SURFACE STUDIES: METHOD OF ANALYSIS AND RESULTS

C. Antoine, A. Aspart, S. Regnault, CEA, DSM/DAPNIA/Service d'Etude des Accélérateurs, CEA-SACLAY, F-91 191 Gif-sur-Yvette Cedex,

A. Chincarini, INFN-Genova, via Dodecaneso 33 - 16146 Genova, Italy

Abstract

Surface studies can support the physical understanding of the behaviour of superconducting material used in RF cavities. As most of the limitations occur in a very small portion of the surface, (typically less than the penetration depth of the material), only a few techniques can give valuable information. Some of these techniques will be discussed here, along with some examples of the results, showing the difficulty of interpretations. The used techniques are most commonly: XPS (X-ray Photoemission spectroscopy), SIMS, and TOF-SIMS (Time Of Flight Secondary Ions Mass Spectroscopy), EBSP (Electron BackScattering Patterns); some comments are also made about Auger, X-Ray reflectometry, GDL (Glow Discharge Luminescence), STM (Scanning Tunnelling Microscopy) and other common surface analyses. The influence of various surface treatments on grain boundary conduction is also explored.

1 INTRODUCTION

At this time, optimum cavity RF performances, especially the Q-slope and the quench field, are deeply influenced by the last surface treatment applied to them. Surface treatments include chemical polishing, electropolishing, baking, ... We have to deal with modifications of the surface that are of the same order or less than the penetration depth of the material.

Electropolishing (EP) followed by a mild baking seems to give the best results [1], but it is quite difficult and expensive to run. If we could understand what are the differences brought by each surface treatment, it could help us to choose conveniently the optimal surface treatment that reproduces the same surface state as EP + baking. Surface studies can give access to the physical understanding of the behaviour of superconducting cavities but could also be a tool to help find new surface treatment methods. Unfortunately, only a few techniques are able to give valuable information, as it will be discussed.

Some of the changes brought by the surface treatments might be large (surface roughness, nature of adsorbed layers, thickness of the oxide layer), but have little influence on the cavity behaviour. On the other hand some very subtle changes in the composition and structure of the surface might play an important role, and may be beyond the sensitivity of most of the analytical methods. These facts explain why it is so difficult to approach the RF superconductivity from the surface science point of view.

1.2 What are we looking for?

In Figure 1, we have schematized a "real surface", trying to summarize the principal physical features that can be explored by surface analyses. We don't know which influence most strongly the cavity performance.
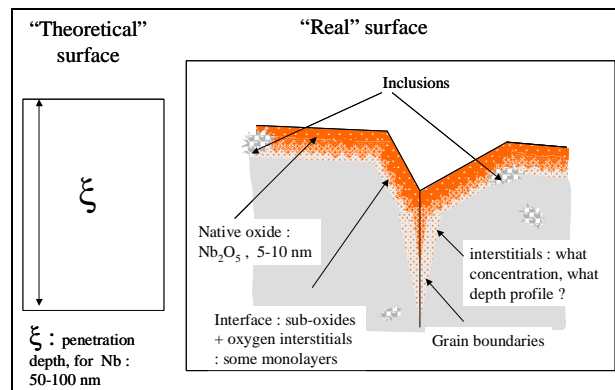

Figure 1: examples of surface features.

Surface roughness can be discarded, because it varies from one cavity to another, depending more from the previous history of the cavity than on its surface preparation, as demonstrated with microroughness and tunneling microscopy measurements in [2]. For remind, Figure 2 gives an example of surface roughness variation with purification annealing for the **same** surface treatment.
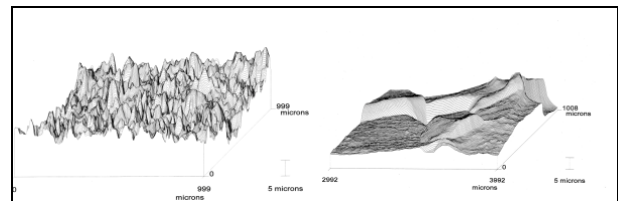

Figure 2 example of variation of surface roughness on 2 Nb samples from the same sheet treated with the same chemical polishing, left: un-annealed, right: annealed sample

To the first order, neither external contamination (adsorbed layers) nor the oxide layer seem to be directly responsible of observed behaviour of RF cavities, although they may vary a lot with the preparation of the surface. We have numerous examples of cavities exposed to air, oxygen, or water vapour with no modification of their results [3]. Nevertheless, modification of the oxide

layer can be either a symptom or the origin of different behaviour, so it is interesting to study it in details.

