EFFECT OF SURFACE METALLURGY ON THE PENETRATION DEPTH AND RF BREAKDOWN FIELD OF SUPERCONDUCTING NIOBIUM*

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ABSTRACT

The surface metallurgy of niobium will be discussed including factors such as impurity distributions at the surface and surface topography. Measurements of the penetration depth are presented both in the clean limit, where there is about a 20 Å region of oxygen at the surface, after high temperature heat treatment, which affects the boundary condition on the GL order parameter; and in the dirty limit where heating in an oxygen atmosphere near 10^{-6} torr can greatly affect the surface roughness. Auger measurements of the surface conditions in a 1% Zr in Nb alloy are also presented. A discussion is given of preliminary results in a special apparatus where rf breakdown experiments can be performed on small samples and correlated with the metallurgical factors mentioned above.

INTRODUCTION

The problem of the low rf breakdown field in superconducting Nb cavities is poorly understood, although it is generally assumed that there is no intrinsic limit below H_{c1} , and in fact there have been some measurements of fields above H_{c1} .¹ It would seem futile to discuss the various factors that could cause rf breakdown until more information about the properties of real Nb surfaces were accumulated, and the work presented here is part of a program in this direction. Hydrogen and nitrogen are removed from Nb with relative ease compared to oxygen, and our philosophy regarding the various problems with Nb has been that oxygen, or possibly carbon, are impurities which could greatly affect the surface properties.

Some of the properties of oxygen in Nb at various temperatures were studied by E. Fromm and H. Jehn² and the problems of surface distributions of oxygen were originally studied by Pasternak and Evans.³ In our work we extended the excellent studies of Pasternak and Evans by using the recently available techniques of LEED and Auger Electron Spectroscopy (AES) and confirmed the segregation of oxygen to the Nb surface upon cooling from high temperature heat treatments.⁴ Further studies to be reported here say more about the nature of this distribution, how it affects other surface properties of Nb, and in particular, how it can influence various superconducting properties.

PROBLEMS INVOLVING THE SURFACE

In initial attempts to measure superconducting properties that are surface dominated, measurements were made of the superconducting penetration depth with different bulk oxygen concentrations.⁴ The idea here was to determine the mean free path (mfp) at the surface caused by oxygen segregation, and also the bulk mfp. When the samples were heated in various oxygen atmospheres at high temperatures to obtain different bulk concentrations it was found⁵ that the

apparent λ increased by factors of two or three, which appeared to indicate that the surface mfp was much smaller than the bulk value. However, it appears that the situation is more complicated than originally expected.⁶ In Fig. 1 the distribution of oxygen as a

Fig. 1. Surface distribution of oxygen in from the sample surface for various oxygen concentrations. Oxygen migrates to the surface when cooling from temperatures greater than 1000°C.

function of distance from the surface is shown for various oxygen concentrations, after cooling from temperatures near 1800°C.⁶ This rapid falloff is, perhaps, expected from Gibbs' adsorption arguments and it would appear to preclude any uniform oxygen distribution (above the ambient bulk concentration) in the surface except for about a 20 Å layer. It is therefore hard to see how oxygen could affect the mfp at the surface of Nb over a distance comparable to λ which is about 500 Å, and the basic explanation for the increased λ probably involves some other effect caused by heating in oxygen.

THE PENETRATION DEPTH IN CLEAN SAMPLES

The problem of the penetration depth in Nb has been studied⁷ in both clean samples and oxygen treated samples and the results are summarized in Fig. 2. In these studies λ is written as

$$\lambda_L(T) = Z_{BCS}(T)\lambda_L(0)$$

where near T_c , $\lambda_L(T) \sim \lambda(T)$. Penetration depth data are often analyzed by the Gorter-Casimir phenomenological function

$$Z_{GC} = \frac{1}{\sqrt{1-t}}$$

and where near T_c , $Z_{BCS} = \sqrt{2}Z_{GC}$. If the clean sample had a perfect surface then near T_c we would expect that $\lambda(T)$ vs Z_{BCS} would be linear. However, it can be seen from the data that this is not the case and that there is slight curvature in

