MORPHOLOGICAL AND CHEMICAL STUDIES OF NB SAMPLES AFTER VARIOUS SURFACE TREATMENT

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Abstract

Surface states generated by chemical or electrochemical treatments seem to be the latter source of limitation for superconducting cavities. How does it affect superconducting RF properties of the material, is this effect due to the morphology of the surface or its local chemical composition ? As an attempt to answer to these questions, Nb samples were submitted to various surface treatment, and studied systematically with various surface techniques either from the morphological point of view (x-rays reflection, profilometry, tunnel microscopy) as from the chemical composition of the very surface point of view (TOF-SIMS, ESCA). In parallel, some attempts to develop new chemical etching are shortly described.

1 SURFACE STATE AND CAVITIES PERFORMANCES

General results on cavities performances have been detailed elsewhere in this workshop proceedings [1].

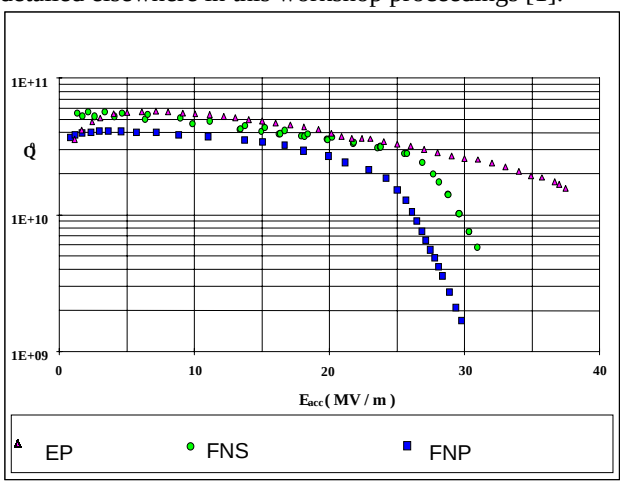

Figure 1 : Typical cavities results for Electropolishing (EP), Chemical polishing with hydroFluoric, Nitric and Sulfuric acids (FNS), and Chemical polishing with hydroFluoric, Nitric and orthoPhosphoric acids (FNP).

We have summarized it in figure 1, where "FNS" is one of the alternative chemical treatment proposed at Saclay (and described more in detail at §2), and FNP is the usual BCP (with hydroFluoric, Nitric and orthoPhosphoric acids). Indeed, looking for alternative chemistry appears to be a way to experiment different surface state on cavities, but for practical reasons, it is impossible to test all of them on cavities.

That is why we also are conducting a complete surface study on sample in order to determine which parameters are modified by the different treatments, and which ones are the most preponderant.

Three main factors can be explored at first sight :

- Influence of surface morphology (roughness at high and low scale).
- Surface chemical composition.
- Nb lattice strain induced by superficial oxide layer. This last point somehow ensues from the previous one as chemical composition of the surface can influence the structure of the oxide layer. We will see in the discussion of § 5 that this hypothesis is fairly probable.

2 SURFACE CHEMICAL TREATMENTS

Literature points out many possible "recipes" for etching niobium, see for example [2] or [3]. In all these mixture we can find the same basics :

- A niobium complexant, i.e. a chemical species that reacts with ions Nb^{5+} and forms a compound soluble into water.
- An oxidant, which reacts with metallic niobium Nb^{0} and turns it into the oxidized form Nb^{5+}, which in its turn will be solubilized.
- Additional compounds like buffer or brightening agents.

Note that in the case of electropolishing, there is no need of an oxidant as a high potential (=oxidant) is already imposed to niobium by the mean of the electrodes and the solution.

The drawback of usual BCP, is that it etches rather than polishes niobium surfaces. After heavy etching, it tends even to etch preferentially at grain boundaries, leaving

some crevices which are difficult to rinse correctly and which enhance the surface roughness. Moreover, ortho-phosphoric acid is known to incorporate into the oxide layer in the form of POx (x~2) ions [4], and is regularly found at the metal-oxide interface by chemical analysis [5].

Even before testing it on cavities, developing alternative chemical polishing among all the possibilities was somehow difficult : what should we privilege ? Roughness, brilliance, etching speed, or safety ?

One of us (A.A.) has made a systematic chemical study of FNS (hydroFluoric, Nitric and Sulfuric acids in various proportions) while various other mixture where tested on sample and/or cavities (see [1] and [6(to be published)] for more details.

Other baths were also developed for in order to change the chemical environment where the oxide layer starts to grow. Indeed as anions presents in the polishing bath are likely to incorporate in the oxide layer, and thus to modify its crystalline structure, change in the chemical media could give indication on its effect on the cavities behavior. For instance, H_2O_2 is known to be oxidant and a niobium complexant. We have tried to develop chemical bath where it replaces HNO_3.

Various mixtures of HF (5-15 $mol.L^{-1}$) and H_2O_2 (2.5-5 $mol.L^{-1}$) were applied on Nb test samples ; but in general, the surface was always degraded : severe grain-boundaries etchings (Nb grains taken off), strong roughness (mean peak-to-valleys > 50 µm) observed by visual and microscope inspections.

