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 Nb₂O₅ phase progressively dissociated and the NbO₂ 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%), HNO₃ (65%) and H₃PO₄ (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 H₂SO₄ (96%) and HF (48%) in the volume ratio of 9:1
under an electric current of 35-40 mA/cm², a voltage of 15-20 V and a temperature ca. 35°C.
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.

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
($\text{Ar}^+$) 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.

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$_2$O$_5$ phases. In case of baking at the highest temperature (180°C) 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
gyrometry of analysis and the energy dependency of the
electron mean free path.

Figure 3 illustrates the shape evolution of the Nb
during baking at 100 and 160°C for EP and
ground+BCP samples. The shape changes at
100°C are not large even for the baking period of 120 h,
but at 160°C 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.
samples as the Nb$^0$/Nb$_2$O$_5$ 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$_2$O$_5$ lines was equal to 201.6, 203.1, 205.4 and 207.2 eV, respectively, with accuracy of ±0.1 eV. At higher temperatures (≥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$_2$O$_5$ 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 Nb2O5 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 Nb2O5 and NbO2. 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.

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 100-180°C 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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