Surface segregation of light impurities is observed in niobium used for SC cavities [4,5], and it is a good candidate for degraded performances in SC RF cavities.

From the SC point of view, the cavity behaviour is consistent with the existence of a thin layer (1-2 nm) at the oxide–metal interface. (See Figure 3).
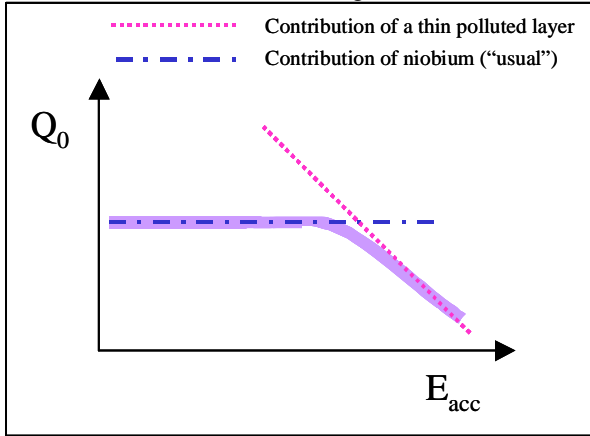

Figure 3: possible origin of the observed slope on Q_0 vs E_{acc} curves

As mentioned in references [6] and [7] interstitial oxygen is the most suspect candidate for the cavity behaviour. Baking experiments are consistent with a thin contaminated layer that becomes diluted as it diffuses during baking, as shown in Figure 4 [7]. The diffusion of a layer of oxygen is modeled there in conditions similar to baking.
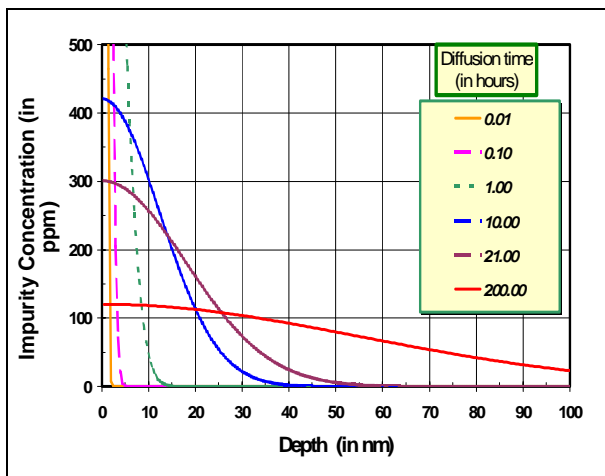

Figure 4 : (from [7]) diffusion model for a thin layer of oxygen inside bulk niobium during baking.

Significant changes in the distribution of oxygen and/or other light elements in the SC material may depend on surface treatment. As will be shown below, surface analyses effectively support this hypothesis, and show that other impurities in addition to oxygen must be taken into consideration.

1.2 What is the origin of the surface segregation and/or contamination?

Surface segregation of light impurities (H, O, C, N, …) is known to occur near the interfaces in many metals, especially if they are quite pure [8,9]. Near these interfaces, the mismatch between neighbouring lattices produces local strain, which in turns interacts with impurities. So a lot of the contamination did reassemble near the surface during the cooling of the metal each time it was annealed. Once it is there, it is very difficult to remove it by chemical polishing. Indeed, during the dissolution process the principal driving force is the local electric potential. In the case of electropolishing, it arises from the externally applied potential while during chemical polishing the electric field is due to adsorption of polar species like H_2O on the surface. In both cases, the local potential can be higher than 10^6 V/m [10] over a few nm, and is readily screened by the growth of an oxide layer. One has to stay aware that the main diffusing species are **ionic**, and that they diffuse **through** a depassivated oxide layer that is not fully dissolved during the polishing process [10 and references therein, 11 and references therein, 12]. Neutral atoms are **trapped behind** the oxide layer, and will diffuse orders of magnitude slower. This phenomenon explains for instance the "memory" effect that we have observed on cavities, where we must remove at least 100 µm of niobium to show stable results for a new surface treatment.

