Surface Characterization: What has been done, what has been learnt?

P. Kneisel
Jefferson Lab, Newport News, Virginia, USA

SRF 2003
Travemuende, Germany
September 8 - 12, 2003

Quote

A. Septier : "Surface Studies and Electron Emission"

Proc. 1.SRF Workshop, Karlsruhe(1981)

" 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"

Objectives

Correlate surface features and surface conditions of a niobium sample surface to cavity performance

Find the "best" procedure to generate the "best" surface with the "best" performance:

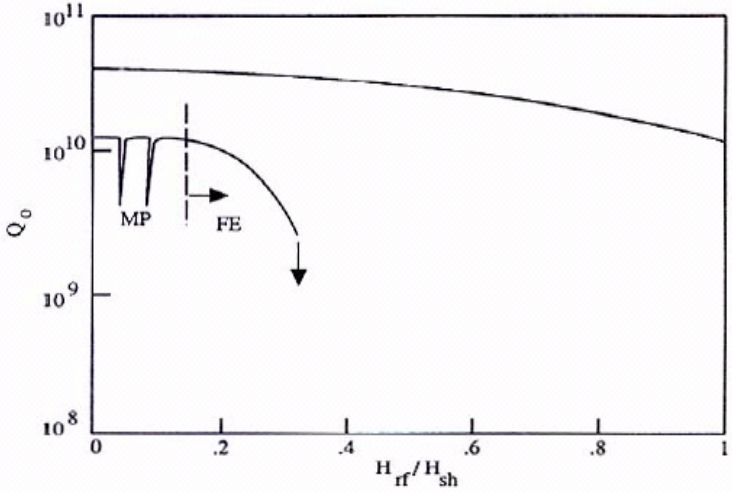
- low residual resistance
- high gradient
- low secondary electron emission coefficient
- low # of emitters or no field emitters
- defect-free surface to achieve "theoretical" quench fields

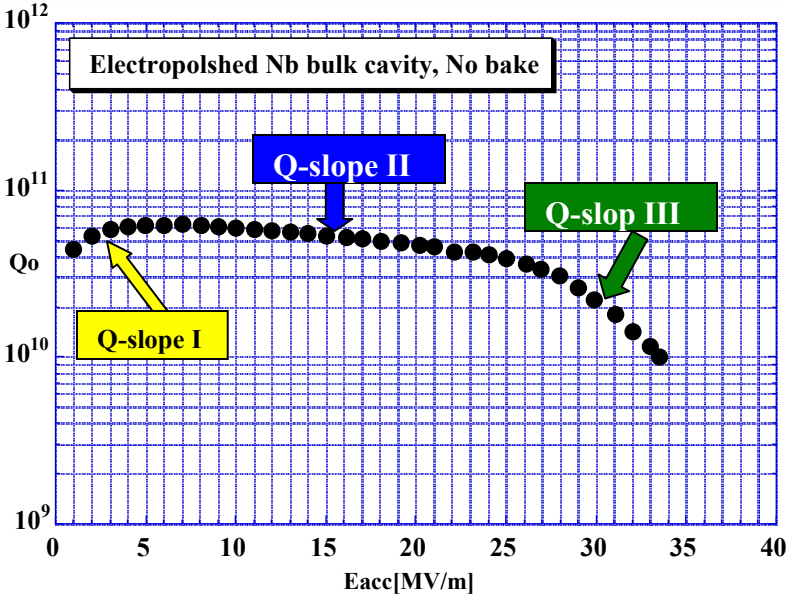
Background

- Observed Q-value lower due to Residual Surface Resistance caused by anomalous losses and defects
- Resonant Electron Loading ("Multipacting") causes Q-drops and barriers, SEE
- Exponential decrease of Q-value at higher gradients due to Non-Resonant Electron Loading (Field Emission) caused by contamination

- "Quench" field levels are generally below H_{SH} : Defects

K. Saito, this conference ⇨





What has been investigated?

Secondary Electron Yield, Field Emission (RF and DC), Photo-Emission

Surface Topography, Surface Structure, Surface Damage Layer, Modification of Surface with Laser or Electron Beam, Grain Boundaries , Hydrogen in Surface and Bulk,

EBW, Weld Structure,Weld Contamination, Contamination Depth Profile of Weld, RRR of Weld

Surface Oxidation Stages for different Preparations, Oxygen Diffusion, Defects, Impurity Distribution (Ta,..), Impurity Clustering, Pinning by Impurities, Penetration depth at different Frequencies, Magnetization, RRR value, Thermal conductivity in Surface Layer, Kapitza Resistance, Mean Free Path

Tools

Surface analytical Instrumentation (" classical")

- scanning electron microscopy (SEM)
- Scanning Tunnel Microscope (STM)
- X-ray photon spectroscopy (XPS, AXPS)
- Auger Electron Microscopy (AES)
- energy dispersive X-ray spectroscopy (EDX)
- e-spectroscopy for chem. analysis (ESCA)
- secondary ion mass spectroscopy (SIMS)
- low energy electron diffraction (LEED)
- ellipsometry
- UV Spectrometry (UVS)
- Nuclear Microprobe

"Superconducting" methods

- penetration depth (cavities or at low frequency)
- Magnetization , Susceptibility
- Pinning
- sample cavities (TE, TEM, tri-axial, quadrupol, "mushroom",strip line,...)
- microwave microscopy

Depth Sampling

The various methods sample different depth of a surface:

nm ⇨ micron ⇨ mm [bulk]

Depth profiling by use of surface analytical instrumentation involves material removal by sputtering

Losses in a rf cavity take place in the penetration depth: ~60 nm for niobium at ~ GHz

However, bulk properties of niobium are also important:

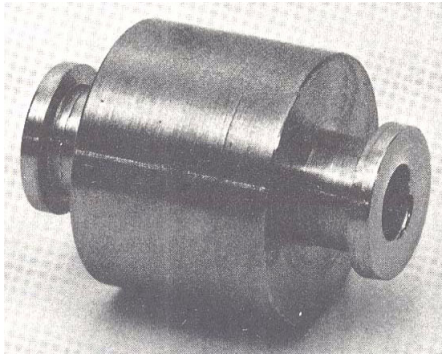
thermal conductivity , Kapitza resistance, Hydrogen concentration

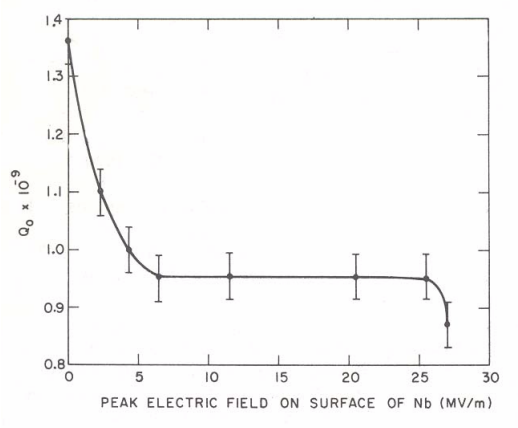
Experience has tought that " environment" has major impact on cavity performance:

leaks, cables,connectors, non-uniform/insufficient material removal, contamination , HOM rejection….

