EFFECT OF SURFACE CONDITIONS ON SOME SUPERCONDUCTING PROPERTIES OF NIOBIUM*
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Although the exact mechanism for rf breakdown is not understood it appears likely that the details of the structure and impurity content at the surface of the superconductor are crucial factors. We discuss measurements of gaseous impurities on the niobium surface which indicate higher oxygen levels than the bulk concentrations. Superconducting penetration depth measurements with various bulk oxygen concentrations are discussed, and they also indicate higher amounts of oxygen in the surface regime. Finally, the properties of thin films of Nb_3Sn grown on niobium, which can be used as a high T_c protective layer for the delicate niobium surface, are discussed.

Introduction

At the present time a major problem limiting the use of superconducting rf cavities¹ is the breakdown at rf fields significantly below H_{c1} . The exact factors contributing to the rf breakdown are not known, but it appears likely that the details of the surface regime must play a crucial role. Our studies, to be discussed briefly here, indicate larger amounts of oxygen on the surface than previously expected and it is possible that this contributes to the low breakdown field. Recently carbon² has also been suggested as a contributing factor, and the final answer remains open. Calculations show³ that a normal region formed on the surface will dissipate enough rf energy to cause the normal region to grow in a fashion which would cause an unstable situation. Impurities such as oxygen might play a doubly adverse role. First, if the impurity concentration in the surface regime is large, and especially at grain boundaries, a low H_{c1} region could be formed which would be the region where initial flux entry begins, and secondly the impurities would reduce the thermal conductivity which would help lead to a runaway condition once dissipation occurs in the normal region.

In this paper we briefly discuss the degassing of niobium and present some work on surface concentrations of oxygen. Also we discuss recent penetration depth measurements with varying oxygen concentrations, which indicate higher surface concentrations relative to bulk concentrations, and finally we discuss possibilities for protecting the surface.

Degassing of Niobium

In general, existing measurements and calculations based on them indicate that to achieve low levels of oxygen and nitrogen in niobium the niobium must be heated above 1800°C at 10^{-8} Torr or less, for many hours depending on the wall thickness of the niobium. At these temperatures the diffusion times for oxygen are of the order of thousands of seconds for a sample about 0.5 cm thick, and the process which limits how rapidly oxygen is removed from the sample is the vapor pressure of NbO ,⁴ since oxygen in this temperature range is removed as NbO . Even at 1800°C for a sample ~ 0.5 cm thick it would take about 10^5 to 10^6 seconds to reduce the oxygen concentration by a factor of 10. In the table we summarize some of the diffusion times. τ_D is defined as the time for the oxygen concentration to drop to 1/10 of its initial value by NbO evaporation, and τ_D is the characteristic time attained from the solution of the diffusion equation for a slab with a uniform initial concentration which goes to zero at the boundary, and is the time for the concentration in the center to drop to about 11% of its initial value. The numerical values computed for τ_D and τ_E are for samples of thickness $2l = 0.2$ cm. For a discussion of the calculation of τ_D and τ_E see ref. 3. Note that the parameter L describes whether the oxygen removal process is diffusion limited or NbO evaporation limited, and it can be seen that for $l \sim 0.5$ cm or less the limiting process is NbO evaporation. At lower temperatures

TABLE

$T^\circ\text{K}$	$D \left(\frac{\text{cm}^2}{\text{sec}} \right)$	$\tau_D = \frac{l^2}{D}$ (sec)	τ_E (sec)	$L = \tau_D / \tau_E$	Log C for $P = 10^{-8}$ Torr
1373	1.61×10^{-5}	621			- 2.43
1973	2.3×10^{-5}	435			- 2.89
2073	3.2×10^{-5}	313	1.9×10^5	1.65×10^{-2}	- 3.29
2173	4.3×10^{-5}	230	3.03×10^4	7.6×10^{-2}	- 3.66
2273	5.7×10^{-5}	175	6.1×10^3	2.9×10^{-1}	- 4.00

*Research supported by the U. S. Atomic Energy Commission.

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and higher concentrations the evaporation of other oxides becomes important, however NbO is the major factor in oxide removal with $C < 1$ a/o at the temperatures we are concerned with. The table also gives the steady state oxygen pressure at $P = 10^{-6}$ Torr. Other concentrations can be derived from the formula $\log C = \log P_{O_2} - 3.35 + 16,700/T$.⁵

It is clear from the table that high temperatures are necessary to get things to happen fast enough and the temperature together with the low pressure environment determines the steady state concentration in the bulk that one attains. In the previous discussion and the discussion to follow it is implicitly assumed that nitrogen is not a problem. This appears to be the case from calculations of the equilibrium concentrations and especially because of the much higher vapor pressure of the nitrides. Also, Auger measurements that we have made show that nitrogen comes off the surface at a lower temperature than the oxides. Recently carbon impurities have been discussed as a possible contaminant.² This question remains for further study.