HF and HNO_3 1-9 in proportion was also tested (FN 1-9, etching rate ~1.2 µM/min) : it leads to mid rough surfaces, without apparent grain boundary etching, but did not produce any change when it was applied to a cavity (quench field ~21MV/m).

Some other media are now under study and will be detailed in [6]

3 MORPHOLOGY

3.1 Available experimental techniques and samples preparation.

It is important to well characterize the surface morphology at different scale : at the micron scale, roughness is not expected to play any role in superconductivity, but might play a role by perturbing the electromagnetic field repartition or by enhancing effective surface. At lower scale (~10-100 nm) surfaces are more difficult to observe ; but it is worthwhile to explore if there are important differences between the different treatments. Moreover it also plays a role in the case of Kapitza resistance where the mechanism of heat transfer is partly due to phonons with ~100 nm wavelength [7].

Arithmetic (Ra) or quadratic (Rq or σ_{rms}) roughness can easily be measured by profilometry, but one has to keep in mind that this parameter does not characterize well a surface : first, different types of morphology can give the same mean roughness as for example on figure 2 , secondly profilometry is generally not able to measure accurately small scale roughness. One can note that brilliance is somehow an indirect indication of this small scale roughness, because it is linked to visible light scattering, but it is rather difficult to measure.

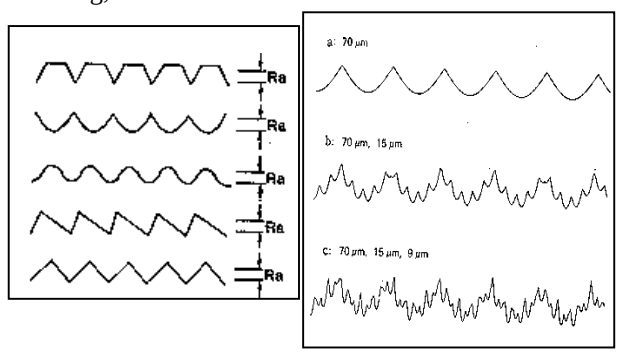

Figure 2 : from Ref [8] : two schemes showing 1) how Ra is insufficiant to well characterize roughness, 2) how different scale roughness can be superimposed.

Reflectivity of X rays can also in principle characterizes roughness at the 10-100 nm scale, but practically it was not possible to get sufficiently plane niobium samples, even after a mechanical polishing (soft metals like Nb are always difficult to prepare). Therefore this technique was not pursued.

In theory, Scanning Tunneling Microscopy (STM) can reach atomic resolution and appears to be an idealistic tool; but because of the limitation in "z" dynamic available results are also tributary from the initial flatness of the samples, and we where again limited on niobium surfaces.

A comparative study of three different surface treatments was done on niobium RRR~135 monocrystals. All the sample were mechanically polished (mirror like), prior the chemical treatments. In this way it was hoped to reduce roughness due to grain boundaries etching or machining that appear on polycrystals, so to be able to explore low scale roughness in the same time as higher level roughness..

The surface treatments were the following :

- Electropolishing (EP) : we have use the process developed at Karlsruhe and now used at KEK, namely in a HF-H_2SO_4 15%-85% in volume, with 8-10 Volts applied on the sample (as an anode). 40-50µm are removed.
- Chemical polishing FNP : standard BCP with HF, HNO_3 and H_3PO_4 1-1-2 in volume. ~100µm removed.
- Chemical polishing FNS : CP with HF, HNO_3, $H_2SO_4$1-1-1 in volume. ~100µm removed.

3.2 Profilometry

Profilometry is a mechanical measurement : a diamond tip with a final radius of ~50 nm skims over the sample surface and corresponding vertical displacements are registered.. It is important to note that explored length play an important role on the results (because of the superimposition of different roughness scale). Indeed, the smallest the explored length, the more we are sensitive to small scale roughness. Roughness is usually not an absolute value and the measuring scale should be mentioned for each comparison.
Figure 3 give examples of the registered profilometry at two different scales. A minimum of 10 measures were taken at random on each sample and the mean roughness was calculated.

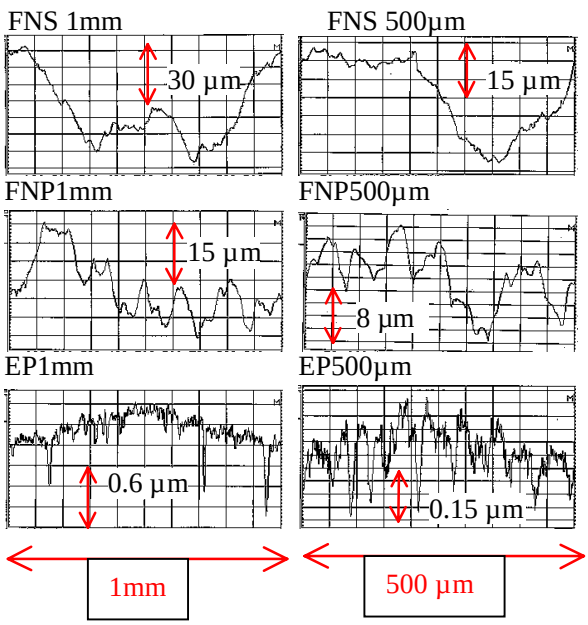

Figure 3 : profilometry at two different observing scale on Nb monocrystasl. Results in term of Ra is showed in figure 5.

