatments were performed in a furnace consisting of a ceramic tubular chamber ( $\varnothing 7$  cm, 1.5 m in length) with a three zone temperature control and water cooled flanges and operates at a maximal temperature of 1000 °C and working pressure of  $\sim 10^{-4}$  Pa. A titanium tube was placed in the middle of the furnace, as a sample holder, with an additional thermocouple close to the samples for more precise temperature control. The gas regulator provided partial gas pressures of a few Pa (30 mTorr) required to reproduce the treatment of cavities described in [1, 2].

The experiments were performed at various temperatures, nitridation times and drive-in diffusion steps ( $T$ ,  $t_{\text{nitridation}}$ ,  $t_{\text{drive-in}}$ ). The typical  $p, T(t)$  plot of one of the treatments is presented in Fig. 1.

Thorough characterisation of LG Nb surface treated at 900\_20N<sub>2</sub>\_30 and 800\_20N<sub>2</sub>\_30 by GDOES, SEM/EDX,

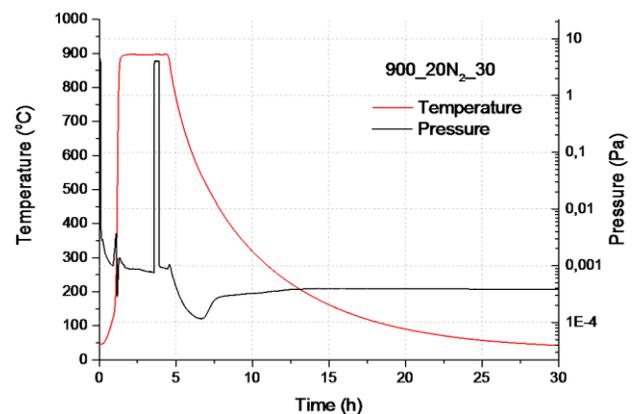


Figure 1: ( $p, T$ ) vs.  $t$  plots during nitridation of Nb samples (900\_20N<sub>2</sub>\_30).

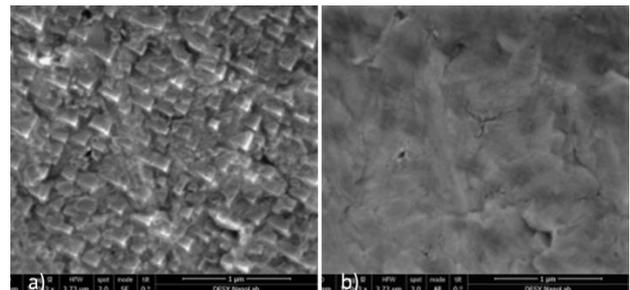


Figure 2: SEM images of the nitrided at 900\_20N<sub>2</sub>\_30 surface obtained with: a – secondary electrons, b – backscattered electrons.

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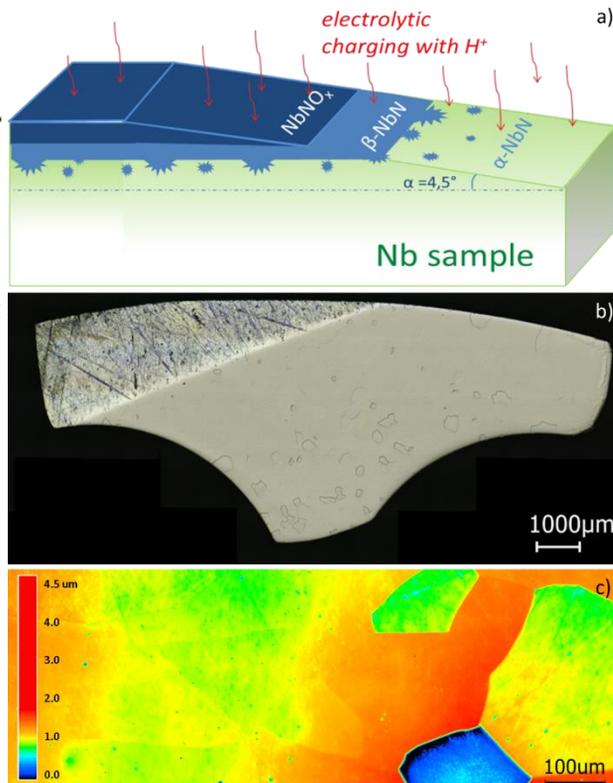


Figure 3: a – schematic view of the sample; b - optical image (top view) of the sample; c – height profile image of the angle polished surface.

