

SURFACE CONDITION OF NIOBIUM FOR SUPERCONDUCTING RF CAVITIES†

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In recent years superconducting rf cavities with extremely small losses have become important for linear electron accelerators and rf beam separators. Niobium appears to be the most favorable metal for these devices; however, the rf field at which 'breakdown' to the normal state occurs is much lower than expected and it is probable that this effect is related to the surface condition of the niobium. In this paper we review previous work in this area, and we present our own measurements. We have made low energy electron diffraction measurements of surface oxides, and Auger spectroscopy has been used to study the amount of surface impurities. Our Auger results show that upon cooling niobium from high temperature treatments, significant amounts of oxygen migrate to the surface. A simple calculation has been made for how surface impurities can influence the value of the 'breakdown' fields, and some ways of protecting the niobium surface with high T_c superconductors are also discussed.

1. INTRODUCTION

In recent years niobium cavities have been shown to have great promise for superconducting rf devices such as linear accelerators and rf beam separators. It has been found that the highest Q 's and surface critical fields are attained in cavities that are treated at high temperatures, above 1800 °C, in an ultra high vacuum furnace.¹ By the combination of firing and chemical or electropolishing, Q values of about 10^{10} which are adequate for practical devices are now commonly obtained at all microwave frequencies investigated. One of the main limitations on the usefulness of superconducting Nb cavities is the lowered value of H_{c1} , the critical magnetic field for flux entry, at rf frequencies. The highest rf critical magnetic fields measured in superconducting cavities at 1.8 °K at various frequencies are as follows: L -band 300 Oe, S -band 550 Oe, and X -band 1000 Oe.

The above achievements are primarily due to four processes taking place during high temperature firing, i.e.,

1. evaporation of oxides from the surface—in particular the metallic NbO,

2. lowering the overall oxygen concentration,
3. thermal polishing,
4. enhanced grain growth.

Due to the highly reactive nature of Nb, both the Q and the peak fields are susceptible to deterioration when the cavities are exposed to the atmosphere or when operated at poor vacuum. Consequently, some protective surface films are needed for practical devices. So far only Nb_2O_5 has been investigated^{2,3} but was found inadequate for the protection of S -band cavities kept at room temperature for a long time.³ It should be pointed out, however, that Diepers and Martens observed no aging in X -band TE_{011} cavities even when exposed to air. These cavities were not heat treated in a UHV furnace but were electropolished and anodized with 3000 Å of Nb_2O_5 . Additional degradation in Q takes place when anodized cavities are irradiated.³

In order to gain more understanding of the above problems, we intend to review what is known about the interaction of Nb surfaces with oxygen and nitrogen, and present our own work on low energy electron diffraction (LEED), and Auger spectroscopy studies of these surfaces.⁴ From these measurements we have been able to study the structure of oxide surface layers, and Auger spectro-

† This work was performed under the auspices of the U.S. Atomic Energy Commission.

scopy measurements allow the determination of surface contaminants to less than $\frac{1}{10}$ of a monolayer.

We have also made preliminary studies of Nb_3Sn layers on the surface,⁵ and this work will be discussed along with the possibilities of other surface coverages such as Nb_3Al and the pentoxide already mentioned.

2. DEGASSING OF NIOBIUM

a. Some General Remarks

The purpose of this section is to give some idea of what factors determine the degassing of niobium and what conditions are necessary to attain oxygen-free surfaces. Oxygen is removed from niobium at high temperatures principally in the form of NbO and NbO_2 . This is true even when the concentration of oxygen in the niobium is too low for actual oxides to precipitate out on the surface or along grain boundaries. Dissolved oxygen that migrates to the surface combines with niobium atoms prior to evaporation in the form of diatomic or triatomic oxide molecules. In general, two major factors can limit the degassing of metals. First, the rate of diffusion of dissolved oxygen to the surface, and secondly, how rapidly the impurities at the surface are removed. It should be emphasized that the surface is a unique situation and it cannot be simply treated as bulk material which has been cut off. Oxide structures form on the surface and the amount of these oxides depends on both the concentration of oxygen in the bulk, and also the partial pressure of oxygen or water vapor in the vacuum chamber, which determines the equilibrium bulk concentration. The general solution of this problem is quite complex since it involves solutions of the diffusion equation in the bulk with a boundary condition at the surface which will depend on the vapor pressure of the oxide at the surface, which in turn depends on the concentration and the vacuum chamber pressure. We will not attempt to solve this general problem, but we will consider the simple cases where we are diffusion limited, i.e. any oxygen which reaches the surface comes off rapidly, and the other limit where degassing is limited by the rate of gas removal from the surface at different equilibrium concentrations in the bulk and where there is relatively rapid diffusion to the surface.

At the high temperatures necessary for removing oxide structures we will find that the oxygen concentrations in the bulk are essentially uniform, and the evaporation of the oxide from the surface determines the rate of gas removal.

b. The Diffusion Limited Case

As mentioned above, we initially consider the simple case of how gaseous impurities will be removed from a Nb sample at various temperatures in the case of a diffusion limited process. We emphasize that this is not the actual case for how oxygen is removed from Nb and this argument is meant to give some physical insight into the various factors. This process will involve the solution of the diffusion equation

$$D\partial^2 C/\partial X^2 = \partial C/\partial t \quad (1)$$

with the boundary condition that at the surface the concentration $C = 0$. The boundary condition that $C = 0$ implies that all gaseous impurities that reach the surface are removed from the sample. For a semi-infinite medium the solution is relatively simple and is given by

$$C = C_0 \operatorname{erf} \frac{X}{2\sqrt{Dt}}. \quad (2)$$

At $X = 0$, $\operatorname{erf} = 0$ and hence the boundary condition is satisfied. In the case of a slab of thickness $2l$ the solution is given by

$$C = \frac{4C_0}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{2n+1} \exp \frac{-D(2n+1)^2 \pi^2 t}{4l^2} \cdot \cos \frac{(2n+1)\pi X}{2l} \quad (3)$$

in Carslaw and Jaeggers,⁶ the function is evaluated for various values of Dt/l^2 . Note that the boundary is at $X = l, -l$ for the above equation. When $Dt/l^2 = 1$, the concentration in the center of the sample is above 0.11 of the initial concentration. It is of some value to compute these times for various temperatures and sample dimensions.

The diffusion coefficient for oxygen in Nb is given by Pasternak⁷ as $D = 0.0212 \exp[-(26910/RT)]$ (cm^2/sec). Values computed from this formula have been used to compute Table I.

TABLE I

$T^{\circ}\text{C}$	$T^{\circ}\text{K}$	$D \left(\frac{\text{cm}^2}{\text{sec}} \right)$	$t = \frac{l^2}{D} \text{ (sec)}$
1600	1873	1.61×10^{-5}	621
1700	1973	2.3×10^{-5}	435
1800	2073	3.2×10^{-5}	313
1900	2173	4.34×10^{-5}	230
2000	2273	5.7×10^{-5}	175

The time in the last column is for a sample of width $2l = 0.2 \text{ cm}$ and is given by the condition $Dt/l^2 = 1$, and $C \sim 0.11 C_0$.

