SURFACE PREPARATION OF NIOBIUM

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1. Introduction

Any discussion of surface preparation for superconducting rf-surfaces is certainly connected with the question what is the best recipe for achieving high Q-values and high break-down fields. Since the break-down in a cavity is not understood so far and because several mechanisms play a role, it also is not possible to give one recipe which always works.

Nevertheless in the past certain preparation techniques for niobium surfaces have been developed and certain rules for preparation can be applied. In the following the to-days state of the art will be described. A description of the physics of the surface and the explanation of the phenomena observed in rf-cavities caused by the state of the surface will be given afterwards [1,2].

It is well known that rf-superconductivity is taking place in a thin surface layer of only a couple of nm. In the case of niobium the electromagnetic field penetrates about 60 nm into the metal depending on the mean free path of the electrons in the surface sheath.

It is also known that from the point of view of rf-superconductivity best results as predicted by the BCS-theory can be achieved for a clean, defect-free metal surface. If this surface is smooth on a microscopic scale the surface resistance is smaller than for a rough surface because the current paths are shorter and therefore less dissipation takes place. A smooth surface is also desirable, if one is interested in establishing high electromagnetic fields on the superconducting surface. As is known rough surfaces lead both to electric field enhancements causing non resonant electron loading, and to magnetic field enhancements initiating rf-breakdown.

In reality of course one is not dealing with ideal surfaces. The niobium is in addition covered with oxide adsorption layers, the effects of which will be discussed in ref. [2].

In the following it is attempted to give a short description of the surface in conjunction with the methods of surface treatments, which generally can be applied to niobium cavities.

2. Surface Treatments

2.1 Machining of a Surface

For the shaping of metal pieces different techniques are used as will be described in detail later during this workshop. [3] Niobium,which is electron beam molten,is usually either machined on a lathe or by milling or die formed (hydroformed, spinned) by sheet metal techniques. In all cases defects are introduced into the metallic surface beside the defects and impurities of the starting material.

Since niobium is already at low temperatures ($\sim 300^\circ$C) reacting with air [4] - oxygen is dissolved in the niobium matrix forming clusters of suboxids which enhance the vickers hardness - great care has to be taken to avoid heating of the niobium part during machining. The choice of the lubricant not only influences the temperature of the work-piece at the tool, but also the surface finish. Generally, all lubricants containing trichlor-ethylene result in smooth surfaces; surface roughnesses of 1-2 μm are obtained. On a macroscopic scale a series of hills and valleys are present, on a microscopic scale smaller irregularities are superimposed as indicated in fig. 1.

As important as the roughness of the surface is the depth of the damage layer introduced by the mechanical deformation of the lattice during machining. The depth of this surface damage layer is depending on the machining condition as well as on the choice of the tool, influencing e.g. the pressure at the tool, or the cutting ability.

Penetration depth measurements by Hauser [5] on niobium samples have indicated that the depth of the surface damage layer for the machining conditions used in our lab [6] is in the order of 50 μm. If die-forming, hydro-forming or spinning techniques are used, one would expect a thinner surface damage layer. Measurements on cavities at Cornell University, where sheet metal techniques have been developed for the fabrication of resonators, [7] indicate that after the removal of about 50 μm

reasonable results are obtained. For helix-resonators, which are build out of
drawn niobium - tubes, the removal of at least 100 μm was necessary.[8] Early
investigations at HEPL indicate a surface damage layer of 250μm.[9]

Prior to the removal of this surface damage layer a visual inspection of the
surface is commonly done. Soaking the niobium in water for a longer period of
time indicates, if there are iron-inclusions in the surface, which show up as
rusty spots and can individually be treated.[10]

2.2 Chemical Surface Treatment

For the removal of this damage layer either electropolishing or chemical poli-
shing is commonly used. Both methods have generally two effects on a surface:

    a) "smoothing" by elimination of large scale irregularities,
    b) "brightening" by removal of superimposed smaller irregularities.