XPS, XRD, AFM will be published elsewhere. Here we will focus on the sample which was specially made for studying the hydrogen trapping phenomenon in H-N-Nb system. For that purpose, one of the samples (FG Nb) after nitridation at 900°C was mechanically polished by metallographic routine followed by "light" electropolishing ( $\text{H}_2\text{SO}_4:\text{HF}=9:1$ ) in order to eliminate possible plastic deformations and inclusions of abrasive particles. Then, hydrogen was loaded electrolytically using a diluted (0.2N) sulfuric acid solution [5].

## RESULTS AND DISCUSSION

The FG and LG Nb samples were nitrided in the regime shown in Fig.1. The analysis with SEM/EDX detected the presence of both O and N in the specimen. In Fig. 2a the topography contrast secondary electron image reveals rectangular shaped precipitates (as shown below, Nb oxides), while in Fig. 2b, in the corresponding backscattered electron image probing information from larger depth, they are not visible meaning the layer with precipitates is quite thin (<10 nm). Based on GDOES and terminal solubility data, the thickness of the nitrided layer was estimated to be ~3  $\mu\text{m}$ . Modelling of a two-step diffusion process using the second Fick's law was realized with forward final differences method. The best fit of the GDOES data resulted in equilibrium concentration of 59.5 at % N and diffusion coefficients in the nitrided layer

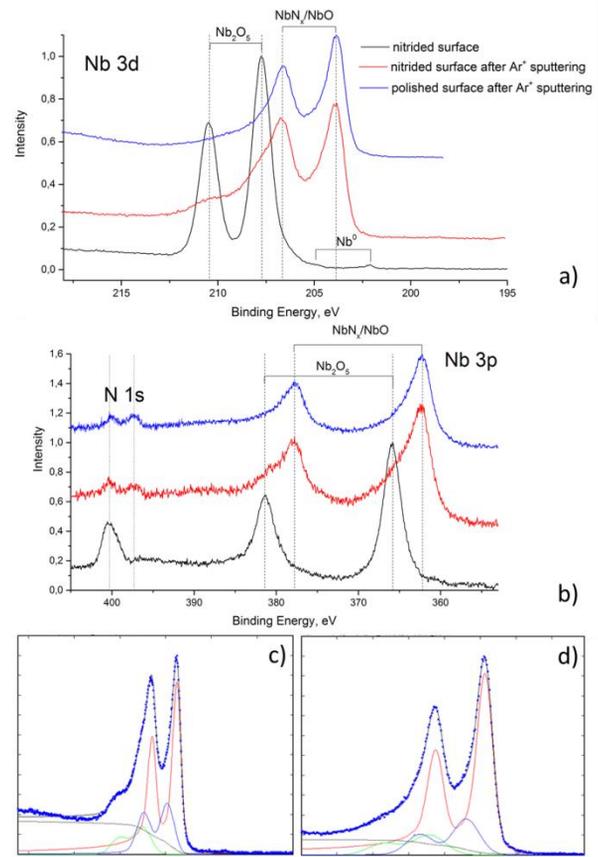


Figure 4: XPS spectra before and after  $\text{Ar}^+$  sputtering: a – Nb 3d levels; b – Nb 3p levels; c, d – deconvolution of the Nb 3d peaks measured on the  $\text{Ar}^+$  sputtered nitrided and polished surfaces, respectively.

and solid solution of  $D_\alpha=4.26 \cdot 10^{-9} \text{ cm}^2/\text{s}$  and  $D_\beta=1.1 \cdot 10^{-11} \text{ cm}^2/\text{s}$ , respectively. Using the data of microhardness measurements at various loads (5-2000 gf) by Vickers method and applying the physical model described in [6], the hardness of the nitrided layer was estimated. The obtained value of 2320 HV is lower than the reported for  $\beta\text{-Nb}_2\text{N}$  (3570 HV, [7]). The lower value can be explained by the fact that the nitrided surface represents a composite of  $\beta\text{-Nb}_2\text{N}$  and NbO, according to XRD studies of this sample.

