'IN SITU' XPS INVESTIGATION OF THE BAKING EFFECT ON THE SURFACE OXIDE STRUCTURE FORMED ON NIOBIUM SHEETS USED FOR SUPERCONDUCTING RF CAVITY PRODUCTION

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Abstract

Investigations were performed for Nb samples prepared by two types of treatment, electro-polishing (EP) and chemical polishing (BCP) preceded by grinding. The chemical structure of thin oxide films naturally formed on the Nb surface changed during baking. This effect was observed 'in situ' by means of the X-ray Photoelectron Spectroscopy (XPS). The experiments were carried out in the temperature range from 100 to 180ºC for 120-hour periods of time. It was found out that the oxide layer for the EP samples was thicker than that for the ground+BCP ones. The Nb_2O_5 phase progressively dissociated and the NbO_2 and NbO oxides developed on baking. This effect was hardly noticeable at 100ºC but considerably revealed at higher temperatures. At the temperature of 180ºC the NbC phase was formed at certain stage of the oxide layer evolution and then it developed during further baking. The tendency of the process was the same for the both EP and BCP samples but the kinetics of the surface oxide composition changes was much faster for the BCP samples what resulted from the thinner oxide layer of BCP samples.

INTRODUCTION

Superconducting properties of niobium depend on structure and composition of surface and near-surface regions. It was documented that the baking procedure of RF cavities at relatively low temperatures improved their quality factor Q and accelerating gradient Eacc [1-3]. Despite considerable amount of works concerning the Nb surface [4-9] this effect is unclear up to now. The aim of this work was to compare the influence of baking on the surface oxide structure for electro-polished and chemically polished flat niobium samples.

EXPERIMENTAL

The surface of niobium sheets was prepared using two standard treatments:

1. Buffered chemical polishing (BCP) in an acid mixture containing HF (40%), HNO_3 (65%) and H_3PO_4 (85%) in the volume ratio of 1:1:2 respectively. Before BCP the samples were ground.

2. Electro-polishing (EP) in an acid mixture containing H_2SO_4 (96%) and HF (48%) in the volume ratio of 9:1

under an electric current of 35-40 mA/cm^2, a voltage of 15-20 V and a temperature ca. 35ºC.

The resulting surface roughness was Ra = 0.1 µm for ground+BCP treated samples and Ra = 0.2 µm for EP samples. The XPS analysis revealed some traces of nitrogen, fluorine and silicon for the BCP samples and nitrogen and silicon for the EP ones. After the surface treatment, the samples were kept in air in the same conditions for few months.

The surface composition of the niobium samples was determined 'in situ' during baking procedure by use of the X-Ray Photoelectron Spectroscopy (XPS) by a VSW apparatus equipped with a hemispherical electron analyzer and an 18-channel detector. The electron analyzer was operated in a fixed-analyze transmission (FAT) mode with constant pass energy of 22.5 eV. The samples were exposed to Al Kα (1486.6 eV, 300 W) radiation. Calibration of the binding energy scale was done by setting the accidental carbon impurity C 1s line that corresponded to the C-C bond at 284.6 eV.

An electron beam heater on which a holder with the sample was installed was applied to heat the samples. The sample temperature was controlled with an accuracy of ±1ºC by use of the K type thermocouple that was in contact with the sample surface. The setting value of temperature was reached for 10 min. The pressure in the analytical chamber was always less than 1×10^{-8} mbar for except first 20 minutes of warming when the pressure achieved for a while $5-7\times10^{-8}$ mbar.

Angle-resolved XPS (AR-XPS) measurements for not baked samples and after each baking procedure were done in aim to control the thickness of the surface niobium oxide.