The obtained results are summarized in figure 5 along with the results of the other techniques. Note that the scattering in the measures results from the non uniformity of the niobium surfaces, and is not due to measure uncertainty.
One can clearly observe difference between the surface morphology of the samples. FNS presents the highest Ra, because the “peak to valley” distances are fairly high ; but the peak frequency is the lowest compared to the two other treatments, and its faces seems to be very sharp (no apparent sub-roughness at this observation scale). This is consistent with the visual aspect of the polycrystalline samples, where the FNS treated surfaces appear very shiny but with grains structure very apparent, as if the grains were not all etched at the same speed. (see photographs in § 2.6). FNP exhibit higher peak frequency, which are about 100 µm wide, with a marked substructure. FNP etches not only preferentially at the grain boundaries (this was observed on photographs on polycrystalline samples), but it also reveals grain substructure, i.e. local defects, dislocations emergence, etc. Nevertheless the peak to valley distance is less than in FNP.
In the case of EP, roughness is reduced a lot (by a factor 6-10), but presents a very fine substructure , that can also be visually observed.

3.3 Scanning Tunneling Microscope

Several images were taken at random, at three different scale. Only a very small portion of the surface could be observed for practical reason (acquisition time), but we have tried to show the most characteristic surface aspects.
The images were then statistically treated in order to get the heights distribution.

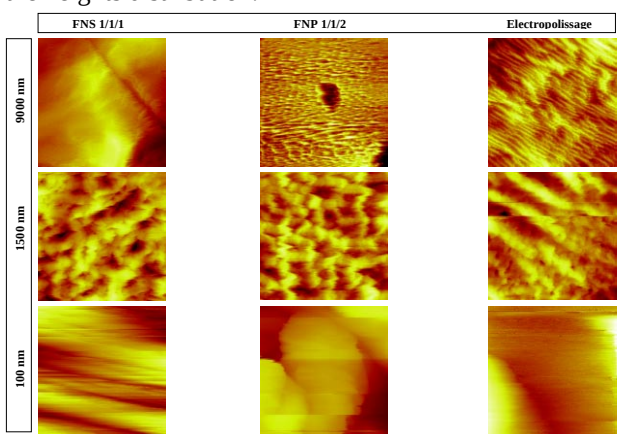

Figure 4 : Scannig Tunneling Microscope Images taken at three different observation scales, on Nb monocrystals treated with resp. FNS, FNP, and EP.

The average value could be compared to Ra and the mid height width was assimilated to the dispersion. Of course further statistical treatment is foreseen in order to better

characterize the surface, and they will be published elsewhere [9].

At higher observation scale (9 µm sided) the differently treated samples present marked difference in aspect. In all samples whatever the treatment, dark spots of different size were frequently encountered, which were attributed to etching pit. The differences appear to be less marked when one observe the samples at lower scale (1.5 µm and 0.1 µm sided). At this last scale, the roughness is still so high compared to the tunneling microscope dynamic, that it was impossible to reach the atomic resolution. Moreover, as we get on the picture only a small portion of the surface, and thus a small portion of, lets's say a "valley" or a "peak", the roughness measurements are obviously "out of range". To get accurate results at such a low scale, we should have imaged a much wider area, with higher dynamic to accommodate the local slope, and with an automated acquisition facility for example.

3.4 Comparison of Ra at different scale

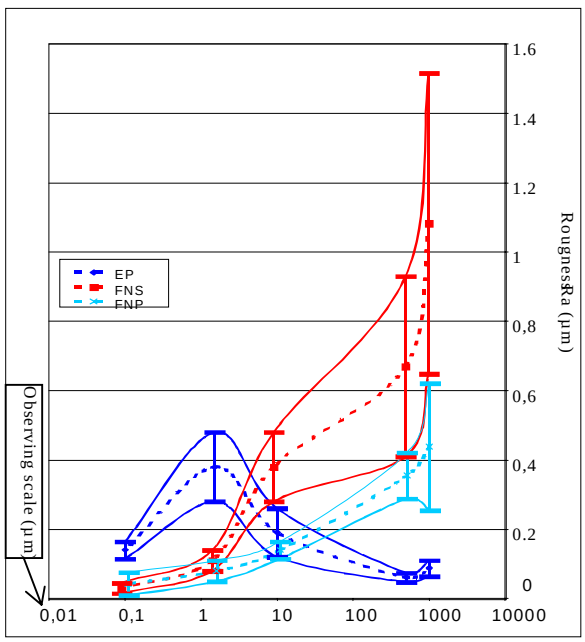

Figure 5 :Comparaison of measured Ra at different observing scale for on Nb monocrystals treated with resp. FNS, FNP, and EP

As pointed out before, the roughness measurements are strongly affected by the observation scale : at lower scale, we are less sensitive to regular micron-sized defects.