Surface Condition

From the table it becomes evident that by heating to 1800°C at a pressure near 10^{-8} Torr a bulk concentration of oxygen near 0.001 a/o can be achieved. In principle this all can be done, and the oxides which form in different temperature ranges can be removed from the sample surface.

Fig. 1. Auger intensity of oxygen line as a function of temperature. The Auger traces were taken after the sample cooled from the high temperature heating. The inserts show some characteristic surface structures. At $\sim 1200^\circ\text{C}$ there is a structure characteristic of a faceted surface, and above about 1800°C a clean Nb surface is seen. Above about 1500°C an NbO structure is commonly seen in our experiments.

In Fig. 1 we give a rough idea how oxygen comes off the surface, and the oxide structures found in the different regimes are also indicated. We have made these studies using low energy electron diffraction (LEED) and Auger spectroscopy. LEED is a relatively new surface tool by which electrons of energy between, say, 50 eV and 500 eV are scattered from the surface. Because of the low electron energy, penetration is small and a diffraction pattern characteristic of the surface is attained. In Auger spectroscopy, again a relatively new technique for surface analysis, electrons at about 1500 eV are used to knock electrons out of inner atomic levels. An electron from the conduction band then drops down into this level and a photon or an electron with this characteristic energy is then emitted. Each element has a characteristic spectrum and in this way surface impurities can be identified, since the electrons which are analyzed are characteristic of a few monolayers at the surface. In Fig. 2 we show an Auger trace of clean and dirty niobium.

Fig. 2. Characteristic Auger spectra of clean niobium and dirty niobium surface. The dirty surface corresponds to sample surface as initially put into vacuum system.

It might appear from the above that oxygen removal from niobium is straightforward. However, this is not the case due to the high heat of adsorption for oxygen on the niobium surface, which causes more oxygen to be in the surface regime than the bulk concentration. Pasternak and Evans⁶ have considered this problem and they give a relationship for the fraction of empty surface sites which goes as

$$\theta_o = \frac{1}{1 + K_2 C}$$

where C is the bulk concentration in a/o and K_2 is the surface distribution coefficient which goes as $K_2 \sim 3 \times 10^{-4} \exp[27,000/RT]$. At 1800°C $K_2 \sim 0.2$, and at 1000°C $K_2 \sim 11$. Hence we can see that during cool down oxygen will build up on the surface. If we assume that significant diffusion to the surface will occur down to, say, 1000°C we can expect to get about 1 a/o oxygen on the surface with 0.001 a/o bulk concentration.

Fig. 3. Oxygen line in Auger spectra as a function of time after heating. Sample was initially heated for 17 minutes at $P \sim 3 \times 10^{-9}$ Torr.

a) 9 minutes into heating cycle $T \sim 1400^\circ\text{C}$,
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, h) 660 sec.

In Fig. 3 we show Auger traces of the oxygen line as a niobium sample is cooled at $P \sim 3 \times 10^{-9}$ Torr. While no oxygen is evident at $\sim 1400^\circ\text{C}$ it can be seen that there is a rapid buildup of oxygen on the surface as the sample is cooled. We emphasize that since the pressure is about 3×10^{-9} Torr during cool down it would take about 15 min to get a monolayer of oxygen on the surface with unit sticking coefficient. This could not explain the rapid buildup in less than a minute and hence the oxygen must come from the interior of

the metal. In Fig. 4 measurements are given of the oxygen buildup with temperature, from our Auger measurements. The number of filled sites is defined as $\theta_2 = 1 - \theta_o$, and then $\theta_2/(1 - \theta_2) = K_2C$. C is estimated from our heating conditions to be about 0.37 a/o and hence K_2C can be estimated from Pasternak and Evans⁶ values of K_2 . These values define the upper curve in Fig. 4.

Fig. 4. $\theta_2/(1 - \theta_2)$ vs $1/T$ determined from Auger measurements for oxygen on the niobium surface. Where θ_2 is the fraction of filled sites and $\theta_2/(1 - \theta_2) = K_2C$. Curve above data point curve is calculated from K_2 values of Pasternak and Evans and the estimated bulk concentration of 0.37% a/o.

It can be seen that our measured values are in good agreement with these estimates.

The above argument assumes that the oxygen rich region is essentially a monolayer or so at the surface, as in segregation arguments⁷ based on Gibbs' adsorption. We feel that this may not be the case, and, in fact, the oxygen may fall from the surface to the bulk concentration over many monolayers. If this occurs it could have a significant effect on both H_{c1} and the thermal conductivity in the surface H_{c1} regime as well as the penetration depth λ . We are preparing to do combined Auger spectroscopy and sputtering so that we can measure oxygen and other impurity concentrations as layers are sputtered off, thereby yielding a plot of impurity concentration vs distance into the sample. Work on grain

boundaries is also contemplated if the niobium can be fractured. We emphasize that this work does not yet connect impurity concentrations to cavity performance and it is also possible that other impurities such as carbon are important. Auger measurements show less than 1% carbon, but this is not sensitive enough to exclude carbon as a problem.