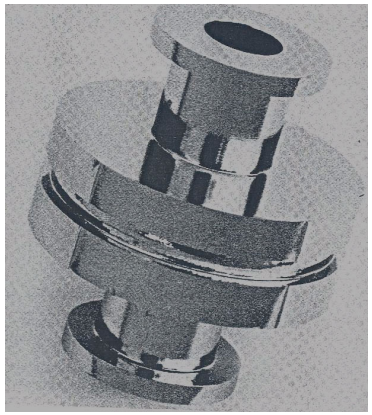
Background(1)

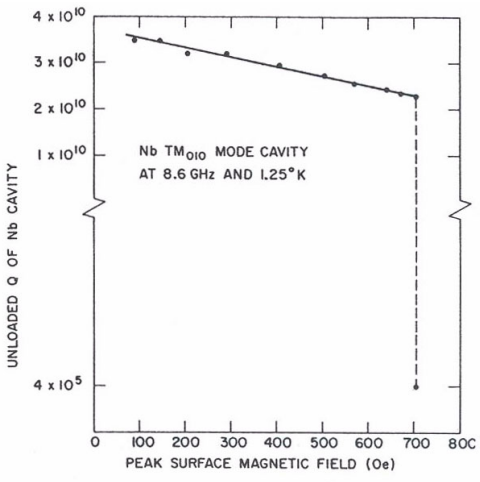
Weissman, J. P. Turneaure; " A Nb TM_{010} – Mode Cavity with High Electric Field and Q_0",
Appl.Phys.Lett 13, 390 (1968)





J.P. Turneaure, N.T. Viet," Superconducting Nb TM_{010} Mode Electron-beam Welded Cavities", Appl.Phys.Lett 16, 333 (1970)





Background (2)

The HEPL results influenced the work in other labs (BNL,SLAC,KFK, Siemens) and high temperature heat treatments became typical.

- Research focussed on understanding effect of heat treatment on cavity performance (R_{res} , H_{peak})
  - Evaporation of oxides from surface (NbO, T_C ~ 1K)
  - Lowering overall oxygen concentration
  - Thermal etching/polishing
  - Grain growth
- At Siemens AG new surface treatment procedures were developed to achieve smoother surfaces
  - Electropolishing with current oscillations
  - Oxipolishing in NH_3OH solution
  - Chemical polishing in $HF:HNO_3:H_2SO_4$ (less grain boundary etching)

Background (3)

- The X-band results of HEPL were not transferable to L-band because of multipacting
  - Secondary electron emission studies
  - Cavity shape
  - Development of computer codes
- Improvement of niobium quality to improve quench fields
  - Better thermal conductivity (multiple melts, post purification..)
  - Defects (eddy current scanning, local RRR measurements, welds, surface imperfections/inclusions…)
  - T – mapping
- Improved "quench fields"
  - Field emission (dc, rf , computer codes, "T-mapping"..)
  - Q-disease, "Q-drop", "in-situ" baking
  - Control of contamination
  - QA

Studies

What has been done?

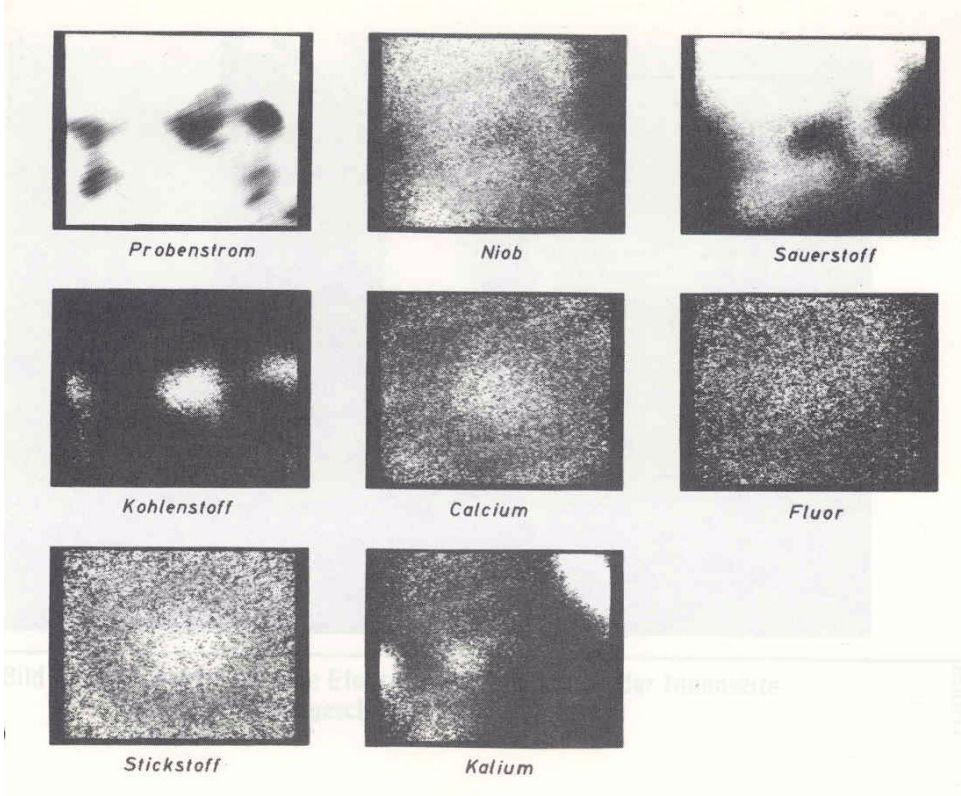
- Some Examples -

Impurities in Niobium(1)

Siemens Report NT 2024 7 (Supraleitende Resonatoren)

Same method applied at CERN 1995 to detect surface defects: C. Benvenuti et al, Proc. 7th SRF workhop, p.491

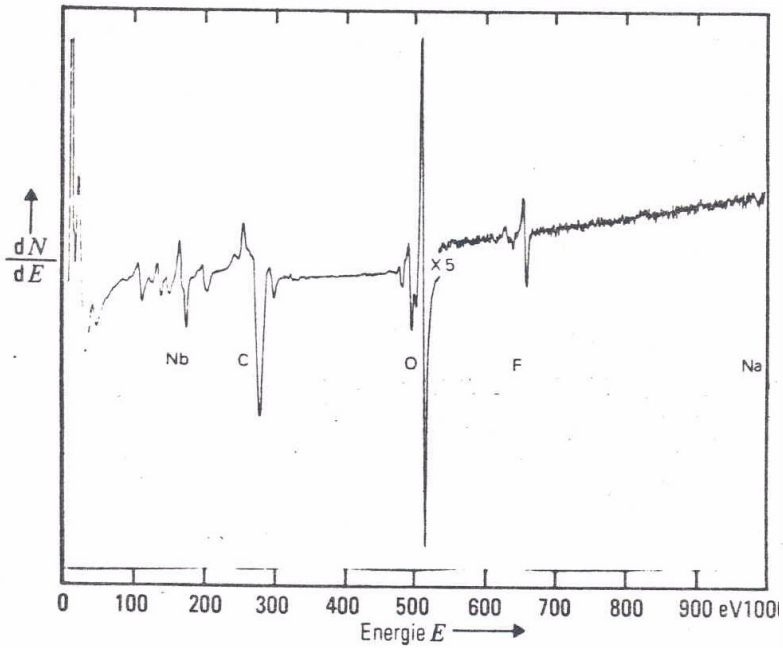
Distribution of some elemental impurities on the surface of a cavity near the electron beam weld; pictures are taken with a Scanning – Auger- Electron – Microprobe (SAM)



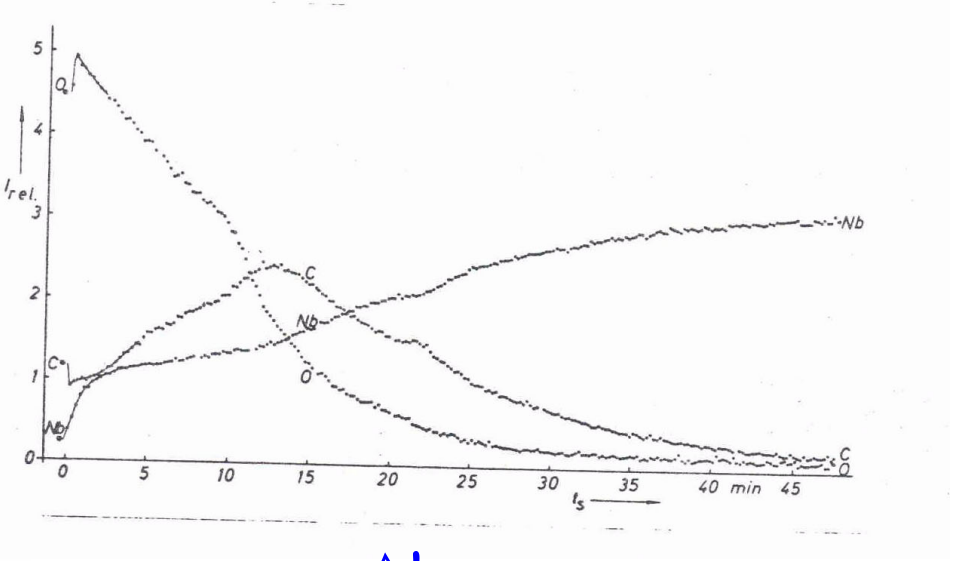
Impurities in Niobium(2)