Essential for the smoothing-effect during electropolishing is the existence of
a layer of high viscosity consisting out of a saturated solution of reaction
products. The rate of removal of metal ions from the surface is determined by
a diffusion process in the viscous layer, which depends on the concentration
gradients, the temperature, the agitation of the solution.[11]

At protrusions of the surface, current densities are high establishing high
concentration gradients, faster diffusion of metal ions through the layer and
therefore a preferential dissolution of the peaks. At valleys the current den-
sities are smaller, as are concentration gradients; and therefore diffusion and
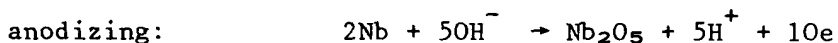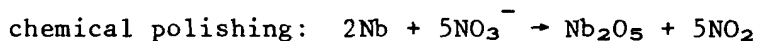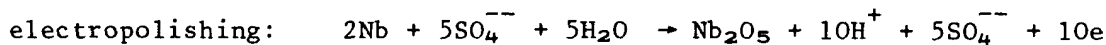dissolution are smaller.

Chemical polishing of niobium is usually associated with a vigorous gas evolution;
in the case of niobium the evolution of the brownish nitrogendioxide takes place;
it has been suggested by several authors[12] that in this case the viscous layer
forms only in the valleys and at the peaks it is swept away by the turbulent flow
of the solution due to the gas evolution. Marked preferential attack then occurs
at the peaks leading to a rapid smoothing.

"Brightening" occurs only if a thin surface oxide film - only a few monolayers
thick - is covering the metal to be polished.[11] It prevents the direct access
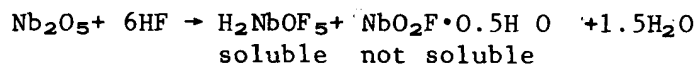
of the solution to the surface, which would cause preferential dissolution of metal from sites of high energy resulting in etching (grain-boundaries, dislocations). It has been suggested that the film undergoes a continous process of dissolution by the acid and renewal. In order to maintain the film, the passage of metal ions across the metal/film interface occurs at the same rate at all points. Such uniform attack of the metal will remove microscopic irregularities from the surface. [13]

Although there exist several methods of chemical treatment of niobium surfaces [11,14,15,16], the methods developed by Siemens company [17] for electropolishing and by ref. [9,18] for chemical polishing are most often used for microwave cavities. Table I shows the summary of the applied surface treatments. Common to all processes is the oxidation of the niobium to niobium - pentoxide, which is dissolved in excess hydrofluoric acid as oxifluorides. The chemistry involved is the following: [19,20,21]
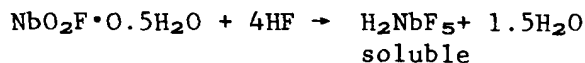
S t e p   1

electropolishing: $2Nb + 5SO_4^{--} + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 5SO_4^{--} + 10e$

chemical polishing: $2Nb + 5NO_3^- \rightarrow Nb_2O_5 + 5NO_2$

anodizing: $2Nb + 5OH^- \rightarrow Nb_2O_5 + 5H^+ + 10e$

S t e p   2 $Nb_2O_5 + 6HF \rightarrow H_2NbOF_5 + NbO_2F \cdot 0.5H O + 1.5H_2O$
 soluble   not soluble

S t e p   3 $NbO_2F \cdot 0.5H_2O + 4HF \rightarrow H_2NbF_5 + 1.5H_2O$
 soluble

The electropolished or chemically polished surfaces are contaminated with reaction products, lower oxides, sulfur and fluorine. [22,23] Proper cleaning is achieved by rinsing in a diluted hydrogenperoxide solution during ultrasonic agitation and/or anodizing (oxipolishing) [10,24,25]; during these steps the insoluble reaction-products are converted into soluble forms. In the case of the oxipolishing process the reactive niobium surface is in addition shifted towards "cleaner" regions of the bulk material. The amorphous Nb_2O_5 can transform into a crystalline modification, which appears as "gray oxide" during numerous subsequent oxipolishing cycles. As Grundner [22] has found, the formation of this oxide starts at certain nucleation sites as NbO, which quickly grow to form a Nb_2O_5-layer. This gray oxide is not soluble in Hf; in most cases chemical methods are too weak, only mechanical methods are successful. The probability of the growth of this crystalline oxide is reduced, if the niobium

was heat-treated prior to oxipolishing, which removes the spots of high energy (nucleation sites) to some extend. The state of the surface - as investigated by Grundner [22] with XPS - is shown schematically in fig. 2.

In the niobium matrix, suboxide clusters are inhomogeneously distributed in a layer of about 10 nm. A 0.5 nm thick sheath of NbO and Nb_2O is sandwiched between this layer and a Nb_2O_5 layer, which is contaminated by adsorbates.

