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IN-SITU EXAFS INVESTIGATIONS OF Nb-TREATMENTS IN N_2, O_2 AND N_2-O_2 MIXTURES AT ELEVATED TEMPERATURES

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Abstract

Smooth polycrystalline Nb metal foils were treated in dilute gas atmospheres using a temperature of 900 °C. Transmission mode X-ray absorption spectroscopy (EXAFS) at the Nb K-edge was used to investigate changes in the atomic short-range order structure of the bulk Nb-material in-situ. The experiments were performed in a dedicated high-vacuum cell that allows treatments in dilute gas atmosphere and temperatures of up to 1200 °C. Typical treatments include (i) pre-heating at 900 °C under high-vacuum, (ii) gas exposure at the desired pressure and temperature, and (iii) cooldown to room temperature under vacuum. EXAFS data were collected during the entire procedure with a time resolution of 1 s. For the treatments in N_2 at T = 900°C, the data show subtle changes in the Nb-EXAFS, that are compatible with N-doping of the bulk Nb, and the results suggest Nb uptake on octahedral interstitial sites. However, even a small O_2-partial pressure leads to a distinct oxidation of the Nb. The results will be discussed in more detail in the presentation.

INTRODUCTION

Nowadays almost all Niobium-cavities for particle accelerators are treated in N_2-gas atmospheres at elevated temperatures to improve their performance in terms of Q-factors, accelerating field gradients, RF-superconductivity etc. Several different recipes have been worked out in the past years to achieve the best possible performance by N-doping [1], N-infusion [2, 3] or mid-T-bake [4] treatments which mainly differ in the applied temperature, the pressure and the duration during which the Nb-cavities are treated in the gas atmosphere.

For the N-doping process, which is performed at a processing temperature of 800 °C, recent studies [5] showed that the N-atoms are likely to occupy the interstitial octahedral sites of the Nb unit cells. It has also been shown that heating under vacuum has no impact on the Nb lattice structure [5], while on the other hand Nb is very sensitive to oxidation even at very small pressures of oxygen at elevated temperatures [6]. Since oxygen is known to prefer the interstitial octahedral sites in the body-centred-cubic lattice of Nb as well [7] this imposes two very interesting questions, i.e. (i) is the N-uptake suppressed or hindered if Nb was pre-heated under poor vacuum conditions and is thus slightly oxidized, and (ii) whether the N-uptake in Nb is still possible in the presence of O_2. To address those two questions polycrystalline Nb metal foils of 7 µm thickness (purity 99.9%) were processed (i) with a pre-heating at 900 °C under a pressure of $2x10^{-4}$ mbar and a subsequent treatment in 3 mbar N_2-atmosphere, and (ii) after a pre-heating phase at 900 °C in a vacuum of 10^{-6} mbar, followed by a treatment in an N_2-air-mixture (3 mbar) with a ratio of 1000:1 at 900 °C. The processes were in-situ investigated using time-resolved, transmission-mode X-ray absorption fine structure (EXAFS and XANES) measurements.

EXPERIMENTAL DETAILS

For the performed in-situ EXAFS experiments a dedicated high-temperature vacuum cell (see Fig. 1) [6] was used. The cell features a ceramic heating plate to allow temperatures of up to a maximum of 1200 °C (heating rate ~ 350 °C/min), a small oil-free turbo-molecular pump (base pressure < 10^{-6} mbar) and a combination of fine leak and magnetic valves to control the treatment processes. The main chamber (150 mm diameter) uses two air-cooled Kapton-windows for X-ray beam transmission and a ZnSe-window for infrared temperature measurements. Additionally, there are two thermocouples installed at the heating plate and at the sample, respectively, with a gradient from the heater to the sample of ~ 100 °C at 900 °C). The sample foils are placed in a Mo-sample holder underneath a Mo-heat shield. The removable dome has a separate water-cooling circle. More details are given in [6].

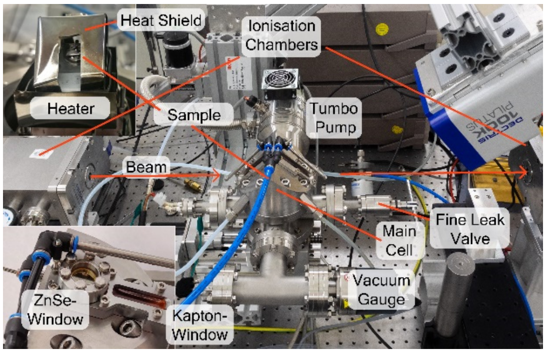

Figure 1: Photography of the high-temperature, vacuum cell [6] mounted on the diffractometer at Beamline P64, PETRA III at DESY. The upper inset displays the Nb sample underneath the heat shield, while the lower inset shows the air cooled Kapton- and ZnSe-windows.