We can conclude from the figure 7 that the three surface treatment that we have tested have a strong effect at high scale, but at lower scale the surfaces states are very alike. We can model the three surface state like on the scheme fig 8.

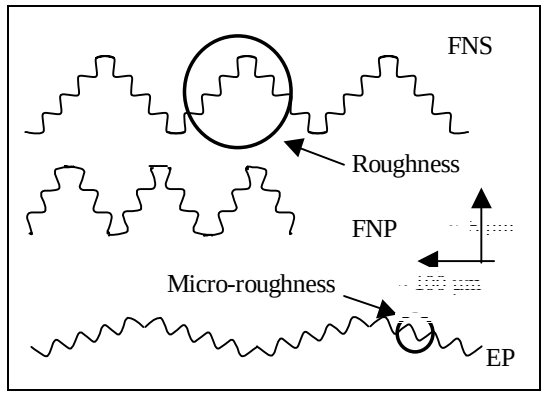

Figure 8 : schematic summary of the roughness measurements.

3.5 Microscopy ,effect of purification annealing on the morphology

Optical microscopy is a first approach to evaluate surface morphology. But one can notice very important differences between monocrystals and polycrystals, and among polycrystals, between normal samples and annealed ones, which underwent heavy recrystalization.

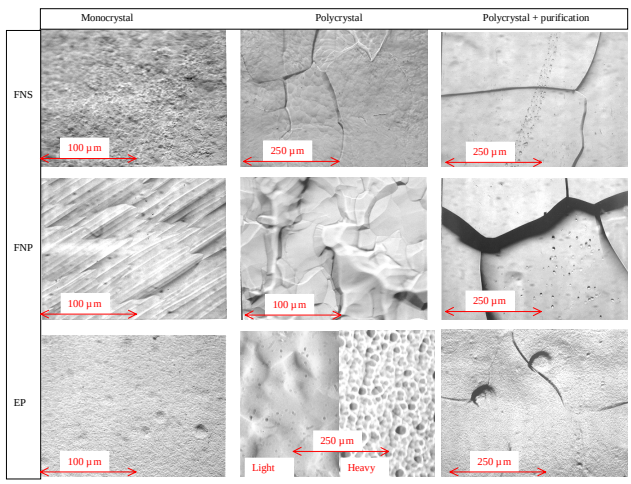

Figure 7 : comparaison of the visual aspect of different crystalline state niobium samples submitted to various chemical treatments.

Note that recrystallisation does not only modify the visual aspect of the samples, it also change the roughness AND the microrughness (see figure 10). As most of the cavities are nowadays annealed, it is obvious that we should complete the experiments described at §3.2 and 3.3. Complementary work on annealed polycrystallinesamples is now underway.

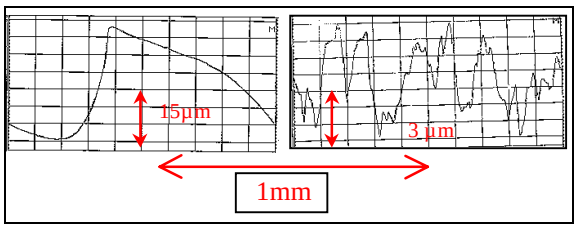

Figure 8 : effect of recrystallisation on roughness (FNP treated samples, same Nb sheet, polycrystalline, after and before annealing).

Anyhow, purification annealing does improve the quench field and Q_0 of cavities but with no appreciable change in the Q slope (the Q curve is only "translated" somewhat) ; moreover this Q slope was also observed on cavities that exhibited visually very different surface state (hydroformed or spinned or grinded cavities…). This tends do demonstrate that the roughness does not play a first order role.

4 SURFACE CHEMICAL ANALYSIS

4.1 Available experimental techniques and samples preparation.

It is quite difficult to find surface analysis techniques sensitive enough to explore the very surface of niobium, without being perturbed or screened by the surface contamination and the oxide layer. Three techniques were retained : SIMS, Time-Of-Flight SIMS and ESCA ; they are shortly described hereafter. More precise explanations can be found in any textbook in surface science.

SIMS and TOF-SIMS are profiling methods. A primary ion beam etches the samples, with a controlled etching rate, but in the case of TOF-SIMS, during analysis static conditions (very low beam intensity) are applied. In this way only ONE monolayer is analyzed at the time ; moreover molecular ions can be detected thanks to the time of flight way of detection. For instance, P alone is not detected by SIMS, while PO_2 is detected by TOF-SIMS in some amounts . The very good depth resolution allows to observe the metal-oxide interface. As it is a very sensitive method (in certain conditions ppm and even ppb can be reached), one can observe also the impurities at the interface or incorporated inside the oxide layer.