2.3 Heat Treatment

Some improvements of the surface condition can be gained by a furnace treatment for temperatures above $T \geq 1600°C$ as indicated in table II. [22] First of all the niobium surface is cleaned from residual contamination, [22] if proper rinsing techniques are not available. [29] But even in a very good vacuum ($p \leq 10^{-8}$ torr) there remain 1-2 atomic layers of surface oxides (NbO, Nb_2O) on the niobium, which are due to oxygen segregation from the bulk. For increasing residual gas pressures the oxides grow as a function of temperature and time. Typically a Nb_2O_5-layer of 1.5 nm is present on top of the niobium after cool-down. Below 700°C the formation of suboxide clusters in the niobium matrix which are due to dissolution of oxygen from the residual gas, starts. Therefore fast cooling below 700°C may be advantageous because of less clustering.[26] Generally the oxide layer after a furnace treatment is thinner than after chemical treatment. There are indications for less electron loading of heat-treated surfaces, if provisions can be taken to avoid adsorption of H_2O, hydrocarbons during the handling of the cavities after the furnace treatment (e.g. glove box with inert gas, fast assembly). The main benefits of a surface treatment rather remain for the bulk than for the surface:

a) The niobium is stress annealed and recrystallized (900°C ≤ T ≤ 1200°C). Investigations [27] at Siemens company have shown that work hardened material with a high density of dislocations gave only moderate values of critical magnetic fields (X-band-TM_{010}-mode, $H_c^{ac} \approx 35$ mT), whereas recrystallization at 1200°C improved the fields to $H_c^{ac} \simeq 110-150$ mT.

b) The niobium is homogenized (1000 ≤ T ≤ 1300°C), which seems to be advantageous for welded cavities. In this temperature range the diffusion rates [49] of impurities like O,C .., which have clustered in the weld during the welding process, are high enough to result in a uniform

distribution. For heavily electropolished surfaces the dissolved hydrogen, which clusters during cool-down to cryogenic temperatures and induces stresses in the lattice, is removed during moderate firing (T $\geq$ 800°C).

c) Above 1600°C <u>grains are growing</u> due to secondary recrystallization. Al-though investigations [27] comparing material of small grain size (< 1 mm) and large grains (> 10 mm) indicate no significant effect on the critical magnetic field of a cavity, smoother surfaces are obtained during electro-polishing for large grain material because of less grain boundary etching.[6]

d) The <u>thermal conductivity</u> of the material is improved to some extend, if the interstitial impurities are removed and the grains are growing (T $\geq$ 1800°C) Better thermal conductivity is desirable for the improvement of break-down fields in cavities. [28]

3. Conclusion

There remain questions like:

- Is electropolishing to be prefered against chemical polishing?
- Is a high temperature firing (T > 1600°C) necessary or can it be avoided?

Let me conclude with a few statements:

Apparently the proper surface treatment has to be developed in each laboratory and for each cavity-type. Also the material purity and homogeneity is important. Nevertheless a few steps seem to be essential:

1) Trivially the surface <u>damage layer</u> has to be removed (50 µm - 250 µm). Whether electropolishing or chemical polishing is the better method for this purpose is not evident. At least it seems to be apparent that <u>electro-polishing</u> results in a more <u>uniform removal</u> of material, whereas chemical polishing tends to cause grain-boundary etching, if large amounts of material have to be removed.

With both methods comparable results have been achieved. In X-band-cavities peak electric field of E_p $\simeq$ 60 to 70 MV/m corresponding to peak magnetic fields of H_p $\simeq$ 110 mT have been obtained at HEPL[30] and SLAC[31] for chemically polished surfaces. At CORNELL[32] and at SIEMENS company[33,34] peak fields of E_p $\simeq$ 55MV/m (H_p $\simeq$ 150 mT) and H_p $\simeq$ 110 - 150 mT, respectively, have been measured. At HEPL,[35] Wuppertal[36] and KfK[6] both methods of chemical surface treatment have been

applied with comparable results at S-band frequencies.

At 500 MHz in the storage ring cavity of CERN [37] accelerating gradients of $E_{acc} \simeq 4.6$ MV/m have been measured after a chemical polishing of the surface. The DORIS - test cavity at KfK was only tested with electropolished surfaces and resulted in $E_{acc} \simeq 4.4$ MV/m. [38]

2) <u>Proper rinsing techniques</u> are essential to remove surface contaminations.

