

# SURFACE CHARACTERIZATION OF BULK NB: WHAT HAS BEEN DONE, WHAT HAS BEEN LEARNT? \*

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## Abstract

Electromagnetic fields penetrate only a distance of ~ 60 nm into the surface of a superconductor such as niobium. Therefore it is obvious that the condition of a cavity surface will affect the performance of this cavity. In at least the last 30 years niobium surfaces as used in superconducting accelerating cavities have been investigated by surface characterization techniques such as scanning electron microscopy (SEM), Auger spectroscopy (AES), X-ray photon spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), electron spectroscopy for chemical analysis (ESCA) and secondary ion mass spectrometry (SIMS). The objective of all these investigations was to establish correlations between surface conditions and cavity performances such as surface resistance and accelerating gradients. Much emphasis was placed on investigating surface topography and the oxidation states of niobium under varying conditions such as buffered chemical polishing, electropolishing, oxipolishing, high temperature heat treatment, post-purification heat treatment and “in-situ” baking. Additional measurements were conducted to characterize the behavior of a niobium surface more relevant to rf cavities such as resonant (multipacting) and non-resonant (field emission) electron loading.

A large amount of knowledge has been extracted by all these investigations; nevertheless, there is still a lack of reproducibility in cavity performance when applying the “best” process to a cavity surface and no clear correlation has been established between niobium surface features and cavity performance.

This contribution gives a review of the attempts to characterize niobium surfaces over the last three decades and tries to extract the “white spots” in our knowledge.

## INTRODUCTION

Approximately four decades ago the use of superconducting cavities in particle accelerators was proposed [1]. Initial work focussed on the use of lead as the superconducting material; however, a few years later niobium became the choice material for these devices and as the developments at HEPL and KFK showed promising results, more research institutions such as Cornell University, Brookhaven National Lab (BNL), Stanford Accelerator Center (SLAC), European Research Center (CERN), Deutsches Elektronen Synchrotron (DESY), Japanese Accelerator Center KEK, CEA in France, the

University of Wuppertal and Siemens AG in Germany started their own developments. The technology turned out to be rather difficult since it combines a variety of disciplines: material science, surface science, solid state physics, chemical processing technology, cleaning techniques, rf technology, vacuum technology, cryogenics and a strict control of contamination. This complexity naturally caused delays and set backs in the developments. A better understanding of the underlying physical phenomena responsible for encountered limitations had to be gained.

Since a high frequency electromagnetic field penetrates only a distance of  $\lambda$  (penetration depth ~ 60 nm for niobium at a frequency of 1500 MHz) into a superconductor, it was rather obvious that the features of this thin surface layer and its influence on cavity performance had to be understood in order to make progress in the development of the technology. Therefore a tremendous amount of investigations of niobium surfaces has been carried out over the last 30 years.

An initial review of the activities was given in a contribution by A. Septier at the 1<sup>st</sup> Workshop on RF Superconductivity [2], and it seems appropriate to repeat a quote from this paper:

*“ It is not yet clear what surface properties are the most important for achieving high Q – values and high peak Rf fields. The answer to this question will be provided by a careful correlation between microwave cavity measurements and surface studies on small samples processed at the same time.”*

This pretty much summarized the objectives of the surface studies: by correlating surface features and surface conditions on sample surfaces one wants to find the “best” procedures to generate the “best” surfaces with the “best” rf performances: *low residual resistances, high accelerating gradient, low secondary electron emission coefficients, few or no field emitters and defect-free surfaces to achieve “theoretical” quench fields.*

However, as the experience has shown, bulk properties of the niobium such as thermal conductivity, Kapitza resistance and interstitial impurity concentration - predominantly hydrogen - are also very important and have major influence on cavity performances. In addition, the “environment” – vacuum, cleanliness level, feedthroughs, cables, peripheral parts – is by no means a negligible factor to cavity performance.

## INVESTIGATIONS, METHODS AND TOOLS

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A large number of sample investigations have been conducted over the years, looking at features as listed below:

- Secondary electron yields for differently treated surfaces
- DC and RF field emission, photo-emission
- Surface topography
- Surface structure and surface damage layer
- Modification of surfaces with a laser or electron beam
- Grain boundaries and segregation of impurities
- Interstitials such as hydrogen in bulk and surfaces
- Electron beam welding: weld structure, weld contamination, contamination depth profile, RRR – value of welds
- Surface oxidation stages for different surface preparations and heat treatments
- Oxygen diffusion
- Surface and bulk defects
- Impurity distribution (Ta,..) and clustering
- Pinning by impurities
- Penetration depth at different frequencies, mean free path
- RRR – value in bulk and surface
- Thermal conductivity and Kapitza resistance

These investigations were carried out with a variety of complementary methods and tools. In most cases “classical” surface analytical instrumentations was used:

- Scanning Electron Microscopy (SEM)
- Scanning Tunnel Microscopy (STM)
- Transmission Electron Microscopy (TEM)
- X – ray Photon Spectroscopy (XPS, AXPS)
- Energy Dispersive X – ray Spectroscopy (EDX)
- Auger Electron Microscopy (AES)
- Electron Spectroscopy for Chemical Analysis (ESCA)
- Secondary Ion mass Spectroscopy (SIMS)
- Low Energy Electron Diffraction (LEED)
- Ellipsometry
- UV Spectrometry (UVS)

However, “non-classical” methods using the superconducting state of the material have been successfully employed in gaining understanding of surface properties and material properties in a depth of  $\mu\text{m}$ :

- Penetration Depth Measurement on Cavities or at Low Frequency
- Magnetization, DC and AC Susceptibility
- Pinning Measurements (Depth profiling)
- Sample Cavities (TE-mode, TEM-mode, Tri-axial, Quadrupol, “Mushroom”, Strip Line..)
- Microwave Microscopy

## A SHORT “HISTORY” OF SRF

Work on superconducting cavities for application in particle accelerators started in the early 1960’s at the High Energy Physics laboratory (HEPL) at Stanford University with lead-plated copper cavities. Around 1965 the HEPL activities were joined by development work at the Kernforschungszentrum Karlsruhe (KFK) in Germany and at Brookhaven National Lab (BNL) in the US. Two years later HEPL developed, in collaboration with Union Carbide Corp., a method to electro-deposit niobium onto a copper substrate from a molten salt bath. About a year later Siemens AG in Germany started a collaboration with KFK and developed the same process. These activities did not produce very satisfactory results, mainly because at the high bath temperature of  $\sim 800\text{ C}$  copper from the substrate diffused into the deposited niobium, polluting the layer and degrading the superconducting properties. At HEPL work started on bulk niobium and in 1968 the first exciting results from an X-band single cell cavity manufactured from a single piece of solid niobium were reported [3] as shown in Figure 1:

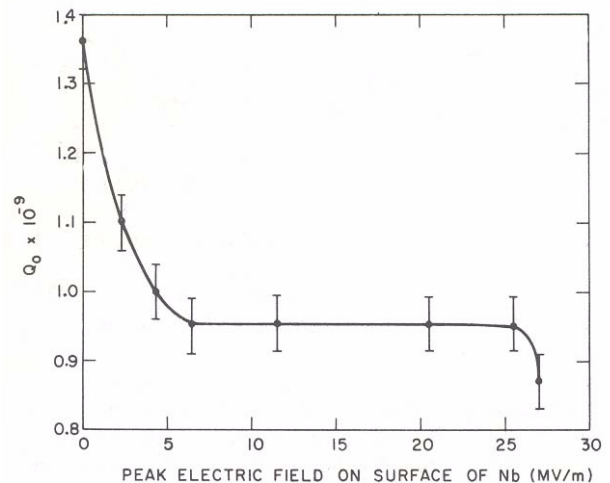
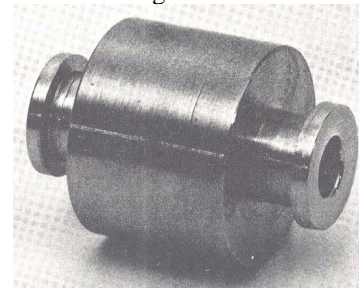


Figure 1: Results from the first solid niobium cavity [3].

