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COMBINED IN-SITU QEXAFS AND XRD INVESTIGATIONS ON Nb-TREATMENTS IN N_2 GAS ATMOSPHERES AT ELEVATED TEMPERATURES*

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Abstract

Thin polycrystalline Nb metal foils were treated in N_2 gas atmospheres at elevated temperatures of 900 °C up to 1200 °C. A combination of transmission mode Quick X-ray absorption spectroscopy (QEXAFS) at the Nb-K-edge and X-ray diffraction (XRD) used in parallel were used to investigate changes in the atomic short and long-range structure of the bulk Nb-material in-situ. A dedicated high-vacuum heating cell with a base pressure of 10^{-6} mbar was used to perform the heat treatments under a vacuum and nitrogen gas atmosphere. The treatments typically included (i) a preheating at 900 °C under high-vacuum, (ii) treatment in 3 mbar nitrogen gas at the desired temperature, and (iii) cooling down to room temperature under vacuum conditions. The QEXAFS and XRD data were collected in parallel during the entire process with a time resolution of 4 s. While the samples treated at 900 °C show the typical N-uptake to the octahedral interstitial sites, the samples treated at higher temperatures show the growth of distinct niobium nitride phases.

INTRODUCTION

Nowadays almost all Nb-cavities used for particle accelerators are treated in N_2-atmospheres to improve their performance, in particular Q-factor, accelerating gradient, superconductivity, etc. Therefore, several different treatment recipes like the Nb-doping [1], Nb-infusion [2] or mid-T-bake [3] have been worked out, variating the treatment temperature duration and used gas pressures. Recent studies on the N-doping have shown that the N-atoms are likely to occupy the interstitial octahedral sites of the Nb unit cells [4]. Additional to this effect Nb is known to tend to build up Nitrides with growing temperatures. This is crucial information to treat the cavities in the way wanted. In the presented work thin Nb metal foils are treated in N_2-atmospheres at temperatures between 900 and 1200 °C, investigated by using in-situ EXAFS and XRD measurements. In the following, the first prom-ising results of the ongoing studies will be presented.

EXPERIMENTAL DETAILS

The EXAFS and XRD measurements were performed in a dedicated high-temperature vacuum cell (Fig. 1) [5]. The cell features a ceramic heating plate allowing tem-peratures up to 1200 °C (heating rate ~350 °C/min), an oil-free turbo-molecular pump (base pressure 10^{-6} mbar), and a combination of fine leak and magnetic valves to control the treatment process. The main chamber has two air-cooled Kapton windows and a ZnSe-window for infra-red-temperature measurements. Additionally, there are two thermocouples inside the cell. The experiments were performed at Beamline P64, PETRA III at Desy [6], for the XRD measurements a Pilatus 100K pixel detector was used.

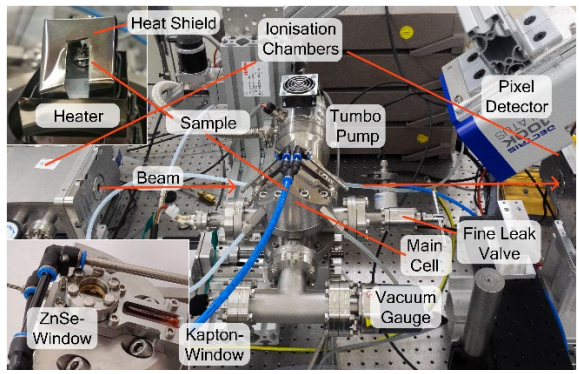

Figure 1: Photography of high-temperature vacuum cell [6] at P64 PETRA III at Desy mounted on the beamlines diffractometer and the Pilatus 100K pixel detector in the upper right-hand corner. The inset in the upper left-hand corner shows an Nb-metal-foil in the sample holder underneath the heat shield., the inset below shows the cell's air-cooled ZnSe- and Kapton windows.

The treatments (Fig. 2) typically consist of a preheating phase in a vacuum at a temperature of 900 °C for 60 min (if not mentioned differently in the following, temperatures are measured at the heater), followed by the treatment in a 3 mbar N_2-atmosphere at a dedicated temperature. After this, the cooldown is performed under vacuum conditions.