3) <u>Heat treatment at moderate temperatures</u> $(T \leq 1300^{\circ}C)$ serves three purposes:

    a. <u>Outgassing</u> of dissolved hydrogen.

    b. <u>Stress annealing</u> , which seems to be essential for heavily cold worked material and is advantageous before electropolishing in order to avoid preferential etching. For cavities made out of solid (electron beam melted) material apparently not many stresses are induced, [27,39] which makes a heat treatment unnecessary.

    c. <u>Homogenization</u>, which seems in most cases to be essential for welded cavities, [29,32,40-43] although there exist exceptions. [36,37]

4) <u>High temperature firing</u> $(T > 1600^{\circ}C)$ causes grain growth, which does not significantly influence the performance of a cavity. [27] In addition at high temperatures and ultra high vacua the niobium is purified due to outgassing of dissolved interstitials, [44] but there seems to be no effect on performance. [45]

Nevertheless high temperature firing is necessary to achieve very high Q-values [46] (e.g. $Q > 10^{10}$ in the TM_{010}-mode at X-band).

5) <u>Dust free assembly</u> is essential both prior to furnace treatment and to rf-testing.

Recently the method of ion sputter cleaning has been picked up at CERN as a method for surface cleaning of niobium cavities. [47] About 2 years ago investigations at CORNELL UNIVERSITY [48] with ion sputter cleaning have been stopped as were tests in our laboratory 8 years ago because of discouraging results. Hopefully the CERN - group can demonstrate the feasibility of this method as a further means to improve superconducting rf-surfaces.
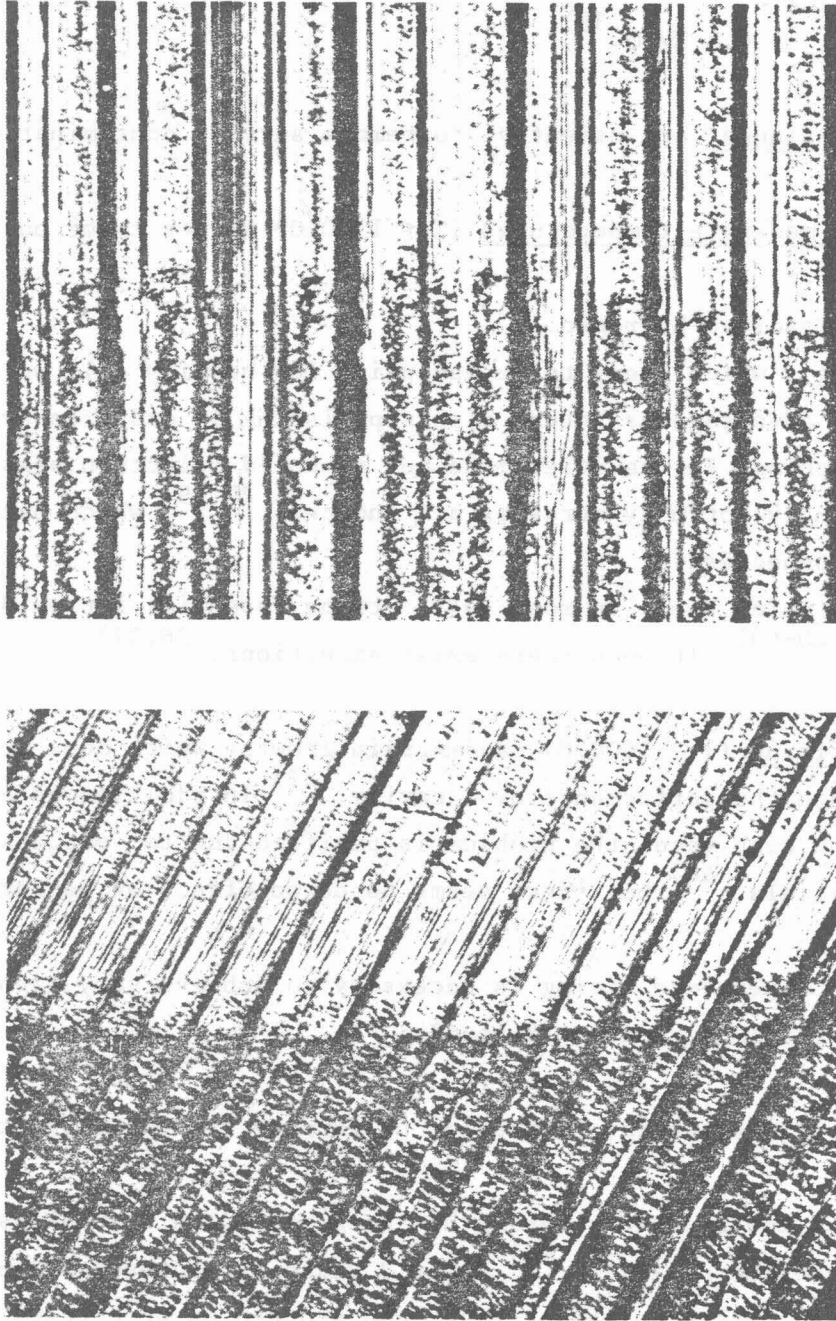
Figure 1: Topography of a niobium surface after machining on a lathe (magnification 200) from ref. 50)
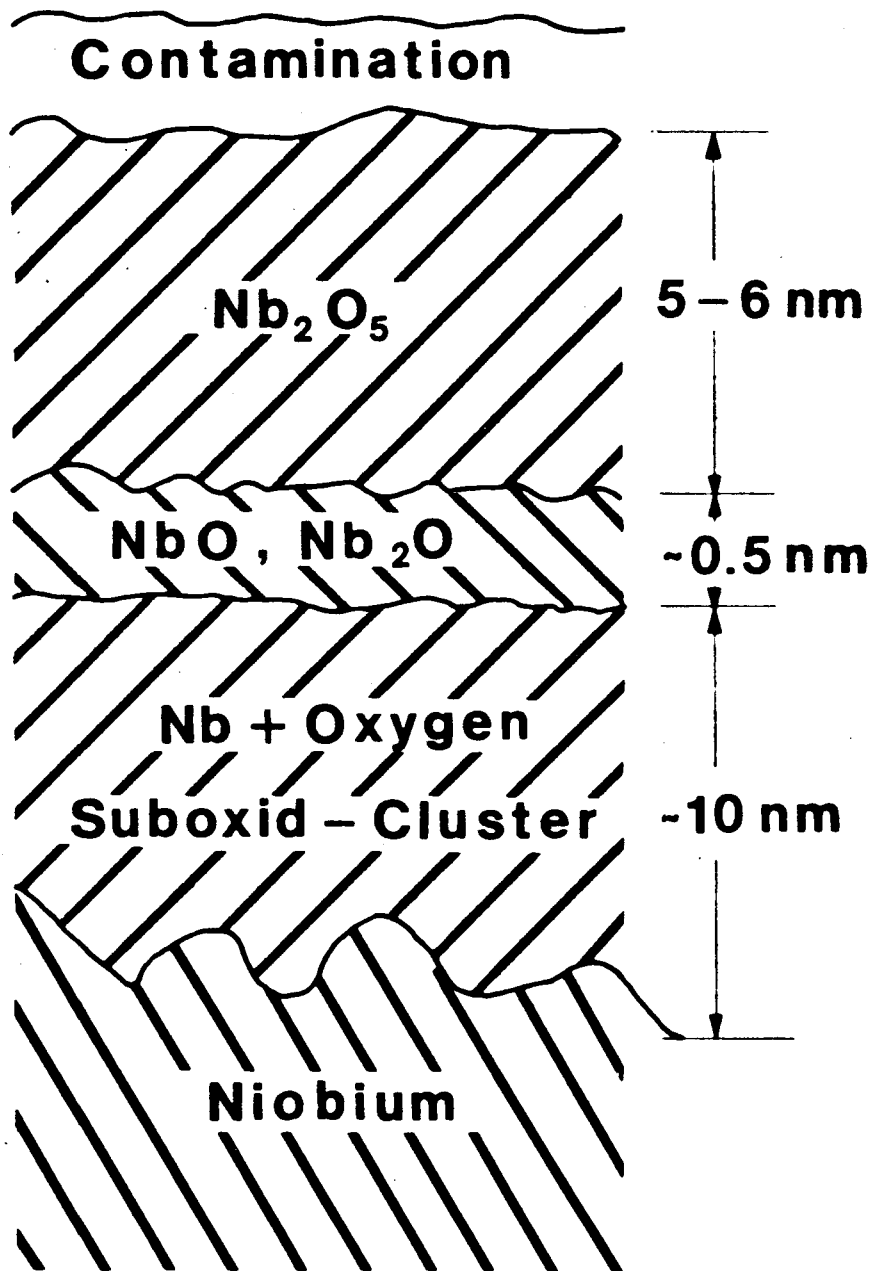
Fig. 2: Schematic diagram of a niobium surface as described by Grundner [22]

