

# **RF MATERIAL INVESTIGATION BY SAMPLE ANALYSIS**

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## **SUMMARY**

Defects or impurities, surface or grain boundaries segregations, are known to be very harmful for superconducting materials, especially for RF applications. A wide range of techniques exists to explore either the global purity or very localized places of the material. This paper reviews some of the techniques which were used at Saclay or with close collaborators, along with their limitations and/or complementarity. Two domains are described : the behavior of material at cryogenic temperature, with our recent improvements in measuring the usual superconducting parameters and localized chemical analysis techniques.

## **INTRODUCTION**

Material characterization is a necessity to be able to trace out any of the origin of defective operation of superconducting cavities. The niobium used now for the elaboration of the cavities is more and more pure : the most harmful impurities, i. e. light element are now reduced to a few At ppm in the bulk, and the thermal conductivity of the niobium has been improved a lot. Nevertheless some margin still exist between the achieved accelerating gradients and the theoretically predicted ones.

Lot of standard procedures are already routinely used, but as performances of cavities have greatly enhanced, we are now confronted to explore more and more finer details, with more and more precision.

In the SC community several tests have been developed to describe the behavior of superconducting material at cryogenic temperature, which need to be continuously improved to fit to our new demands. With  $T_c$ , RRR, thermal conductivity and Kapitza resistance, we can predict the global behavior of a superconducting cavity, but not directly its surface resistance. We need to use more specific techniques to explore the very

narrow area just under the surface where dissipations occur. Indeed, in metals, interfaces like grain boundaries or metal-oxide interface act like a trapping defect and/or a short-circuit diffusing path. Paradoxically, the purer the material, the more likely we are to get some segregation phenomena, because surface is nearly the only remaining trapping defects.

## CRYOGENIC EXPERIMENTS

Residual Resistivity Ratio (RRR), thermal conductivity ( $\lambda$ ), and Kapitza resistance are mainly aimed to determine the ability of the superconductor to evacuate thermal dissipation toward the helium bath. In addition, Transition Temperature ( $T_c$ ) and surface resistance ( $R_s$ ) can be a useful tool to study compound superconductors of higher  $T_c$ .

Thermal conductivity ( $\lambda$ ) and Transition Temperature ( $T_c$ ) are classical although delicate 4-wires measurements, already described elsewhere, [1]. They are now automated with Labview™ which gives a gain 2 to 3 in time, and allows to measure more samples systematically.

RRR measurement where improved a lot with the introduction of two new processes : the "extrapolation method" and RRR mapping.

The "extrapolation method" is a classical 4-wire measurement ; it became feasible with the use of a thermostatic tank with fine temperature regulation. As can be seen on Figure 1, the normal resistivity is extrapolated toward 0 K with a simple polynomial law :  $\rho \sim A + B.T^3$  and then reintroduced in the ratio. (Details about this measure and its validation will be given in [2]). Advantages of this method is that we do not need a magnetic coil nor magnetic transition, and we are then far less sensitive to the surface state of the samples. For instance, samples without chemical treatments or with a titanium layer can be measured without troubles, which represents a big gain in time. Measurements are taken continuously during the natural heating up of the cryostat and we do not need any complex system of thermal stabilization.