Penetration Depth Measurements

To get some idea of oxygen concentration in the surface region compared to the bulk, we have measured the penetration depth in niobium along with the bulk resistance ratio at different oxygen concentrations. The oxygen was added to the sample by heating at a temperature and pressure (see Table) so that our estimated bulk concentration ranged from about 0.003 a/o to about 0.05a/o. After heating for about 5 hours at the high temperature, usually from 1700°C for the high concentrations to about 1900°C for the low concentrations, at pressures from 2×10^{-8} to 7×10^{-7} Torr, the sample was cooled in high vacuum (2×10^{-8} Torr) and during this process oxygen could migrate to the surface from the bulk if, indeed, this happens during the cooling process. Since the sample cools fairly rapidly to 500°C or 600°C in the order of 20 secs, it is unlikely that much more than a fraction of a monolayer of oxygen could hit the sample from the high vacuum environment. This would also be the same for all samples and certainly could not explain the differences in λ discussed below. In our experiments the bulk oxygen concentration is estimated from the relationship that $\lambda \propto c^{0.3/a/o}$.⁶ If we assume that the resistance ratio of 300°K to 410°K is effectively $c/\Delta c$ then we can estimate the percentage impurity. Our preliminary data showing λ vs $\rho_{300^\circ K}/\rho_{410^\circ K}$ is given in Fig. 5.

Fig. 5. Penetration depth vs bulk resistance ratio for sample heated in oxygen for 3 to 5 hrs at 1700°C at pressures from 1×10^{-7} Torr to 7×10^{-7} Torr. Lower curve is calculated curve from bulk resistance ratios. Upper measured curve which shows larger λ values indicates lower surface mean free path.

At a resistance ratio of 1000 we get $\lambda = 465 \pm 20 \text{ Å}$ which checks well with Maxfield and McLean.⁸ They give the mean free path $\lambda = 4000 \text{ Å}$ at $300^\circ K / 4.2^\circ K^{1/2}$ for their niobium sample. Using this value we can estimate λ for our bulk resistance ratios of 140, from the work of Miller,⁹ as about 500 Å which is much lower than our measured value of near 600 Å. In fact using this 600 Å value of λ we need $\lambda = 630 \text{ Å}$ in the surface regime compared to about 4900 Å in the bulk. Hence our penetration depth measurements clearly indicate more oxygen in the surface regime than the bulk. It should be mentioned that all data was taken on the same sample and after oxygen was added it could be removed by heating in ultra high vacuum whereby the resistance ratio increased and λ decreased. The heavy curve in Fig. 5 is the behavior estimated from the bulk resistance ratio. While these experiments certainly appear to indicate higher surface oxygen concentrations, the final answer will be obtained by direct Auger and sputtering measurements.

In the experiments described here it has been mentioned that the sample was heated for three to five hours at some pressure of oxygen. We have indicated that this time is much longer than the characteristic diffusion time which for our size sample is hundreds of seconds, and, in fact, the heating time is longer than the time required to reach the steady state oxygen concentration. In view of this it is assumed that any inhomogeneities in the oxygen concentration near the surface are due to intrinsic surface effects. However, it is conceivable, although improbable, that some unknown mechanism at the surface determines the diffusion rate out of the surface regime, and this is what we see in our experiment. Further work and direct measurements will be necessary to exclude such possibilities.

Alloys on the Niobium Surface

Because of the sensitivity of the niobium surface to oxygen there is great interest in protective layers. It has recently been found that $^{10} \text{Nb}_2\text{O}_5$ grown on the niobium surface protects the niobium while still providing high Q's, and more will be said about this promising process in this conference. A scheme that we have tried¹¹ is to grow thin layers of Nb_3Sn on Nb and some of these experiments are briefly discussed here.

In the apparatus used in these measurements samples can be heated to over 1800°C for cleaning, then about 900°C for alloy formation and then cooled to cryogenic temperatures where the T_c is then measured. All this occurs in an ultra-high vacuum environment, so that the T_c of the samples can be measured without deterioration due to oxygen or other gases. To make a Nb_3Sn or Nb_3Al layer either Sn or Al is evaporated from a filament source onto the niobium foil, which has been previously outgassed. After the metal was deposited the sample was heated from 700°C to 1000°C to form the layer of Nb_3Sn or Nb_3Al .

Fig. 6. Data showing the effect of annealing temperature on a 220Å 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.

In Fig. 6 we show how the Nb_3Sn T_c changes with various heat treatments and in Fig. 7 we show how the T_c increases as the layer is made thicker.