It can be seen from Table I that the time to reduce the concentration of impurities at the center of a sample 0.2 cm thick to about 10 per cent of its original value is about 300 sec at 1800°C . The time for larger samples will go as l^2 . To find out how rapidly the concentration changes for large times, it is easiest to use our previous approximation for a semi-infinite medium where $C = C_0 \text{erf } X/2\sqrt{Dt}$. For small values of the argument β , $\text{erf } \beta \rightarrow 2\beta/\sqrt{\pi}$. Hence to reduce the concentration another factor of 10 to say 1 per cent of the original concentration would require something like 100 times the time as the initial factor of ten. The samples used in our LEED investigations were about 0.02 cm thick. Hence, in the diffusion limited case, in only about 3 sec at 1800°C we should have 1/10 of the initial concentration of, probably about 0.1 a/o oxygen (the abbreviation a/o is used for atomic per cent), and in about 300 sec we should be down to about 0.001 a/o oxygen. At this high temperature we emphasize that the amount of impurity at the surface is fairly small. However, upon cooling, the surface concentration will increase and this will be estimated later. For an rf cavity of wall thickness of about 0.5 cm the times will clearly be much longer.

c. Evaporation of Oxides from the Niobium Surface

In this section we discuss the rate at which oxygen is removed from the surface, assuming bulk diffusion is rapid. Actually we will show that this limit is a good approximation to the actual degassing of Nb. First, it is well to mention that the oxygen producing reactions such as $\text{NbO} \rightleftharpoons \text{Nb} + 1/2 \text{O}_2$ and $\text{NbO}_2 \rightleftharpoons \text{Nb} + \text{O}_2$ are negligible. Formulas for the pressures given in Pasternak⁷ yield at 1800°C , $5.8 \times 10^{-12} \text{ torr}$ for the oxygen partial pressure in the first reaction and about $4 \times 10^{-11} \text{ torr}$ for the second reaction. Data are also given for the pentoxide, which give about $1 \times 10^{-10} \text{ torr}$ at this temperature. These low pressures agree with the mass spectrographic data of Rovner *et al.*,⁸ and show that oxygen is not appreciably removed from the sample as O_2 . At high temperatures the oxygen is essentially removed as the diatomic molecule NbO . This is shown in the work of Rovner *et al.*,⁸ where they also give the rate of NbO removal as $Z = K_3 C$ and for NbO_2 removal $Z_2 = K_4 C^2$. Z is essentially the number of atoms per unit area per unit time coming off the surface and the constant K_3 has units of centimetres/second. We mention that at high concentrations NbO_2 evaporation is an important process, but at low concentrations it is sufficient to assume that the rate of oxygen removal from the surface goes as $Z = K_3 C$ and that the NbO_2 process is negligible. For Nb, K_3 is given as $\log K_3 = 10.98 - 3.5 \times 10^4/T$ and $\log K_4 = 9.64 - 3.56 \times 10^4/T$. In Table II we show how much NbO will come off at higher temperatures.

The easiest way to estimate how long it will take to reduce the concentration to 10 per cent of its original value is to write the rate equation for gas leaving the surface as $dC/dt = -K_3 C/l$. Where $2l$ is the sample thickness and it is assumed that

TABLE II

$T^{\circ}\text{C}$	$T^{\circ}\text{K}$	$\log K_3$	$\log C$	$\log Z$	$Z \left(\frac{\text{a/o cm}}{\text{sec}} \right)$	$Z \left(\frac{\text{atoms}^{\dagger}}{\text{cm}^2 \text{sec}} \right)$
1800	2073	-5.90	-1	-6.90	1.2×10^{-7}	6.72×10^{13}
1900	2173	-5.12	-1	-6.12	7.6×10^{-7}	4.26×10^{14}
2000	2273	-4.42	-1	-5.42	3.8×10^{-6}	2.13×10^{15}

[†] 1 a/o = 5.6×10^{20} atoms/cc

gas is coming off from two surfaces

then

$$t = -\frac{l \ln C_0/C}{K_3}. \quad (4)$$

Where $l \sim 0.1$ cm and we take $C_0/C = 10$

then

$$t = 2.3 \times 10^{-1}/K_3.$$

It is clear from Table III that the times for the monoxide leaving the surface are much longer than the times calculated for the diffusion limited case.

TABLE III

T °C	t (sec)
1800	1.9×10^5
1900	3.02×10^4
2000	6.1×10^3

Hence the best approximation is that the removal of oxygen is limited by the rate of oxide evaporation and therefore the distribution of oxygen in the sample during the degassing process is that of a relatively uniform concentration, which drops as the oxide comes off from the surface. It is well to point out that the results of Rovner *et al.* show that at relatively high concentrations at 1800 °C, NbO_2 comes off at about the same rate as NbO , and at 2000 °C NbO comes off at about 10 times the rate for the dioxide. Since the flux goes as the second power of the concentration for NbO_2 and the first power for NbO it is clear that for low oxygen concentrations, which is the case we are interested in, NbO will be the major component. Hence the times we have calculated are sufficiently accurate to estimate the time necessary to degas Nb. To achieve $C_0/C = 100$, twice as much time is required as for $C_0/C = 10$.

d. Some Remarks About the More General Case

From the preceding sections it is clear that we are in the case where oxygen removal is evaporation limited. We can describe this somewhat more formally by defining a dimensionless parameter $L = \tau_D/\tau_E$. For $L \leq 1$ then $\tau_E > \tau_D$ and we get the evaporation limited case. For $L \geq 1$ we have the diffusion limited case. Besides some small numerical factors we can write $\tau_D = l^2/D$ and τ_E , which we define as the time for the oxygen concentration to

drop to 0.1 of its original value, due to evaporation of NbO is given by $\tau_E = 2.3l/K_3 = l/\alpha$. Then $\tau_D/\tau_E = l\alpha/D$. We can then see from Table IV that $L \leq 1$ for the cases we are interested in.

TABLE IV

T °C	D (cm ² /sec)	α (cm/sec)	$L = l\alpha/D$
1800	3.1×10^{-5}	5.25×10^{-7}	$1.7 \times 10^{-2}l$
1900	4.1×10^{-5}	3.3×10^{-6}	$8.1 \times 10^{-2}l$
2000	5.5×10^{-5}	1.6×10^{-5}	$3 \times 10^{-1}l$

It is clear from the table that for wall thicknesses $2l$ of about 0.5 cm, $L \ll 1$.

e. Steady-State Concentrations at Various Pressures

To compute the steady-state concentration of oxygen at various pressures we have constructed Table V. The steady-state concentrations at various pressures are calculated from the results of Fromm and Jahn⁹ that

$$\log C_0 = \log P_{\text{O}_2} - 3.35 + 16,700/T$$

It is easily seen from Table V that at 10^{-6} torr the steady-state concentrations are quite high, and