Two years later the HEPL team reported another stunning result from an electron beam welded X-band niobium cavity with superior performance after ultra high vacuum high temperature heat treatment [4]:

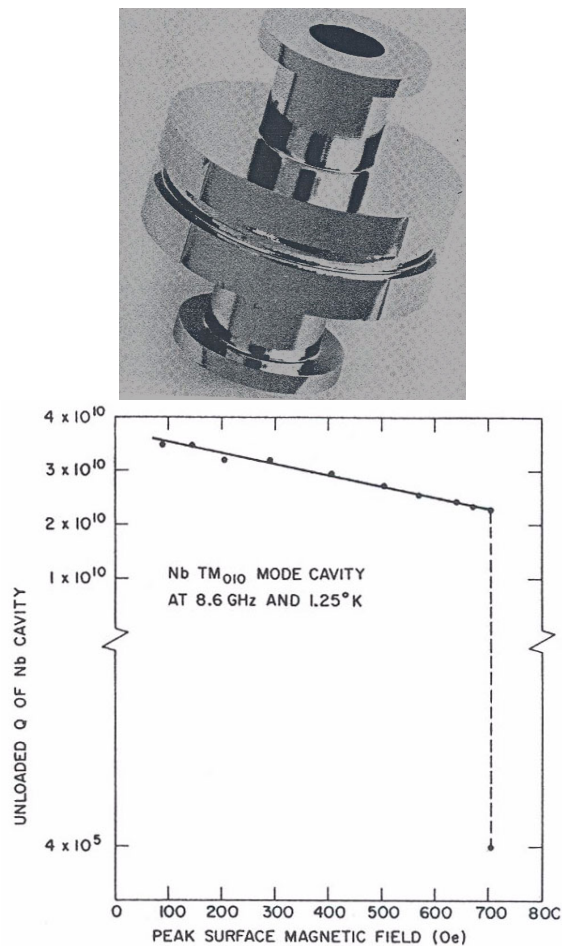


Figure 2: Electron beam welded  $TM_{010}$  X-band cavity [4].

These developments at HEPL influenced the direction of the work at other laboratories (BNL, SLAC, KFK and Siemens) and high temperature heat treatments at or above 1800 C became typical as a final surface treatment following chemical polishing in HF/HNO<sub>3</sub> acid solutions.

The research focussed on understanding the effect of heat treatment on cavity performance; in particular, the evaporation of oxides from the niobium surface was investigated as well as the reduction of interstitial impurities such as oxygen carbon, nitrogen and hydrogen as a function of the vacuum conditions in the UHV furnace. Grain growth at elevated temperatures for prolonged times as well as thermal etching or thermal polishing under those conditions became subject to material studies.

Because of grain boundary etching with the standard chemical polishing solution of equal parts of hydrofluoric and nitric acids and the thermal etching during high temperature heat treatment, at Siemens AG new surface treatment procedures were developed with the goal to achieve smoother surfaces and to avoid magnetic field enhancements at the rather sharp grain boundaries. Electropolishing in a solution of ~ 90% concentrated sulphuric acid and ~ 10% hydrofluoric acid was developed based on current oscillations at a constant voltage. This method, which had been abandoned in the

early 1980's by most laboratories except for KEK in Japan and which has been popularised again in recent years in a modified form by spectacular results reported by K. Saito of KEK [5], gave very smooth surfaces lacking grain boundary etching. A comparison of a chemically polished (CP) surface and an electropolished (EP) surface is shown in Figure 3 [6].

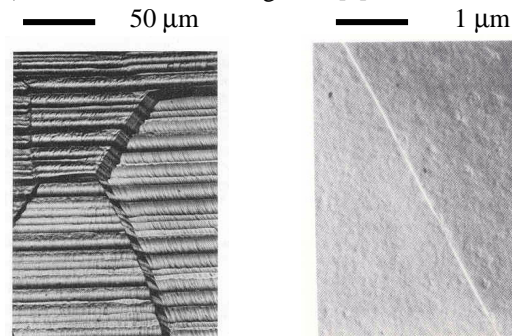


Figure 3: Roughness of a CP and an EP niobium surface [6].

In addition, at Siemens AG a process called “oxipolishing” was developed as a final surface treatment/cleaning step. In this process, the niobium surface is anodically oxidized in a solution of ammonium-hydroxide at voltages up to 80 V. A dense Nb<sub>2</sub>O<sub>5</sub>-layer of a thickness of 2 nm/V is forming, which provides a better defined interface at the bulk niobium than is achieved without the process. By dissolving the anodic oxide in hydrofluoric acid and repeating the process of anodization, a well defined Nb/ Nb<sub>2</sub>O<sub>5</sub> interface with less sub-oxides of the nature NbO<sub>x</sub> can be formed.

The developments at Siemens AG made it possible to reduce the use of high temperature heat treatments as a final preparation technique for rf cavities. However, when attempting to transfer the HEPL and Siemens results from X-band cavity studies to actual accelerating devices operating at lower frequencies (S-band and L-band), strong multipacting barriers were encountered, which limited the achievable gradients to 2 – 4 MV/m. These limitations triggered a new area of research: study of the secondary electron emission yields of surfaces treated under various conditions. In addition, computer codes developed at several laboratories indicated that the trajectories of multipacting electrons and their impact energies on the niobium surface when returning to a cavity wall after excursions into the cavity volume could be influenced by the cavity shape. Multipacting could be avoided by reducing the impact energies below ~ 50 eV or increasing them above ~ 2000 eV by appropriate shaping of the cavities and therefore shaping of the electromagnetic fields; at these energies the secondary electron emission yields from reasonably clean niobium surfaces were below 1.

Once the multipacting limitations in accelerating cavities were understood and could be overcome, defects in the material became the next limitation because of “quenching” at field levels far below the theoretically expected fields. Material with better thermal conductivity,

which would thermally stabilize the cavities, started to appear on the market in the late 1970's triggered by investigations at Cornell University [7]. Improvements in the thermal conductivity of a factor of 8 – 10 could be achieved commercially by multiple electron beam melting steps under improved vacuum conditions and further improvements could be realized by post-purification heat treatments in the presence of a material such as Yttrium or Titanium with higher affinity to interstitial impurities in niobium.

Diagnostic methods – predominantly temperature mapping in superfluid or subcooled helium [8] – became the most powerful tools to identify defects, anomalous losses and quench locations in cavities. By “guided repair” such locations could be eliminated and higher fields could be obtained. Further improvements of the quality of a niobium surface were achieved by eddy current scanning – this development took place at DESY [9] - of the niobium sheets for defects prior to cavity fabrication. This way a pre-selection and elimination of sheets with suspicious surface features could avoid the costly fabrication of cavities with sub-standard performance.