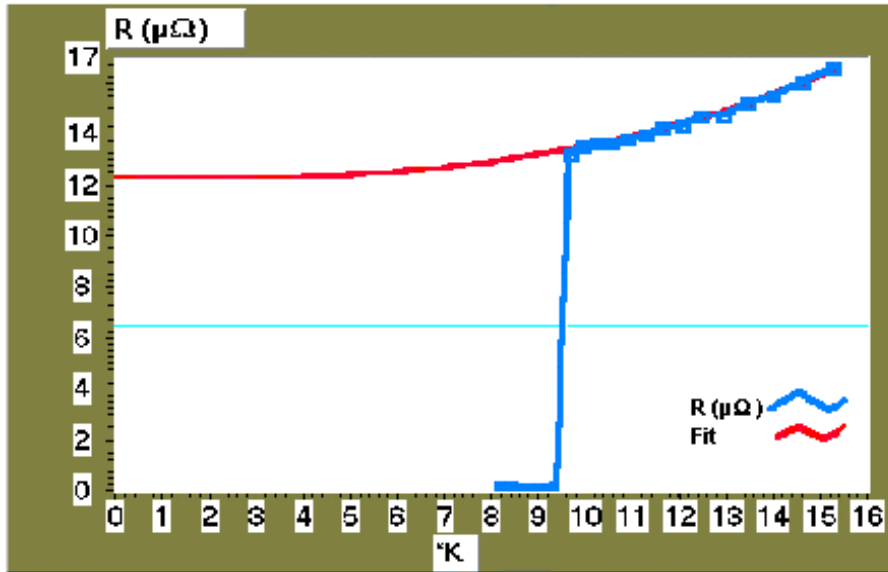


Figure 1 : The curve in blue is the resistance of a niobium sample. In red is the fit of this curve with a  $A + B.T^3$  function which allows to extrapolate the results toward 0 K.

Figure 2 shows a moveable arm which allows RRR mapping on 1.3 GHz cavities. Each sensor is a set of two coupled inductances powered by an electromagnetic sinewave. Variations of their mutual inductance with the frequency of the sinewave is dependent on the resistivity of the underlying metal. Measures at low and high temperature give access to local RRR measurements of samples and cavities. This technique has shown inhomogeneities in the starting material, and in the completed cavity. For more details see [3].

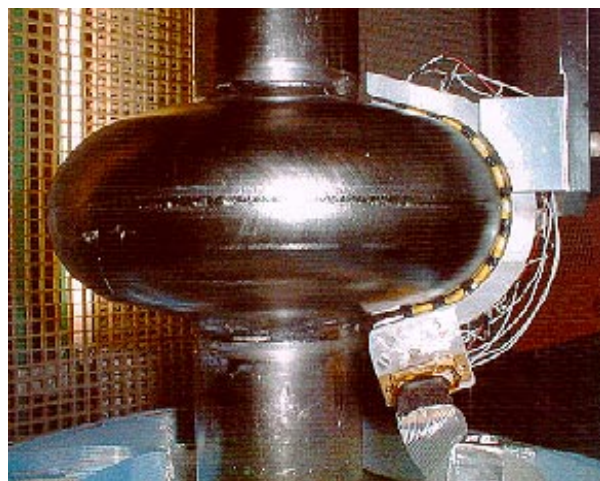
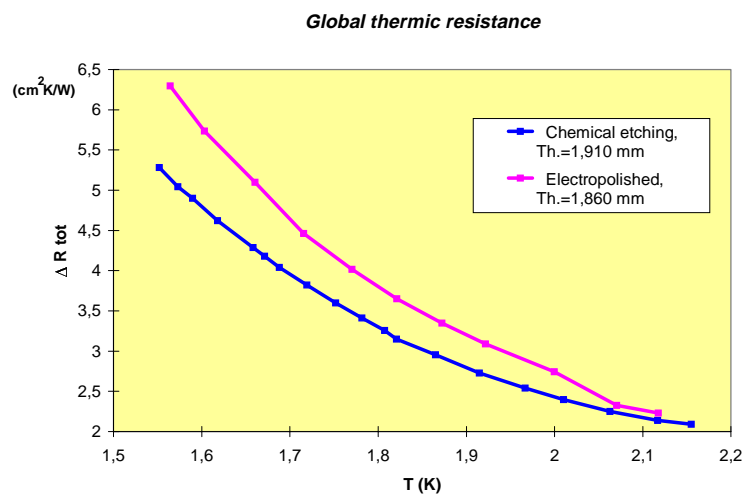


Figure 2 : RRR mapping : moveable arm installed on a 1.3 GHz cavity.

A collaboration with the LIMSI (CNRS) is underway for measuring the Kapitza resistance (thermal resistance at the superfluid He-Nb interface) and the parameters that can influence its value (purity, surface condition, etc.). Figure 3 shows the difference of global thermal resistance between chemically polished samples, and electropolished samples of the same Nb sheet material. Obviously, an increase of the contact surface with Helium improves the thermal transfer.