Incorporation of the solution's electrolytes also modifies the properties of the oxide layer (structure, kinetics of growth…), and might influence the composition of the metal near the oxide-metal interface. Moreover, Halbritter showed modification of the metal-oxide interface (serration) during the growth of the oxide layer in wet conditions [13]. Such a phenomena was also observed in other oxidation conditions [14]. Our experimental results also confirm that the thickness of the oxide layer is not homogeneous.

2 SURFACE TECHNIQUES

Among the available surface techniques, some cannot be applied to cavity surface states at operating conditions. For instance, some techniques are sensitive only to a very thin surface layer (Scanning Tunnelling Microscopy, Low Energy Electron Diffraction. for instance). Others integrate a thick layer without enough depth resolution, and the outer contamination layer, and/or the oxide layer might mask any interesting information. EDX (Electron Dispersive X-rays analysis), for instance, explore more or less 1 µm depth.. Some other techniques, like X-ray reflectometry can be applied to "perfect material" like monocrystals, but cannot be applied to "real" surfaces like etched polycrystalline niobium, which are too rough [15]. Of course results obtained on "perfect" samples, can give us some hints in the understanding of the material

behaviour, but one has to remember to be cautious in trying to extend these results to real conditions.

Profiling techniques, with a depth resolution less than 10 nm if possible, are interesting for surface impurity distribution. Most of these techniques consist in sputtering the surface either with an ion beam or a plasma, and to detect some of the sputtered species (e. g. ions in the case of SIMS, neutral atoms in the case of GDL), or to perform a surface analysis of the freshly sputtered surfaces (e.g. XPS, Auger) One has to be very careful with these techniques because preferential sputtering is known to occur in many metallic systems [16] and especially in niobium [17], so that except for very low etching rates in very high vacuum, most of the profiles that we obtain, especially for oxygen, are not accurate. Another difficulty with oxygen is that the oxide-metal interface is quite difficult to localise, due to a combination of the depth resolution of the chosen technique and the surface and interface roughness. Then, unless we have chemical information (like in XPS) we need to have some standard samples as a reference to be able to exploit the observed profiles.

3 SURFACE STUDIES

3.1 Sample preparation

It is very important to mimic the standard surface preparation applied to cavities. All Nb samples were cut from the same sheet (RRR ~320, supplied by Oremet-Wah-Chang). Half of them underwent a purification annealing and reached RRR ~570. Samples were submitted to various chemical treatments described below, followed by high pressure rinsing with de-ionized water. As some of the surface treatments, like electropolishing are sensitive air exposure, samples were held in vacuum within 1-2 hours after the rinsing, until their surface analysis.

3.2 XPS

XPS gives us information on the nature of the oxide layer and the interface region. Unfortunately it does not go deeper than 7-8 nm, and profiling does not give enough depth resolution due to the preferential oxygen sputtering. Moreover it is not very sensitive and impurities concentration below about tenth of atomic % won't be detected. The last drawback of this technique is that the contribution of the different chemical species has to be determined by deconvolution of complex spectra. To be physically significant such results need to be confirmed by other techniques.

Figure 5, extracted from [18], shows a Nb spectra obtained by photoemission spectroscopy with synchrotron radiation on a sample of clean mono-crystalline niobium covered with ~ 2 monolayers of NbO. Synchrotron radiation allows varying the incident X-rays energy with a better energy resolution than conventional XPS. This, combined with various angles of detection allows to get an explored depth of ~ 2 nm with a very good depth

resolution. With such a good energy resolution, the deconvolution of the niobium region shows 3 components in the doublet generally attributed to metallic Nb. From valance considerations, these 3 peaks can respectively be attributed to Nb°, Nb_6O and Nb_4O, i.e. bulk niobium, and niobium in contact with an oxygen in an octahedral interstitial site and in a tetrahedral site.
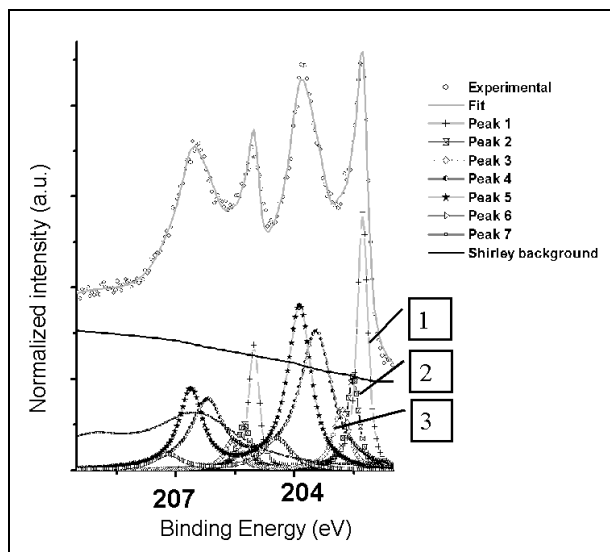