Because of the better niobium and improved QA procedures, single cell cavity performances with gradients of  $E_{acc} \sim 40$  MV/m corresponding to magnetic surface fields around 180 mT were reported first in the early 1990's. These results were an indication of the potential of niobium as the material of choice for accelerating devices. However, more often than not were/are cavity performances severely limited by onset of field emission loading, which was traced back to “artificial” contamination on the surfaces. Both DC field emission studies on samples and on actual cavities in connection with T-mapping and SEM/XPS investigations showed, that in most cases field emission was caused by “dirt” on the surfaces, stemming from insufficient cleaning procedures or recontamination by hardware used during assembly steps. The need for stringent contamination control measures was recognized and the use of high purity chemicals for surface processing, extensive rinsing at high pressure with ultrapure water and clean room assembly has become standard practice and helped to shift the onset fields for field emission in many cases beyond surface electric fields of  $E_{surf} \sim 50$  MV/m. At such field levels corresponding to surface magnetic fields  $> 100$  mT often a degradation of the Q-value in the absence of field emission loading is observed. This so called “Q-drop” is presently not yet fully understood, even though there exist several models to explain these observations [10]. It has consistently been observed that this “Q-drop” could be eliminated to a large extent by “in-situ” baking at temperatures around 120 C for prolonged times [11-13].

This “Q-drop” and its reduction by in-situ baking, which is more often observed on electropolished niobium, but is also present on chemically polished surfaces, has been subject of several studies on samples using “classical” surface analytical methods such as XPS and SIMS. These studies showed that the surface oxide

composition on niobium surfaces changes as a function of heat treatment. Even more solid information with regard to cavity performance could be extracted from DC magnetization and AC susceptibility measurements on samples as discussed below. These measurements directly probe the transport current properties of the superconducting material and seem to be well suited to correlate variations of properties such as critical fields due to different surface treatment procedures with observations on cavities.

With ever improving cavity performances, the subject of the theoretical performance limit of bulk niobium has been raised more often. There are indications that the superheated critical field  $H_{SH} \sim 180$  mT (for niobium) might be the limit as discussed in [14].

In the following sections a selected number of surface characterization studies, which contributed to the present understanding and the successes in improving the performance levels of superconducting niobium cavities, are being discussed.

## A SELECTION OF Nb SURFACE INVESTIGATIONS

### *Surface Topology and Impurities*

As already mentioned earlier, surface roughness possibly causing magnetic field enhancements was a concern from the start of the development of the SRF technology and a large number of topological studies have been made, triggering the development of treatment methods to reduce the surface roughness. A typical niobium surface after chemical polishing and high temperature heat treatment is shown in Figure 4 [15].

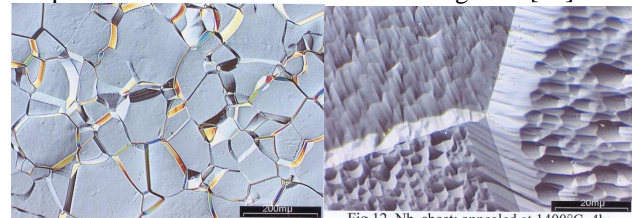


Fig.1. Annealed 800°C, 4h(Heraeus)

Fig.12. Nb, sheet; annealed at 1400°C, 4h; 100μ removed by CP

Figure 4: Typical niobium surfaces after treatments as indicated [15]

Electropolishing as developed at Siemens AG [16] significantly reduced the grain boundary exposure and smoothed the surfaces dramatically. An example of an electro-polished S-band cavity based on the current oscillations at constant voltage is shown in Figure 5. In addition the cavity has been anodised with an  $Nb_2O_5$  layer of 40 nm.

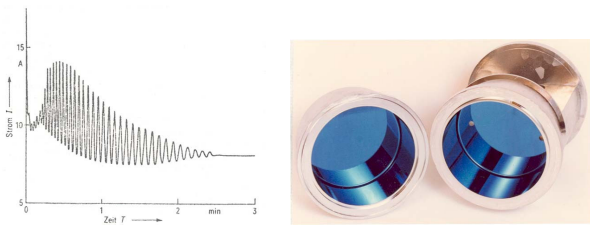


Figure 5: Example of an electropolished and anodised cavity using current oscillations. [16, 17].

Also at Siemens AG a new chemical polishing solution was evaluated: instead of the commonly used buffered [BCP] solution of equal parts of  $\text{HF}/\text{HNO}_3/\text{H}_3\text{PO}_4$  at room temperature, the new mixture contained 1:1:2 volume ratio of  $\text{HF}/\text{HNO}_3/\text{H}_2\text{SO}_4$  and was applied at 50 C. This mixture drastically reduced the grain boundary etching experienced with the BCP solution, whereas the smoothing effect within the grains remained the same. However, use of the mixture at lower temperatures extinguished its benefits.

The effectiveness of both mixtures was investigated in a series of tests with a spherical x-band sheet metal cavity [18] which alternately was treated with one of the mixtures. As can be seen from Figure 6, the treatment with the sulphuric acid mixture consistently gave superior results. As an explanation the authors of ref. 18 concluded:

*“...this may be understood if one takes into account the field enhancement at peaks and sharp edges of the surfaces. The power loss related to these regions exceeds that of the surrounding smooth area giving rise to local surface temperature spots. These spots tend to grow because of their enlarged surface resistance, thereby causing an overproportional increase in the average resistance”.*

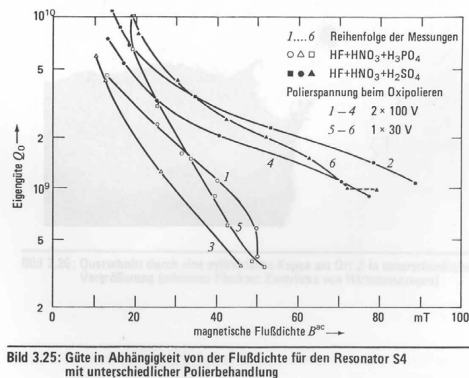


Figure 6: Comparison of cavity performance after alternating surface treatments with two different acid mixtures [18].

Studies of the morphology of niobium sample surfaces after various surface treatments were reported in 1999 at the 9<sup>th</sup> Workshop on RF Superconductivity [19]. Profilometry measurements confirmed the findings reported in [18]; in addition, marked differences were found in the appearance of the grain structures.

Whereas the sulphuric acid containing mixture produced shiny surfaces with pronounced grain structure, the standard BCP solution acted preferentially on grain boundaries and revealed grain substructures such as defects and dislocations.

Micro-structure of buffered chemically polished niobium surfaces continued to be subject of profilometric investigations [20]. Especially in the region of the equator electron beam weld on a cavity, which has to sustain the highest magnetic surface field, sharp grain boundary steps with step heights up to 30  $\mu\text{m}$  were found depending on the amount of material removal. Leveling of such strong grain boundary edges requires an electropolishing of the surface with the removal of at least 150  $\mu\text{m}$ .

These micro-structure studies were the basis of one of the proposed models [21] to explain the “Q-drop” at high gradients based on magnetic field enhancements at the grain boundary edges. As discussed in [10], this model cannot explain all experimental observations associated with the “Q-drop”.

Figure 7 shows the alignment of grains in the electron beam weld and a detailed picture of a grain boundary after BCP of 117  $\mu\text{m}$ .