Investigation of Electron Beam Weld (Hillenbrand,Diepers,Report NT124 II, Siemens AG)

Auger Spectrum of Electron Beam Weld



Depth profile of weld contamination



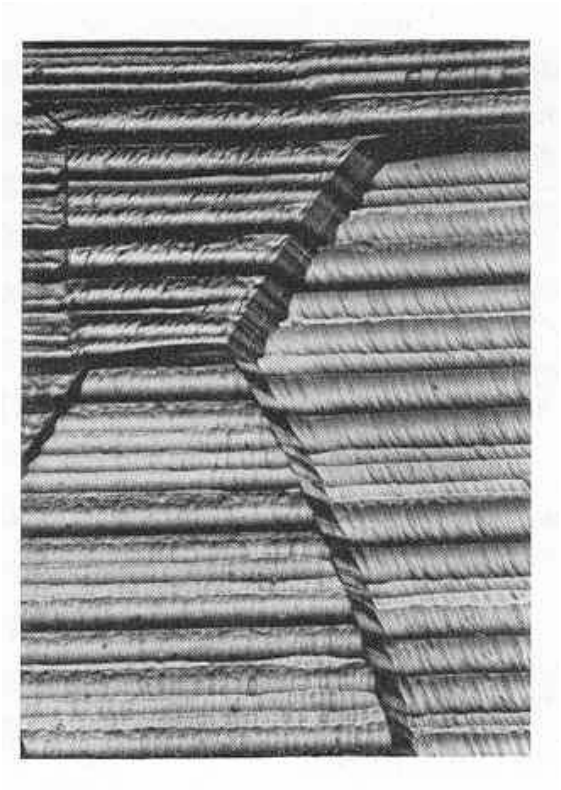
⇨t_s

Niobium Surfaces(1)

Chem. Polished Nb (HNO_3 + HF)

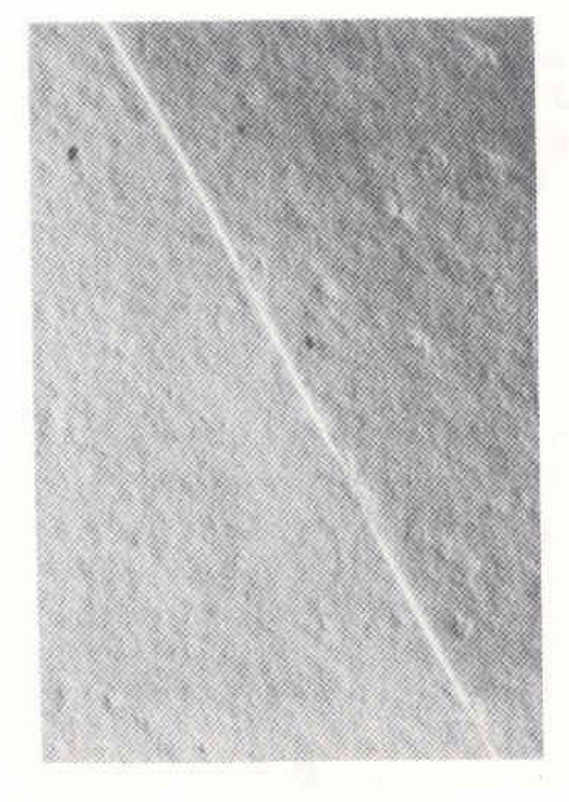
H. Diepers et al, IEEE Trans.Nucl.Sci NS-20, 68(1973)

50 micron



Electropolished Nb (current oscillations, HF + H_3SO_4)

1 micron



Niobium Surfaces (2)

X. Singer, DESY, private communication

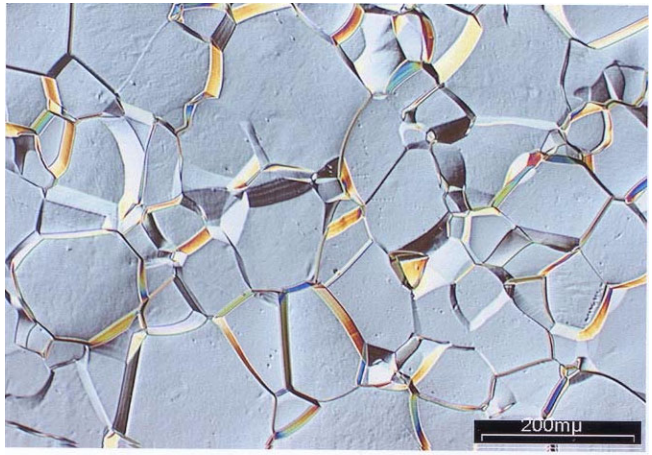


Fig.1. Annealed 800°C, 4h(Heraeus)

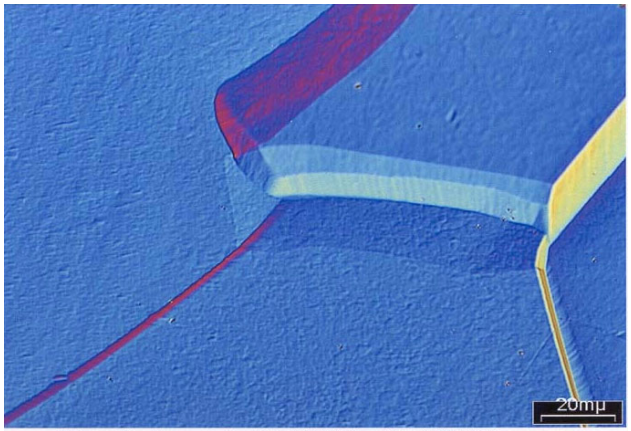


Fig. 2. Annealed 1000°C, 4h (TWC)

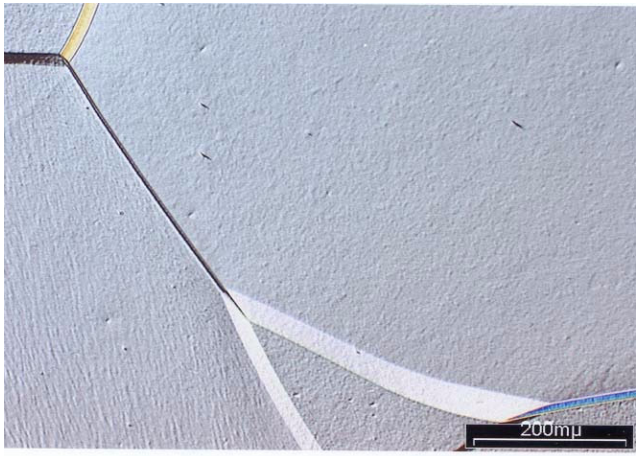


Fig. 3. Annealed 1200°C, 4h (Heraeus)