*Figure 3 : Global thermic resistance for two samples of a same niobium sheet (RRR ~180) with two different surface treatments.*

Nevertheless, the dielectric resonator presented at the last workshop [4] has shown to be able to measure effective resistance only above  $\sim 100$  n $\Omega$  at 2 K due to electronic noise, and is only available for high  $T_c$  superconductors unless a significant modification of the measuring system.

## CHEMICAL ANALYSIS NEAR THE SURFACE

Interfacial segregation can be as thin as some atomic monolayers. To evidence such local concentration, we need to have very high sensitivity and/or good lateral resolution. It is possible to detect light impurities like hydrogen, carbon and oxygen, as more heavy metallic impurities with many surface techniques, provided that they can afford for sufficient spatial resolution and sensitivity. The challenge is to detect some monolayers of impurities in a volume that is some 50 to 100 nm deep under the surface (penetration depth of the electromagnetic field), in spite of the fact that the surface also

includes a natural oxide layer and a contamination layer. Two categories of analysis methods are described in more details hereafter : nuclear methods and profiling methods. Very classic methods like SEM (phase contrast, EDX) or ESCA have also been used but have shown to be not very well adapted to trace very low concentrations and/or very narrow segregations. TEM has also been attempted but the preparation of the samples was too long and delicate.

**Nuclear methods** : Among Nuclear methods, Ion Induced X-Ray Emission allows to detect with a good sensitivity a wide range of metallic impurities like Ti or Ta ; It is semi-quantitative, by comparison with a standard sample, but has no depth resolution : some micron depth are explored altogether. Lateral imaging is possible by the use of a microprobe, as it is detailed in [5, 6]. Figure 4 shows an example taken from [6] : we could correlate anomalous thermal losses at high accelerating gradients of a cavity with the presence of Titanium at grain boundaries.

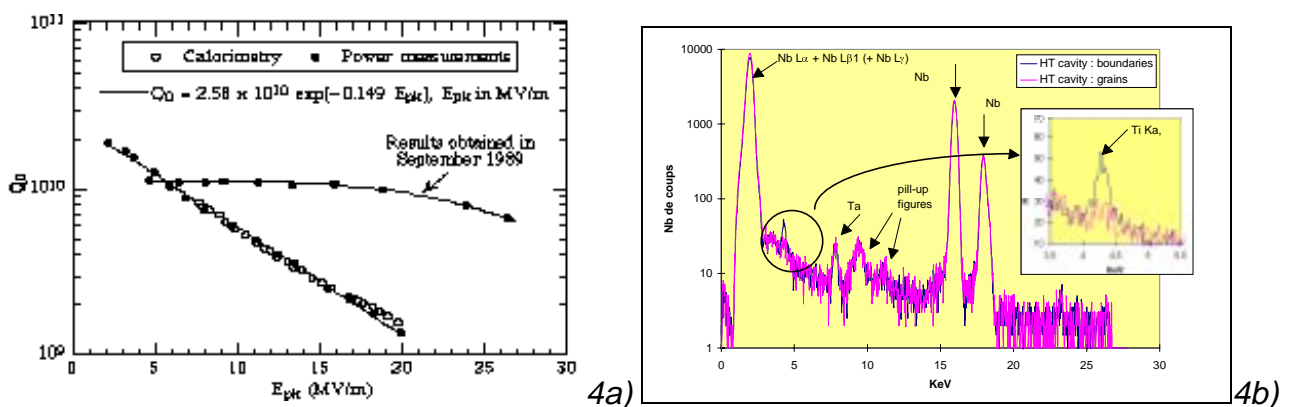
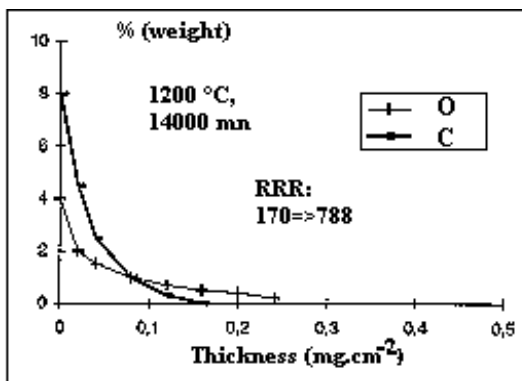


Figure 4a)  $Q_0$  versus  $E_{pk}$  of a cavity heat treated at very high temperatures. Both (conventional) if power measurements and results from the thermometry system are included. For comparison, results from 1989, where no  $Q$ -degradation was observed, are also depicted. 4b) PIXE spectra for a sample cut from the cavity (internal surface).