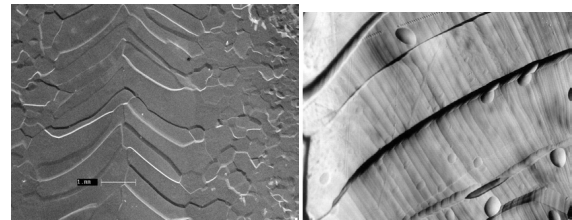


Figure 7: Micro-structure of an electron beam weld [20]

The impurity levels in the commercially available niobium and especially their distribution was investigated at Siemens AG in the early 1970's [22]. This was of interest since a non-uniform distribution of impurities could influence the performance of a cavity by, e.g., clusters of carbide, nitride or tantalum. In addition it was suspected that the high temperature heat treatments could also alter the distribution. The method used for these investigations was the “Scanning Auger Electron Microprobe Technique “ (SAM) for the lighter impurities such as oxygen, nitrogen, carbon, fluor, calcium and potassium; for heavy elements such as tantalum and tungsten autoradiography was employed, during which the sample after irradiation and generation of short life time nuclids was placed on a photographic film. From the blackening of the film a distribution of the impurities could be deduced. SAM has also been applied to the inner surfaces of LEP cavities at CERN for the investigation of defects [23].

An example of the Ta distribution in reactor grade material, which was at that time the only available material, is shown in Figure 8.

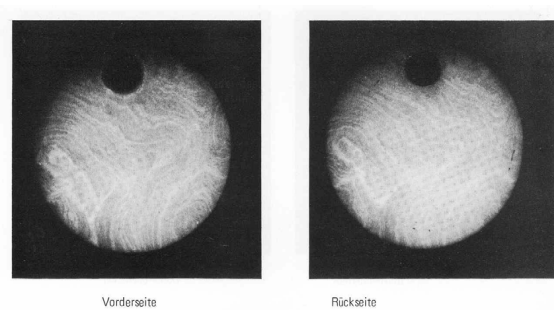


Figure 8: Ta distribution in a reactor grade niobium sheet, viewed from the front and the back [22].

An example of the elemental distribution near an electron beam weld as seen by SAM is shown in Figure 9.

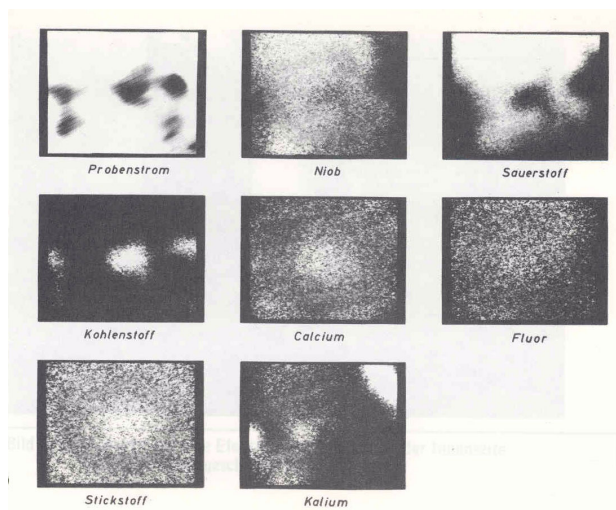


Figure 9: Distribution of elements such as carbon, oxygen, nitrogen, fluorine, calcium and potassium near an electron beam weld [22].

For a long time and sometimes even nowadays electron beam welds have been the causes for sub-standard cavity performance. They can either exhibit voids, if inappropriate weld parameters are applied, or they can be the reason for impurity segregation near the heat affected zone of the weld [71]. Comparative measurements at Siemens AG on X-band cavities made either from a solid piece of niobium or by electron beam welding had resulted in inferior performance of the welded cavities [24]. Therefore, investigations of the impurity distribution near an electron beam weld were carried out [25]. Depth profiles as shown in Figure 10 indicated that an enhancement of the carbon concentration occurred in a depth of up to 100 nm and it was concluded that this is most likely caused by formation of niobium carbide. The weld contamination could be removed by electropolishing and after 100  $\mu\text{m}$  of material removal a clean Nb surface appeared in the Auger spectrum (Figure 11).

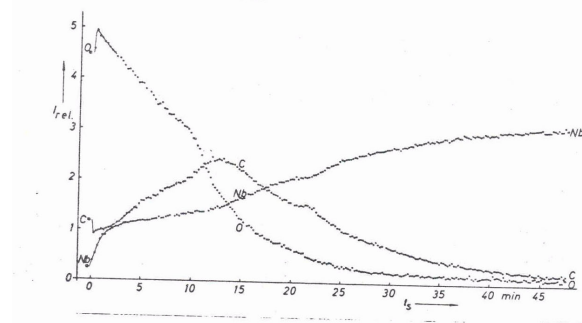


Figure 10: Depth profile of the electron beam weld contamination [25].

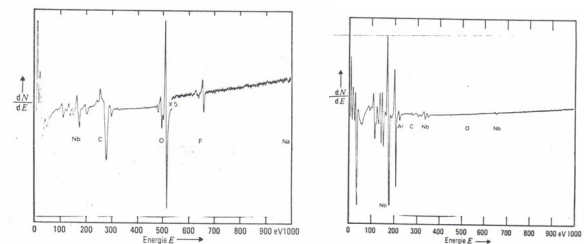


Figure 11: Auger spectrum near an electron beam weld; left: as welded, right: after 100  $\mu\text{m}$  of EP [25]

### Oxidation

The features of the oxide layers on top of the niobium and its growth have been the subject of a large number of investigations, both on samples using “classical” surface analytical methods as well as on rf cavities by “exposure” tests. It has been established that these features can influence cavity performances and since niobium is a metal with very high solubility and binding energy for elements such as oxygen, nitrogen, carbon and hydrogen, care has to be taken during room temperature surface treatments of niobium and high temperature annealing procedures to avoid detrimental degradations of the material.

In [26], LEED and Auger spectroscopy have been used to study the amount of surface impurities appearing during high temperature heat treatments and during cooldown. Among the processes taking place during UHV firing – evaporation of oxides and volatile impurities from the surface, degassing of hydrogen, oxygen and carbon and grain growth as well as thermal etching or polishing – these investigations were concerned with the processes taking place during cooldown. The investigations showed that during cooldown in UHV significant amounts of oxygen migrate from the bulk to the surface and form surface oxides. This may lead to a shortening of the mean free path, lowering therefore the thermal conductivity in the surface and might be responsible for breakdown in cavities. In addition, the critical field  $H_{c1}$  will be lowered at grain boundaries or other disordered regions in the material.

The initial stages in oxidation of niobium have been studied in [27] with uv-photoemission technique and the

changes in the electron distributions curves for different oxygen exposures at varying temperatures have been recorded. At least three different oxides or mixtures of oxides have been found: NbO<sub>2</sub> and NbO seem to form first as a thin protective layer and Nb<sub>2</sub>O<sub>5</sub> forms after heavier oxidation.

Auger electron spectroscopy measurements on samples, which were treated according to the typical procedures for rf cavity preparation – UHV degassing, BCP, EP and anodization – were carried out at BNL with the objective to determine the oxygen depth profile in the niobium surface [28]. These investigations confirmed earlier results: the surface treatments typically applied to rf cavities result in surfaces covered by layer of a two-phase mixture of NbO and NbO<sub>2</sub> suboxides of ~5 nm thickness and a layer of two-phase NbO+Nb, also ~ 5 nm thick. It is speculated, that the performance of rf cavities could be influenced by these oxides because of their low critical temperatures.