Table I: Chemical methods of surface preparation of niobium cavities

METHOD	SOLUTION	CONDITIONS	EFFECT	SURFACE
Electro-polishing	H_2SO_4(97%):HF (40%) = 85 : 10 by volume	10 - 15 V 25 - 35°C current oscillations	Smoothing brightening surface roughness ~.5 nm	Contaminated by reaction products S, F ...
Chemical-polishing	HNO_3(65%):HF (40%) = 60 : 40 by volume	Room-temp. (RT) or T<RT for smaller reaction rates 25 μm/min at 0°C	Smoothing (brightening) grain boundary edging	Contamination with reaction products
	HNO_3(65%):HF(40%): H_3PO_4(85%) = 1:1:1	room-temp. 10 μm/min		
Anodizing (oxipolishing)	20% NH_4OH or any diluted acid except HF	Room-temp. 0 ... 100 V voltage defines thickness ~ 2.4 nm/V	a) oxidation of residual oxides b) removal of S,F c) neutralization of acids	Sulfur removed fluorine reduced
Rinsing	H_2O_2 + dist. H_2O + ultrasonic	Room-temp. 15 - 30 min with repeated renewal	Very efficient removal of surface contamination	

Table II: Effect of high temperature firing on a niobium surface

METHOD	CONDITIONS	EFFECT	SURFACE	REMARKS
Ultra high vacuum high temperature firing	$1600 - 1900\,^{\circ}C$ for high β-structures $\leq 1200\,^{\circ}C$ for low β-structures	Degassing of material surface cleaning: F removed S reduced C contamination due to rinsing in hydrocarbons reduced to 1 monolayer	State strongly depending on residual gas pressure in furnace: A) $<10^{-8}$ Torr: 1-2 monolayers of NbO, Nb_2O B) P increased: formation of Nb_2O_5 by further oxidation as function of T,t ~ 1.5 nm C) $T < 700\,^{\circ}C$: formation of suboxide-clusters	e.g. Grundner → due to segregation of oxygen from bulk → responsible for A) step in $\Delta\lambda(T)$ around 7 K B) (Δ/kT_c) exp $< (\Delta/kT_c)_{BCS}$ C) $R \neq R(f^2)$ Fast cool-down may reduce suboxide clustering.

R e f e r e n c e s

1) A. Septier,
    "Surface Studies and Electron Emission", this workshop

2) J. Halbritter
    "Theoretical Aspects in RF-Superconductivity", this workshop

3) W. Bauer,
    "Fabrication of Niobium Cavities", this workshop

4) W. Schwarz, J. Halbritter,
    J. Appl. Phys. 48, p. 4618 (1977)

5) W. Hauser,
    KfK-Ext. Ber. 3/74-7, Kernforschungszentrum Karlsruhe (1974)

6) P. Kneisel,
    KfK-Bericht 1645, Kernforschungszentrum Karlsruhe (1972)

7) H. Padamsee, J. Kirchgessner, M. Tigner, R. Sundelin, M. Banner, J. Stimmell,
    L. Philips
    IEEE Trans. Magnetics, MAG-13, p. 346 (1977)

8) K.W. Zieher
    private communication

9) J.P. Turneaure, I. Weisman
    J. Appl. Phys. 38, p. 4417 (1968)

10) H. Padamsee, private communication

11) e.g. W.J. McTegart,
    The electrolytic and chemical polishing of metals, Pergamon Press (1959)

12) W.J. McTegart, R.G. Vines
    Trans. Aust. Inst. Metals 5, p. 107 (1952)

13) J. Edwards,
    J. Electrodep. Tech. Soc. 28, p. 133 (1952)

14) V. Sorajic,
    Metalloberflächen - Angewandte Elektrochem. 27, p. 80 (1973)

15) J. Votruba
    private communication

16) H. Lengeler
    private communication

17) H. Diepers, O. Schmidt, H. Martens, F.S. Sun
    Phys. Lett. 37A, p. 139 (1971)

18) M.L. Kinter, I. Weisman, W.W. Stein,
    J. Appl. Phys. 41, p. 828 (1970)