Figure 5: upper: Nb spectra obtained by photoemission spectroscopy with synchrotron radiation on a sample of clean niobium covered with ~ 2 monolayers of NbO. Lower: Decomposition of Nb levels using the Rainbow software. At least, 3 components are required for fitting the first peak, that can be attributed to Nb°, Nb6O and Nb4O, i.e. metallic Nb with oxygen interstitials (from ref [18]).

With this technique it was even possible to quantify the interstitial oxygen in contact with metallic Nb: 10 ± 2 At%, which is ~200 larger than the bulk solubility (see [18,19] for details).

Similar results were obtained by X-ray reflectometry on Nb samples epitaxied on sapphire. Oxidation in various media (air, dry oxygen, partial pressure), at room or higher temperatures, leads to an over-saturation of Nb films with interstitial oxygen. Concentration as high as 70 At %, accompanied by a lattice distortion, is observed even before the oxide forms [14]. (NB : [O] in Nb_2O_5 is 71.4 At %)

How can we extend those results to chemically polished bulk Nb? Synchrotron radiation does not penetrate sufficiently inside fully-grown oxide, and our samples are too rough to be studied by X-rays reflectometry. Conventional XPS can explore the oxide-metal interface; but slight signals like NbO, or even interstitials O are difficult to model accurately as Nb_2O_5 and Nb° signals dominate the spectra.

Figure 6 shows the evolution of conventional XPS spectra of an electropolished sample during a 3 days baking at 120°C. Degradation of the Nb_2O_5 to NbO_2 is obvious [2], but on deconvolution basis it is rather

difficult to make a decision on the existence of the species at low concentration (NbO, Nb_4O Nb_6O.
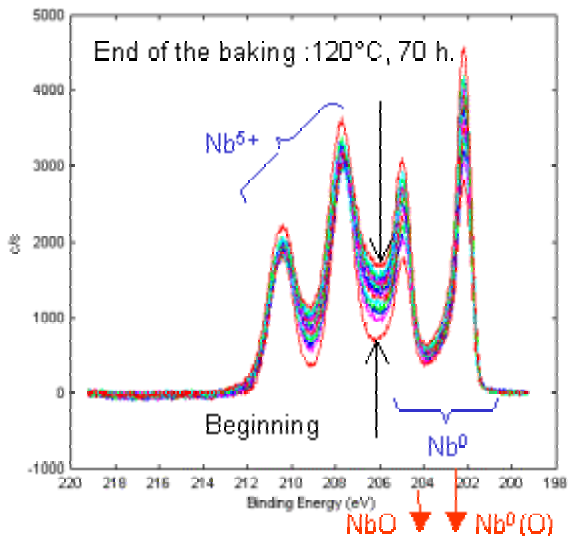

Figure 6: evolution of the Nb signal during a 3 days baking at 120°C. The 2 peaks at the right side correspond to Nb° while the 2 peaks at the left side correspond to Nb^{5+}; the apparition of a 3rd component (Nb^{4+}) can be inferred from the enlargement of the middle of the spectra.

Statistical treatment of the spectra allows us to confirm the existence of small fractions. For instance, with Principal Components Analysis (PCA), all spectra constitute a "matrix" whose eigenvalues are calculated. In Figure 7, it is seen that at least 6 components are relevant to fit the spectra. It may therefore be legitimate to think that those 6 components are linear combinations from species like Nb_2O_5, NbO_2, NbO, Nb_4O, Nb_6O, Nb°... This suggests that the existence of interstitial atoms is statistically demonstrated, even though deconvolution with 12 peaks would have been rather hazardous. More detail about the statistical treatment of XPS experimental results can be seen in [20]

In addition we have observed the following features :