These analysis were conducted on samples prepared in a way as close as possible as for cavities : samples were RRR 200 niobium which underwent a further purification annealing, then surface treatment (EP 40-50 µm, or 100 µm FNS or FNP according to the case), then HPR, and then analyses after a determined period in the air.

We have been trying , in a first step, discover whatever differences there was in surface chemical composition between FNP, FNS and EP, and also the influence of air exposure.

ESCA : samples are submitted to a monoenergetic X-rays beam. Electrons from the core orbitals of the atoms are ejected by photoelectric effect and their kinetic energy is correlated to their initial binding energy, which is characteristic of one orbital of an element. Moreover, if this element is linked to a more or less electronegative specie, its binding energy will be slightly displaced, allowing to know the chemical environment of the considered atom. In our case, it is very easy to distinguish metallic niobium (Nb^0) from its oxide(s), we can also get some information about the presence of an hydroxide and their relative thickness. Indeed the photoelectrons don't travel much across the material, and this technique explores only 30 to 80 nm on the surface, depending on the mean free path of the electrons inside the material an d the detection angle. Unfortunately it is not a very sensitive method and one cannot analyze traces (~< 0.1 %). Meanwhile, by varying the detection angle it is possible to determine approximately the oxide layer thickness [10] with a relative error.

4.1 SIMS and TOF-SIMS results

A first series of experiment[1] showed us that high pressure rinsing and air exposure could modify the surface ; and there was clear indications that different surface treatments could induce change in the oxide thickness. Figure 9 gives an example of such a spectra, showing the influence of High Pressure Rinsing on the surface composition of a Nb sample (same Nb sheet, same chemical treatment).

Fluor was found in any case, but its concentration is greatly reduced after HPR. Other contaminants like hydrogen or carbon were also found but more deep into the material, as was already observed previously [5].

Unfortunately most of the samples from this first set were not HP rinsed, and were allowed to stay in the air for 2-3 day before the experiment. That is why we have try to prepare more carefully a second set of experiments.

[1] SIMS, performed at Evans Europa-Brunell University-Uxbridge-Middlesex UB8 3PH-U.K.

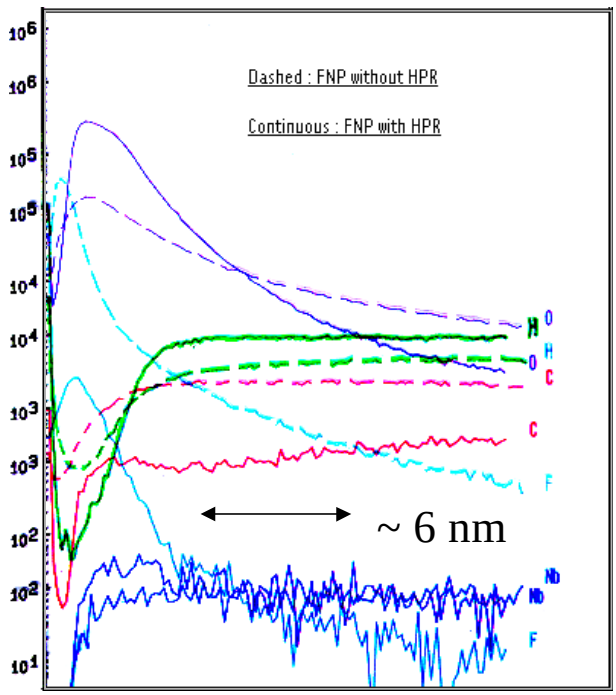

Figure 9 : SIMS profiling of FNP treated Nb samples, with or without high pressure rinsing. Depth scale deduced from ESCA results.

For the second set of sample[2], we put apart one electroplolished sample in dry ultrapure Ar, less than one hour after the HPR. It was introduced in the experimental setup the day after, being exposed to the air less than 5 min. Results are partially showed on figure 10.

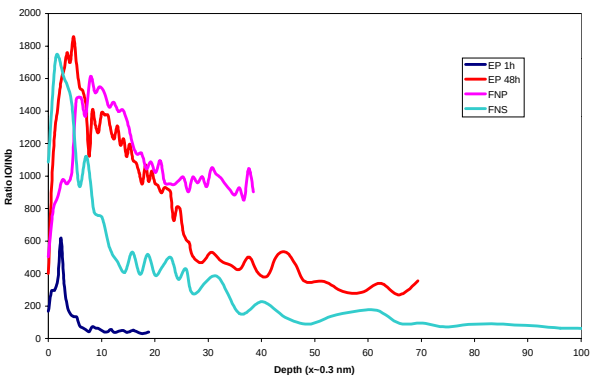

Figure 10 : TOF-SIMS profiling Nb samples treated with various treatment, showing the variation of the oxygen/niobium signal.