XPS combined with AES for depth profiling was employed to further study the oxide growth and oxide coatings on niobium surfaces being subjected to different treatments [29, 30]. For the different surface preparation techniques applied to rf cavities the oxidation process proceeds as following: at the niobium surface an inhomogeneous layer of NbO- NbO<sub>2</sub> of < 1nm thickness forms pretty much independent of the oxidation technique. A homogeneous, dielectric Nb<sub>2</sub>O<sub>5</sub> layer grows in UHV or after oxipolishing, whereas electropolishing yielded rough oxide layers, which picked up impurities easily. After some time the oxide layer grows to a stable thickness of ~ 6 nm. A chemical shift of ~ 0.3 eV to higher binding energies was seen on “wet” prepared samples, when compared to UHV treated niobium.

In Figure 12 two spectra taken on an electropolished surface and for a sample UHV annealed at 1850 C are shown. After deconvolution, different ratios of sub-oxides can be recognized.

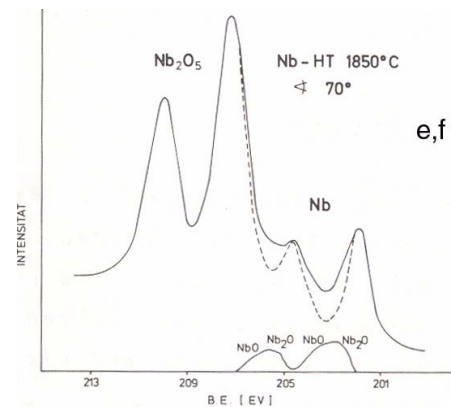


Figure 12: XPS spectra for electropolished and UHV degassed niobium [30].

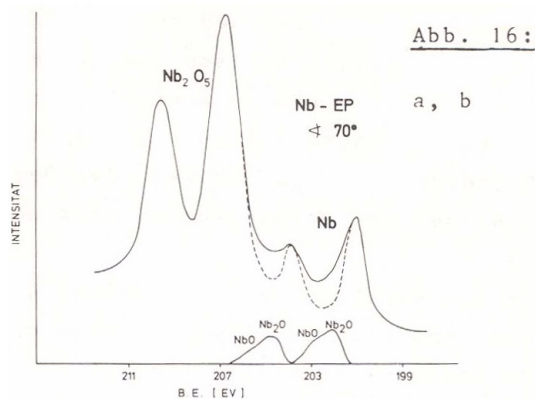
Similar measurements with similar results were obtained in a study at KEK, which concentrated on the surface conditions of the niobium after “wet” chemical treatments [31]. It was found that an ultrasonic rinsing of an electropolished surface with hydrogen-peroxide resulted in a stable Nb<sub>2</sub>O<sub>5</sub>, which also removed contaminants such as C and N.

While all the investigations discussed above have been conducted on reactor grade niobium, more recent measurements have been carried out with high purity niobium samples. Of particular interest in these investigations were the modifications of the surface by high pressure water rinsing, air exposure or “in-situ” baking [32]. Some of these investigations have been done with better resolution and improved analytical tools. After “in-situ” baking at 120 C and deconvolution of the XPS data, the pentoxide on the niobium seems to have transformed into NbO<sub>2</sub> with possibly other species like NbO, Nb<sub>4</sub>O, Nb<sub>6</sub>O [33].

Experiments at INFN Genova by XPS and AXPS confirmed earlier results obtained on reactor grade niobium [34, 35]. After deconvolution of the Nb3d line, four chemical states of an air exposed niobium, which was heat treated at 1950 C, could be identified: pure Nb, NbO, NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. From angle-resolved XPS it became clear that the Nb was first covered with a layer of NbO, followed by NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. On top of these oxides there are adsorbates of carbon with C=O and C-OH – bonds with 1-2 monolayers of Nb-OH .

Thermal and electron-beam irradiation effects on surfaces of niobium for rf cavity production were reported in [36]. “In-situ” baking of the 99.99% pure, chemically cleaned niobium samples in UHV at increasing temperatures up to 230 C resulted in the decomposition of the pentoxide and the formation of distinct layers of NbO<sub>x</sub> (1<x<2.5) and Nb<sub>2</sub>O close to the Nb. Hydrocarbons on the surface decomposed also at the higher temperatures and eventually formed niobium carbide.

In a paper presented at this workshop [37] results from XPS investigations on electropolished and mechanically polished + BCP treated samples were reported. Whereas the initial oxide layer thickness on the EP samples was thicker than on the other one, the decomposition kinetics



of the oxide during “in-situ” baking was faster for the BCP sample, most likely because of the thinner initial oxide. Initial measurements of the near surface composition of electropolished niobium using variable photon energy XPS are reported in [38].

All investigations discussed above were carried out on samples and revealed the nature of the oxide on a niobium surface. However, the impact of the oxide distribution on the performance of a rf cavity – in particular on the surface resistance – can only be investigated with a cavity. In a controlled study by Palmer [39, 40] the contribution of surface oxides to the residual resistance was investigated: in these experiments X-band niobium cavities were fired at 1400 C in UHV, which resulted in the dissolution of the natural surface oxide into the bulk as confirmed by AES. The residual resistances of these oxide-free cavities (they were never exposed to atmosphere prior to the test) were 5 -10 n $\Omega$  – comparable to oxidized surfaces. When oxide layers were carefully regrown under controlled exposure to dry oxygen, the increase in resistance gave a contribution of 1-2 n $\Omega$  for the oxide layer.

In recent years the so called “Q-drop” at high gradients has triggered an appreciable number of investigations at various labs. As already mentioned earlier, this Q-degradation can be reduced by “in-situ” baking and is among other effects related to a redistribution of oxygen/surface oxides at the niobium-oxide interface. Recent measurements on an L-band cavity as reported at this workshop [13] showed marked changes in material parameters such as mean free path and penetration depth, and there is a tendency of increased residual losses with increased baking temperature. One can speculate that the contribution of increased metallic sub-oxide layers as discussed above can cause additional losses. However, further confirmations are needed.

### Magnetization, Susceptibility, Penetration Depth

In the early 1970’s a program was started at KFZ Karlsruhe to develop new methods to investigate superconducting niobium surfaces, using the conduction electrons as a probe to sample material properties at different depth in the material. Volume properties such as residual resistivity and bulk mean free path were investigated with dc and 10 kHz penetration depth measurements. Flux pinning measurements and magnetization ( $B_{c2}$ ) explore depths between 1 and 50  $\mu\text{m}$ , penetration depth in a magnetic field parallel to the niobium surface sample a depth of 0.04 to 1  $\mu\text{m}$  and are useful to determine surface mean free path and sub-oxide precipitates and the niobium/oxide interface can be sampled with  $B_{c3}$  and tunnel measurements to a depth of 1-5 nm [41].

An example of a 10 kHz magnetic penetration measurement is shown in Figure 13 for 2 samples, which were after heat treatment at 1800 C cooled down in the UHV furnace under different conditions as indicated [ 42].

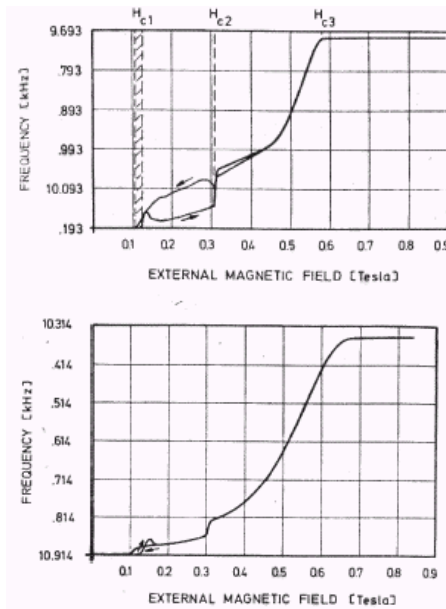


Figure 13: Magnetic field penetration  $\lambda$  at 10 kHz in a niobium sample cooled down within 12 hrs to 50 C after heat treatment (top) and accelerated cooldown by filling the furnace with 1 atm  $\text{N}_2$  at 400 C (bottom) [42].