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Fig. 2. Effect of oxygen on apparent λ
 Curve (1) clean Nb
 Curve (2) RRR 170 heated at 8×10^{-7} torr at 1800°C
 Curve (3) RRR 85 heated over 1900°C at 2×10^{-6} torr
 Curve (4) RRR 8 heated over 1800°C at 2×10^{-6} torr

the data. This slight curvature can be explained by assuming that the Nb surface is smooth to first order but that there is a thin layer, $\sim 20\text{\AA}$ thick, of normal material on the surface. This could be a highly doped oxygen layer as shown in Fig. 1, realizing that the T_c of Nb falls at $1^\circ\text{K/at.}\%$. The origin of the curvature comes about because of the boundary condition on the Ginzburg-Landau order parameter which is usually taken as

$$\frac{1}{\psi} \frac{d\psi}{dx} \sim \frac{1}{b}$$

As one approaches T_c , $\xi(T)$ increases hence $d\psi/dx$ decreases and therefore one could expect $1/\psi$ to increase, since the product must stay constant. Then λ , which goes as $1/\psi^2$, can be expected to increase due to this effect. A solution of the GL equations yields a complex expression⁸ for the ratio of the effective penetration depth at boundary and the usual λ for the metal vacuum interface. Some values of $\lambda_{\text{eff}}(T)/\lambda(T)$ are given in Table 1 for $\kappa \sim 0.8$. From the

Table 1

Variation of $\lambda_{\text{eff}}/\lambda$ with $\xi(T)/b$

$\xi(T)/b$	$\lambda_{\text{eff}}/\lambda$
0.01	1.005
0.03	1.014
0.05	1.023
0.07	1.032
0.1	1.045
0.16	1.072
0.2	1.090
0.3	1.135
0.4	1.179
0.6	1.264
1.0	1.413
3.01	1.806
5.01	1.943
7.01	2.009
9.96	2.059

data one can estimate what value of $\xi(0)/b$ removes the curvature and this turns out to be ~ 0.02 which we estimate would be caused by about $20\text{\AA}$ of normal metal

on the surface. From this type of analysis it would appear that relatively clean surfaces can be understood in some detail.

THE PENETRATION DEPTH IN NON-IDEAL SAMPLES

Samples that are heated in an oxygen atmosphere have different behavior from the ideal behavior discussed and some results on such samples are shown in the other curves in Fig. 2. The effect of oxygen discussed above is not nearly large enough to explain these changes on the basis of a sharp distribution, as in Fig. 1, and the explanation for the large changes must be found elsewhere. Examination of the surface shows that heating to temperatures near 1800°C in an oxygen atmosphere of 10^{-6} torr causes thermal faceting. It is probable that the increased surface area caused by this process accounts for some of the variations of λ in the following way. In an inductive measurement λ is measured by determining the area of flux penetration which ideally goes as $2\pi R \lambda(0) Z(T)$. However, if the surface is rough then the area is $2\pi R f \lambda(0) Z(T)$, where f is a geometrical factor >1 , and the product of f and $\lambda(0)$ cannot be separated. The conditions for the phenomenon of thermal faceting are, in general, not completely understood, and there appears to be some controversy over whether gaseous environments are necessary for this process to take place. In our own work we find that an oxygen environment is necessary for the large effects shown in Fig. 3, although we have not established what the lower limit on

Fig. 3. Faceting of niobium surface caused by heating to over 1950°C for 10 hr at 10^{-6} torr.

the oxygen pressure is. Certainly at 10^{-6} torr and 1800°C faceting is very significant and we suspect it will be significant at somewhat lower pressures. We have not observed faceting on the scale shown in Fig. 3 at pressures near 10^{-9} torr, and a faceted surface could be made smooth by high temperature heating at this pressure. It appears that the phenomenon is caused by NbO forming on preferential sites, possibly along certain crystallographic directions, and then evaporating from these sites. Preliminary Auger measurements, that we have made on Ta support this view. Upon heating, Ta in an oxygen pressure near 10^{-6} torr the main oxygen line decreases as the temperature increases, as expected. However, a second structure can be seen when the main oxygen line is small enough. The second peak decreases more slowly with temperature, and above about 1900°C it becomes larger than the main oxygen peak. This could indicate

preferential bonding along different crystallographic directions, with obvious implications to the causes of faceting and possibly other types of surface inhomogeneities.