RESULTS AND DISCUSSION

The Nb 3d spectral line consisted of several doublets of different niobium phases. Some preliminary experiments, not reported here, allowed establishing a procedure of the correct deconvolution of the Nb 3d lines. These measurements were done at temperatures between 140 and 300ºC. A complete dissolution of the niobium pentoxide and dioxide phases occurred during baking for several minutes at the temperatures 250ºC and higher. At

this condition only niobium monoxide and niobium carbide was present at the surface (Figure 1). Argon ion (Ar^+) sputtering of the niobium surface at room temperature removed completely all oxide phases and the XPS analysis showed Nb^0 and NbC phases only. That latter was formed by the ion bombardment. The deconvolution of these relatively simple Nb 3d spectra allowed setting parameters of the peaks, especially the asymmetry parameters of the lines of Nb^0 and NbO phases.
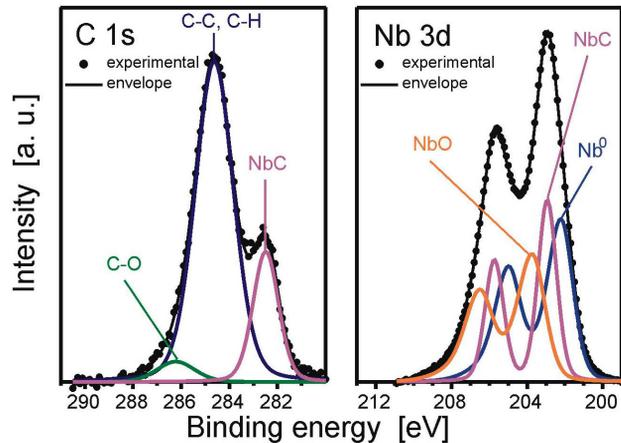
Figure 1: Deconvolution of C 1s and Nb 3d spectra for the EP sample baked at 300ºC for 15 min.
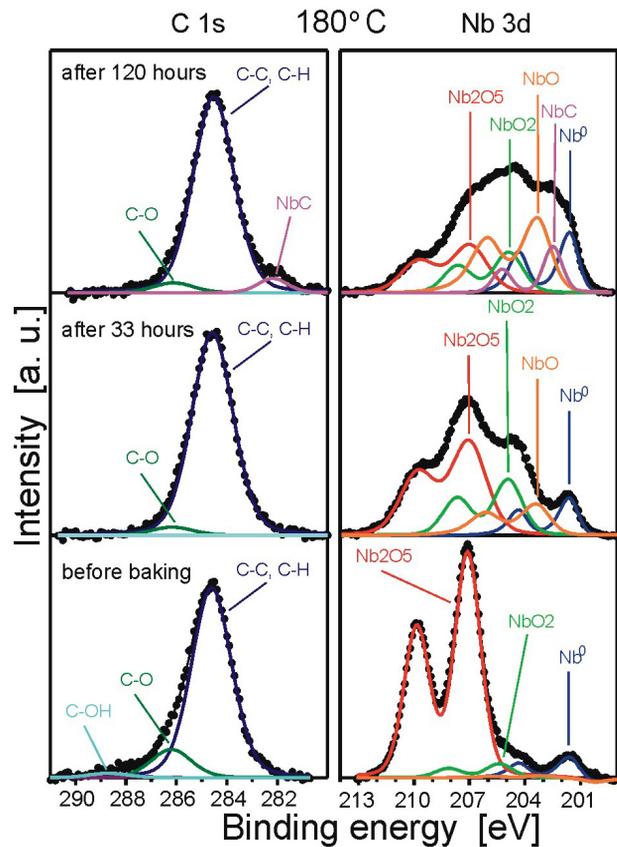
Figure 2: Deconvolution of C 1s and Nb 3d spectra for the EP sample at 180ºC at different time of baking.