It was a huge surprise to notice that even after high pressure rinsing, the oxide layer on electropolished sample was extremely thin, even though former results (measured on air exposed samples, not shown here) had given indication of the contrary. This means that the oxide formed on electropolished sample is extremely sensitive to air and grows to its equilibrium thickness in a different way from the oxide formed in FNP baths. This difference of growing rate can be correlated either a different crystallographic structure, and/or a difference of local composition of the oxide.

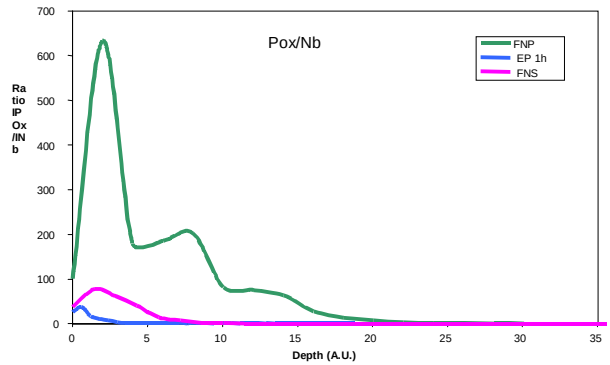

Figure 11 : TOF-SIMS profiling Nb samples treated with various treatment, showing the variation of the POx/niobium signal.

Indeed the microcrystalline-amorphous structure of Nb pentoxide is very particular and can accommodate a wide range of defective stoechiometry around the formula Nb_2O_5, by the mean of more or less regular defects distribution (see ref [11] and it very nice transmission micrographies !). Incorporation of foreign atoms at these defects is very easy and can give rise to stabilization of certain kinds of defects “substructures” that could be at the origin of the observed effects.

Moreover, we could confirm the incorporation of several solution anions inside the material (for instance POx in the case of FNP, S in the case of electropolishing) as can be see for instance on figure 11.

This is a strong indication that the structure of the surface oxide plays a major role in the high field cavities behavior.

4.2 ESCA results

As ESCA[3] can give us some information about the chemical neighborhood of a considered element, it was worthwhile to attempt to determine chemical differences between EP and the classical FNP.

Influence of high pressure rinsing and stay in the air on a classical FNP treated sample. As can be observed on figure 11, even after a thorough normal rinsing, the oxide layer has not reach its maximum thickness. HPR allows

[2] Analysis performed at “Biophy Research”, 6 Rue A. GACON, F-13016 Marseille.

[3] Analysis performed at the Laboratoire de chimie des surfaces et interfaces, CEA, DSM/DRECAM/Service de Recherche sur les Surfaces et l’Irradiation de la Matière. F-91 191 Gif-sur-Yvette cedex.

the oxide layer to grow somewhat further. These results confirm what has been observed with SIMS techniques.

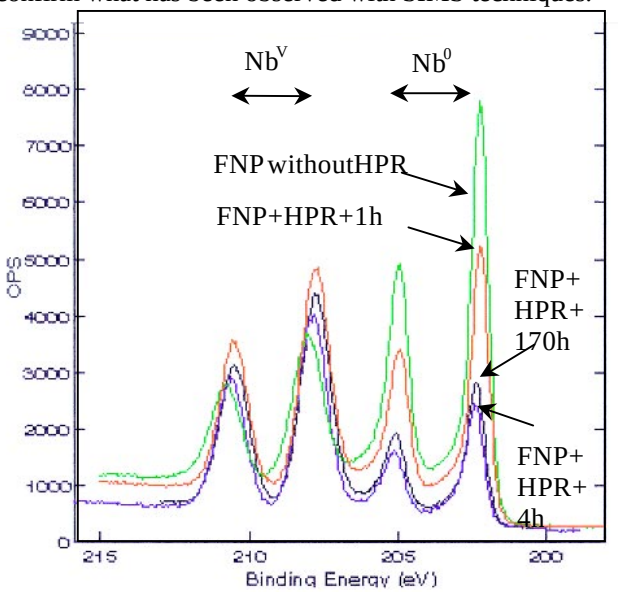

Figure 12 : Influence of high pressure rinsing and stay in the air on a classical FNP treated sample.

But this result is slightly in contradiction with Halbritter [10, 12, 14], which states that the oxide layer should reach its maximum thickness after less than 5 min in contact with water. But we must notice that we use a much more pure niobium, that has underwent an important annealing, and that the oxide seems to grow slower in this case.

On the contrary further exposure to the air after HPR, and ~ 4 hours exposure does not appear to bring much changes : after FNP treatment the oxide layer reaches its equilibrium thickness within some hours.

Influence of air exposure on EP treated samples. One can observe that the Nb° signal on EP samples is still very intense after only one our in the air, although they were HP rinsed, i. e. that the oxide layer is very thin. It increases after air exposure , rapidly during the first 21 hours, then slower. But even after 45 h in the air, the oxide layer is still thinner compared to FNP treated samples (cf. figure 13). These results confirm the observations made by TOF-SIMS and are to be compared with results obtained at KEK on air exposed cavities [13].