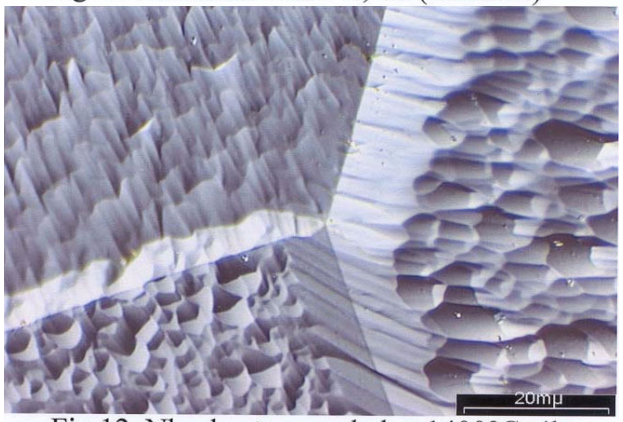
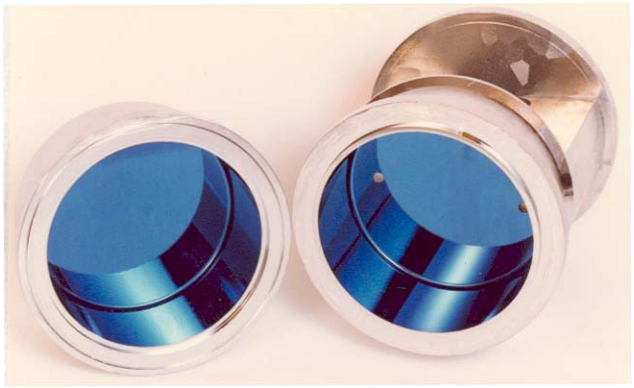


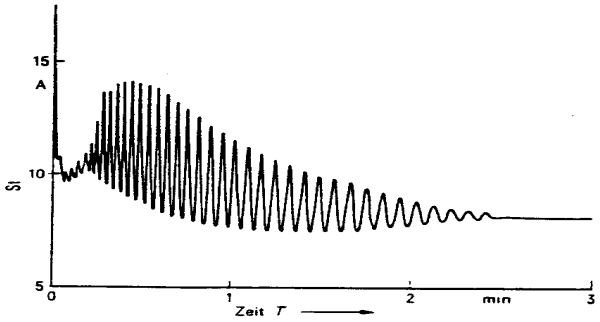
Fig.12. Nb, sheet; annealed at 1400°C, 4h;
100μ removed by CP

Electropolishing/Anodizing

Multi-mode pill box cavity, electropolished and anodized (20 V and 60 V)



H.Diepers et al., Phys. Lett. 37A, 139 (1971



Niobium Surfaces (3)

Different polishing solutions were investigated over the years aimed at achieving smooth surfaces:

- HF (50%)/HNO_3(100%) 1:1 @ 42C: good surface finish, fast reaction
- HF (48%)/ HNO_3(100%)/H_3PO_4 (85%) 1:1:1 @ 37C, grain boundary etching
- HF (40%)/ HNO_3(65%)/H_2SO_4 (96%) 1:1:2 @ 78 C,good surface finish, fast reaction

  Y. Uzel et al.;Appl. Phys. A30 (1983), 185

- HF (40%)/ HNO_3(65%)/H_2SO_4 (96%) 1:1:2 @ RT

  C. Z. Antoine et al.;"Alternative Approaches for Surface Treatment of Nb SC Cavities", 9th SRF Workshop,Santa Fe (1999),109

- E-polishing : Lactic acid/sulfuric acid/hydrofluoric acid

  J.Delayen et al.,"Alternate Electrolyte Composition for E-Polishing of Nb Surfaces", SRF2001, Tsukuba (2001), 499

Niobium Surfaces

Y. Uzel et al.,

All measurements following the polishing with addition of H_3PO_4 belong to the steeper gradient group, verifying the adverse influence of the stronger grain boundary etching. This may be understood, if one takes into account the field enhancement at peaks and sharp edges of the surface. 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 enlarges surface resistance, thereby causing an overproportional increase in the average resistance

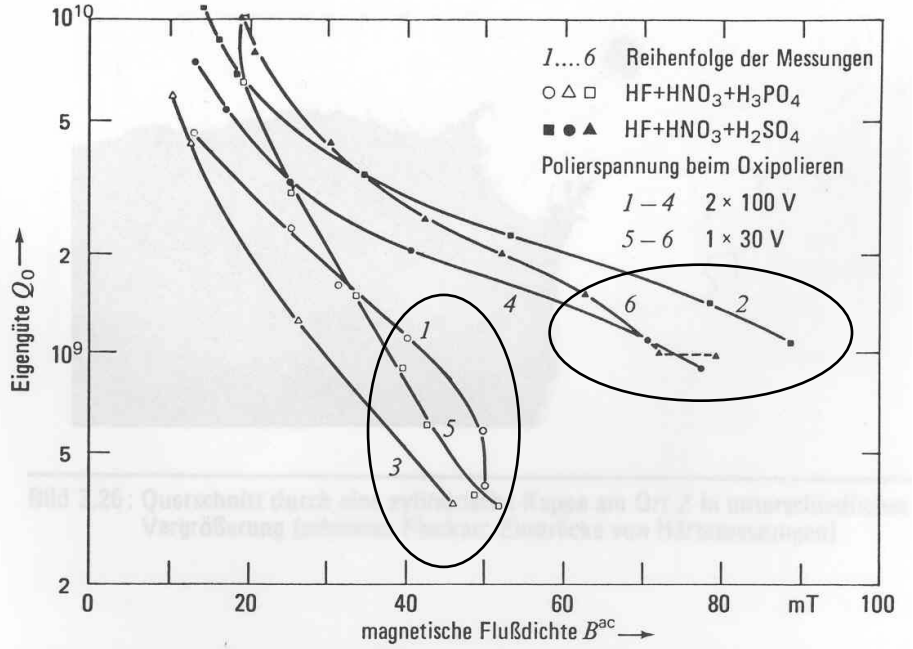


Bild 3.25: Güte in Abhängigkeit von der Flußdichte für den Resonator S4 mit unterschiedlicher Polierbehandlung

Niobium Surfaces (4)

M.Strongin et al,"Surface condition of niobium for sc rf cavities", Part.Acc 3, 209ff(1972)

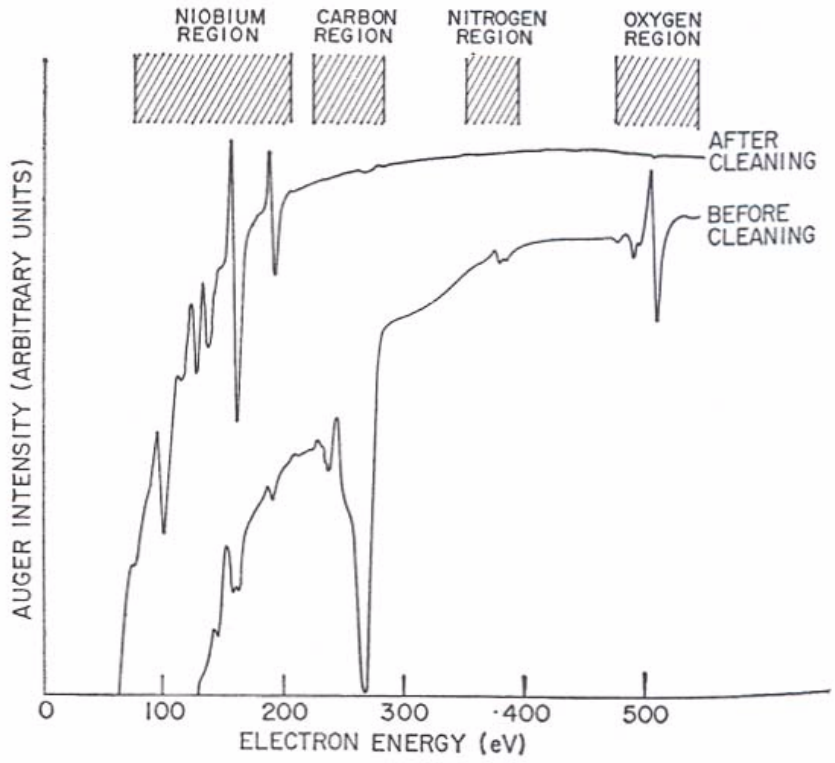
Nb heat treated @ ~ 1400 C

- LEED and Auger spectroscopy used to study amount of surface impurities

- During cooldown in UHV significant amounts of oxygen migrate to the surface, forming surface oxides