The Nb 3d spectra were deconvoluted using four doublet lines (3d5/2 and 3d3/2 with separating distance of 2.75 eV) attributed to Nb^0, NbO, NbO_2 and Nb_2O_5 phases. In case of baking at the highest temperature (180ºC) an additional doublet of the NbC phase was added after 35 hours of baking. The apparition of this new phase was evident from the C 1s spectra where the carbide line at 282.3 eV was well separated from the main C-C line at 284.6 eV. An example of such deconvolution is presented in Figure 2. The intensities of the carbide line in the Nb spectra were calculated by multiplying the intensity of the carbide C 1s line by the Nb relative atomic sensitivity factor, equal in our case to 7.16. This factor was determined taking into account the Scofield's Nb 3d cross-section, the transmission of the spectrometer, the geometry of analysis and the energy dependency of the electron mean free path.
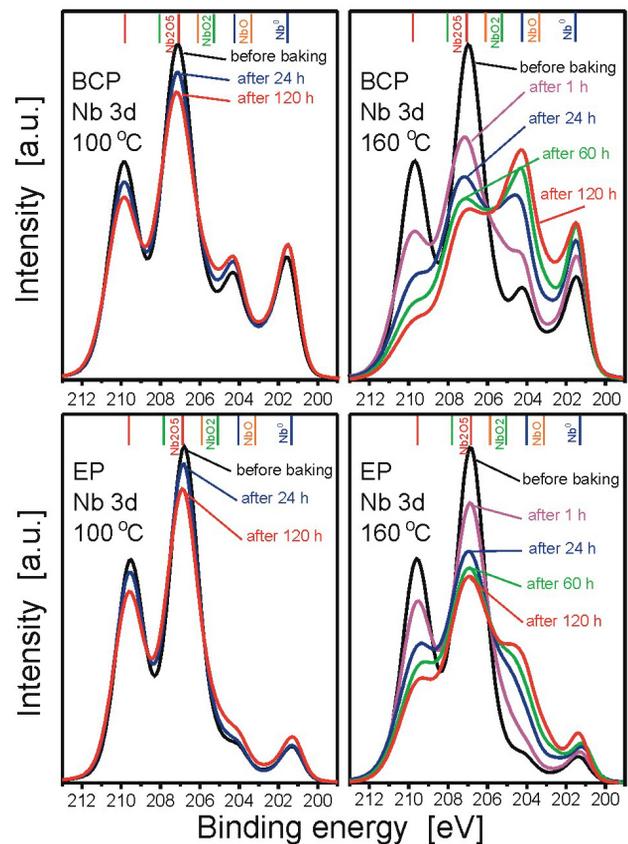
Figure 3: Comparison of the shape changes of the Nb 3d spectra during baking at 100 and 160ºC for EP and ground+BCP samples.

Figure 3 illustrates the shape evolution of the Nb spectrum during baking at 100 and 160ºC for ground +BCP and EP treated samples. The shape changes at 100ºC are not large even for the baking period of 120 h, but at 160ºC the shape changes are very considerable. The decomposition of the pentoxide and the growth of the mono- and dioxide are evident. The spectrum evolution is much faster for the BCP sample. This figure also shows that the initial oxide thickness is smaller for the BCP

samples as the Nb^0/Nb_2O_5 signal ratio for these samples is higher in comparison to the EP ones.

The binding energy of the Nb^0, NbO, NbO_2 and Nb_2O_5 lines was equal to 201.6, 203.1, 205.4 and 207.2 eV, respectively, with accuracy of ±0.1 eV. At higher temperatures ($\geq$ 140ºC) and for sufficiently long time of baking (shorter for higher temperatures) the binding energy of the NbO line was shifted gradually up to 203.5 eV and the binding energy of NbO_2 line was shifted in the opposite direction down to 205.0 eV. This effect testified that probably the stoichiometry of the NbO and NbO_2 phase was not stable. Nb ions in NbO bonding oxidised while those ones in NbO_2 bonding reduced. Moreover, the Nb_2O_5 peaks broadened from 1.8 to 2.4 eV what indicated that the crystallographic defects in this phase increased.
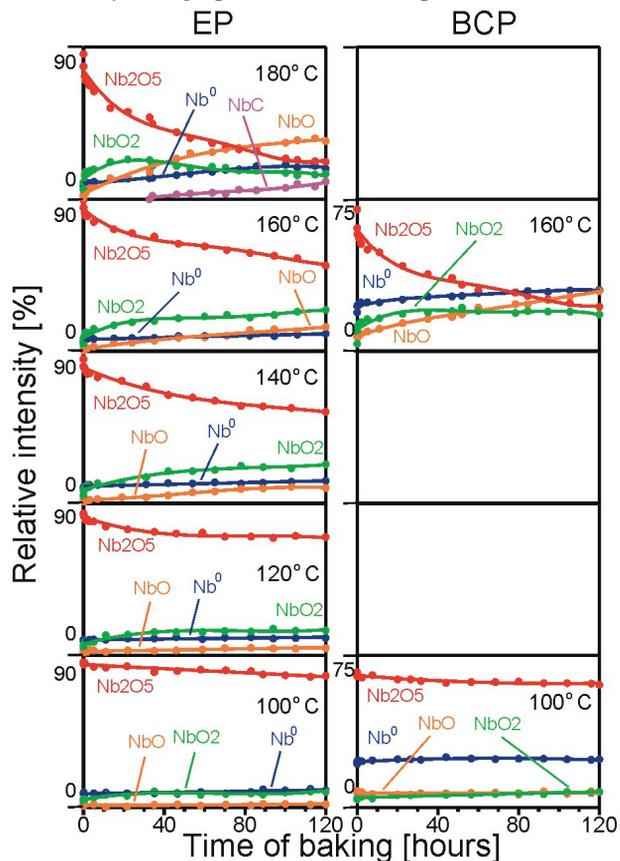
Figure 4: Changes of the Nb 3d lines intensities of different niobium phases during baking at different temperatures for EP and ground+BCP samples.