TABLE V

T °C	T °K	$P = 10^{-6}$ torr	$\log C$	$P = 10^{-8}$ torr	$\log C$	$P = 10^{-9}$ torr	$\log C$
1600	1873		-0.43		-2.43		-3.43
1700	1973		-0.89		-2.89		-3.89
1800	2073		-1.29		-3.29		-4.29
1900	2173		-1.66		-3.66		-4.66
2000	2273		-2		-4		-5

it will be seen later that this will lead to almost complete oxide layers when the sample is cooled down. At 10^{-8} torr and at 1800 °C, which approximates the usual conditions in furnaces for annealing cavities the steady-state concentrations will be of the order of 0.001 a/o. We will show later that even this can lead to significant surface coverage when the sample is cooled. However, we emphasize that large times are necessary to achieve this small steady-state value, in fact, larger than those commonly used. This point will be discussed later. We mention that the steady-state concentrations computed here check fairly well with the mass spectrographic data of Rovner *et al.*⁸

f. Equilibrium Between Surface and Bulk Concentrations

The next factor to be considered is the equilibrium between the surface and the bulk. For reasonably clean surfaces attained after heating in ultra high vacuum and oxygen concentrations of about 0.01 a/o one might have expected a negligible fraction of a monolayer on the surface; this is probably not the case. The problem we want to consider here is how much oxygen will eventually find its way to the surface when the sample is cooled in high vacuum after a given heat treatment. The problem of the distribution coefficient between the surface and the bulk has been studied by Pasternak and Evans.¹⁰ While our LEED measurements, to be described later, do not confirm their model of two surface species, we can essentially take over their expression for the distribution coefficient between the surface and the bulk, and write that the fraction of empty sites on the surface defined as θ_0 goes as

$$\theta_0 = \frac{1}{1 + K_2 C}, \quad (5)$$

where K_2 is the distribution coefficient and C is the concentration in atomic per cent. This result can easily be derived by writing down the equilibrium between the surface layer and the bulk. For instance, the steady state between surface oxygen and oxygen in the bulk is given by the equation that oxide at surface $\xrightleftharpoons[v_-]{v_+}$ oxygen in bulk.

where $v_+ = k_+ \theta_2 (1 - C) \sim k_+ \theta_2$

and $v_- = k_- C \theta_0$.

k_+ and k_- are the rate constants in the two directions, θ_0 and θ_2 are the fraction of clean sites and occupied surface sites, and C is the bulk concentration in atomic per cent. In the steady-state $k_- C \theta_0 = k_+ \theta_2$, and $\theta_2/\theta_0 = (k_-/k_+) C = K_2 C$. Since $\theta_2 = 1 - \theta_0$ we have $(1 - \theta_0)/\theta_0 = K_2 C$ or $\theta_0 = 1/(1 + K_2 C)$. From Pasternak and Evans¹⁰ K_2 is given as

$$K_2 = K_0 \exp [27,000 \text{ cal/mole/RT}].$$

An evaluation from their data yields a value of $K_0 = 2.88 \times 10^{-4}$ a/o. Our data which we will briefly discuss later give a somewhat smaller value for the argument of the exponential.

Even with this result it is still difficult to estimate how much oxygen will migrate to the surface during cooling. If one evaluates K_2 for a sample at room temperature (probably an unreasonable extrapolation) then it appears that K_2 is very large and there will then be a large amount of oxygen at the surface. However at lower temperatures the diffusion times become large and the oxygen stays in the bulk. A reasonable estimate of how much oxygen will migrate to the surface during cooling can be attained by assuming rapid diffusion down to about 800 °C. At this temperature $K_2 = 83$. Then the fraction of empty surface sites is $\theta_0 = 1/(1 + 83C)$. Hence at 0.1 a/o there will be about 10 a/o empty sites and at 0.01 a/o there will be about 50 a/o empty sites. Note that at 1800 °C, $\theta_0 = 1/(1 + 0.2C)$. Hence with 0.1 a/o in the bulk there will be about 98 a/o empty sites at the surface or about 2 a/o impurities. Thus upon cooling from 1800 °C to about 800 °C with 0.1 a/o oxygen in the bulk the concentration at the surface will go from 2 a/o to 90 a/o, at 0.01 a/o the concentration at the surface will go from about 0.2 a/o to 50 a/o and finally at 0.001 a/o the surface concentration will go from 0.02 a/o at 1800 °C to about 10 a/o upon cooling. For a clean surface it is clearly necessary to reduce the bulk concentration to about 0.001 a/o. In the above discussion we have considered along with Pasternak and Evans that any oxygen that goes to the surface is in a monolayer at the surface. This does not have to be the case and there is probably a gradient of oxygen in the surface regime as the concentration falls from the surface to the bulk amount. Also during a rapid cooling cycle, oxygen that was migrating to the surface could be frozen in the surface regime in larger than equilibrium amounts. At present we have no way of estimating the size of this regime, but we expect that a region of the order of a couple of hundred angstroms will be very important to the rf properties. This will be discussed later in the section on Auger spectroscopy where we will briefly discuss some estimates of the size of this diffusion regime.

3. THE EFFECT OF RESIDUAL NITROGEN

In the previous section our main interest has focused on the removal of oxygen from niobium.

Oxygen appears to be the major concern for the reasons which follow. The problem appears to be not so much the removal of impurities from the bulk metal, but the removal of impurities from the surface regime. In the case of oxygen the heat of 'adsorption' to the surface is much higher than the heat of solution,¹⁰ whereas for nitrogen impurities the heat of 'adsorption' is comparable to the heat of solution. Hence, the discussion of the previous section would lead one to believe that much more oxygen would be left in the surface regime, which, of course, is the important consideration in the performance of rf cavities. From a recent discussion of Meyerhoff¹¹ one would expect slightly more nitrogen impurities in the bulk niobium than oxygen since the steady-state concentration at low pressures seems to be slightly higher. Although within any reasonable error one can consider the residual bulk concentrations of oxygen and nitrogen to be about equal.

We emphasize that nitrogen removal rates under the heating conditions that we have discussed should be comparable to oxygen removal. The dynamics of nitrogen removal will not be discussed here, but it appears to be somewhat different than the oxygen case. First the diffusion constant for nitrogen is somewhat lower. At 1800°C for $l \sim 0.1$ cm we calculate for nitrogen in niobium that $D \sim 1.84 \times 10^{-6}$ cm²/sec and $t = l^2/D \sim 5000$ sec. For oxygen we have that $D \sim 3.1 \times 10^{-5}$ cm²/sec and $t \sim 326$ sec. However the longer diffusion times for nitrogen does not appear to be particularly important since we have previously mentioned that oxygen removal is governed by the low NbO flux from the surface and characteristic times are more like 10⁵ sec for oxygen removal. According to Pasternak, Evans, and Bergsnov-Hansen¹² the rate for nitrogen removal appears to be faster than this. Also we emphasize again that nitrogen does not appear to form large surface concentrations as oxygen does, and in general it appears that nitrogen is probably not a problem in cavity performance.