- Peaks are sharper in purification-annealed samples, than in the normal ones showing that the lattice is better ordered.
- We observed slightly different chemical shift of the niobium oxide signals, depending on surface treatment and also if the sample is annealed or not. This confirms that although the oxide is still a pentoxide, the chemical environment changes slightly, suggesting varying concentrations of hydroxide or foreign atom.
- Fluoride can be detected on all samples, and it is in bulk rather than surface; it disappears with baking (i.e. the concentration decreases under the limit of detection).
- Baking results in the degradation of the pentoxide to NbO_2, and in the increase of the disorder and the injection of some oxygen atoms from the oxide into the matrix. This is certainly balanced by

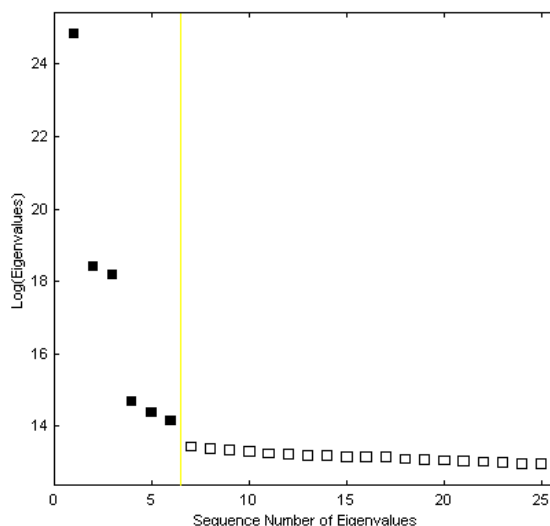dilution of oxygen in bulk Nb due to thermal diffusion.

Figure 7 : Principal Components Analysis (PCA) of 46 spectra acquired during baking, showing the respective statistical weight of each eigenvalue

3.3 SIMS

SIMS is in theory more sensitive, and allows profiling with a good depth resolution, provided that it is conducted slowly, in UHV conditions ($<<10^{-5}$ Pascals), and with a primary ion beam at grazing angle. Well-characterized samples were necessary to evaluate the depth and intensity scale. They were made of monocrystalline Nb and Nb_2O_5 epitaxied on a sapphire substrate (less than 10 $\pm$ 5 Å in roughness). The Nb sample was covered with 85 Å Pt in order to prevent oxidation*.

As can be seen by example on Figure 8 some behavior differences can be observed on annealed samples between chemically polished and electropolished samples. The oxygen contamination penetrates in the depth of the material, but a similar behavior is also observed for other impurities: F, C, H, and S (S not shown here). The same spectra made on un-annealed samples do not exhibit such a pronounced difference. But we can observe that the oxide layer is thicker, and that oxygen contamination behind the oxide layer is also thicker not annealed samples.

The baking of such samples also exhibit a redistribution of mainly O, C, F, P... revealing some diffusion of each species. Unfortunately, it was not possible to evaluate these effects quantitatively, because of several limitations due to experimental conditions:

- We have some indication that ~10-15 % of the grains behave a little different than the rest of the material, probably due to their crystalline orientation.