The sketch of the sample (not to scale) and the optical image of a ready-made specimen are shown in Fig. 3a and b, respectively. The measured solid angle with the initial surface plane was  $4.5^\circ$ . The height profile image of the polished surface made with laser scanning microscope is presented in Fig. 3c. The peak-to-valley distance measured over the area of  $1 \times 0.3 \text{ mm}^2$  is 4.5  $\mu\text{m}$ . Such a roughness is explained by the presence of the steps at grain boundaries, which showed up after the mechanical polishing and did not exceed 1.1  $\mu\text{m}$ , and the waviness parameter which is not taken into account by the software of the microscope. A surface prepared in this way reveals the gradual depletion of nitrogen on the surface while a required hydrogen concentration is easily attained by adjusting the parameters of electrolytic hydrogen charging (Fig. 3a). The *in-situ* studies of such a surface upon cool-

ing would allow demonstrating the influence of N content on the precipitation dynamics of niobium hydrides via trapping effect. Recently, first experiments have been performed with *in situ* dynamic XPS at P04 beamline PETRA III, DESY.

The XPS spectra (see Fig. 4a,b) were collected from the nitrated and angle polished surface using 1 keV photons of primary X-ray beam. The spectral analysis of the Nb 3d and 3p levels shows that the unpolished surface (black curve) was oxidized to pentoxide upon nitridation in our furnace. N 1s peak at 400 eV corresponds to adsorbed nitrogen (N<sub>2</sub>) at grain boundaries and surface inhomogeneity due to high roughness of the unpolished surface [8]. Upon Ar<sup>+</sup> ion sputtering, the pentoxide was almost completely removed (red curves) on the unpolished surface. A new peak at 397.3 eV within N 1s region corresponding to Nb-N bonding became visible after sputtering of the both surfaces. Spectral deconvolution of Nb 3d peak showed that the resulted surfaces contain both NbN<sub>x</sub> and NbO phases with Nb 3d<sub>5/2</sub> positioned at 203.7 eV and 204.7 eV, respectively (Fig.4c,d). The XRD studies support this finding. The XPS were also measured upon cooling to 130 K and warming up to room temperature in a dynamic XPS mode. The data are currently being analysed. The 3D topography image made with a laser profilometer showing the defect left by the precipitated hydride is presented in Fig. 5.

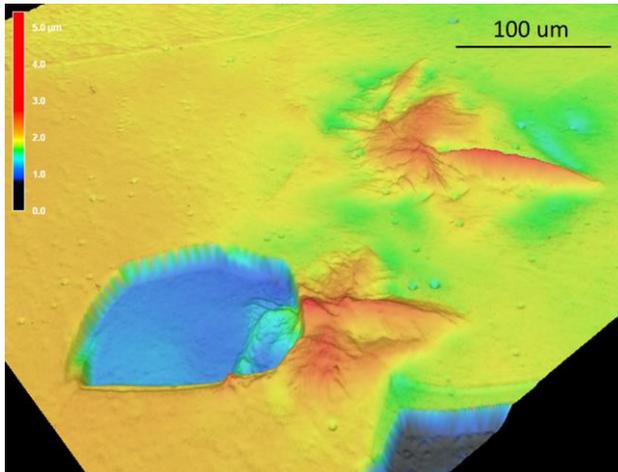


Figure 5: 3D topography image (laser profilometry) of the defects left by niobium hydrides revealed after cooling.

### Ongoing Research Activities

Presently our studies are focused on the samples subjected to the same treatments as TESLA cavities (standard treatment of EXFEL cavities), as well as new treatments reported by Fermi National Laboratory, i.e. N-doping and N-infusion. In particular, we perform thorough investigation of N-infused samples. SEM of the N-infused samples (800°C\_N<sub>2</sub>120°C, 48h at 30 mTorr of N<sub>2</sub> partial pressure) did not reveal any additional features on the sample surface (as opposed to thermal treatments of cavities at DESY, see [9]). The room temperature XPS studies are being performed at PETRAIII beamline at various energies of the incident photon beam. The preliminary results

revealed Nb<sub>2</sub>O<sub>5</sub> on the sample surface. Also, Nb 3d level of the N-infused sample has a hardly pronounced feature at around 203.9 eV as compared to 800°C annealed sample which can not be assigned to a Nb-N bond since N 1s did not reveal a chemically bound nitrogen with niobium. C 1s peak neither revealed carbide phases. It is to be clarified whether the differences observed in oxide-related features in the spectra are the peculiarity of the treatment or the difference in crystal orientation of the surface. In order to clarify this future experiments on N-infused samples at higher temperatures and different crystal orientations are to be performed.

Magnetic properties of Nb samples after various thermal processing are being performed jointly with JCMS, Jülich. In particular, magnetisation curves and complex magnetic susceptibility have been measured over a wide temperature range and dc magnetic fields up to 10 kOe. As an example, the M(H) curves and ac susceptibility of the N-infused sample are presented in Fig. 6a and b, respectively.