4. LEED AND AUGER SPECTROSCOPY STUDIES OF THE Nb SURFACE

Low energy electron diffraction is a technique that can yield the structure of the surface layers of a metal.¹³ Because of the energy range of the elec-

trons, from about 10 eV to 500 eV, the electrons penetrate into the sample a few monolayers, and so the diffraction patterns that are obtained are characteristic of these surface layers. Initial studies of the types of surface structures of Nb have been made and in general the LEED studies allow some estimates to be made about the condition of the Nb surface. We have studied the (100) face of Nb and the structures that have been identified can in principle be different for other surfaces. Our analysis of work by Haas, Jackson and Hooker¹⁴ on the (110) surface indicates that essentially the same oxides are forming on this surface and hence it is probable that the structural identification given here will also be characteristic of the large grain polycrystalline surfaces used for rf cavities. Of course, after heating for an adequate time near 1900°C the diffraction pattern of the clean Nb is evident as shown in Fig. 1. If the

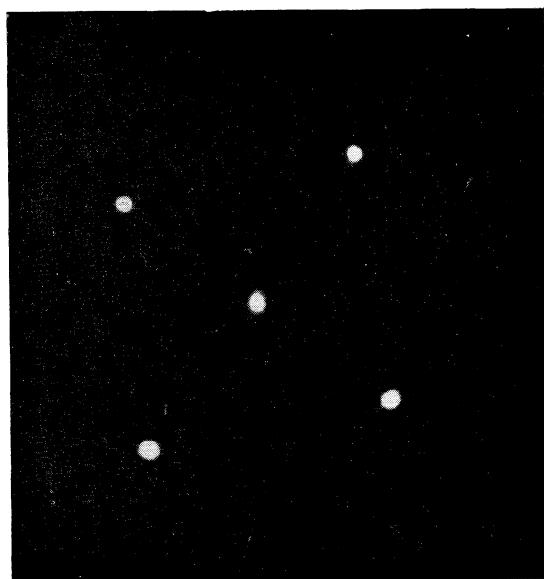


FIG. 1. Low energy diffraction pattern of clean (100) niobium surface.

sample is not completely degassed and the initial heating is from about 1500–1800°C we find that an NbO-like structure is evident on the surface as illustrated in Fig. 2 (top). Strictly speaking this compound is not bulk NbO but a specific surface compound whose lattice parameters, and probably

other properties are somewhat different. When NbO is mentioned on the surface we are referring to this compound. Since bulk NbO is a semimetal with a T_c of ~ 1 °K this can possibly be a factor in lowering the Q of microwave cavities. If the sample is initially heated in the 800 to 1500 °C range

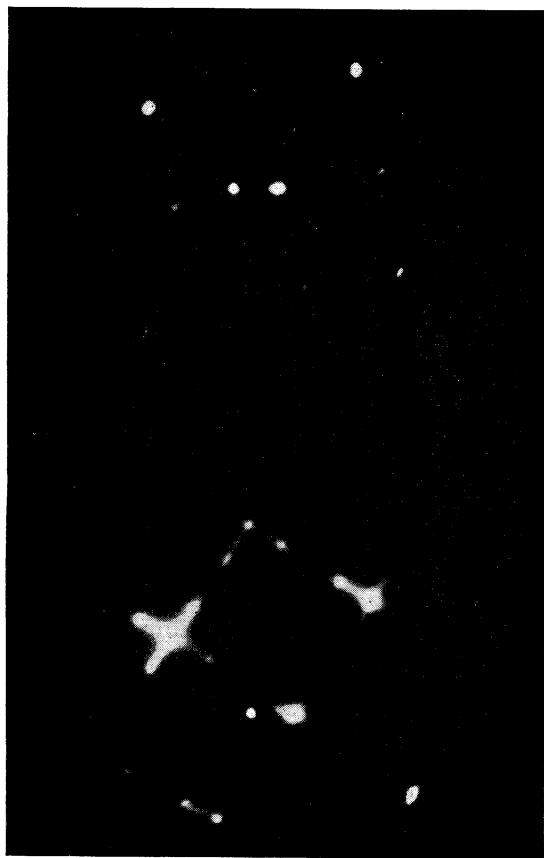


FIG. 2. (Top) Diffraction pattern characteristic of NbO-like structure can be seen as faint spots between more intense spots characteristic of clean Nb. (Bottom) Structure showing faceted structure on surface.

without adequately removing all the oxygen, then a faceted structure is evident, as shown in Fig. 2 (bottom). The diffraction studies of this structure indicate that the satellite spots do not move together with the central spot which implies that there are regions about a few hundred angstroms in extent that are not parallel to the surface. This kind of structure implies an increased surface roughness and can possibly lead to electric and

magnetic field breakdown. Finally, if the sample is initially only heated to a few hundred °C an amorphous structure is seen, indicating that the initial adsorbed oxygen is still on the surface. It should be emphasized at this point that the LEED measurements are made after cooling the sample to room temperature. At the high temperatures used for annealing, atomic motion smears out the diffraction patterns, so that the structures cannot be seen.

Another problem of interest in estimating the condition of Nb cavities after degassing, is the following. Suppose the cavity is heated for a long time at 1800 °C or higher at a pressure near 10^{-8} torr. Upon cooling the sample, gas atoms from the vacuum chamber will hit the surface and will form oxide structures. For example, at 10^{-8} torr about one monolayer of gas will hit the surface every four minutes. Hence if the cavity is slowly cooled from its annealing temperature at this pressure, oxides will form on the surface. We have tried to simulate this condition in the following way. Samples were heated for 1 min at different ambient pressures at 1850 °C. For our sample which was about 0.01 in. thick the diffusion time calculated from I^2/D is of the order of seconds (see Table I), at about 1800–1900 °C. Hence over this heating period we can expect a uniform oxygen concentration, except for the surface regime. We estimate the bulk concentration to be about 0.01 a/o or less after the initial heating (see Table V). This initial heating simulates the cleaning stage used in cavity preparation. Of course the actual cavity wall thicknesses are much greater than the sample thickness used here and longer times are required than those estimated here. The sample was then heated at different ambient oxygen pressures at different temperatures from say, 1000 to 1850 °C. This was done to simulate the cooldown period during cavity preparation. As soon as the heating period was over, the chamber was pumped out rapidly to ultra high vacuum conditions, i.e., pressures below 5×10^{-9} torr. At this point the sample was cooled to room temperature and the LEED pattern was observed. We assumed that once the pressure was below 5×10^{-9} torr little gas would collect on the surface in the observation time and that any structures which were observed were formed during heating in the 1000 to 1850 °C range at higher

TABLE VI

Heating	Pressure of O ₂ (torr)	Temperature °C	Condition after heating
1 min	3×10^{-8}	1850	clean (very very weak smearing)
1 min	3×10^{-8}	1850	
then 1 min	3×10^{-8}	950	weak faceting
1 min	3×10^{-8}	1850	{weak NbO-like structure
then 3 min	3×10^{-8}	950	{some faceting
1 min	3×10^{-8}	1850	
then 3 min	3×10^{-8}	~950	NbO stronger, some faceting
1 min	3×10^{-8}	1850	
then 5 min	3×10^{-8}	~950	NbO stronger and faceting

pressures, or were formed by oxygen coming to the surface as discussed earlier.

In Table VI we also show a summary of the LEED observations when the sample is heated in an oxygen pressure of 3×10^{-8} torr. At 10^{-7} torr similar experiments showed even stronger oxide structures. It is clear from Table VI that as the final heating temperature is lowered the oxide structures are observable and become stronger as the time is increased. We think this roughly simulates the cooling of the cavity after it is heated to 1850 °C. The above experiments show that even at 3×10^{-8} torr of O₂ at 950 °C oxide structures are formed. Hence a cavity cooling from its heat treatment temperature of 1850 °C will pick up oxide structures either from the bulk or from gas in the chamber with $P \sim 3 \times 10^{-8}$. To avoid part of this problem O₂ pressures near 10^{-9} torr are necessary during cooldown, since at this pressure about 1 monolayer of gas will hit the sample surface in 40 min. This will minimize impurities from the chamber. However there is still the problem discussed earlier of the bulk impurities coming to the surface.