Figure 4 summarises the evolution kinetics of the oxide layer structure during baking for BCP and EP treated samples at different temperatures. The results are presented in the form of relative intensities of the Nb spectral lines of different niobium phases measured at the electron emission angle equal to 90º. The comparison of the results indicates that the oxide composition evolution is much faster for the BCP samples. It may be explained by the fact that the oxide thickness is smaller for the BCP samples and assuming that the rate of the niobium pentoxide dissolution is comparable for each type of

sample. The most pronounced surface changes occurred during first several hours of baking at each temperature.

The Angle-Resolved XPS analyses confirmed that the total thickness of the oxide films decreased during baking and that the thin internal layers of niobium mono- and dioxide developed at the cost of the niobium pentoxide thickness decrease. Figure 4 presents a comparison of the AR-XPS results for the EP samples baked at 160 and 180ºC where the differences are very pronounced. The intensity of the Nb^0 line for the sample baked at 180ºC is strong and do not disappear at the emission angle of 20º contrary to the sample baked at 160ºC. This fact indicates that the oxide layer is much thicker for the sample baked at 160ºC.
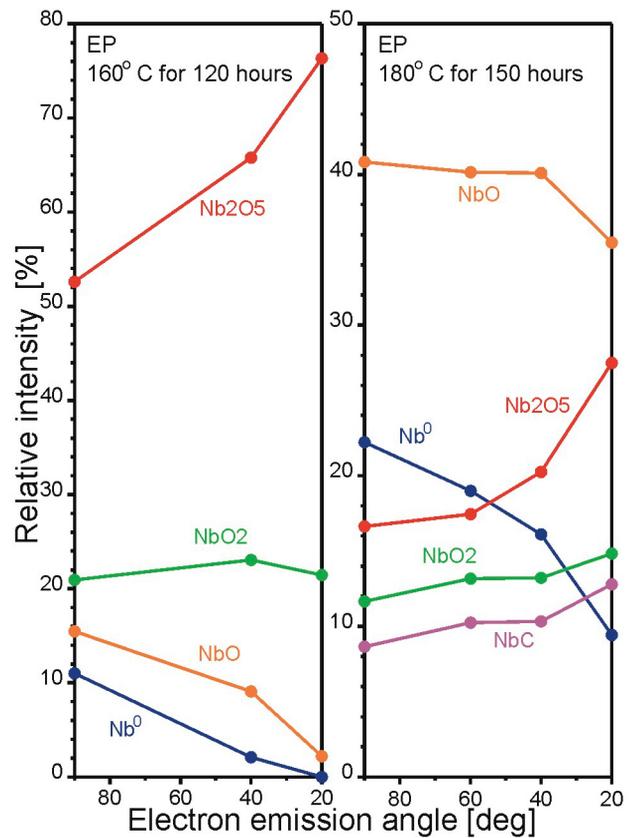
Figure 5: The AR-XPS results for the EP sample at the highest temperatures. The emission angle is related to the sample surface.