The change of  $\lambda$  with external magnetic field is attributed to both the penetration of fluxoids and sampling of the shielding current ( $\lambda_s \sim 1/n_s^{0.5}$ ), which depends on the mean density  $n_s$  of the superconducting charge carriers. As Figure 13 indicates, no fluxoids penetrate below  $H_{c1}$  and hence  $\lambda_s$  remains constant; above  $H_{c1}$  fluxoids penetrate and gradually increase the 10-kHz small field penetration depth. At  $H_{c2}$  the normal conducting state becomes stable in the bulk, whereas superconductivity exists beyond  $H_{c2}$  at the surface. Hence at  $H_{c2}$ ,  $\lambda$  increases suddenly to values reflecting the shielding ability of surface superconductivity. At  $H_{c3}$ ,  $\lambda$  reaches the normal state value [300  $\mu\text{m}$  at 10 kHz]. With decreasing external magnetic field,  $\lambda$  decreases similarly as described above, but with some pronounced irreversibilities, which depend on surface treatment as shown in Figure 13.

Measurements of the pinning of fluxoids as a function of temperature is one of the most sensitive methods to gain information about precipitation of Nb-O compounds in the niobium matrix. Measurements of the dependence of the critical current density  $j_c(x)$  and the critical field  $H_{c2}(x)$  on distance  $x$  from the surface were carried out for samples treated by the same procedures as used for rf cavities [43]. The measurements indicated the presence of highly inhomogeneous, disturbed surfaces to a depth of  $\sim 50 \mu\text{m}$ ; the presence of two superconducting phases near the surface were observed, one of which has the same nature as the bulk material (with  $H_{c2} \sim 0.3$  T), but constitutes a matrix, in which superconducting regions of another phase with  $T_c \sim 7\text{K}$  are dispersed, most likely  $\text{NbO}_x$  precipitates. In low frequency penetration depth measurements  $\lambda(T)$  deviations from the BCS behaviour



were seen as a step at  $T \sim 7$  K, confirming the presence of inhomogeneous phases in the niobium matrix [44].

Figure 14 shows the depth profile of the oxygen concentration as deduced from the pinning measurements.

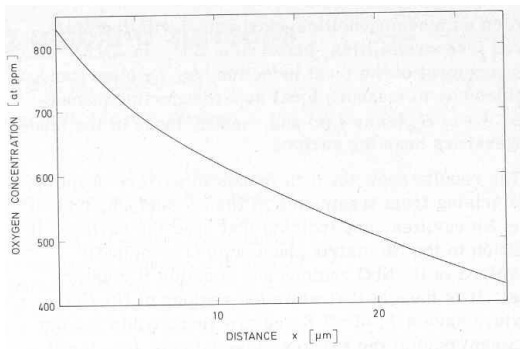


Figure 14: Profile of the dissolved oxygen content near the surface of a niobium sample after 1200 C heat treatment and 5 x oxipolishing at 100 V [43].

It was concluded from these investigations that for good rf performances of cavities a damaged layer of  $> 50 \mu\text{m}$  had to be removed by BCP or EP. These results were “confirmed” by a series of cavity tests, in which material was successively removed and the cavity performance ( $Q$ -value and peak electric fields  $E_{\text{peak}}$ ) was recorded, see Figure 15 [45].

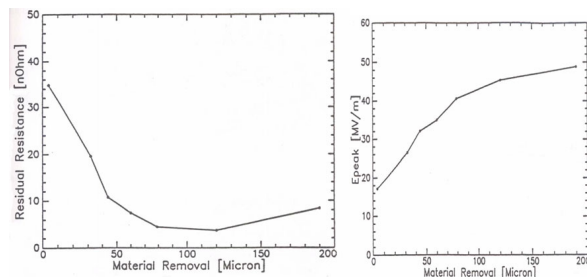


Figure 15: Effect of removal of surface damage layer on the performance of a single cell, 1500 MHz niobium cavity [45]

Magnetization and susceptibility measurements have been recognized in recent years as a powerful method to gain information about surfaces subjected to different treatments such as BCP, EP, heat treatment, “in-situ” baking [46-49] and several contributions to this workshop have reported on additional measurements [50, 51].

Figure 16 shows the temperature dependence of  $H_{c3}$  for niobium surfaces treated by different processes as indicated. Highest  $H_{c3}$  values are obtained on EP surfaces.

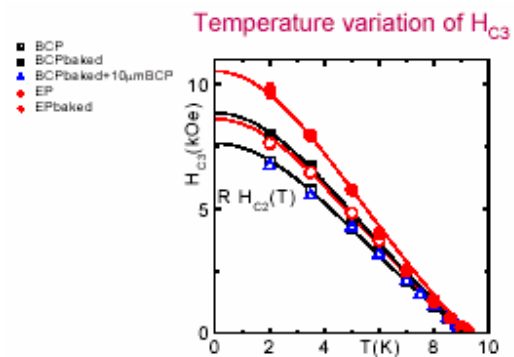


Figure 16: Temperature dependence of  $H_{c3}$  for niobium surfaces treated by different processes as indicated [50].

These results might be an additional clue to explain the generally superior performance of electropolished and baked cavities compared to those with chemically polished surfaces.

### Tunnel Spectroscopy

In contrast to the “superconducting” methods described in the previous section, which sample the “inner” surface of a niobium sample as probed by conduction electrons, the “classical” surface analytical methods probe the “outer” niobium surface, which is covered with oxides and adsorbates and give information about the chemical composition of a surface. Tunnel spectroscopy looks at surface states near the Fermi level of the niobium and they determine the transport properties of the material such as surface resistance and residual resistance, but are also important for electronic emission from the surface. As discussed in [52], a niobium surface gets instantaneously oxidized at pressures above  $10^{-10}$  torr (Cabrera-Mott mechanism) as a result of the energetic conditions existing for metallic interface oxides and dielectric oxides. As a consequence of the oxidation process the niobium is highly strained and crack corrosion takes place. Oxygen vacancies are generated and at 300 K a large number of localized states near the Fermi energy exist. These states are in fast interface tunnel exchange (ITE) with conduction electrons in the niobium and account under the influence of a rf electric field for dielectric interface losses. This mechanism can explain the observed reduction or elimination of the aforementioned “ $Q$ - drop” by “in-situ” baking, which reduces the number of localized states and therefore the losses.

In [53] measurements of tunnel characteristics of Nb-Nb<sub>2</sub>O<sub>5</sub>-Pb tunnel junctions are reported. The analysis of the current-voltage characteristics showed that tunneling in these junctions is governed by two tunneling mechanisms: direct tunneling through a potential barrier and resonance tunneling via localized states in the barrier (Nb<sub>2</sub>O<sub>5</sub>). For this mechanism the tunneling current can be described by a model of mono-energetic localized states in the barrier. Changes in the number of localized states by e.g. “in-situ” baking should therefore be visible as a change in tunnel characteristics.