The standard treatment (see Fig. 2) that is used for all processed samples consists of a pre-heating phase at 900 °C (temperature at the heater, sample at ca. 800 °C) under vacuum conditions for 60 min. This is followed by the main treatment in the desired gas atmosphere at a certain temperature and gas pressure that varies between the different treatments. After this there is a cool down phase which is performed under vacuum condition again.

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The shown experiments were performed at beamline P64 at the PETRA III storage ring (DESY, Hamburg, Germany) [8]. The time-resolved Quick-EXAFS data at the Nb *K*-edge (18986 eV) were collected in-situ prior, during and after the treatment with a time-resolution of 1 Hz and employing a Si (111) channel-cut monochromator [9].

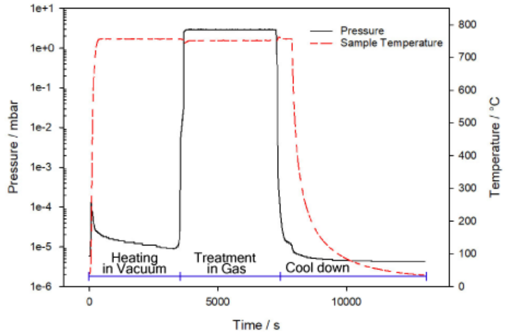

Figure 2: Exemplary treatment process with a pre-heating phase at 750 °C sample temperature, a treatment phase in gas at a certain temperature and 3 mbar pressure and a final cool down phase in vacuum.

RESULTS AND DISCUSSION

In the following the results obtained for two types of treatments are presented and discussed.

Pre-heating in Poor Vacuum and High-purity N_2 Treatment Afterwards

This treatment consisted of two phases, i.e. pre-heating under poor vacuum conditions at a pressure of $2x10^{-4}$ mbar at 900 °C for one hour and the subsequent treatment in high-purity N_2 at a pressure of 3 mbar and 900 °C. The normalized X-ray absorption spectroscopy data of both phases are presented in Fig. 3. During the pre-heating (blue to green color of the spectra) there is a slight but significant shift of the Nb K-edge energy to higher energies with the time of the treatment. This can be explained by an oxidation of the Nb sample caused by the oxygen remaining in the cell because of the vacuum conditions. In parallel, clear changes are detectable in the near edge data (XANES) as well. The experimental data reveal isosbestic points, i.e. energies in which all measured XANES spectra intersect, e.g. at 19030 eV and 19052 eV. Isosbestic points in general are a clear indication for the presence of only to types of phases within the set of spectra, i.e. in the present case the pristine Nb-metal and an oxide phase, most likely with an oxygen atom occupying the interstitial octahedral site.

With the initiation of the N_2-treatment, no additional shifts of the edge energy are detected, indicating that there is no additional oxidation of Nb. However, there are ongoing changes of the XANES, with new X-ray absorption features developing with time. For example, a new peak is formed at about 19010 eV, and a systematic shift of the peak from ca. 19028 eV to about 19022 eV can be seen. Moreover, the positions of the previously observed isosbestic points shift as well.

All these observations suggest that the N_2-exposure results in an uptake of N-atoms within the oxidized Nb-lattice, most likely by a continuous occupation of interstitial octahedral sites of the Nb unit cells. The observations are thus consistent with a co-existence of three phases, i.e. pristine Nb, oxidized Nb and N-doped Nb with different amounts changing with time.

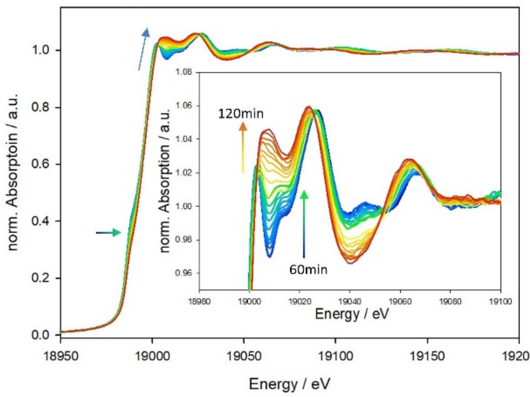

Figure 3: Selected X-ray absorption near edge spectra from thin Nb metal foils (7 µm thickness) measured during a heat treatment in poor vacuum of $2x10^{-4}$ mbar (60 min at 900 °C, blue to green curves) and a subsequent treatment in a N_2-atmosphere of 3 mbar (120 min at 900 °C, yellow to red curves).