Fig. 7. Progressive buildup of a film by alternately depositing layers of Sn and then reacting and annealing. a) Pure Nb, b) 40Å of Sn annealed at 800°C for 15 min., c) 40Å more of Sn annealed at 825°C for 15 min., d) 40Å more of Sn annealed at 900°C for 3 min., 940°C for 2 min., and 775°C for 5 min., e) 40Å more annealed at 825°C for 15 min., f) 200Å annealed at 860°C for 10 min., g) no tin deposited, annealed 10 min. at 900°C, h) no tin deposited, annealed 40 min. at 900°C.

From such measurements it is possible to get some estimate of the coherence length of the Nb_3Sn . Clearly, for films much thinner than the coherence length it would be expected to see the T_c of bulk niobium rather than the high T_c film, and as the layer is built up the T_c approaches that of bulk Nb_3Sn . An analysis of this data leads to an estimate of about 200Å for the Nb_3Sn coherence length which checks reasonably well with other estimates. Of course, if part of the low T_c in the Nb_3Sn film

is due to increased disorder, which becomes less important in the thicker films, then the coherence length would be smaller than our estimate.

There are certain interesting features which must be considered when making the films as opposed to thicker Nb_3Sn layers. Since the films are extremely thin it is important not to lose any Sn during the formation process. This can happen by diffusion into the niobium or by evaporation off the surface. It turns out that diffusion into the niobium is fairly negligible, however, evaporation from the surface is a significant problem. It can be seen from Fig. 6 that heating to about 900°C deteriorates the film. We think this is due to evaporation of the Sn from the Nb_3Sn , which we would expect to have a vapor pressure about 1/10 that of pure Sn. At 900°C significant tin will be lost from a thin Nb_3Sn layer. Note in a bulk diffusion process or a bulk sample, tin lost at the Nb_3Sn surface will not be an important problem since the layers are of macroscopic thickness. It should be mentioned that the calculated times for the Nb_3Sn layer formation are quite small, about 0.05 sec to form a layer 100Å thick at 850°C¹² and we would not expect much pure tin to be lost during this part of the layer formation since at 850°C we would expect to lose 0.5 monolayers/sec from the Sn surface.¹³ It appears that the greatest Sn loss occurs during the annealing process at elevated temperatures. It is clear from the above considerations that the thinner the layers that must be formed the lower the reaction temperature. We always want as low a temperature as possible to prevent tin evaporation, however, we must have a high enough temperature to get significant Sn diffusion to cause the Nb_3Sn to form. It is interesting to speculate on whether Sn depletion in the Nb_3Sn surface, after annealing bulk samples is a cause of poor energy gap characteristics attained in tunneling measurements. At 950°C we would expect¹⁴ to lose about 0.5 monolayers of Sn from the Nb_3Sn surface in a second, which is certainly adequate to cause a poor gap characteristic.

We have also been able to form Nb_3Al layers; however, better results have been attained so far with Nb_3Sn . Although LEED measurements indicate that Nb_3Al monolayers can be formed, we have been unsuccessful with thicker surface layers. We suspect that any layers much thicker than a monolayer will be extremely difficult to form on the niobium surface, since the diffusion coefficient for nitrogen into niobium is large and it will be lost from the surface layer under the necessary temperatures for nitride formation. Of course, by heating in a relatively high nitrogen pressure the whole sample can be nitrided.

We feel that Nb_3Sn layers seem promising enough to try in an actual cavity. The layer can be made thin enough so that it protects the Nb surface, while the microwave properties are essentially determined by the niobium underneath which has a higher H_{c1} . It might also be possible to use thicker H_{c1} layers of Nb_3Sn . However, in

this case it is expected that the low H_{c1} will lead to less favorable results than are possible with niobium. In future experiments it should be possible to investigate the performance of actual cavities coated with Nb_3Sn .

Acknowledgements

We have discussed these problems with many colleagues. In particular we are indebted to D. H. Gurinsky, H. Hahn, J. Halbritter and H. Isaacs for many discussions of the problems considered here. We also thank N. Garcia who collaborated on the Nb_3Al and NbN work which we have briefly mentioned in the text.

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14. These estimates are outlined in reference 11, where it is estimated from the heats of formation that the vapor pressure of Sn above Nb_3Sn is about 1/10 that of pure Sn.

Note added in proof: Recent experiments that we have made in the course of penetration depth measurements, show that in polycrystalline niobium grain growth and high resistance ratios are attained when the sample is heated in oxygen before the final heating in high vacuum. This process probably removes carbon² and it appears that carbon on grain boundaries might inhibit grain growth in the niobium. It is possible that the regions where grain boundaries meet the surface have even higher oxygen and carbon concentrations than the rest of the surface. These regions would have lower H_{c1} due to the smaller meanfree path and are the places where instabilities are likely.