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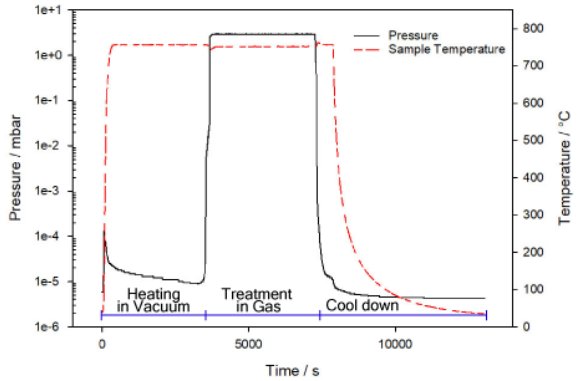

Figure 2: Time course of an exemplary treatment process consisting of three steps: (i) heating in vacuum at 900 °C of 60 min, (ii) treatment in N_2 gas atmosphere at a pressure of 3.3 mbar and a certain temperature between 900 °C and 1200 °C and (iii) the cool down to room temperature under vacuum condition.

RESULTS AND DISCUSSION

In the following, the results of the in-situ XRD and QEXAFS investigations will be shown.

The QEXAFS Measurements

Figure 3 shows the time development of the X-ray absorption near-edge spectra (XANES) of an Nb-metal-foil treated in an N_2 gas atmosphere for 60 min at 900 °C and a pressure of 3.3 mbar. The time development is shown from blue to green. In the data it can be seen, that during the process there is a slight edge shift to higher energies visible, so there is no oxidation measurable, which would cause a more pronounced shift in the binding energy, while the N-uptake to the octahedral interstitial sites of the Nb unit cell is the reason for it. At the same time, the N-uptake causes a change in the XANES structure. Here isosbestic points are visible that hint towards the assumption of the presence of just two different phases in the sample which consists of normal Nb unit cells and Nb unit cells with an N-atom in the octahedral interstitial site. This could already be shown in previous investigations [4].

For the foil treated at 1100 °C (Fig. 4) a shift of the absorption edge to higher energies can be obtained. This underpins the assumption of oxidation at this temperature from the XRD data is either caused by nitrogen or oxygen. Additionally, the development in the XANES is more intense than for the foil treated at 900 °C. This will be caused by the oxidation as well, but at the same time by a faster N-uptake to the octahedral interstitial sites caused by higher activation energy. At the same time, an out washing of the isosbestic points is notable which is a sign of the development of at least one additional phase. To get a clearer result on which of the two new phases is the more dominant one phase fits have to be done in the future as well.

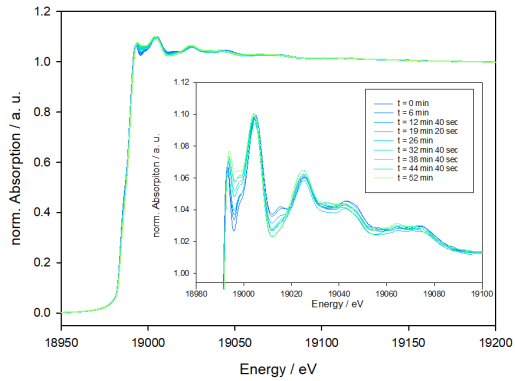

Figure 3: EXAFS and XANES data of an Nb-metal-foil treated in an N_2 atmosphere for 60 min at 900 °C and a pressure of 3.3 mbar with the time development from blue to green.

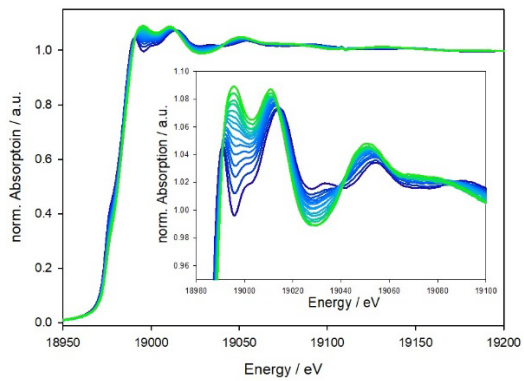

Figure 4: Time development from blue to green for the EXAFS and XANES data of an Nb-metal-foil treated for 60 min at 1100 °C in an N_2 atmosphere at a pressure of 3.3 mbar.