## Grain Boundaries

Grain boundaries have for a long time been suspected to contribute to performance limitations in superconducting rf cavities [54]. Grain boundaries represent a “weak” link with degraded superconducting properties because of preferential segregation of impurities such as oxygen, hydrogen, and carbon. In electromagnetic fields at rf frequencies currents are forced to flow across these boundaries, which will suffer a transition to the normal conducting state at field levels below the bulk critical fields.

In order to verify this picture, measurements of the specific resistance of a grain boundary in high purity niobium were carried out at CEA Saclay [55]. To separate the contribution of the grain boundary from the grain itself, very high purity niobium was obtained by post purification in the presence of Ti as a getter material and used for the measurements. The experimental set-up is schematically shown in Figure 17: the resistance across the boundary is measured by applying micropins on both sides of the boundary.

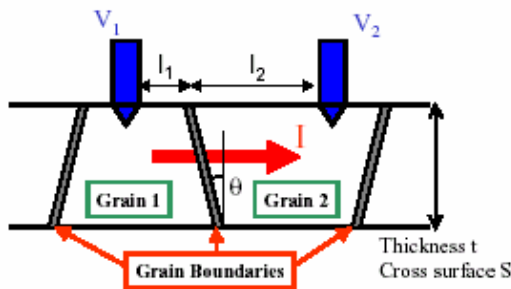


Figure 17: Principle of grain boundary measurement [55]

This investigation showed that there is a non-uniform distribution of residual resistance and therefore variations in local RRR-values; the grain boundary resistance is the major contribution to local RRR-values and the average resistance is a factor of 1000 larger than commonly assumed.

These measurements were continued on samples, which underwent different surface treatment such as BCP, EP and “in-situ” baking [33]. The results are summarized in Figure 18 and clearly show that grain boundaries are affected by the surface treatment. Electropolishing gives superior results to BCP, whereas baking seems not to influence the local RRR. This observation could indicate that the depth affected by the baking goes much deeper inside grain boundaries than on the surface of grains, not inconsistent with the known fact that diffusion processes in a grain boundary occur much faster than inside the bulk of a grain.

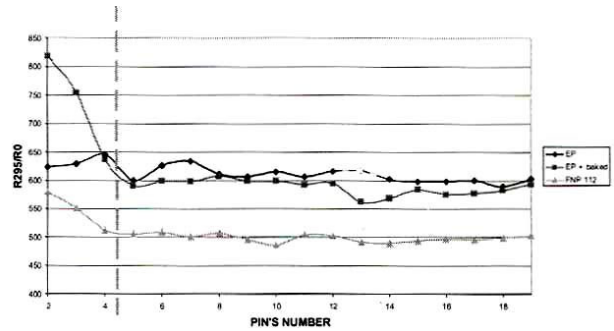


Figure 18: Experimental RRR measurements of several grain boundaries measured sequentially on the same sample after different surface treatment as indicated [33]

Preferential diffusion of titanium along grain boundaries occurs during post purification solid state gettering and has been studied using proton-induced x-ray emission [56]. Noticeable concentrations of titanium have been found in a depth of several microns, confirming the observation that good rf performance in cavities after post-purification could only be obtained after the removal of at least 50  $\mu\text{m}$ .

## Electronic Emission from Niobium Surfaces

Electrons are emitted from a surface in the form of secondary electrons resulting from e.g. impact of primary electrons, or as field emitted electrons, which tunnel out of a surface under the influence of an external electric field, or as photo-electrons. Photo-electrons are not discussed here, because they are not relevant to performance levels of superconducting accelerating cavities. However, they are important in the context of superconducting photo-injectors as proposed by BNL [57], where the niobium surface is used as the source of electrons, when irradiated with strong laser pulses.

Emission of secondary electrons in response to impinging primary electrons can lead to **multipacting** barriers in superconducting cavities, if the following conditions are fulfilled:

- An electron emitted from a cavity wall is under the influence of the EM fields returning resonantly to the emitting surface
- The impacting electrons produce more than one electron, if the impact energy is high enough. For niobium the secondary electron emission coefficient (SEE) is  $> 1$  for impact energies  $E_{\text{imp}}$  between  $50 \text{ eV} < E_{\text{imp}} < 2000 \text{ eV}$  as shown in Figure 19 [58].

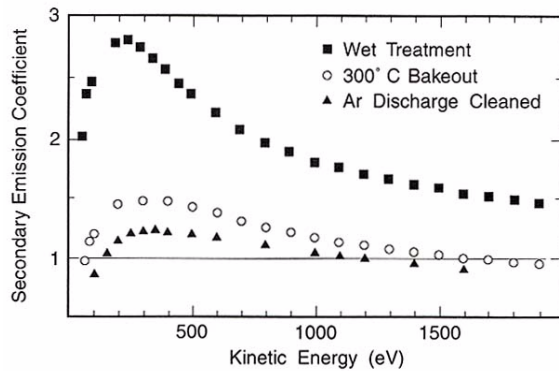


Figure 19: Secondary electron yield for niobium as used in superconducting cavities [ 58]

As can be seen in Figure 19, SEE is also very sensitive to surface conditions. This was confirmed by measurements reported in [59] and summarized as following (see also Figure 20):

- SEE is more determined by surface preparation than by the base metal “Wonder Surfaces” with very low SEE need to be generated “in situ” or by baking Electron bombardment (“conditioning”) decreases the secondary electron yield. Usually condensed gases have little effect on SEE.

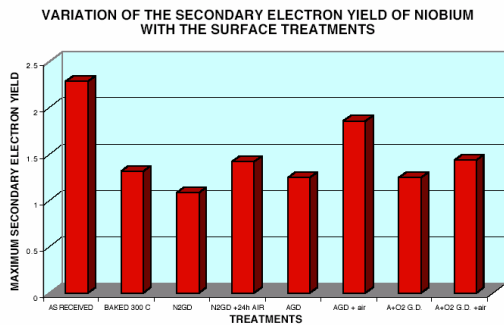


Figure 20: Modification of secondary electron yield of niobium with surface treatments [59].

At the 2001 SRF workshop R. Noer et al. [60] presented a new study of secondary electron emission yield of the niobium surfaces after various treatments. They concluded:

- Annealing at 700 C is effective in reducing SEE
- Subsequent electropolishing and baking tend to increase SEE.
- The effect of rinsing the niobium with ozonized water on SEE – this process is being used in the KEKB cavity production – is small compared to the use of ultrapure water.
- Exposing a niobium surface after bake-out to a gas affects the SEE; nitrogen is worse than air or argon.

Results are shown in Figure 21.

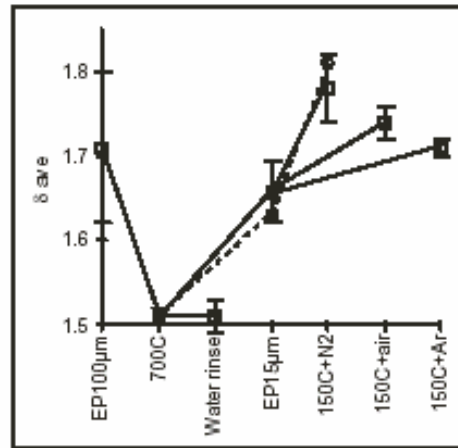


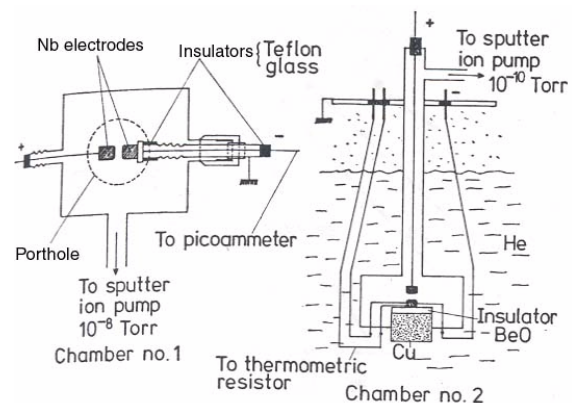
Figure 21: Dependence of SEE on surface treatment [60].