Treatments in N_2-O_2 Atmospheres

The second treatment is performed after a pre-heating in best possible vacuum (around 10^{-6} mbar), which has been proven to have no impact on the Nb lattice structure [5, 6]. The subsequent treatment is performed in a N_2-air-mixture (N/O ratio of 1000:1) and a total pressure of 3 mbar. The development of the normalized X-ray absorption data with time is shown in Fig. 4 (blue to green). In contrast to the first experiment in the previous section, here no obvious shift of the edge position is visible, which leads to the conclusion that the oxidation is substantially suppressed in comparison to the first sample, although the oxygen (air) partial pressure is around ~10^{-4} mbar in both cases. Nevertheless, there is a clear development of the XANES as a function of time again, but in this case, there are no distinct isosbestic points recognizable. This intends that there are at least three different phases right from the beginning, unoccupied Nb unit cells, those with a N-atom and those with an O-atom on the interstitial octahedral site, however the latter with substantially smaller contributions. In order to quantify the identified species as a function of the time of the treatment, multi-phase fits are planned for the future. From the absence of absorption edge shifts, it can be expected that N-doping effects are much stronger compared to the oxygen uptake or niobium oxidation.

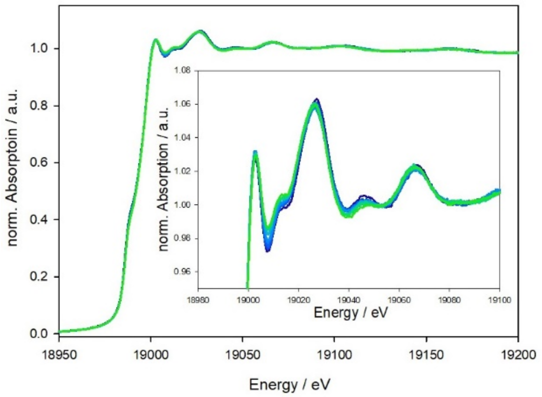

Figure 4: Series of time-developed Nb K-edge XANES spectra from Nb metal foils (7 µm thickness) detected in the course of a high-temperature treatment at 900 °C in a N_2-O_2-atmosphere with an oxygen to nitrogen ratio of 1/1000 and a total pressure of 3 mbar (blue to green).

This conclusion is supported by a closer inspection of the magnitude of the Fourier-transform of the a k^2-weighted EXAFS fine structure data (see Fig. 5). Here it can be seen, that the peaks related to the first Nb-Nb shell at 2 and 2.8 Å decrease with the time of the treatment, which is related to the increase of disorder due to the uptake of oxygen and nitrogen on interstitial sites. In parallel, a growth of the peak for the Nb-N or Nb-O bonding can be seen at ca. 1.5 Å radial distance (see Fig. 5), which can be expected for the present experimental conditions.

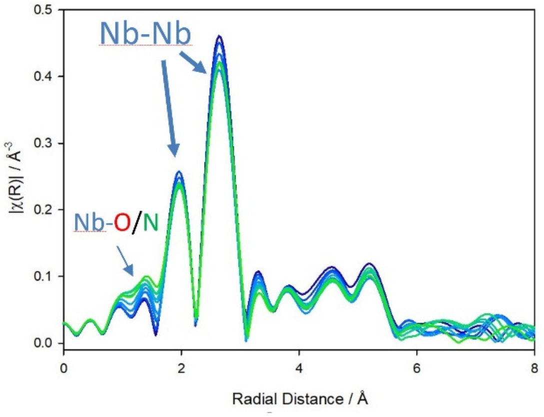

Figure 5: Development of the magnitude of the Fourier-transform $|\text{FT}[\chi(k)k^2]|$ of the k^2-weighted EXAFS fine stucture measured during the treatment of thin Nb metal foils treated at 900 °C in a N_2-O_2-atmosphere (N_2/O_2 composition ratio 1000:1, p = 3 mbar).

CONCLUSION

According to the presented EXAFS experiments it can be concluded, that for Nb treatments in N_2-atmosphere at 900 °C even the presence of small amounts of O_2 has a significant impact on the short-range structure of the treated Nb material. It has been shown that oxygen and nitrogen compete for the interstitial octahedral sites of the body-centered cubic (bcc) Nb lattice, here it still has to be quantified how the ratio of N_2 and air/O_2 has an effect on the process of occupation. Obviously, oxygen levels should be decreased to minimal levels already in the pre-heating stages of the treatments, where the impact of oxidation appears larger in comparison to small oxygen levels as contaminations of the N_2-gas used for the subsequent doping processes. A quantification of the measured effects by performing multi-phase fitting as well as conventional multi-shell EXAFS fits is currently in preparation.

In the light of the importance of oxygen contaminations for high temperature treatments such as the N-doping processes, additional in-situ EXAFS experiments are planned for N-infusion and mid-T-bake processes at substantially lower temperatures in the range from ca. 120 °C to 400 °C as well. Furthermore, since there are indications that the effects of N_2-treatments on Nb-cavities irrespective of the actual temperature are caused by the prevention of the hydrogen-accumulation by occupying the interstitial octahedral sites [10] which can be done by N- or O-atoms respectively [11], it has to be investigated whether the occupation with O-atoms instead of N-atoms has an effect on the cavities' performance such as Q-factor, RF-superconductivity etc. as well.

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