After ~ one week in the air, the two samples are very alike from the ESCA point of view. One can summary them by saying that the oxide grown after FNP is thicker and more stable than the one grown after EP : while it takes only a few hours for the oxide layer to be complete on FNP treated samples, it takes several days for the EP treated ones. This means obviously that they are different in nature.

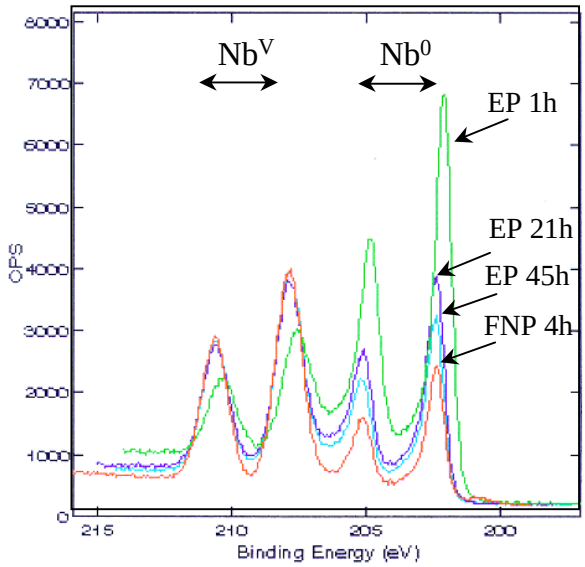

Figure 13 : Influence of air exposure on EP treated samples for the Nb signal.

Hydroxides could be observed on all the samples especially at grazing angles. When they are shortly exposed to air EP samples seems to present a little less hydroxide than the FNP ones, but the differences vanish after several hours. Moreover, at grazing angle, on the spectrum for oxygen, one can observe that the part of the oxygen signal which is in the form of hydroxide increases after a long stay in the air, whatever the former treatment (figure 14). Note that with detection angle perpendicular to the surface, the hydroxide part of the oxygen signal is only a few percent ; this confirms that the hydroxide layers form on the external part of the oxide layer. It is somewhat surprising that this hydroxide grows rather in air than in aqueous media during rinsing ; but once again this can be correlated with growth mechanism and kinetics.

All samples exhibit carbon contamination. The main part of the signal is C analogous to graphite and is generally attributed to hydrocarbon pollution on the surface. A small part of the signal can be attributed C linked to O. This pollution signal is usually also attributed to superficial contamination, but in our case it is not detected on grazing angle spectra while it is with normal incidence, which does mean that this contamination is more internal. EP samples seem to have a more important inner carbon contamination than the other samples. Note that oxygen and carbon contamination at the metal-oxide interface was already observed with other surface analysis techniques [5].

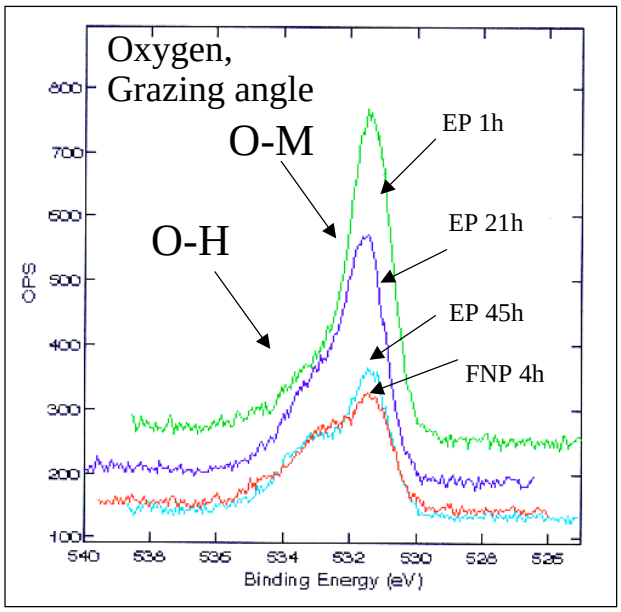

Figure 14 : Transformation of the oxide signal with air exposure, apparition of the hydroxide signal, at grazing angle (20°).

Table 1 shows the estimated thickness of niobium oxide, calculated like in reference [10]. Calculation were done with two different angle of detection, and uncertainty is deduced from the difference of results at the two angles. Note that as the thickness grows the uncertainty also grows , which can be correlated with inhomogeneous thickness of the oxide layer [10, 12, 14].

Table 1 : Calculated oxide thickness

Surf. Treatment/ Air exposure	Nb_2O_5 thickness nm
FNP 4h	5 ± 2
EP 1h	2,5 ± 0,1
EP 21h	3,9 ± 0,8
EP 45h	4,6 ± 0,8
EP 220 h	5,0 ± 1,5

FNP + 48h 110°C, 10^{-9} bar	
Nb V	4,0 ± 1
Nb IV (?)	2.84 ± 0.08
FNP + 170 h in air	5,0 ± 1,5

Effect of baking. Baking does affect the oxide layer, as can be seen on figure 15. It is quite surprising that the oxide dissociates at so a low temperature, but surface phenomena are often different than the bulk equivalents. Deconvolution of the spectra of the baked sample (figure 16) gives three distinct group of peaks. The doublet attributed to Nb_2O_5, the one attributed to metallic Nb and a larger one that can be attributed to intermediate oxidation value, for instance a mixture of Nb^{IV} compounds[15].