To summarize, heating in high vacuum, 10^{-8} torr or below, and high temperatures will reduce the concentration of gas in the bulk and at the surface. See Table V for the steady-state concentrations. However upon cooling there is still the possibility that at lower temperatures oxide structures will form and persist due to the residual gas in the chamber and from oxygen coming from the bulk metal. It is clear that cooling must be done in ultra high vacuum and the bulk impurity content must be as low as possible for a clean surface.

5. AUGER STUDIES OF SURFACE OXYGEN CONCENTRATION

The total amount of oxygen on the Nb surface can be studied by Auger spectroscopy. In this technique one observes the inelastically scattered electrons after bombarding the sample with energies near 1500 eV. These incident electrons knock electrons out of the inner shells of the metal. When this happens an electron drops down from the conduction band, and to conserve energy an electron or X-ray is emitted with the energy characteristic of this transition. By energy analyzing the electrons that come back, one can determine what elements are on a surface in amounts of less than 0.1 monolayers. In Fig. 3 we show an Auger

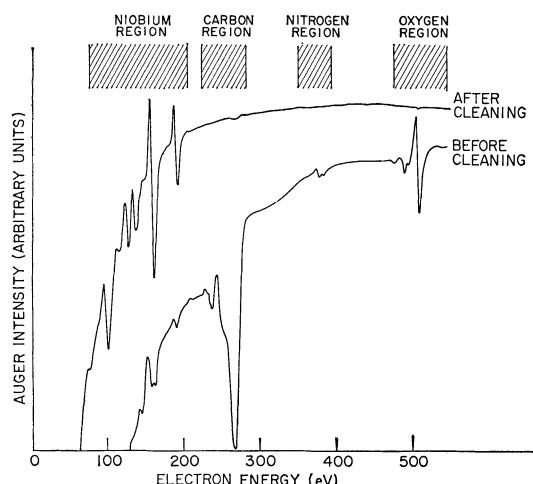


FIG. 3. Characteristic Auger spectra of clean niobium and dirty niobium surface. The dirty surface corresponds to sample surface as initially put into the vacuum system.

trace of Nb before cleaning. After moderate cleaning small carbon, nitrogen and oxygen peaks are observed and of course the characteristic Nb lines. The Auger spectra shows that after heating for sufficient time under high vacuum conditions a clean surface is finally attained, and the Auger measurements of the conditions necessary to attain the clean surface agree with LEED and mass spectroscopic data.

By Auger spectroscopy we have also been able to study the amount of gases that diffuse to the surface as the sample is cooled. In Fig. 4 Auger traces are shown for a sample heated to about 1370 °C at 3×10^{-8} torr of O₂. While hot, the Auger pattern shows that the oxygen concentration on the surface is less than 1/10 of a monolayer. This is reasonable

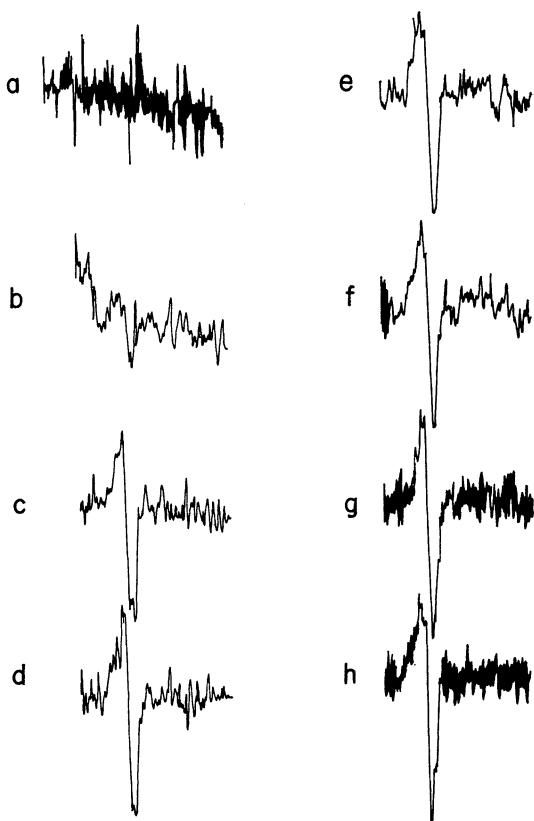


FIG. 4. Oxygen line in Auger spectra as a function of time after heating. Sample was initially heated for 17 min at $P \sim 3 \times 10^{-8}$ torr. (a) 9 min into heating cycle at $T \sim 1400$ °C, (b) 15 sec after heating cycle, $P \sim 3 \times 10^{-9}$ torr, (c) 30 sec after heating, (d) 45 sec, (e) 70 sec, (f) 150 sec, (g) 220 sec, and (h) 660 sec.

for the following argument. First at 1370 °C and a pressure of O₂ of 3×10^{-8} torr the equilibrium oxygen concentration from the formula given previously is about 0.1 a/o and the surface distribution coefficient K_2 is 1. The fraction of empty sites on the surface should then be ~ 0.9 . Hence with our sensitivity of about 0.1 monolayers, this would be just about the noise level and we would not expect to see an oxygen peak. Actually the clean sample should have had less than 0.1 a/o oxygen, which would also yield a smaller amount of oxygen on the surface. In this experiment the sample was heated for 17 min at about 1370 °C which is not enough time from previous estimates to reach the equilibrium concentration of about 0.1 a/o at 3×10^{-8} torr. It is interesting that even at this relatively low pressure a clean sample will absorb gas from the system, at this temperature. Upon cooling, the curves in Fig. 4 show almost a monolayer of oxygen is detectable in about 45 sec. This indicates diffusion from the bulk to the surface. At the ambient pressure of about 3×10^{-9} torr a monolayer of gas can hit the surface in about 12 minutes. Thus even with a sticking coefficient of unity there is not enough gas hitting the sample to account for the rapid build-up of oxygen on the surface. If we assume as before that rapid diffusion will occur down to about 1000 °C we get a surface distribution coefficient of about 11. Hence from $\theta_0 = 1/(1+K_2C)$ there should be about $\frac{1}{2}$ a monolayer of oxygen at the surface in agreement with our results. Of course if there was diffusion to 800 °C the distribution coefficient would be ~ 90 yielding about 0.9 monolayers of oxygen. Since we do not know the details of the cooling rates and where rapid diffusion stops we can only make rough estimates which appear to be in agreement with the Auger measurements. In the preceding discussion it was implied that the oxygen at the surface is concentrated in a monolayer. This may not be the case and it is possible that during cooldown oxygen is 'frozen' in a large region near the surface. In fact, the equilibrium oxygen distribution in the surface may extend over many layers before the bulk concentration is reached. If this conjecture is true it might drastically affect cavity performance. We discuss this in a later section.

Using this technique we have also been able to measure how oxygen comes off the surface as a

function of time and while our results are not precise, they are in general agreement with the mass spectrographic results discussed previously.