The XRD Measurements

While the data of the Nb-foil treated at 900 °C did not show any visible changes in the XRD data during the treatment, this can be explained by the fact, that the amount of Nb unit cells with N-occupied interstitial octahedral sites is still below a percentage of 2 % [4] (apart of small reversible changes caused by the heating and cooling itself). The foil treated at 1100 °C shows changes in the diffractogram during the time of processing. This time development is shown in Fig. 5 (a) as a comparison of the heated sample before and after the treatment. Fig. 5 (b) shows reference data of the Nb cubic and hexagonal unit cell and for beta-Nb_2N. It is visible that the Bragg-Peaks of the cubic Nb-metal cell, that exist already before the treatment show a slight shift to smaller angles after the treatment. This might be caused by the uptake of N to at least some of the octahedral interstitial sites of Nb-cubic unit cells. Additionally, during the treatment new peaks arise that can be related to the beta-Nb_2N unit cell, which is the typical phase for Nb with an amount of up to 10 % of N atoms, and the hexagonal Nb-metal unit cell. This unit cell normally occurs typically in high-pressure or very high-temperature environments. For this phase, additional investigations have to be performed to evaluate the

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reason for its formation. Additionally, phase fits of the data should be performed in the near future.

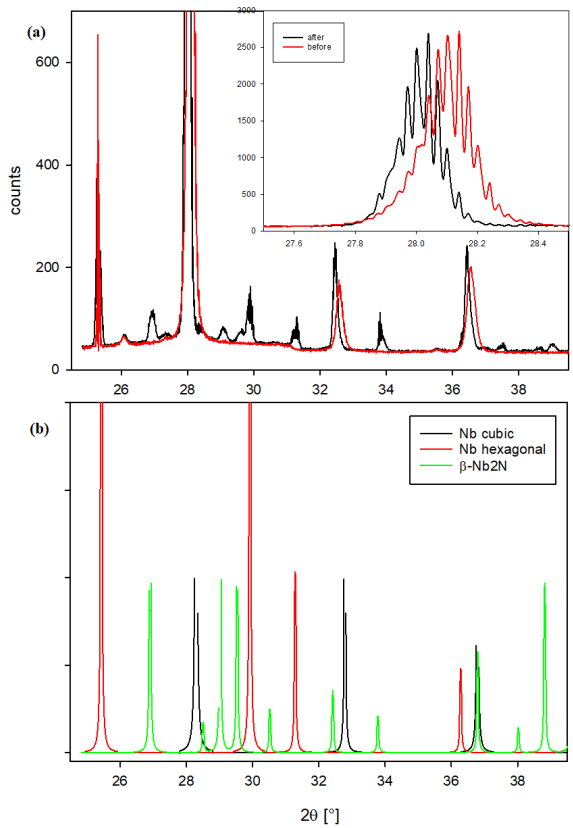

Figure 5: (a) XRD data of the hot Nb-metal-foil before (red) and after (black) the treatment in the N_2 atmosphere for 60 min at 1100 °C and a pressure of 3.3 mbar, (b) calculated reference diffractograms for cubic (black) and hexagonal Nb-metal unit cells (red) as wells as the beta-Nb_2N phase unit cell (green).

CONCLUSION

According to the results shown for the QEXAFS measurements significant different processes could be obtained for treatments at 900 °C and 1100 °C. While the sample treated at 900 °C shows evidences for the N-uptake into the interstitial octahedral sites of the Nb-cubic unit cell, the sample treated at 1100 °C seemed to develop at least three different phases and the XANES data shows a higher impact of structural changes in the short range. This assumption is supported by the result from the in parallel measured XRD data. Here the treatment showed a high impact even on the far range structure of the sample in form of peak shifting and the development of new peaks related to the hexagonal Nb-metal phase and the beta-Nb_2N phase. For further, more precise assumptions additional phase fittings of the QEXAFS- and XRD-data should be performed in the near future.

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