19) Gmelin Handbuch der Anorganischen Chemie, Band 49 "NIOB"

20) D. Günzel, L. List
    private communication

21) J. Pagetti, J. Talbot
    Corrosion-Traitements-Protection-Finition 15, p. 171 (1967)

22) e.g. M. Grundner
    KfK-Bericht 2565, Kernforschungszentrum Karlsruhe (1977)
    M. Grundner, J. Halbritter
    J. Appl. Phys. 51, p. 397 (1980)

23) G. Beranger, P. Boisot, P. Lacombe, G. Amsel, D. David
Revue de Physique Appliquée 5, p. 383 (1970)

24) H. Martens, H. Diepers, R.K. Sun
Phys. Lett. 34A, p. 439 (1971)

25) P. Kneisel, O. Stoltz, J. Halbritter, H. Diepers, H. Martens, R.K. Sun
Proc. of the 8th Intern. Conf. on High Energy Accelerators, p. 275
CERN, Geneva (1972)

26) P. Kneisel, O. Stoltz, J. Halbritter
J. Appl. Phys. 45, p. 2296 (1974)

27) H. Pfister et al.
private communication

28) H. Padamsee
"Heat Transfer", this workshop

29) A. Citron, G. Dammertz, M. Grundner, L. Husson, R. Lehm,
Nucl. Instr. and Methods 164, p. 31 (1979)

30) J.P. Turneaure, N.T. Viet
Appl.Phys. Lett. 16, p. 333 (1970)

31) P. B. Wilson, Z.D. Farkas, H.A. Hogg, E.W. Hoyt,
IEEE Trans. Nucl. Sci. NS-20, p. 104 (1973)

32) H. Padamsee, M. Banner, J. Kirchgessner, M. Tigner, R. Sundelin,
IEEE Trans. Magnetics. MAG-15, p. 602 (1979)

33) K. Schnitzke, H. Martens, B. Hillenbrand, H. Diepers
Phys. Lett. 45A, p. 241 (1973)

34) H. Martens, H. Diepers, R.K. Sun
Phys. Lett. 44A, p. 213 (1973)

35) P. Kneisel, C. Lyneis, J.P. Turneaure,
IEEE Trans. Nucl. Sci. NS-22, p. 1197 (1975)

36) U. Klein, D. Proch, H. Lengeler
Report WU B 80-16, Gesamthochschule Wuppertal (1980)

37) Ph. Bernard, G. Cavalleri, E. Chiaveri, E. Haebel, H. Heinrichs, H. Lengeler
E. Picasso, V. Picciarelli, H. Piel
Proc. of the 11th Intern. Conf. on High Energy Accelerators, CERN, Geneva (1980)

38) Sh. Noguchi, Y. Kojima, J. Halbritter
submitted to Nucl. Instr. and Methods (1980)

39) P. Kneisel, H. Padamsee
CLNS-Report 79/433, Cornell University (1979)

40) G. Arnolds, H. Heinrichs, W. Hoffmann, R. Mayer, N. Minatti, H. Piel,
D. Proch, W. Weingarten
J. Appl. PHys. 47, p. 1134 (1976)

41) V. Lagomarsino, G.Manuzio, R. Parodi
8th Intern. Cryogenic Engeneering Conf., Genova, Italy (1980)

42) T. Furuya, K. Hosoyama, T. Kato, Y. Kojima, O. Konno
Proceedings of the 1979 Linear Acc. Conf., Brookhaven (1979)

43) J. P. Turneaure, H.A. Schwettman, H.D. Schwarz, M.S. McAshan
Appl. Phys. Lett. 25, p. 247 (1974)

44) M. Strongin, H.H. Farrell, H.J. Halama, O.F. Kammerer, C. Varmazis,
J.M. Dickey
Part. Acc. 3, p. 209 (1972)

45) H. Pfister
Cryogenics 16, p. 17 (1976)

46) C.M. Lyneis,
    private communication

47) H. Lengeler
    private communication

48) H. Padamsee
    private communication

49) A. Joshi, M. Strongin
    Scripta Metallurgica 8, p. 413 (1974)

    A. Joshi, C. Varmazis, M. Strongin
    "Role of Carbon and Oxygen Interaction on Grain Growth and Purification
    of Niobium", BNL-Report, Brookhaven

50) H. Pfister et al.
    private communication