Finally it is well to mention that by using Auger spectroscopy, we have been able to estimate K_2 in the formula for the fraction of empty sites, i.e., that $\theta_0 = 1/(1+K_2C)$. By heating the sample at 10^{-6} torr of O_2 for about 8 min we should have a bulk concentration of 0.37 a/o. At each temperature we now measure θ_2 from the height of the Auger line and hence K_2 can be calculated at each temperature. Our initial values of K_2 vs. temperature are shown in Fig. 5. These values lie

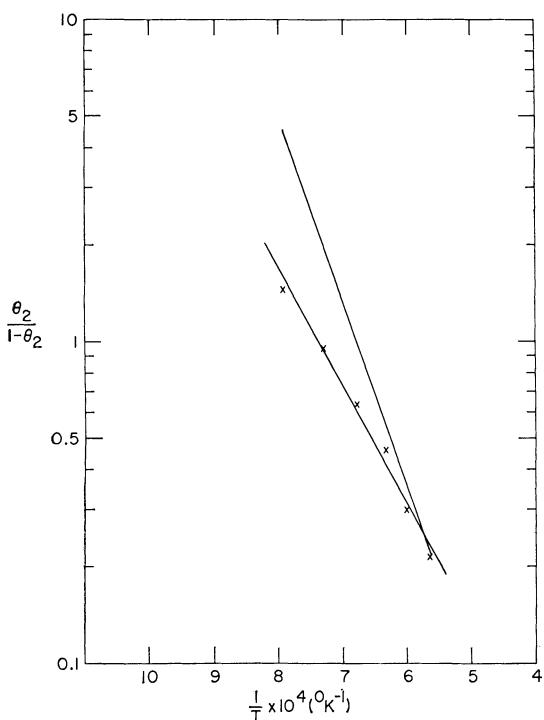


FIG. 5. $\theta_2/(1-\theta_2)$ vs. $1/T$ for oxygen line on niobium surface, where θ_2 is the fraction of filled sites and $\theta_2/(1-\theta_2) = K_2C$.

somewhat below the values of Pasternak although in general the agreement is fairly reasonable. Note we have plotted $\theta_2/(1-\theta_2) = K_2C$, where $\theta_2 = 1 - \theta_0$, and is the number of filled sites.

6. RELATIONSHIP TO THE rf CAVITY PROBLEM

Initial work by Turneaure and coworkers¹ indicates very high quality factors, Q , as well as

high surface magnetic fields (~ 1 kG) in X -band rf cavities. To attain the high values it was found that the cavities had to be heat treated to above 1800°C in high vacuum. Upon cooling the cavities were put in a nitrogen atmosphere, cooled, and measured. As long as the cavities were kept at cryogenic temperatures the high Q 's remained. However unless the cavities were sealed off or used with a high vacuum system the Q 's were degraded upon warmup. Recent measurements on larger cavities operating at S and L bands which were also fired about 1800°C in UHV furnaces show lower surface magnetic and electric fields¹⁵ than those achieved at X -band. At the present time the rf fields in simple cavities appear to be limited by the superconducting to normal transition caused by the formation of normal nuclei.³ This problem will be discussed later. In more complex structures, on the other hand, multipacting or field emission¹⁶ also impose an upper limit on the rf field. In this present work we have studied the conditions necessary to attain a clean surface, however we emphasize that it is not clear what conditions are necessary for the best microwave properties. From the studies that we have made we estimate that the surfaces used in the existing cavities are not completely free of surface oxides and the rf properties of perfect surfaces remain to be studied. We hope to correlate the results from the above studies with microwave measurements in the near future when our high vacuum temperature furnace is installed.

7. MECHANISM FOR DEGASSING A CAVITY

From the previous sections some estimate can be made of the time necessary to clean the inner surface of an rf cavity of some average dimensions. To discuss this problem we write an equation for the change of NbO pressure within the cavity as follows

$$P\gamma + \frac{FP}{kT} - C A K_3 = \frac{dN}{dt} = \frac{V}{kT} \frac{dP}{dt}. \quad (6)$$

The term FP/kT is the rate at which gas leaves the interior of the cavity through the orifice, where F is the pumping speed out of the cavity and into the pumping chamber. C is the concentration of oxygen in the bulk metal in atoms/cm³, A is the

total surface area of the outer and inner surfaces, and K_3 was defined previously as the rate constant for evaporation of NbO from the surface. For a typical cavity A is about 1000 cm^2 , the volume is about 1 liter and $2l$ is about 0.5 cm. The term $P\gamma$ describes the rate at which NbO redeposits on the inner cavity surface. Hence the above equation describes the net change of gas in the enclosed volume of the cavity, as the difference between the net amount of gas coming off the inner surface and the amount being pumped out.

In the case of degassing a cavity we make the approximation that most of the oxygen is lost as oxide from the outer surface, since the pumping speed is higher and the ambient pressure is lower, than for the gas coming off the inner surface of the cavity. We have already indicated that the times for diffusion, at least in the thicknesses we are concerned with, are small compared to the characteristic time for NbO to come off the surface. Hence in this case we can assume a uniform oxygen concentration in the sample. Thus we can write the following expression for the removal of oxygen from the cavity

$$\frac{dC}{dt} = -K_3 C/2l. \quad (7)$$

Hence $C/C_0 = \exp(-K_3 t/2l)$, where C is the number of oxygen atoms per unit volume in the niobium. If we put this into the Eq. (6) we get

$$\frac{dP}{dt} = -\frac{(F+\gamma kT)P}{V} + \frac{[K_3 C_0 A \exp(-K_3 t/2l)] kT}{V} \quad (8)$$

whose solution is

$$P = P_0 \exp[-(F+\gamma kT)t/V] + \frac{K_3 C_0 A kT}{V} \cdot \frac{\exp(-K_3 t/2l)}{-K_3/2l + (F+\gamma kT)/V}. \quad (9)$$

The first term is just the rate at which the initial NbO in the cavity is pumped through the orifice and redeposited on the surface and the second term describes the pressure in the cavity due to the NbO, coming off the wall. In most cases

$$(F+\gamma kT)/V \gg K_3/2l$$

and thus a steady state is achieved where the pressure changes slowly and

$$P \sim [K_3 C_0 A kT/(F+\gamma kT)] \exp(-K_3 t/2l).$$

From our initial equation γP was the number of NbO molecules being redeposited on the surface at pressure P per unit time. In the steady state at pressure P this number must be equal to the flux from the surface neglecting the pumping speed out of the cavity F . By knowing the flux from the wall at say, 0.01 per cent concentration, which from Table II is about $10^{13} \text{ atoms/cm}^2 \text{ sec}$, we can calculate an equivalent steady-state pressure above the surface. The pressure P we calculate at 1800°C is $\sim 1.25 \times 10^{-7} \text{ torr}$. If C_0 is 0.01 a/o we then have $P \sim 10^{-7} \exp(-K_3 t/2l) \text{ torr}$, as the approximate description for how the pressure falls off in the cavity, since the first term will be negligible.

It should be clear that since the pumping speed F is small, the main removal of NbO must take place at the outer surface of the cavity, and the concentration will fall approximately as $\exp(-K_3 t/2l)$. We have indicated previously that this is about 10^5 sec at 1800°C for $l \sim 0.1 \text{ cm}$.

In principle we should have an equation describing any other gases in the cavity where

$$P_0' = P_0' \exp[-(F'+\gamma' kT)t/V],$$

where P_0' is the initial pressure of other gases, F' is the pumping speed out of the cavity and $\gamma' kT$ describes the gas in the cavity redepositing on the metal again. It appears that P_0' will be rapidly reduced and the equation for NbO removal is more important for describing the pressure in the cavity and how rapidly the cavity is degassed.