- Short mean free path and therefore low thermal conductivity in surface can cause breakdown

- Especially at grain boundaries or other disordered regions H_{c1} is lowered from the 1200 Oe value

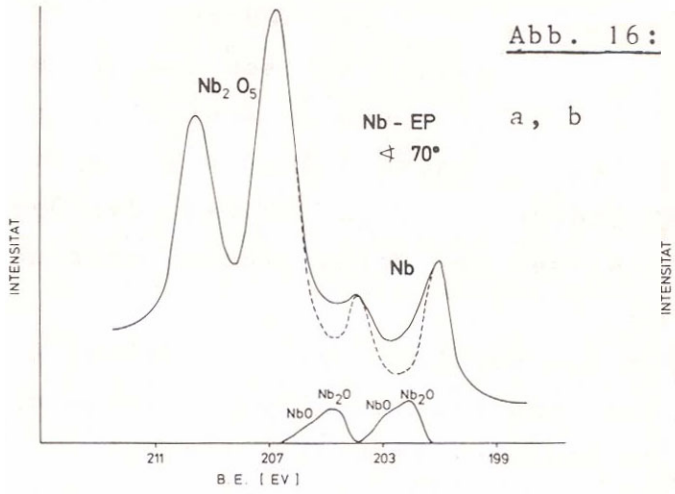


Niobium Surfaces(5)

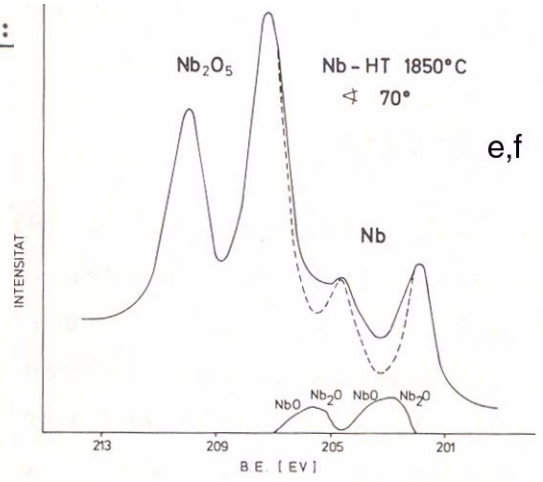
M. Grunder, " Surface Investigations on Nb used for SC cavities using ESCA and AES", Thesis KFK, 1977

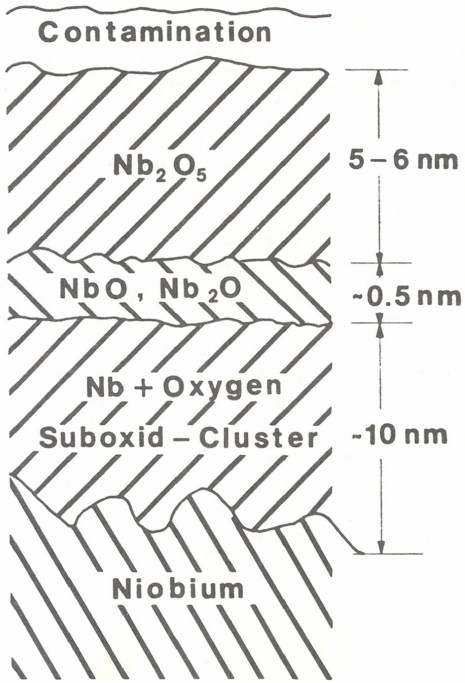
- 5 - 6 nm Nb_2O_5
- Transition layer of 2-3 monolayers of inhomogeneous NbO, NbO_2
- Nb matrix of 1-10 nm enriched by oxygen (few at %)
- Electron Bombardment converts Nb_2O_5 to NbO_2

Nb Electropolished



Nb heat treated @ 1850C in UHV





Magnetization/Penetration Depth

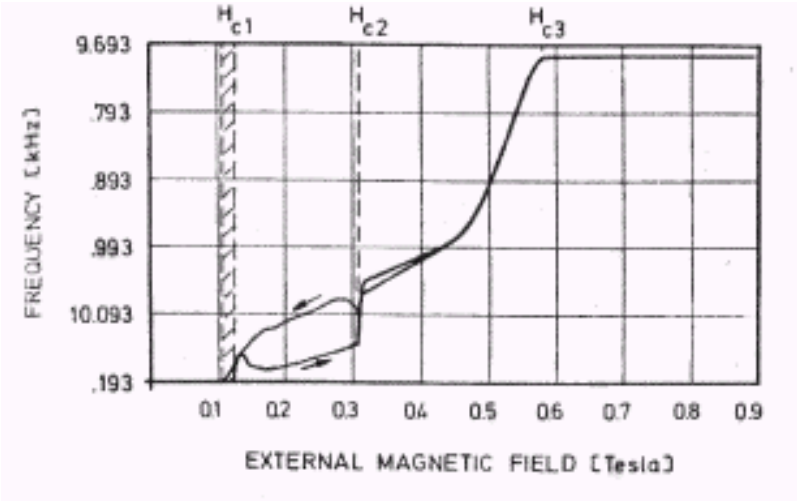
In 1973 we used magnetization and low frequency penetration depth measurements to investigate bulk and surface properties of niobium at KFK

P. Kneisel, O. Stoltz, J. Halbritter, "On Surface preparation and Measurement of Niobium used in High Frequency Cavities", JAP 45,2296 (1974)

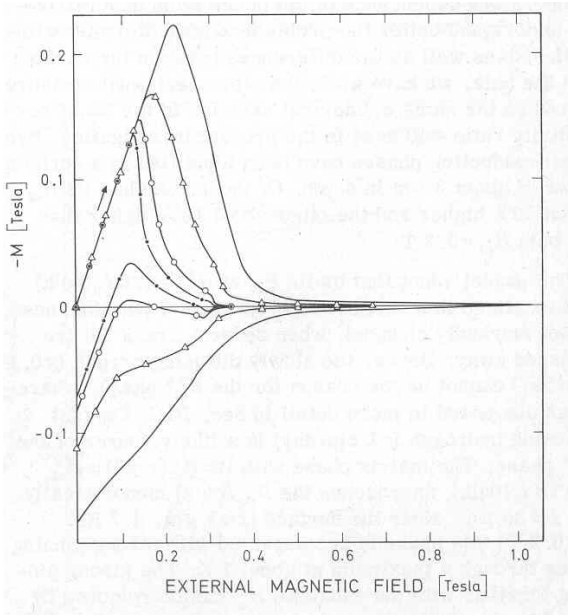
Das Gupta et al.; " Inhomogeneities in Superconducting Niobium Surfaces", JAP 47 (5), 2146 (1976)

Both methods are sensitive to surface conditions (~ 50 μm)

Heat treated Nb sample cooled within 12 hrs to 50C



As received, 3.2 μm ,10 μm, 30 μm bcp



Magnetization (3)

- E. Mahner, " Induktive T_c and H_{c2} -Messungen an Niob,Nb_3Sn and $YBa_2Cu_3O_{7-x}$ ", Diplom-Thesis, Uni Wuppertal 1989
- K.Saito, M. Wake, :"A New Material Evaluation Method on Niobium by Magnetization Measurement", Proc. 7th SRF Workshop (1995), p. 553

Effects in magnetic behaviour for different treatments such as CP, annealing, dissolved hydrogen clearly observed

- M. Bahte et al,"Magnetization and Susceptibility Measurements on Niobium Samples for Cavity Production", Proc. 8th SRF Workshop, Abano (1997),881

Investigation of effects of chemical treatments, annealing, surface damage. BCP and annealing remove pinning and as a result the magnetization is nearly reversible