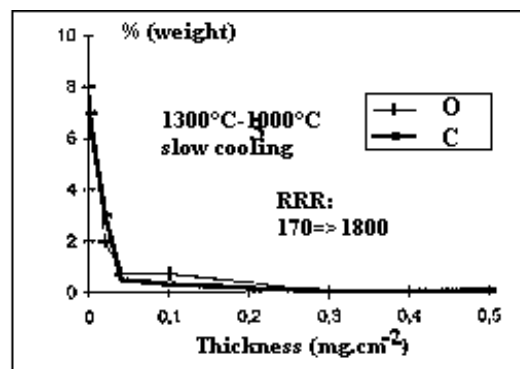
Nuclear Reactions can give the signature of individual atoms like oxygen or carbon. One can get profile concentration with 50 nm to 100 nm depth resolution. With the use of a microprobe one can even explore grain boundaries. Anyhow these measures are always delicate because of the presence of a natural oxide layer about 5-10 nm and a contamination layer, the most accurate/safer results are obtained by comparison.

As can be observed on figure 5a) and 5b), samples with high RRR value can exhibit fairly high concentration of impurities near the surface. Moreover, samples with close value of RRR like the ones in 5c) and 5d) can have a very different composition near the surface.

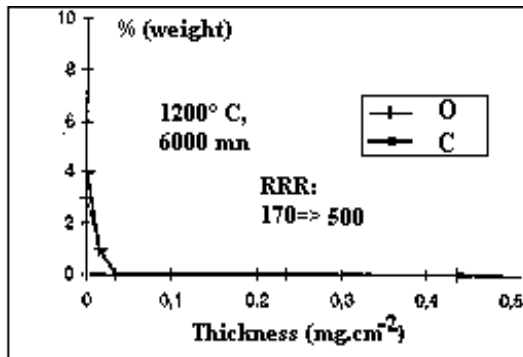
RRR measurements obviously don't give sufficient indications about the local purity near the surface. An increase in thermal conductivity can be counterbalanced by a local pollution that increases surface resistance.



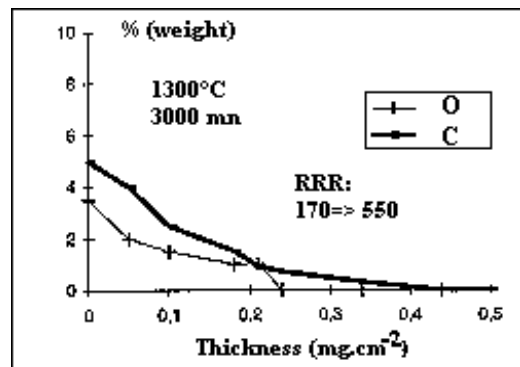
5a)



5b)



5c)



5d)

Figure 5 : profile concentration of oxygen and carbon for four different annealing conditions, along with RRR measurement. 500- 600 nm of depth are explored ( $\sim 5 \text{ mg.cm}^2$ ) : this means that except for 5c), the polluted region is far more thick than the natural oxide layer (= 5-10 nm).