8. ESTIMATES OF GAS CONTENT AND SURFACE CONDITION FOR A TYPICAL CAVITY TREATMENT

In Fig. 6 we show the heating curve for a cavity used for microwave work in the 3 GHz regime.¹⁷ The pressure on the graph is the pressure in the furnace and we can see from our previous analysis that the pressure inside the cavity, due to NbO, is comparable. If we assume that the pressure measured in the cool part of the chamber is mostly hydrogen, nitrogen, and CO then we would estimate that in the 10^{-7} torr regime, on the heating curve in Fig. 6, the partial pressure of O_2 is in the low 10^{-8} torr

range and O_2 is being removed from the sample as NbO , which should be pumped very effectively by the chamber surface. From Fig. 6 it can be seen that the sample spends about 6 h at $1800^\circ C$ or higher, and as indicated above, it is assumed oxygen is removed during this time. We have

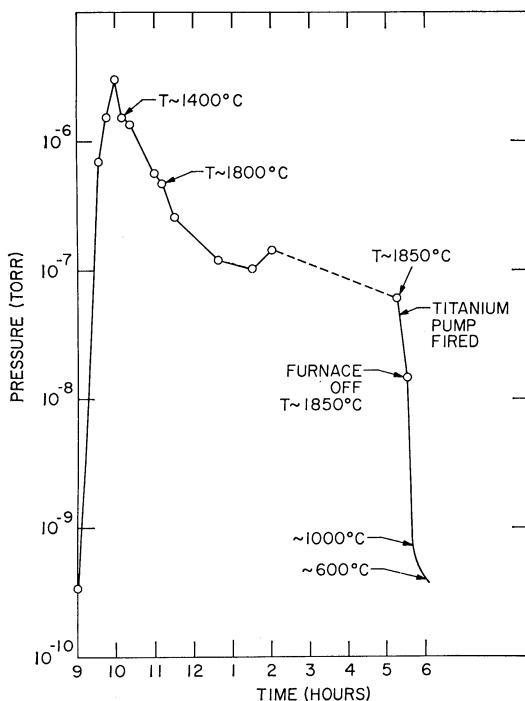


FIG. 6. Heating cycle for a niobium cavity.

calculated a time to reduce the O_2 concentration by 10 of near 10^5 sec at about $1850^\circ C$ (see Table III), and 6 h is not enough time at the lowest pressures; about 30 h would be more reasonable. Finally, Fig. 6 shows that when the furnace is shut off the pressure drops into the low 10^{-9} torr range in about 2 min. If the initial gaseous content in the niobium was about 0.01 per cent then it is probable under the above annealing times that the oxygen content was reduced by a factor of 3 to 10. If the final gaseous content in the Nb was 0.001 a/o, we would expect at least 1 a/o concentration in the surface regime during cooling, and at about 3×10^{-3} a/o we would expect at least 3 a/o oxygen concentration on or near the surface. These numbers are estimated for rapid diffusion to the surface as the cavity cools through $1000^\circ C$. If rapid diffusion can occur down to say $800^\circ C$ even

more oxygen than estimated above should come to the surface. The physical extent of this surface regime is under investigation. In the next section we discuss some detrimental effects of oxygen near the surface.

9. THE SENSITIVITY OF THE SUPERCONDUCTIVE SURFACE PROPERTIES AND BREAKDOWN AT HIGH rf FIELDS

Since rf fields react with the metal in a very thin layer of $\sim 500 \text{ \AA}$ only, the surface preparation is extremely important to achieve high Q 's and high surface electromagnetic fields.

We have previously¹⁸ given some reasons why the usual arguments for the proximity effect between superconducting regions may have to be modified and that a few normal metal surface layers could have a large detrimental effect. The T_c , and therefore the energy gap, in niobium is very sensitive to oxygen contamination and T_c drops at the rate of $1^\circ K/a/o$, hence oxygen contaminated layers would have a lower T_c and would thereby have poorer microwave performance. We have also shown that NbO or a closely related compound is a possible surface contaminant. Bulk NbO is a semimetal with a low T_c near $1^\circ K$. Again, such a layer would affect the microwave properties adversely. In general, nonmetallic oxides should not have an adverse effect unless they caused surface faceting, or if they caused losses in the dielectric.

In the above discussion we have been concerned mainly with those features which would affect the low field Q . In general with the preparations previously described or with the surface coatings to be discussed, it is our opinion that, this part of the cavity problem will eventually be solved. However at present it appears that the breakdown of rf cavities in a high ac field will be a major problem. In the discussion to follow we present some ideas on this problem.

We think that the present evidence is consistent with breakdown caused by low thermal conductivity at the surface which is in turn caused by a short electron mean free path (mfp) at the surface. The losses in the superconducting and normal state and the influence of the thermal conductivity have been estimated by Halbritter.¹⁹ In the following

analysis we emphasize the possible role of oxygen and its influence on the thermal conductivity. In the usual estimates of surface impurities, it is assumed that oxygen only comes to a narrow region at the surface. However, as previously mentioned, there is a distinct possibility that in cooling down a cavity oxygen diffusing towards the surface is 'frozen-in' over a significant region. Experiments are under way to test this conjecture and to also measure the steady oxygen distribution as one goes from the surface concentration to the bulk amount.

The following simple model would appear to describe some of the features of breakdown. Suppose that due to the oxygen which diffuses to the surface and especially at grain boundaries or other disordered regions, there is a low H_{cl} compared to the expected value of 1200 Oe. Then the region is effectively normal for our purposes and there are losses comparable to the normal state losses. For a hemispherical normal region, as shown in Fig. 7, with no heat flow out of the flat

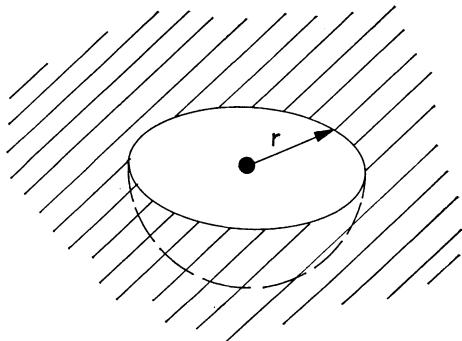


FIG. 7. Hemispherical region on niobium surface that is assumed to go normal because of greatly reduced H_{cl} . This can possibly come about from oxygen on the surface.

surface the solution is similar to heat flow out of a sphere in an infinite medium.²⁰ In this case

$$\Delta T = \frac{Q}{4\pi K r}, \quad (10)$$

where Q is the heat flow out of the sphere, K is the thermal conductivity in the superconducting state and r is the radial distance to the surface between the normal and superconducting regions.

Then the power dissipation in the normal region is $P = R H_{ac}^2/2$ W/cm², assuming the region is of the order of the normal state penetration depth.

We estimate the surface resistance R in the normal state as about 0.05 Ω and if we take H_{ac} as 300 Oe, then $P \sim 1500$ W/cm² in the normal state. Because of the low surface mfp we can take K as 0.01 W/cm °K. In pure superconducting Nb, K can be as high as 0.1 W/cm °K because of the increased phonon conduction due to the condensation of normal electrons. Data by Calverly, Mendelsohn and Rowell²¹ show that strains cause this value to decrease and we feel ~ 0.01 W/cm °K is a reasonable estimate. Then $\Delta T \sim 375 r/K$. For a rise of about 5 °K at the boundary, which we assume is adequate to make Nb go normal and therefore propagate a phase transition, we have $r \sim 10^{-4}$ cm. Hence a normal region with a radius of about 10,000 Å will have a boundary at 5 °K above ambient. In this case H_{cl} will be lowered, the normal region will grow and this will cause ΔT to increase since it is proportional to r . This leads to an unstable situation and we think it can cause rf breakdown. Note at 900 Oe the region for a 5 °K rise would only have a radius of about 1000 Å, which is near the coherence length. Eventually order parameter fluctuations in a region with a radius of the order of the coherence length could lead to an upper limit on the ac field.