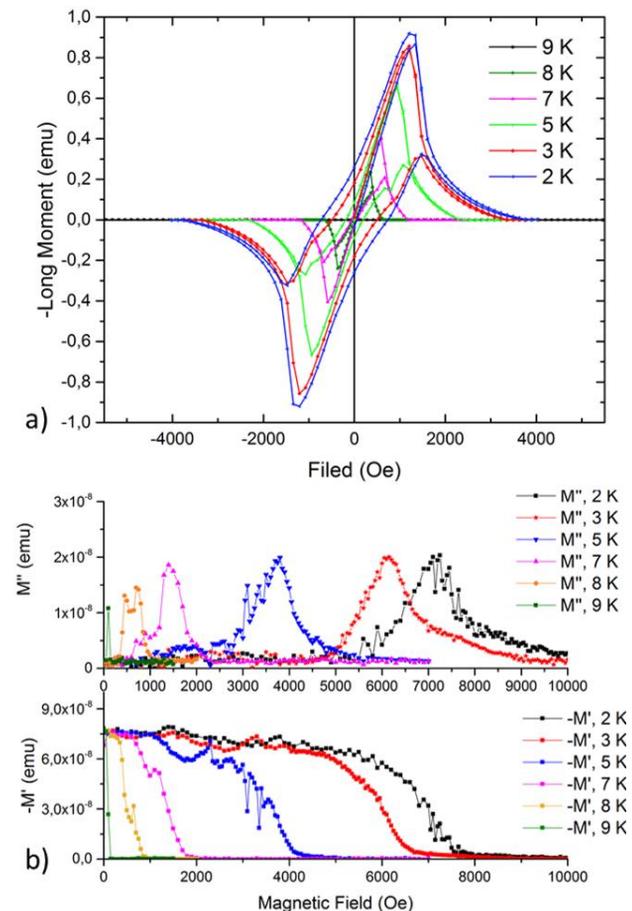


Figure 6: the M(H) curves (a) and ac susceptibility (b) of the N-infused Nb sample. The data were not corrected for the demagnetization factor.

Similar measurements have been performed on nitrated and BCP-ed samples and are yet to be analysed.

## CONCLUSION

In this paper we briefly described our activities on niobium sample treatments related to TESLA cavities and their characterization by various techniques. A technique for sample preparation for studying the N-H interaction in Nb with varied nitrogen content at the surface was proposed. The as-prepared surface was characterized by XPS at room temperature before and after the Ar<sup>+</sup> ion sputtering. The current activities on studying of N-infused samples were briefly outlined.

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## REFERENCES

[1] A. Grassellino *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 p. 102001, 2013.

[2] A. Grassellino *et al*, "Unprecedented Quality Factors at Accelerating Gradients up to 45 MV/m in Niobium Superconducting Resonators via Low Temperature Nitrogen Infusion", arXiv:1701.06077.

[3] H. Padamsee, J. Knobloch, T. Hays, *RF Superconductivity for Accelerators*, 2<sup>nd</sup> Edition, Wiley, Weinheim, ISBN: 978-3-527-40842-9, 2008.

[4] G. Pfeiffer, H. Wipf, "The trapping of hydrogen in niobium by nitrogen interstitials", *J. Phys. F: Metal Phys.*, vol. 6, No. 2, pp. 167-179, 1976.

[5] M. Yono *et al*, "Electrolytic Hydrogen Charging in Niobium Single Crystals", *Trans. JIM*, vol. 8, pp. 276-277, 1967.

[6] B. Jönsson, S. Hogmark, "Hardness measurements of thin films", *Thin Sol. Films*, 114 (1984), pp. 257-269.

[7] M. Benkahoul, "Niobium nitride based thin films deposited by DC reactive magnetron sputtering: NbN, NbSiN and NbAlN", Master Thesis, École Polytechnique Fédérale De Lausanne, Lausanne, Switzerland, 2005.

[8] R. M. Oliveira *et al*, "Evaluation of the resistance to oxidation of niobium treated by high temperature nitrogen Plasma Based Ion Implantation", *Surf. Coat. Tech.*, vol. 312, pp. 110-116, 2017.

[9] M. Wenskat *et al*, "Nitrogen infusion R&D on single cell cavities at DESY", presented at SRF'15, Lanzhou, China, July 2017, paper THPB007, this conference.