- B. Steffen ;" Bestimmung der kritischen Felder von oberflaechen- und temperaturbehandeltem Niob durch Wechselfeld-Suszeptometrie", DESY Thesis-2003014

AC suszeptibility measurements are used to investigate the dependence of critical surface fields and critical surface current density on surface treatment (ep,bcp,"in-situ"baking)

E-polishing of 80 –160 micron leads to increased B_{c3} as well as "in-situ" baking at 120C; Effect of baking depends on baking parameters, affected layer < 5 micron

Magnetization (3)

More during this workshop:

L.v.Sawalski et al.; "Surface Superconductivity of Niobium: Onset of Long Range Coherence"

S. Casalbuoni et al.; " Superconductivity above the Upper Critical Field as a Probe for Niobium RF Cavity Surfaces"

Oxidation

The processes in the natural oxide layer taking place during "in-situ" baking of niobium surfaces were investigated by several groups:

A.Dacca, Ph.D. Thesis, INFN and Universita` di Genova, 2000
R. Ballantini et al., "Improvement of the maximum field of accelerating cavities By dry oxidation", 9th SRF Workshop ,Santa Fe(1999),p.211
Q. Ma, R.A. Rosenberg, "Thermal and electron-beam irradiation effects on the surfaces of niobium for RF cavity production", SRF 2001, Tsukuba, 368

- Both investigations confirmed the results by Grunder as far as the structure of the oxide layer on top of Nb is concerned
- During "in-situ" baking the Nb_2O_5 is converted to suboxides (NbO_x , $x<2.5$), which turns into NbO_2 of several monolayers at higher temperature
- AXPS: atmospheric contamination layer of C=O, C-OH and Nb-OH bonds
- Hydrocarbon contamination decomposes and starts to form NbC at T >200 C

Niobium Surfaces

C.Z.Antoine et al, "Morphological and Chemical Studies of Niobium Samples after Various Surface Treatments",9th SRF Workshop,Santa Fe (1999),295
C.Antoine at al. "Surface studies: method of analysis and results", SRF 2001, Tsukuba, Japan

- Morphology of Nb subjected to different treatments (FNP,FNS,EP) investigated with x-ray reflection,profilometry,STM)
- Chemical composition explored with TOF-SIMS and ESCA

- Oxide growth on EP surfaces much slower than on FNP surfaces (> 45 hrs vs ~ 4 hrs)
- Morphology of surface different for the different chemical treatments; heat treatment leads to recrystallization and therefore to changes in roughness/microroughness

- "In-situ" baking (**120C, 96hr**) converts Nb_2O_5 to NbO_2 and oxygen diffuses into the Nb matrix

- What is the role played by surface impurities, since there is an indication of some diffusion of species like C, F, P after baking?

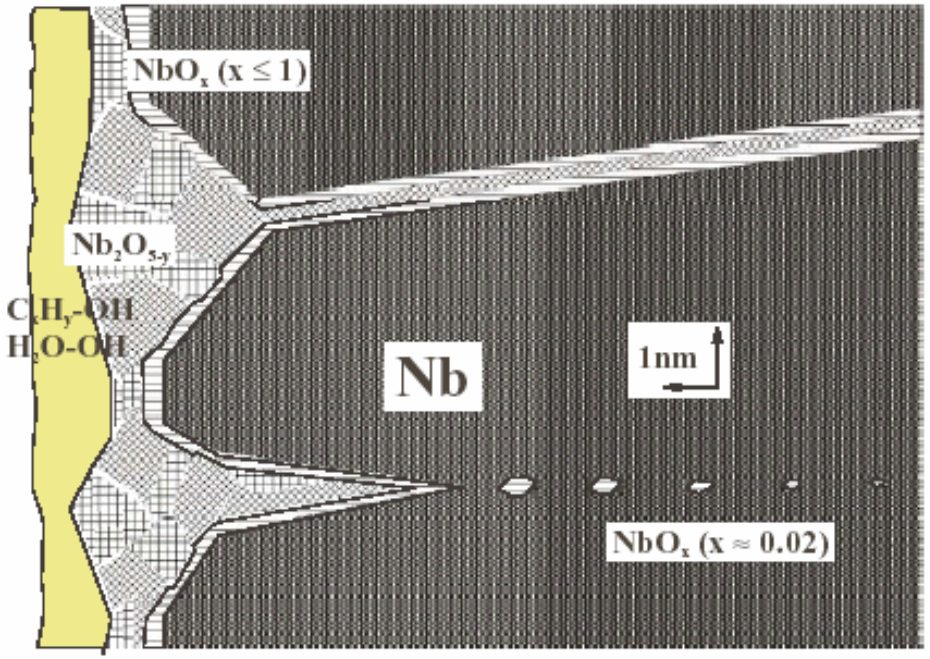
Oxidation

F. Palmer," Surface Resistance of Superconductors- Examples from Nb-O Systems", 3rd SRF Workshop, Argonne (1987), Report ANL-PHY-88-1,309

X-band cavities heat treated "in-situ" at 1100 C for 20 min , surface oxide dissolved into bulk as confirmed by AES studies on samples; after baseline measurements, the cavities were exposed to clean oxygen at 0.1 torr for 2 –16 hrs. Increase in residual resistance 1 – 2 nΩ

Niobium Surface

J. Halbritter, Proc. SRF2001,KEK Proceedings 2003-2, p.292



Contamination Studies

B. Piosczyk, KFK Report 1991, Kernforschungszentrum Karlsruhe (1974)
Condensation of gases such as O_2 , N_2 , CO_2 , O_2/N_2 on cold niobium surfaces at 100 Mhz cause dielectric losses: magnetic moment of O_2

P. Kneisel," Effect of cavity Vacuum on Performance of SC Niobium Cavities", 7th SRF Workshop, Gif sur Yvette (1995),443
Prior to cooldown only a partial vacuum was established in the cavity
For "clean" surfaces: significant losses for p> 3 torr
For contaminated surfaces: losses + strong influence on electron loading

T. Habermann et al.;"Influence of Adsorbates and Surface Compounds on the Field Emission of Niobium", 8th SRF Workshop, Abano (1997),972
FE behaviour is influenced by adsorbates and surface compounds,
Unrealistically high emitting areas, correlation between enhancement factor and emitting area

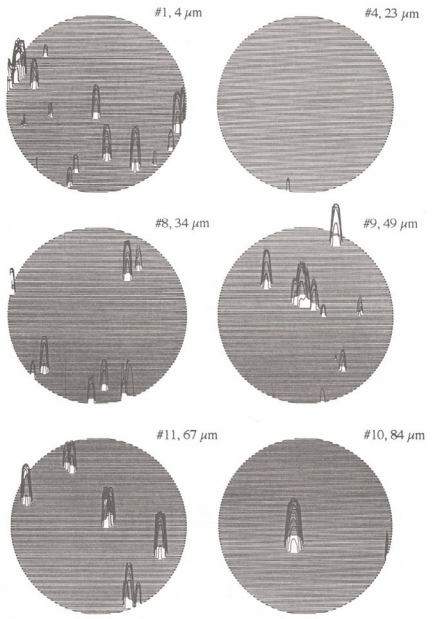
Material Removal

E. Mahner et al.; "Effect of CP on Electron Field Emission of Nb samples and cavities", 6th SRF Workshop(1993),1085

- Systematic removal of material from cavity surface and samples
- Measurement FE behaviour, X-ray diffraction, R_{res} and E_{peak}

100 MV/m

#1, 4 μm
#4, 23 μm
#8, 34 μm
#9, 49 μm
#11, 67 μm
#10, 84 μm



- X-ray diffraction: material is textured, removal of ~ 10 μm removes damage from rolling
- no systematic change in # of emitters with material removal up to ~ 90 μm
- removal of ~ 70 μm necessary to achieve low R_{res} , ~ 200 μm for max. E_{peak}

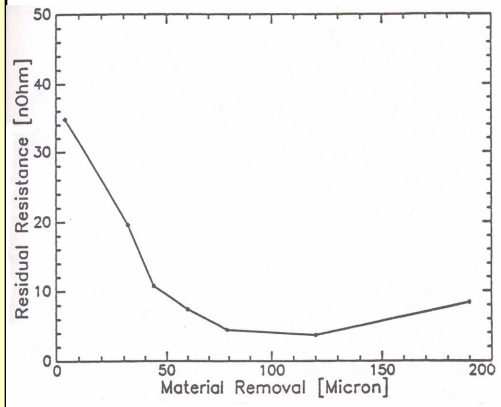


Fig. 3. Effect of material removal on the residual surface resistance R_{res}.