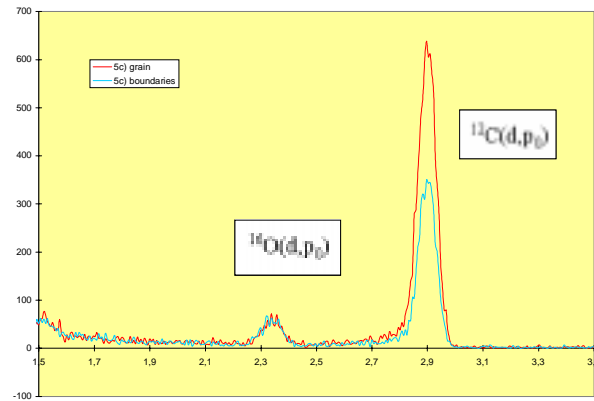
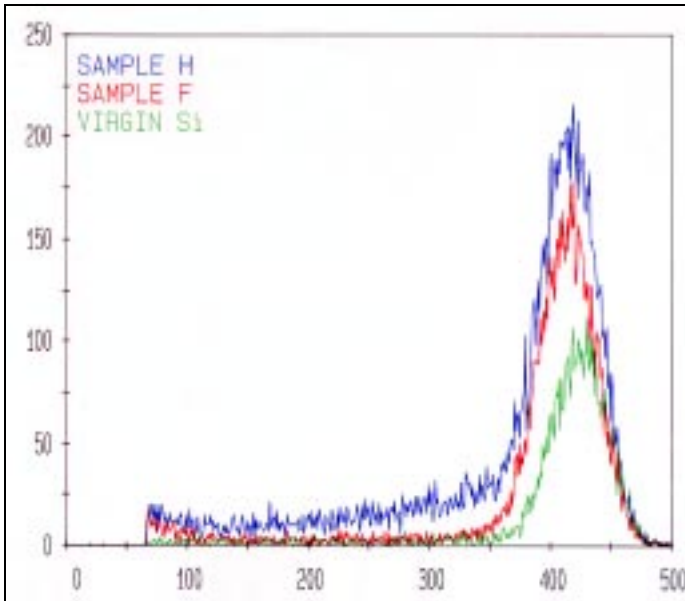


Figure 6 :example of comparison grain/boundary for the 4c) sample

Elastic Recoil Detection Analysis can measure atomic hydrogen concentration up to 0.2 At%, with  $\sim 30$  nm depth resolution ; on rough surfaces, the use of a microprobe is impossible and we get the signal from an area about  $1 \text{ mm}^2$ . Figure 7 gives an example of two niobium samples, with and without a heat treatment, along with a silicon sample which does not contain atomic hydrogen in the bulk. Note that the surface signal goes up to some At %, but includes surface contamination layers (adsorbates, hydrocarbons...) which are always present on surfaces, even under vacuum. Nevertheless, the presence of about 1% of H more than 30nm deep into the sample without heat treatment proves that surface segregation has occurred. Indeed, global measurements give only some 100 At ppm for this type of niobium, i.e. at least 10 times less. Heat treated samples do not exhibit hydrogen contamination except near the very surface ; but note that if they stay several months exposed to the humidity of the air, one shall recover hydrogen at some depth in the material. Inside the material, hydrogen is in the form of individual atoms which abandon their unique electron to the fermi level of the metal. They are then very mobile even at low temperature, although they are attracted by the surface defects (for more details about this phenomena see [7]).



Sample	Depth (Å)	At %
F	0-300	5.0
	300-600	<0.1
	600-900	<0.1
	900-1200	<0.1
	1200-1500	<0.1
	1500-1800	<0.1
H	0-300	7.5
	300-600	1.4
	600-900	1.1
	900-1200	0.8
	1200-1500	0.6
	1500-1800	0.5

Figure 7: ERDA spectra for hydrogen : the blue spectrum (H) is taken on a standard sample (RRR ~170), the red signal (F) comes from the same sample after an heat treatment (800° C, 2h), and the green one comes from a silicon probe which does not contain hydrogen in the bulk. In this last case, the hydrogen signal originates from the contamination layer.

**profiling methods** : they are all based on the same principle : samples are eroded (plasma discharge, ion beam, ...) and emitted particles are detected in function of time. Most of the time, the depth resolution needed for RF applications is not reached within a standard application and one has to cross check carefully the results of several techniques. Among these techniques, SIMS, GDS, and ESCA can give a depth profile of the material, and in some case can be coupled with lateral imaging.

Glow Discharge Spectroscopy is based on the luminous emission of neutral particles of the plasma created by the glow discharge ; it allows to study many species at the same time, although it is not quantitative for such low concentration. It has the advantage of showing a very good depth resolution : as can be observed on figure 8a one can distinguish the surface contamination (before the oxygen signal) from the inner one (after the oxide layer). It confirms what was assumed from the nuclear reaction studies :



there is impurities segregation at the metal-oxide interface. Note that just after a heat treatment the whole contamination and the oxide layer is reduced a lot (fig 8b)<sup>1</sup>.