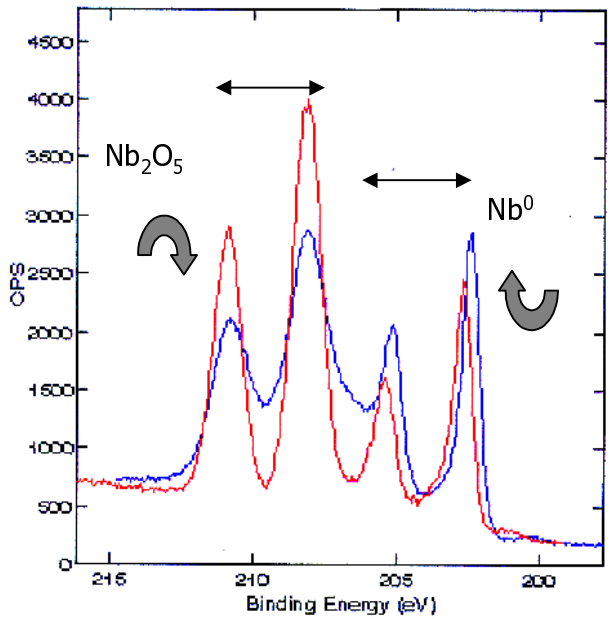

Figure 15 : Transformation of the niobium signal with baking : the Nb_2O_5 signal decreases and gets wider will the Nb^0 signal increases slightly : the oxide layer has disassociated partly into suboxides and has got thinned.

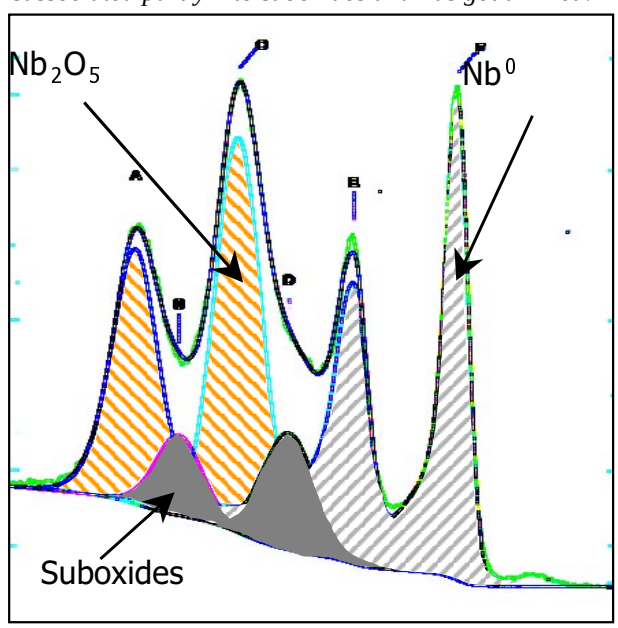

Figure 16 : Deconvolution of the niobium signal for the baked sample. The large signal of suboxides can probably be attributed to a mixture of Nb^{IV} coupounds.

Note that some authors also propose a feeble signal that is attributed to NbO at the bottom of the Nb^0 signal. NbO signal is waited at binding energy 1.4 eV lower than the metal signal as was observed on bulk NbO samples [15, 16], and also by ourselves on clean Nb surfaces with low energy radiation17. Moreover for high Fermi Level density metals like Nb, it is more accurate to use an asymmetric shape to fit the Nb^0 peak [18]. Therefore we can not state about the existence of a NbO layer in these samples.

5 DISCUSION AND CONCLUSION.

Although it needs to be completed, this work gives us some general orientation about our next experimental approaches.

Roughness seems a doubtful explanation for the Q slope as the recrystallisation brings a lot of change to the niobium surface while it is does not change the slope (even if the quench field is improved). Cavities with very different surface aspect due to their previous "history", exhibit the same type of Q variation, providing indication that the overall surface roughness does not play a noticeable role.

The oxide thickness and its sensitivity to air exposure was the only noticeable difference that could be observed on samples. We don't know yet if it is the oxide thickness itself that play a role or only the fact that it traduces impurities presence in and near the oxide layer. The presence of impurities inside the first layers of the metal itself has been suggested several times but need further exploration. Anion incorporation in oxide layers is a well known phenomena and is known to influence oxide structures. Different structures of oxide may have an influence on the underlying metallic lattice.

A more complete study of the influence of air exposure is also highly necessary.

Another aspect should also be explored : the apparent "memory" effect that occur when we change from one treatment to another.

It seems now evident that the "real" surfaces need far more further exploration before we could be able to master their RF properties.

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