- On annealed samples, the beam touches only one grain while on "normal" samples it integrates several grains.
- We need a reliable reference for each element, and as we deal with very low concentrations, references are quite difficult to obtain.
- Vacuum has to be improved, because H signal was close to saturation.
- The roughness of the oxide-metal interface convoluted with the roughness of the sample itself is detrimental to the depth resolution and might play a role in the impurities distribution.
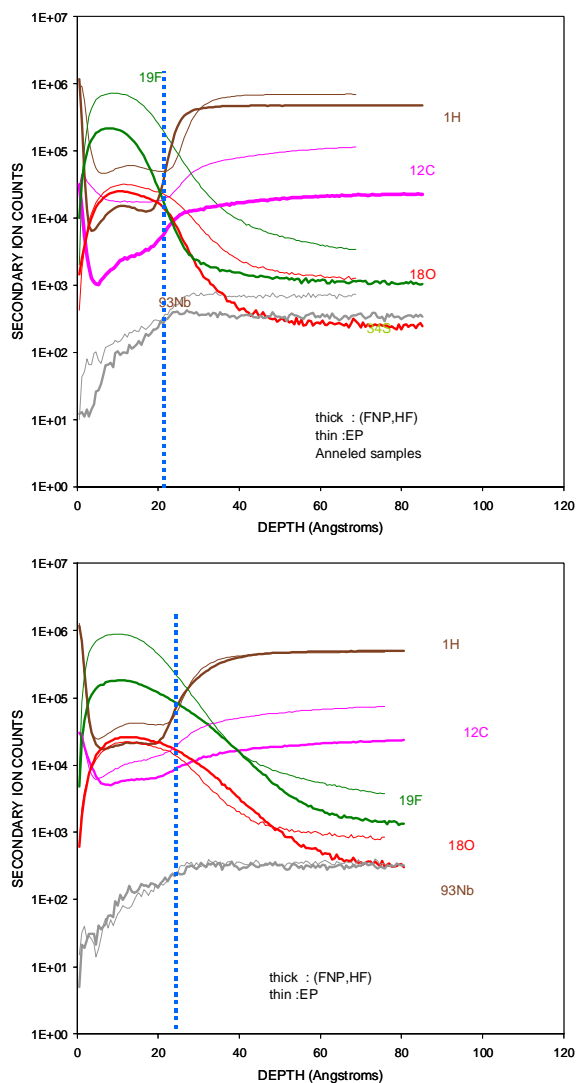

Figure 8: comparative SIMS profile of a chemical polished sample (named FNP) and an electropolished sample. Dotted line indicates approximately the interface, as deduced from Nb signal intensity. Up: annealed samples, down un-annealed samples.

Although the combination of XPS and SIMS should be well adapted to our problem, we see trends but no strong evidence of a very different behavior of the samples depending on their surface treatment. This difficulty could be overcome with the use of better-defined samples like in reference [14]. In the case of well-controlled samples of very low roughness, the variation of the metal-oxide interface can be monitored by X-ray reflectometry, as well as the distribution of interstitials. If polishing of such samples is not possible, the modification of the oxide layer in presence of various electrolytes can nevertheless be explored.

3.4 EBSP

Electron BackScattering Patterns is an example of the difficulty to find accurate surface studies techniques. Although it appears like a promising technique, the obtained results are rather puzzling and difficult to interpret. Indeed, diffracted electrons cannot escape from more than some tens of nm from the material; we explore a sample thickness comparable to the penetration depth. Moreover, the oxide layer, as it is amorphous, doesn't exhibit diffraction patterns (N.B. X-rays penetrate much deeper inside the material and are not accurate for surface measurement).
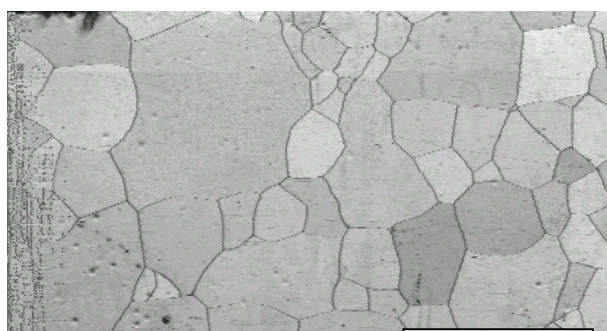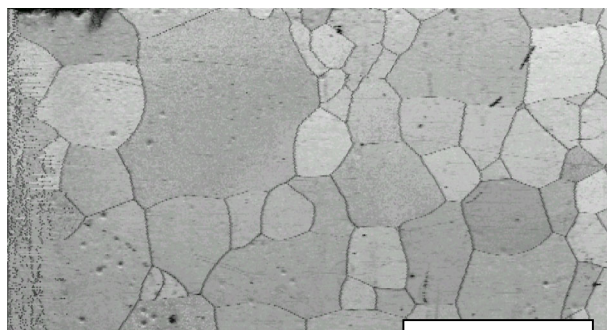

Figure 9 a)

2250.0 µm = 90 steps   IQ 39.7...466.7

Figure 9b)

2250.0 µm = 90 steps   IQ 50...471.8

Figure 9: Quality Indices of diffraction pattern obtained on a niobium sample, a): after electropolishing; b): the same sample after baking. Darker grains correspond to more diffuse diffraction patterns (grain boundaries, where disorder is maximum, appear in black). After baking the relative grey level of some grains has changed., in particular on the right part of the photograph.