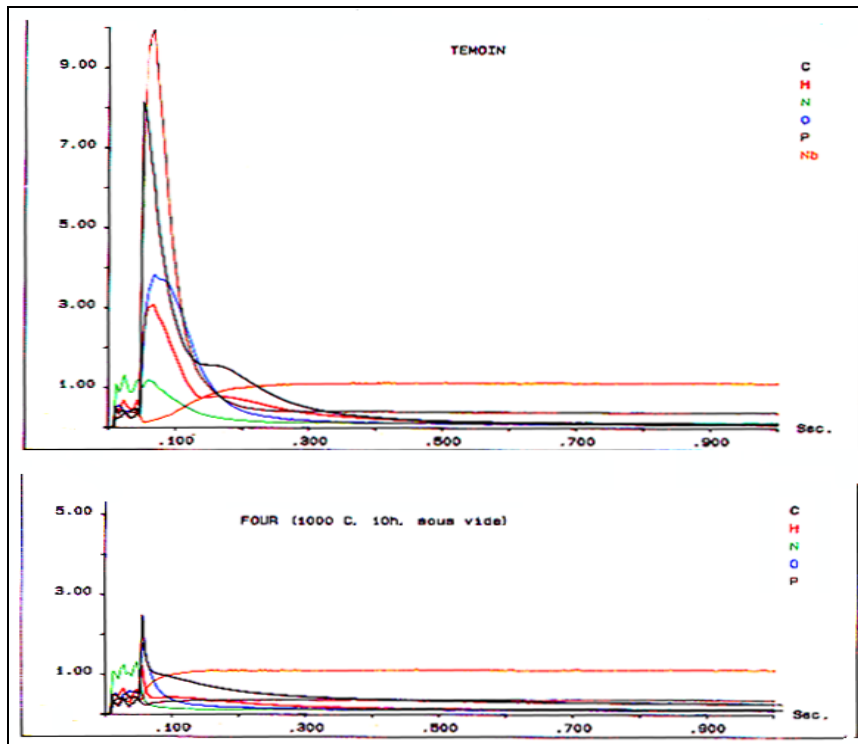


figure 8 SDL spectra for a standard niobium sample and a heat treated one : the blue signal represents oxygen while the orange is niobium in function of etching time. Impurities atoms like hydrogen, carbon, phosphorous... can be observed before and after the oxygen signal, proving two different kinds of contamination.

TOF-SIMS (Time Of Flight Secondary Ion Mass Spectroscopy) is done in a UHV chamber with a very slow rate of abrasion : more or less one atomic layer at each cycle. The reduced size of the ion beam allows also lateral imaging. In Fig 9 the cesium ion source is chosen to get the better sensitivity for carbon and oxygen. Once again carbon segregation can be observed just under the oxide layer on standard niobium sample (RRR~200) ; moreover the lateral imaging shows that this carbon is gathered in little aggregates with a diameter about several microns, and coupled with an oxygen signal.

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<sup>1</sup> Measure at the beginning of the discharge is sometime delicate. In our case, the well resolved oxygen signal allows us to identify the location of the other elements. Moreover the thickness of the oxide layer calculated with the mean abrasion rate was consistent with the given thickness of the natural oxide layer (5-10 nm).