Multipacting can nowadays be avoided by appropriate shaping of the cavities (elliptical or spherical cross sections) and by careful surface preparations minimizing surface contamination.

Under the influence of the rf-electric surface fields in an accelerating cavity electrons are drawn out of the surface, are accelerated in the rf fields and gain sufficient energy to produce heat and bremsstrahlung when impinging on an opposing surface. This loading is presently still in many cases limiting the performance of superconducting cavities and great efforts are exercised by many SRF laboratories to find techniques to shift the limits to higher values.

Field emission has been thoroughly investigated in the case of dc emission and rf emission, supported by surface analytical investigations of emitters.

Field emission currents can be described by a modified Fowler-Nordheim correlation for broad area electrodes. Early dc studies at Orsay [61] on anodized niobium samples at room temperature and at 4.2 K showed that the threshold field for onset of field emission and the breakdown voltages increased with oxide layer thickness. The experimental set-up and results are shown in Figure 22.



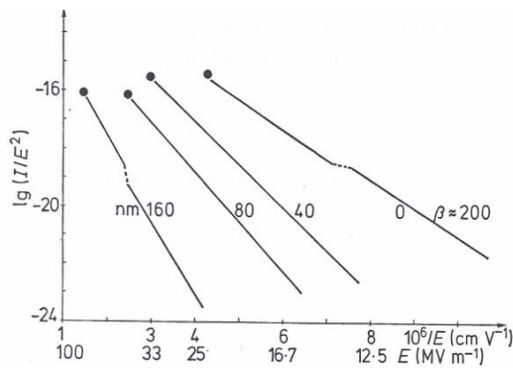


Figure 22: Test set-up used for the measurement of Fowler-Nordheim plots of anodised niobium samples (top) and Fowler-Nordheim plots (bottom) [61]

More sophisticated dc studies have been done subsequently in UHV field emission scanning microscopes, initially developed at the University of Geneva [62] and later duplicated at the University of Wuppertal [66-68], at Saclay [69], and at Jlab [70]. Results can be summarized as following:

- emitters are localized, in many cases foreign/artificial contaminants, loosely attached to the surface;
- only a small number of particles found on a surface are active emitters, which can cause geometrical field enhancements;
- many of the emitters can be removed by “in situ” heat treatment at  $T > 1400$  C under UHV conditions, probably due to dissolution of surface impurities into the niobium bulk material.
- UHV heat treatment between 200 C and 800 C activates “intrinsic” emitters – sulfur and carbon segregation emitters, which can have a crystalline microstructure.
- Adsorbates can enhance field emission.

The rf studies conducted at Cornell University [63] involved special “break-apart” cavities or mechanical destruction of cavities; the emitting sites have been identified after their destruction in cavity tests with SEM and energy dispersive x-ray spectroscopy.

After their destruction the emitters appeared as starbursts, ripple pattern, craters and regions of molten niobium. They included materials such as Fe, SS, In, Cu, Ti, Teflon and C and residues from rinse water. The emitters seemed to be “artificial” and most likely are contaminants from treatment and assembly procedures. Field emission is no fundamental limit in rf cavities.

## SUMMARY AND OUTLOOK

The last 4 decades of research on superconducting niobium surfaces and cavities have resulted in a model of the niobium surface as shown in Figure 23 [52]: the

surface is covered with a layer of hydro-carbon contaminants, followed by non-uniform layers of Nb-pentoxide with oxygen vacancies, which is on top of sub-oxide layers of NbO and Nb<sub>2</sub>O. Crack corrosion causes deeper penetration of the oxides into the niobium matrix and in grain boundaries segregation of impurities takes place. Clusters of oxygen deep in the niobium matrix are responsible for a mixed phase with degraded material properties.

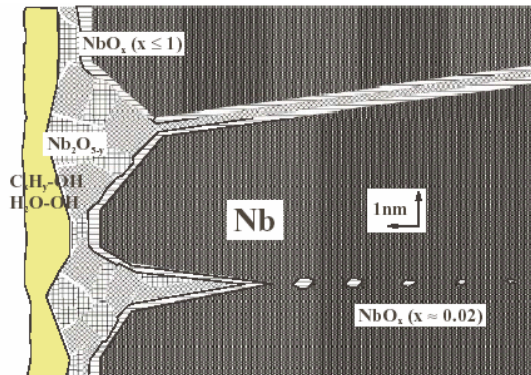


Figure 23: Model of a niobium surface as seen by a rf field [52].

Despite the complicated composition of the niobium surface, treatment procedures for niobium cavities have been developed, which result – if applied properly – in reproducible high performance cavities for application in accelerators [64]. In many cases the niobium used for manufacturing these cavities has reached the theoretical performance or close to it, both in BCS surface resistance and critical field. Therefore, the niobium surface oxidation does not seem to play an as important role as thought of in the years prior to the advent of RRR niobium.

In contrast, bulk properties of the material such as thermal conductivity, Kapitza resistance, concentration of dissolved impurities such a hydrogen, which can cause “Q-disease”, and the elimination of defects are very important for cavity performance.

Investigations on samples using “classical” surface analytical tools are useful, but it seems to be a “dream” for now to correlate the findings from such sample tests to cavity performance. After all, these methods use “outer” (valence) electrons, whereas the superconducting properties are determined by conduction electrons. Therefore, “superconducting” methods such as penetration depth, magnetization, pinning and susceptibility seem to be better suited to correlate sample features to cavity performance.

Secondary electron emission studies and field emission studies on samples seem to be directly applicable to rf cavities; however, no sample measurement ever “beats” a cavity test. As an example, much of the knowledge for the causes of field emission in cavities was learnt from destructive tests on cavities at Cornell after rf testing.

With the improved material quality, “environmental” effects such as breakdown of rf cables, heating of connectors, leaks, sub-standard performance of treatment facilities, “flaws” in auxiliary parts and surface contamination are becoming the dominant limitations. Stringent requirements for quality control and meticulously applied quality assurance measures are essential for future applications of the technology in high performance devices. This is particularly true when high Q – values at high gradients are required. However, there are still some open questions such as:

“What exactly limits the residual resistance and why are there variations observed between supposedly equal surface treatments?”

“What exactly is the cause for the “Q-drop” and why is it not always observed in field emission free cavities, not limited by early quenches?”

“Is the Q-drop an electric or magnetic field effect?”

“What causes the “Q-peak” at low fields and the “Q-slope” at medium fields?”

“How can the “Q-slope” be eliminated to get higher Q-values at high fields?”

For some of these questions explanations have been given by J. Halbritter [66], which still might need some experimental verifications. His model for the “Q-drop” employs interface tunnel exchange between charge carriers close to the Fermi energy and localized states in the Nb/Nb-oxide interface. The density of these localized states changes with oxide thickness and heat treatment. Direct measurements of these changes by e.g. tunneling experiments should be carried out besides cavity measurements with, e.g., thicker oxide layers (should decrease the onset field for the Q-drop) or “in-situ” baking (has been verified to increase the onset field).

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