Of course, the conductivity and mfp get higher as one goes away from the surface and it is plausible that the instability region grows along the surface where the thermal conductivity is lower.

10. POSSIBILITIES FOR PROTECTING THE NIOBIUM SURFACE

For ease in handling the rf cavities it would be of great value to have a stable surface condition. There are several possibilities for protecting the surfaces of niobium cavities. At present a process of anodic oxidation of niobium surface (formation of Nb_2O_5) has been developed by Siemens² and it has also been investigated at Brookhaven.³ Anodized cavities exhibit initially higher Q 's which might be due to the conversion of various oxides and suboxides notably NbO as well as oxygen present in the surface layer into Nb_2O_5 , a low-loss insulator.

Another possibility for protecting the surface is a thin layer of some high T_c material such as Nb_3Sn , Nb_3Al or other alloys. We have studied the

formation of thin Nb_3Sn layers on Nb surfaces and it appears plausible that good quality thin layers can be made.⁵ Figure 8 shows the Nb_3Sn transition as the layers are made thicker. The diffusion coefficient of Sn into niobium is extremely small and this may provide an adequate coating without having to worry about diffusion from the protecting layer into the Nb. In practice, the proper amount of Sn can be vaporized inside the cavity at a temperature above 1000 °C. Then, upon cooling to about 900 °C, the tin will condense on the cavity

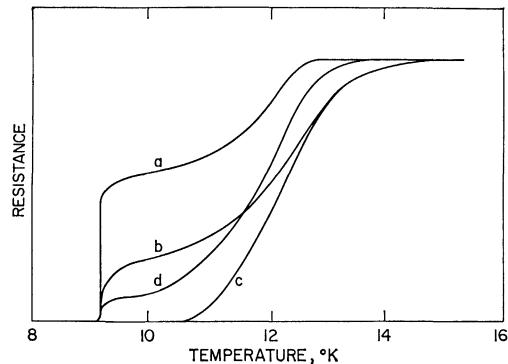


FIG. 8. Data showing the effect of annealing temperature on a 220 Å Sn film. (a) 5 min at 825 °C, (b) 30 min at 825 °C, (c) 10 min at 875 °C—a further 10 min at 900 °C did not change the curve noticeably, (d) 10 min at 950 °C.

walls and then form Nb_3Sn . The thickness of the Nb_3Sn layer would be determined by the amount of Sn that was used. Our previous experiments show that about 900 °C would be a good formation temperature for a layer of Sn a couple of hundred angstrom thick. Some experiments showing the effect of the annealing temperature are given in Fig. 9.

NbN is another possibility that we have tried, however we find that we cannot form a good surface layer by heating a niobium ribbon in about 10^{-5} torr of nitrogen at about 300–800 °C. In this range there is some possibility that one can form a surface layer without too much diffusion into the bulk. However, we have had little success with this compound. Also, even if the layer could be made we would expect significant amounts of nitrogen from the NbN to diffuse a few hundred angstrom into the bulk in about 10^4 or 10^5 seconds. Nb_3Al has also been tried, however the T_c 's are

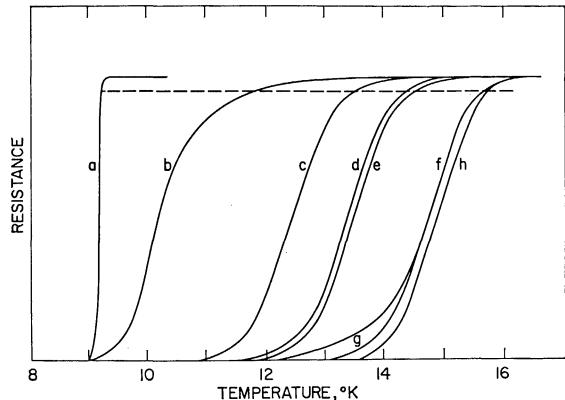


FIG. 9. Progressive buildup of a film by alternately depositing layers of Sn and then reacting and annealing. (a) Pure Nb, (b) 40 Å of Sn annealed at 800 °C for 15 min, (c) 40 Å more of Sn annealed at 825 °C for 15 min, (d) 40 Å more of Sn annealed at 900 °C for 3 min, (e) 40 Å more annealed at 940 °C for 2 min and 775 °C for 5 min, (f) 200 Å more annealed at 860 °C for 10 min, (g) no tin deposited, annealed 10 min at 900 °C, and (h) no tin deposited, annealed 40 min at 900 °C.

somewhat lower and in general it appears more difficult to make good Nb_3Al layers compared to Nb_3Sn layers. However, Nb_3Al is still a reasonable possibility. More experiments in this area will be carried out at Brookhaven with the arrival of a vacuum annealing furnace.

11. RADIATION DAMAGE TO Nb CAVITIES

Recent work at Brookhaven²² has indicated small degradation in pure niobium surfaces when exposed to a total flux of 10^{16} protons from the Brookhaven 200-MeV linac. However, similar experiments on Nb_2O_5 coated surfaces³ have shown large degradation in the residual surface resistance which is probably due to enhanced oxygen diffusion into the bulk and large possible change in the loss tangent of Nb_2O_5 . These experiments indicate that Nb_2O_5 coatings on Nb surfaces will not be suitable as protective films due to much higher radiation damage in insulators as compared to the damage in pure metals which are annealable at relatively low temperatures. From the radiation experiments we can infer that if we could produce clean Nb surfaces, radiation damage at least for

the exposure up to $\sim 5 \times 10^{15}$ protons/cm² would be negligible.

12. SUMMARY

In this paper we have tried to summarize what structures can be expected on the surface of niobium under cleaning conditions approximating those used for microwave cavities. It is clear from the assembled data and our LEED studies that the surfaces used at present are not free of oxide layers due to, essentially, the inadequate heating times at elevated temperatures and rapid migration of oxygen to the surface on cooldown. It is also clear that firing at much higher temperatures ($\approx 2000^\circ\text{C}$) could seriously deform the cavities and impair their usefulness for applications envisioned. Furthermore, the inadvertent handling during installation into any equipment will degrade their performance. On the other hand, it is not clear what surface properties are the most important for achieving high Q 's and peak rf fields. The answer to this question will hopefully be provided by a careful correlation between microwave cavity measurements and surface studies on small samples processed at the same time in the high temperature, high vacuum furnace now being installed. In view of the above arguments it is possible that some suitable surface coatings may finally provide the best compromise.

ACKNOWLEDGMENTS

We have discussed these problems with many colleagues, and we express our appreciation to them. In particular, we are indebted to D. H. Gurinsky, H. Hahn, J. Halbritter, and H. Isaacs for many discussions on the problems considered here. We also thank N. Garcia who collaborated on the Nb₅Al and NbN work which we have briefly mentioned in the text.

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Received 7 February 1972