Some experiments [10] indicated that the factor Q, and especially the Q-slope for high accelerating gradients, was better when the cavity was baked at 100-120ºC but the baking procedure at 150ºC worsened the Q values. However, Q regained its good values for baking above 250ºC. It is supposed that the chemical treatment of niobium surface (BCP or EP) remove the oxides, but a new oxide layer grows immediately when the contact with air take place [11]. The surface of the niobium cavity consists of the external oxide layer of few nanometers formed by the oxidation process and of much thicker region of dissolved oxygen in Nb metal [3, 8]. The presence of the oxygen atoms in the near-surface region,

among other effects, lead to deterioration of the factor Q. On the basis of the kinetic data obtained in this work one can propose a model of the oxygen concentration changes in the near-surface region (Figure 6). Baking at 100-120°C for about 50 hours causes diffusion of the dissolved oxygen into the bulk and in consequence the decrease of its concentration in the near-surface region. During this process the external oxide layer remains almost unchanged. After such treatment the Q-slope at high field of the cavity is improved. Baking at 140-200°C causes even faster diffusion of oxygen into the bulk but also a fast dissociation of the Nb_2O_5 external layer that yields oxygen that during baking continuously penetrates into the near surface region. Thus, the concentration of

oxygen in the near-surface region after such treatment may be even higher than before the baking and the values of Q decrease and the Q-slope appears for lower accelerating field. Baking at 250-300°C causes a very fast (within few minutes) complete dissolution of the Nb_2O_5 and NbO_2. The final structure of the Nb surface becomes the NbO and NbC stable phases that thickness is much thinner than the initial oxide layer. Very fast, compared to lower temperatures of baking, oxygen diffusion into the Nb bulk again dilutes and makes more homogenous the near-surface region thus improving the parameter Q. This model is consistent with the experimental results concerning the Q after baking; especially it explains the bad baking phenomenon for temperatures 150-200°C.
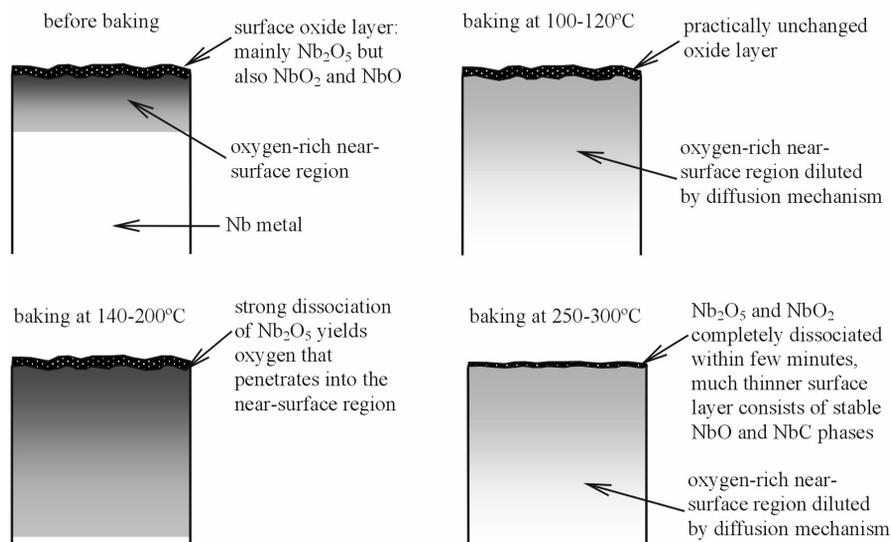
Figure 6 : Model of the oxygen-rich near-surface region of the Nb sample after baking at different temperatures.

CONCLUSIONS

The initial oxide film on the Nb sheets is thicker for the electro-polished (EP) samples in comparison to ground + chemically polished (BCP) ones.

Baking procedure in the range of 100-180ºC causes dissolution of the thickest external layer of niobium pentoxide and growth of the much thinner internal layers of niobium dioxide and monoxide. The total thickness of the oxide gets smaller during baking.

The kinetics of the oxide composition changes is faster for ground+BCP samples in comparison to EP samples what results from the thinner initial oxide layer of the ground+BCP samples.

On the basis of the kinetic data a model of the oxygen concentration changes in the near-surface region is proposed. This model is consistent with the results of the Q measurements at different temperatures.

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