If there are some differences in the distribution of interstitial atoms due to the surface treatment, there should also be differences in the strain state (whatever it is the cause or the consequence of the presence of these foreign atoms). In theory [21], strain should be detected by this technique, because disorder or strain induce

diffuseness in the diffraction diagram. Figure 9 gives an example of visualization of the quality indices, which are automatically deduced from the "diffuseness" of the diffraction diagrams

Several treatments were tested, showing that only a part (12-13 %, whatever the treatment!) of the grains exhibit significant changes, probably dependant on their crystalline orientation. We need now to find if these changes are related to small changes of the lattice parameter, which could indicate effective strain of the lattice.

4 GRAIN BOUNDARIES SPECIFIC RESISTANCE

Grain Boundaries (GB) are also interfaces inside the material; thus one can expect that phenomena similar to surface segregation may occur. Classical surface studies are difficult to apply to this problem; that is why a specific apparatus was developed at Saclay for the direct measurement of the specific resistance of grain boundaries. It has already been described in detail elsewhere [22]. It is a 4-wires method, where we measure ac-cumulated voltages with 19 sequential pins at 300 K and 10K. The samples are annealed, with grain diameter about 2mm so that each pin touches in principle a different grain. By comparison, we obtain an equivalent "RRR" of the grain boundaries. Influence of grain boundary behavior was theoretically explored in [23]. We present hereafter the first results obtained on samples that underwent different surface treatment.
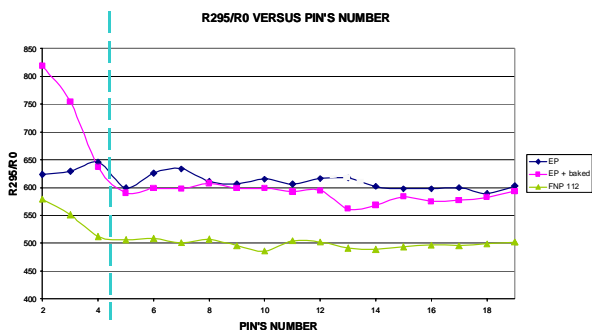

Figure 10: experimental RRR measurement of several grain boundaries measured sequentially on the same sample by a four-wire method. The first values correspond to very low voltage measurements and can be put aside. Blue curve corresponds to an electropolished sample, the pink one corresponds to the same sample after baking and green curve corresponds to the chemically polished sample. Except for the 5 first measurements, the error bars are of the same size as the experimental dots. Variations arise from the fact that each grain boundary is different from the others.

Figure 10 shows an example of the measured RRR of a series of grain boundaries. This figure shows clearly that grain boundaries are affected by the surface treatment, and that chemical polishing gives poorer results than electropolishing. Apparently, baking influences less the

measurement. This could indicate that the depth affected inside grain boundaries goes much deeper than the affected depth at the surface of the grains. This is consistent with the fact that GB are a very disordered phase, where diffusion is known to occur much faster than inside the bulk of the grains. This technique seems to be a convenient tool to roughly evaluate different surface treatments: it is far more rapid and less expensive than cavity testing.

5 CONCLUSION

Surface segregation seems to explain well the "Q-slope" observed on every cavity before baking, whatever the surface treatment. Segregation of many atomic species (O, C, F, …), can be inferred from most of the studies cited here. At this point, only qualitative trends can be drawn, and we were unable to evidence measurable variations depending on the surface treatment, although surface contamination was observed on all of them.

To be able to quantify such effects, only more "sophisticated" experiments done on better-characterized samples like monocrystals are needed. But if monocrystalline samples were studied, one would have to test many different crystalline orientations in order to be representative. Nevertheless, such research has to be conducted within the framework of solid physics community rather than RF superconductivity.

It is more difficult to determinate why we observe quench field variation with surface treatments. We already have some indication of non-uniformity of the surface, which could explain that local differences appear. Another explanation could be related to the curvature radius of the surface steps [24] (N.B.: this is different from the roughness as it is usually measured). Indeed, J. Knobloch, for instance demonstrated that we can have localized field enhancement for sharp step edges [25]. Change in the edge sharpness, less easily measurable than roughness, still needs to be experimentally demonstrated.