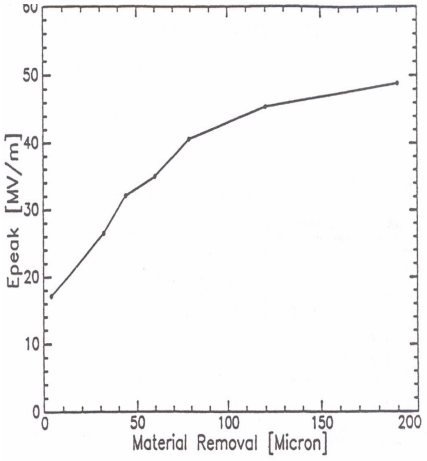
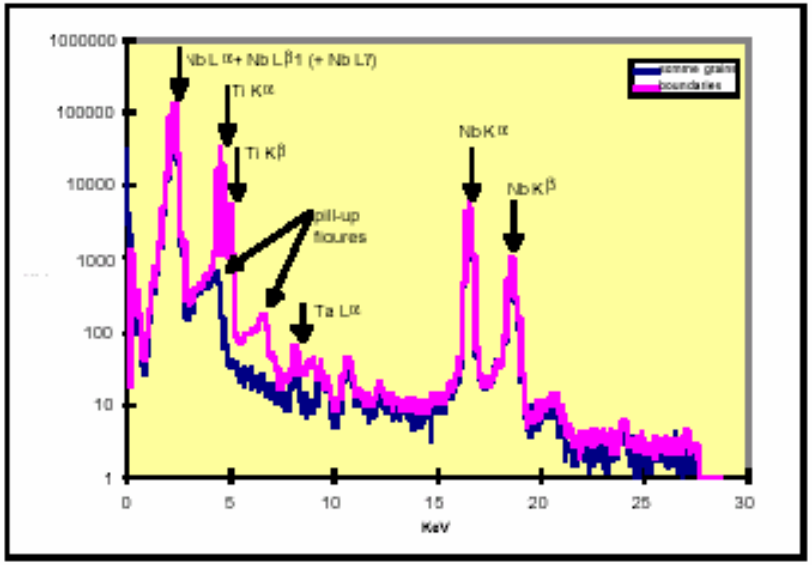


Fig. 2. Effect of material removal on the peak surface electric field E_{peak}.

Grain Boundaries(1)

C. Antoine et al.;"Nuclear Microprobe Studies of Impurity Segregation in Nb used for rf Cavities", 8th SRF Workshop,Abano(1997) LNL-INFN(rep)133/98,p.911

Nuclear Microprobe spectra showing the global contamination of titanium at grain boundaries for annealed samples (sum of several spectra)



- Titanium from purification annealing can be readily detected in grain boundaries.

  Subsequent sufficient chemical treatment is necessary to remove the Ti

- Ta seems to be evenly distributed in the first few microns of the surface (no clusters) (see Siemens)

- Carbon contamination mostly found in grain boundaries (see Siemens)

- Oxygen: no difference found between grains and boundaries, but contamination extends deeper into the material

Grain Boundaries (2)

H. Safa et al.; " Specific Resistance Measurement of a Single Grain Boundary in Pure Niobium",9th SRF Workshop, Santa Fe (1999),267

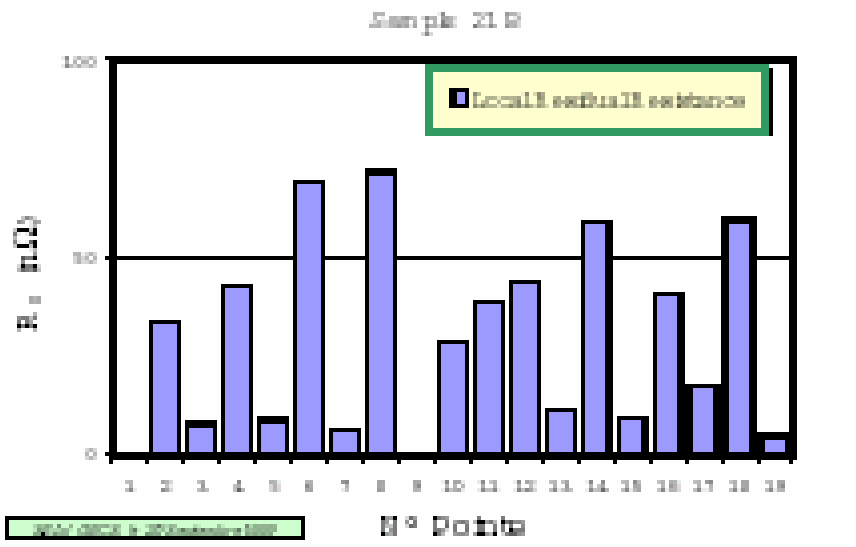


Figure 5 - Local measured residual resistance. Note that the value may vary by more than one order of magnitude from one place to another.

- Grain boundaries are "weak links" and will become normal above a critical field
- Very high RRR niobium needed to separate grain boundary resistance from grain resistance
- Resistance across boundary measured by applying micropins on both sides of the boundary.
- Specific resistance value averaged over 10 boundaries:

$$G = 2 \times 10^{-13}\ \Omega m^2$$

a factor of 1000 higher than typically assumed

More at this workshop:

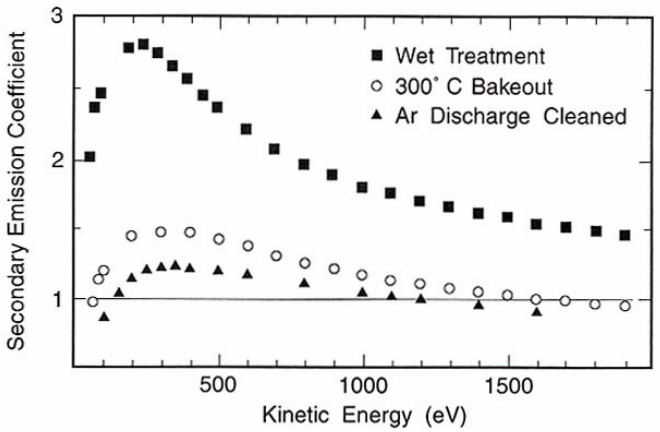
S. Berry et al.,"Grain Boundary Specific Resistance and RRR Measurements in Large Grain Pure Niobium"

Electron Loading

Multipacting

Primary electrons are resonantly re-accelerated to a cavity wall and generate secondary electrons

SEY and impact energy are important



R.Calder et al.;Nucl. Instr.&Meth. Phys.Res.B 13, 631 (1986)

The SEE is very sensitive to surface conditions

Field Emission

DC Scanning systems have been developed at Univ. of Geneva (PH.Niedermann), Univ. of Wuppertal (E.Mahner, N.Pupeter, T. Habermann, G. Mueller),Saclay/Orsay (J.Tan et al,M.Fouaidy et al) and Jlab (T.Wang)

Rf field emission investigated mainly at Cornell University (D. Moffat,T. Hays, J. Knobloch, H. Padamsee) with

Special cavities + SEM + EDX + AFM

Field Emission

DC

UHV field emission scanning microscope + surface analysis (AES)