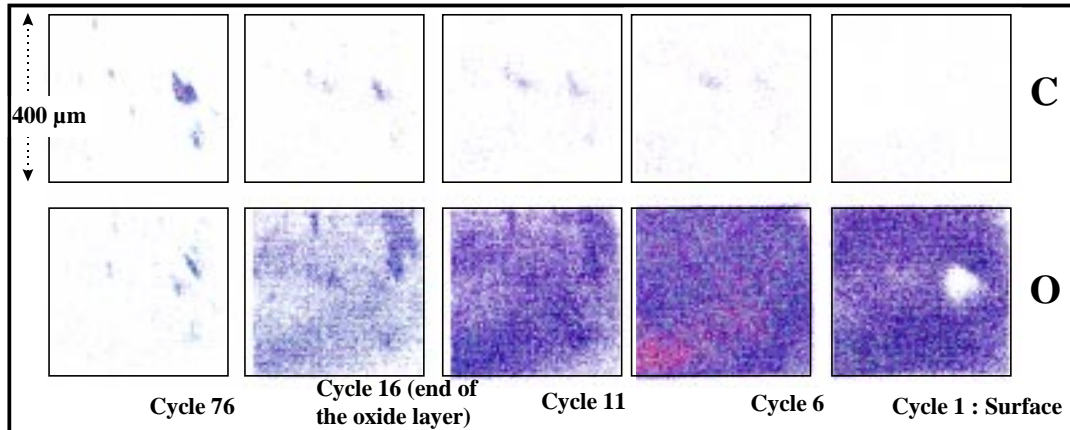


figure 9 : extracts from a TOF-SIMS analysis : segregates has also been observed at the metal-oxide interface on this niobium sample

Such features, with local enrichment of carbon and oxygen have also been observed on rolled samples from different suppliers by Scanning Electronic Microscopy coupled with EDX. They were also tested for field emission activity but they showed to have no DC field emission. Nuclear microprobe allows us to quantify this type of contamination : locally we can get concentration as high as At % level for carbon an oxygen. It seems that this contamination originates from the elaboration process : when the melted metal cools down, the light elements still diffuse very quickly in the bulk, and can reassemble into small "bubbles" of lower density. During the rolling process these bubbles are flattened out, and can give rise to irregular features like the ones we have observed.

The presence of chemically linked carbon has also been confirmed by XPS coupled with ion beam erosion. When the oxide layer disappears, a slight carbide signal can be observed which disappear in his turn quickly. (The exact erosion rate was not known). XPS limit of detection ranges about some 0.1 At% ; once again we can see that this contamination is not negligible.

One strange aspect of these contaminations is that it is not withdrawn by the usual chemical treatment applied to cavities (all the studied samples were chemically etched with a usual 1-1-2 acid bath, with removed thickness ranging from some microns to 100 microns). Some indications can be found in the literature, that during etching, metallic ions migrate through a contamination layer without dragging it, or very slowly. (For example, in [8 ], such a phenomenon was demonstrated on iron for impurities as different as Co, Na or S with activation experiments).

## CONCLUSION

The presence of contaminant, mainly carbon and oxygen near the surface of the niobium has been clearly demonstrated, even on high RRR material, by the use of different techniques. Our usual chemical treatment is insufficient to withdraw it, and even heat treatments in certain conditions do not improve the surface purity.

Surface composition might be an explanation of the anomalous thermal losses observed at Saclay at high fields, as well as for the superiority of electropolishing as a surface treatment as claimed by KEK [9]. Now that we are less often limited by field emission or localized "macroscopic" defects, it could be interesting to start a more systematic and comparative study of the local surface composition for different surface treatments, and try to correlate it with the RF behavior of the corresponding cavities.

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1 see for instance P. Dolegeviez & F. Koechlin , Proc. Of ICMAS, Grenoble, Oct. 16-19 (1990), ITTT France (1990)

2 H. Safa, to be published, + ref 3

3 This workshop : H. Safa et al, "RRR mapping of SRF cavities by a magnetometric method"

4 D. Moffat et al, "Measurement of the anomalous RF surface resistance of Nb using a dielectric resonator" 7<sup>th</sup> SRF workshop, Gif sur Yvette, Oct 17-20 (1995)

5 C. Z. Antoine et al, "Evidence of preferential diffusion and segregation of impurities in very pure niobium used for radiofrequency cavities", JAP 81(4), (1997), 1677-82

6 This workshop, C.Z. Antoine et al, "nuclear microprobe studies of impurities segregation in niobium used for radiofrequency cavities.",

7 CZ Antoine, "Hydrogen in Niobium : the analytical approach", Proceedings of the 5th Workshop on RF superconductivity, Aug 19-23 1991 at DESY, HAMBURG, Germany

8 R. Delmas, PhD Thesis , Paris 6 (1982)

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9 Saito et al, this workshop