6 REFERENCES

[1] E. Kako, S. Noguchi, M. Ono, K. Saito, T. Shishido, H.Safa, J. Knobloch, L. Lilje, "Improvement of cavity performance in the Saclay/Cornell/DESY's SC cavities", 9th Workshop on RF Superconductivity, Santa Fe, Nov.1-5, 1999, pp179-186

[2] C.Z. Antoine et al, "morphological and chemical studies of Nb Samples after various surface treatments", 9th Workshop on RF Superconductivity, Santa Fe, Nov.1-5, 1999, pp 295-303

[3] See e.g. B. Visentin, "Change of RF superconductivity parameters induced by heat treatment on Nb cavities", proc. of PAC 2001,

[4] C. Z. Antoine "RF material investigation by sample analysis", Inv. Conf, 8th Workshop on RF Superconductivity, Abano Terme (Padova), 6-10 Oct. 1997

[5] C. Z. Antoine et al, "nuclear microbrobe studies of impurities segregation in niobium used for radiofrequency cavities.", 8th Workshop on RF Superconductivity, Abano Terme (Padova), 6-10 Oct. 1997

[6] B. Visentin et al, "improvement of superconducting performances at high accelerating gradients", proc. EPAC 1998, pp 1885-1887

[7] H. Safa, "progress and trends in SCRF cavities for future accelerators, proc. of EPAC 2000, pp197-201

[8] Grain boundary structure and kinetics", ASM Material Science Seminar Books, (1979)

[9] "Fundamentals of grain and interphase boundary diffusion", I KAUR, W GUST Ed, Ziegler Press, Stuttgart, (1989)

[10] M.J. Dignam , "Oxides and oxides films", Vol 1, chap 2 : "ionic transport through oxide films", NY (1973), J. Diggle Ed

[11] Encyclopedia of electrochemistry of elements, Vol.II, A.J. Bard, M. Deklev ed, New York, (1974), pp 111-112 and ref therein

[12] R. Delmas, M. Fedoroff, G. Revel, "delayed dissolution of superficial impurities as an error cause in activation analysis of metals", Journal of trace and microprobe techniques, vol.2, No 1, p 67 (1984).
R. Delmas, "Contribution à l'étude des causes d'erreur en analyse par activation", PhD Thesis, Paris VI (France), (1982).

[13] M. Grudner, J. Halbritter, "On the natural Nb2O5 growth on Nb at room temperature", Surf. Sc., 136, (1984), pp 144-145.

[14] O. Hellwig, "Oxidation of epitaxial Nb(110) films : oxygen dissolution and oxide formation", PhD Thesis, Bochum (Germany), April 2000.

[15] M. Berthelot, Training Period Report, SEA- Saclay, June-Sept., 1999

[16] P.S. Ho, J.E. Lewis, "Deconvolution method for composition profiling by Auger sputtering technique", Surface-Science, vol.55, no.1; April 1976; p.335-48.

[17] P.C. Karulkar, "Effects of sputtering on the surface composition of niobium oxides", Journal-of-Vacuum-Science-and-Technology., vol.18, no.2; March 1981; p.169-74.

[18] I. Arfaoui, C Guillot, J. Cousty, C. Antoine; "Evidence for a huge enrichment of interstitial oxygen atoms in the nanometer-thick metal layer at the NbO/Nb (110) interface", submitted to JAP

[19] I. Arfaoui, "stoechiométrie, structure et tenue en champs électrique d'un film mince de NbOx~1 sur Nb(110) », PhD Thesis, Ecole centrale de Paris, March 2001.

[20] A. Chincarini et al, this workshop

[21] A.J. Wilkinson, D.J. Dingley, "quantitative deformation studies using back scatter patterns", Acta metal. mater., 39(12), (1991), pp 3047-3055.

[22] H. Safa, M. Bolore, Y. Boudigou, S. Jaidane, R. Keller, P. Nardin, G. Szegedi, "Specific resistance measurment of a single grain boundary in pure niobium", 9th Workshop on RF Superconductivity, Santa Fe, Nov.1-5, 1999, pp 267-269

[23] B Bonin, H Safa, "power dissipation at high fields in granular RF superconductivity", Superconducting Sc. & Technol., 4, 257-261, (1991)

[24] L. Lilje, personal communication, see also H. Safa, this workshop.

[25] J. Knobloch, "microstructure of RF surface in the EB-weld regions of Nb", 9th Workshop on RF Superconductivity, Santa Fe, Nov.1-5, 1999, pp 238-245