In Fig. 4 we illustrate some related effects of

Fig. 4. λ vs Z_{BCS} for a cylindrical Nb single crystal. The apparent λ was 668 Å in the as machined sample and 485 Å after etching. This is still significantly higher than the $\lambda_L(0)$ value for pure Nb of about 315 Å.

inhomogeneities in the low temperature part of the apparent λ vs T curve for a machined unannealed surface. At the lowest temperatures, below $Z \sim 1.2$, there is a rapid increase in the screening. This appears to be due to an oxygen rich surface region going superconducting near 6°K. One can make a simple model for the effect of a uniform layer on a bulk sample and we find that $\lambda_{eff}(T) = \lambda'(T)(1 - e^{-d/\lambda'}) + \lambda(T)e^{-d/\lambda'}$. Where d is the thickness of the low T_c layer, λ is the penetration depth of the bulk material, and λ' is the penetration depth of the low T_c layer below its T_c . Of course when $\lambda'(T) = \lambda(T)$ and T_c is the same for both regions, then $\lambda_{eff}(T) = \lambda(T)$ as expected for a uniform sample. When $\lambda' \rightarrow \infty$, i.e. a normal layer, then $\lambda_{eff} = \lambda + d$. For $d \ll \lambda'$, $\lambda_{eff} \approx \lambda + d(1 - \lambda/\lambda')$. Hence above T_c of the layer $\lambda_{eff}(T) = \lambda(T) + d$ and below the T_c of the layer the factor of d is reduced by $(1 - \lambda/\lambda')$ which appears as an additional screening. This rapid increase in screening shows up even in the cleanest samples that we have made and we estimate that in these samples it corresponds to a region from 20 Å to 40 Å in extent. In Fig. 4, the screening corresponds to a layer from 60 Å to 125 Å. There is also an extended plateau region above $Z \sim 1.2$ which could indicate normal inclusions mixed in the superconductor which cause λ to limit, until these regions finally go superconducting below $Z \sim 1.2$ where the additional screening is observed. It is interesting that this plateau region is not explained by the simple model already discussed and it probably must be explained by other inhomogeneities at the Nb surface such as the normal inclusions mentioned above. As yet we have made no convincing model to explain these results. We also mention that at higher Z the slope is also much higher than in the cleanest samples as expected.

After etching the machined region it can be seen from Fig. 4 that the λ vs T curve shows both less

structure at low temperatures and a smaller slope at high Z .

SURFACE PROPERTIES OF A Nb-Zr ALLOY

Type II superconducting alloys have been suggested as possible candidates for rf cavities on the assumption that it might be possible to achieve breakdown fields significantly above H_{c1} .⁹ This problem is discussed in another paper in the conference.¹⁰ It should be mentioned that the surface problems of alloys are probably even more complicated than the pure material. Surface segregation in a 1% Zr in Nb alloy has been studied and has led to some surprising results which we briefly mention here. If a 1% alloy of Zr in Nb is heated, Fig. 5 indicates

Fig. 5. AES peak heights of Nb, Zr, O and N as a function of temperature. The data were taken with the sample at room temperature after the sample was cooled from a temperature on the abscissa.

that oxygen segregation to the surface starts at about 500°C and similar Zr segregation starts at about 800°C. At about 1300° the Zr segregation is maximum and it is estimated that it covers from 1/4 to 1/2 of the surface. As in the case of oxygen, the zirconium concentration falls off from the surface to the bulk concentration in a few monolayers. It is also interesting that when Zr is present the segregated oxygen behaves differently than without Zr and does not come off the surface as the temperature is raised. This appears to indicate that the oxygen combines with Zr in the surface region and therefore does not redistribute into the bulk from the surface as interstitial oxygen does. It is clear that this type of segregation problem will affect any superconducting properties of Type II superconductors which are surface sensitive, and great care is necessary in preparing a surface that resembles the bulk material.

RF PROPERTIES

Besides the intrinsic scientific interest in better understanding phenomena at surfaces, a motive for our work in this area is improving the rf properties of superconductors. In this regard a sample cavity¹⁰ has been designed where the rf breakdown field can be obtained on cylindrical superconductors of the order 0.2" dia. In this way metallurgical and surface analysis can be done on samples which can then be tested for the rf breakdown field. The work

at present involves the properties of alloy Type II superconductors which are described in another paper,¹⁰ although some preliminary work involves the properties of niobium. The breakdown field of the as machined single crystal Nb sample discussed in Fig. 4 is 400 gauss.

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