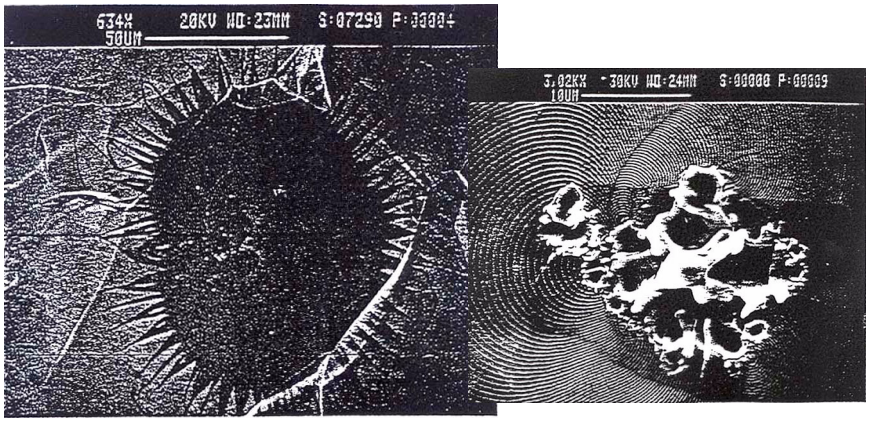
- emitters are localized
- Loosely attached foreign particles, but only a few are active emitters: geometrical field enhancements
- Heat treatment at T > 1400 C removes artificial emitters
- UHV heat treatment between 200C and 800C activates " intrinsic" emitters: Sulfur, Carbon segregation emitters can have crystalline microstructure
- adsorbates and surface compound increase FE

RF

- Remains of emitters after destruction

Topology: Starbursts, ripple pattern, craters, molten Nb

Materials: Fe,SS,In,Cu,Ti,Teflon,C, residue from rinse water



- emitters seem to be "artificial" and FE is no fundamental limit

Field Emission(3)

G.J. Sayag et al.; "Field Emission from Oxidized Niobium Electrodes at 295 and 4.2K", Journ.Phys.E10(1977),176

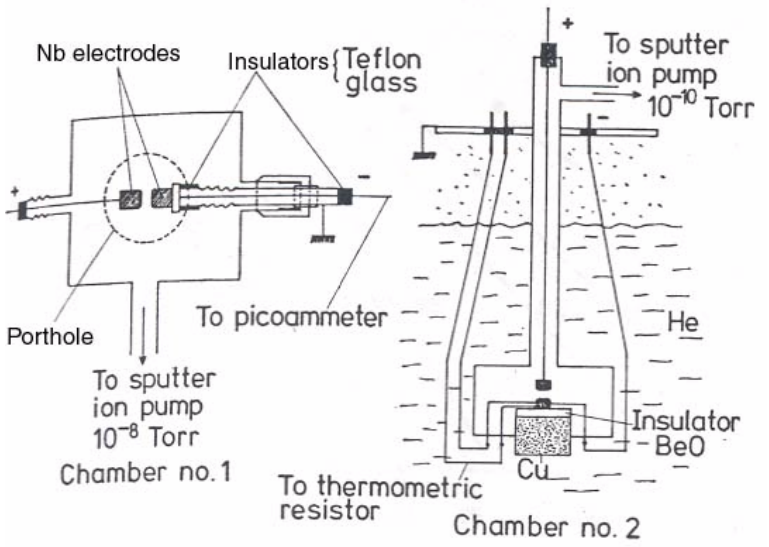


Figure 1: The two UHB diodes

- 99.9% niobium, heat treated at 1800 C, electropolished, anodized up to 160 nm
- FN – plots after some conditioning taken at RT and 4.2K

- Anodic oxide layer protects niobium, FE threshold and BD voltage increase with oxide thickness
- Efficiency independent of temperature

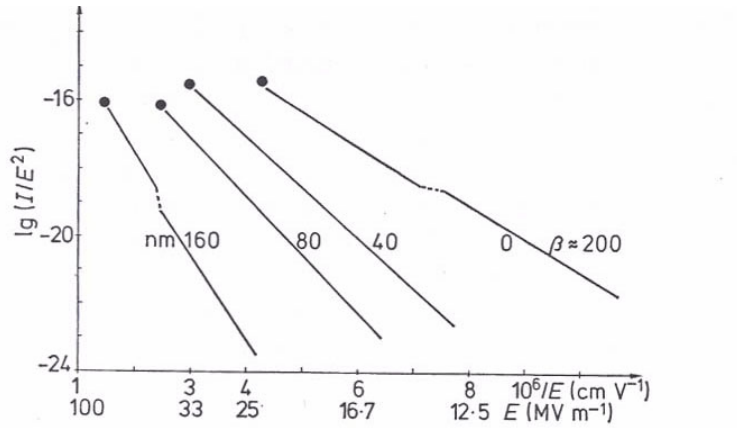


Figure 3 FN plots of plane electrodes with various oxide layer thicknesses

Experience (1)

What has been learnt?

Estimated costs over last ~30 years in the following laboratories:
ANL,BNL,Cornell,FNAL,HEPL,Jlab,LANL,SLAC,Stony Brook,UCLA,
CERN,DESY,INFN Milano, INFN Legnaro, INFN Genoa, KFK,
Orsay, Saclay,Univ.Wuppertal,
KEK,JAERI,Beijing Univ, Protvino

~ 1000 man years , ~ M$ 50 - 100
~ 40 - 50 PHD's

Experience (2)

- Surface Physics is reproducible, both in space and in time
- The life time of an investigation in the area of SRF is 5 – 10 years
- Over the last 4 decades much has been learnt about niobium surfaces, treatment procedures and cavity manufacturing; existing procedures – if applied properly – will result in high performance cavities for application in an accelerator (e.g. TESLA)
- The niobium surface - its oxide structure – is very complex and can influence cavity performance. Especially localized states in the interface may contribute to losses, to a smearing of the DOS and to ITE ("Q – drop") [Halbritter]

Experience (3)

- Investigations on samples using "traditional" surface analytical tools have been useful and most likely continue to give insights in the complex composition of Nb surfaces .

- However, it seems to be a "dream" (and so far the past has confirmed that) to be able to correlate the findings from such sample tests to cavity performance . After all, these methods use " outer" electrons (valence electron), whereas the sc properties are determined by conduction electrons.

- Bulk properties such as thermal conductivity, Kapitza resistance, dissolved impurities (Hydrogen), defect elimination are very important for achieving high gradients

Experience (4)

- Therefore methods such as penetration depth, magnetization, pinning, suszeptibility seem to be well suited to correlate sample features to cavity performance

- SEY measurements and FE studies on samples seem to directly applicable to cavities; however, no sample measurement ever "beats" a cavity test. Example: Cornell studies on FE with cavities, which were subsequently disected and the surfaces/field emitters were observed in an SEM

- With the improved material quality, resulting in thermally more stable cavities, "environmental" effects and surface contamination causing FE have become the dominant limitations

Experience (5)

- 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 in particular true , when high Q-values at high gradients are required

Future

What is missing?

- Q vs E_{acc} typically show the 3 different slopes as mentioned earlier. The low field slope ("peak") is sensitive to baking/oxygen diffusion and has been explained [Halbritter] as a smearing of the DOS due to oxygen clusters and a thermal non-equilibrium (overheating) between the Nb-O clusters and the surrounding niobium: we should measure the DOS and its changes as a function of treatment

- Slopes II and III are explained [K. Saito, PAC 2003, this conference] by a H –field dependence of the energy gap and heating of the rf surface. Data taken at Jlab [G. Ciovati] fit better to the ITE [Halbritter] between charge carriers and localized states in the Nb/Nb-oxide interface: the density of localized states in the interface should be measured as function of "in situ" baking conditions

Future

- What causes a Q – drop in a cavity and why does it not always occur? Is the "Field-Enhancement-at Grain-Boundaries" – model by J. Knobloch still valid? [news at this conference?]

- Is the Q-drop an electric or magnetic field effect and under which physical conditions is it eliminated ?

- Does Hydrogen play a role beyond Q – disease?