# Temperature Dependence of the Surface Resistance of Niobium at 1300 MHz - Comparison to BCS Theory -

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### Abstract

We have carefully measured the temperature dependence of the surface resistance of three 1300 MHz single cell niobium cavities manufactured from high purity niobium of RRR=200. The cavities had undergone different surface treatment such as BCP, EP, "in-situ" baking at 85°C and 140°C, and the data were analyzed by using Halbritter's surface resistance program. Whereas between chemically polished and electropolished surface differences in surface resistance can be explained by mean free path effect, this is no longer true for "in-situ:" 140°C baked cavities. To explain the data obtained in these tests, additional material parameters such as energy gap and London penetration depth are changing. After an "in-situ" 140°C baking for app. 40 hrs the BCS surface resistance between 1.8K and 4.3K is lowered by nearly a factor 2 compared to a chemically polished surface. This contribution describes the measurements and attempts to analyze the obtained data.

# **1 INTRODUCTION**

One of us (P. K) has since several months investigated the effects of " in-situ" baking of niobium cavities at  $140^{\circ}$ C for longer periods of time [1]. The interest in this research was triggered by earlier successful attempts to decrease Q-degradation in high purity niobium cavities by "in-situ" diffusion of oxygen into the surface at 250°C [2] and more recently by reports in ref. [3, 4] of the benefits of baking at elevated temperatures.

The observations collected during app. 10 - 15 experiments on chemically treated niobium surface can be summarized as following:

- 1) The BCS surface resistance decreases by nearly a factor 2 in the temperature range between 4.3K and 2K in high purity niobium cavities,
- 2) After the baking the resonance frequency of the cavity has changed slightly towards lower frequency,
- 3) The gap energy is even slightly increased,
- 4) These effects remain after air exposure of the cavity or high pressure ultrapure water rinsing,
- 5) Only after the removal of app. 3000 Å of material from the surface does the surface resistance return to its original value.

In this investigation we used electropolished 1300 MHz KEK-type single cell niobium cavities with the goal to

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verify the above effects also on electropolished surfaces. As discussed in detail in this paper, the same effects were observed, leaving us with the task to interpret the experimental data. As is well known, the BCS surface resistance is strongly dependent on mean free path ( or rather the ratio of coherence length to mean free path) and has a minimum at 1300 MHz around 200 Å. Therefore the first attempt was to explain the observed reduction in surface resistance by a change in mean free path caused by diffusion of interstitials or surface oxides into the niobium.

We tried to fit the experimentally observed temperature dependence of the surface resistance to the BCS theory using Halbritter's code [5]. This fit will result based on earlier experience in values for mean free path  $\Lambda$  and the energy gap  $\Delta/k_{\rm B} = \alpha$  (k<sub>B</sub> : Boltzman's constant). However, by using this procedure we could not obtain consistent results which would explain the reduction in BCS surface resistance and the frequency shift at the same time. Only if we allowed a change in the London penetration depth after the baking and treated this material parameter as another fit parameter, we obtained a reasonable fitting of the experimental results to the BCS theory. Using this procedure, we re-analyzed all experimental data from just electropolished surface as well as after baking at 85°C and 140°C for both electropolished and chemically polished surfaces. From this analysis we noticed a very interesting effect, namely that the niobium surface can change from a Type-I superconductor to a Type-II superconductor after the baking. Especially, an electropolished surface seems to be a perfect Type-I superconductor.

In the following section we present first the results from the baking experiments, then describe the method used for data analysis based on Halbritter's surface resistance code, and finally discuss the transition from Type-I to Type-II superconductor.

# 2 140°C BAKING EFFECT ON THE ELECTROPOLISHED CAVITIES

For this investigation we used two 1300 MHz KEK cavities: K-15 and K-16 manufacture from niobium of RRR=200. These cavities had previously been tested for extensive chemical polishing [6]. For these experiments  $30\mu m$  were newly removed by elecropolishing from the surface. Subsequently the cavities were evacuated to  $3.5 \times 10^{-7}$  torr with O-ring sealed blank-offs. No baking for improvement of the cavity vacuum was applied prior to shipping them under vacuum to Jlab.

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Cavity K-16 was cold tested several times at Jlab; only high pressure water rinsing (HPR) was applied as a cleaning step. After four months of storage in the class 100 clean room - exposed to air - the cavity was re-tested for the baking experiment : after a baseline test following a high pressure water rinsing of the cavity interior the cavity was baked "in-situ" in the vertical test dewar in the helium gas environment. During the baking for app. 40 hrs at 140°C ( temperature rise app. 8°C per hour ) the cavity was pumped by a turbo-pump (50 l/sec) / scroll pump (500 l/min.) pumping arrangement. The pressure during the baking was in the  $10^{-6}$ - $10^{-8}$  torr range.

Cavity K-15 was still under vacuum (at 200 mtorr) when used for the baking experiment. As with K-16, only HPR was applied for the baseline test followed by the baking step as described before.

We measured the temperature dependence of the Q-value between 4.3 K and 2K as well as the Q vs. Eacc dependence at 2K. The BCS surface resistance was obtained by subtracting the residual surface resistance Rres from the measured surface resistance Rs;



Figure 1 : Reduction of BCS surface resistance after 140<sup>o</sup>C baking with electropolished K-15 cavity



Figure 2 : 140°C baking effect the high gradient performance for the electropolished K-15 cavity

As an example, in Figure 1 the temperature dependence of the BCS surface resistance before and after baking is shown for cavity K-15. In Figure 2 Qo-Eacc curves are plotted for both cases. For both cavities the BCS surface resistance with electropolishied surface was lowered by nearly a factor of 2 as was observed in earlier experiments with chemically polished surface. In these tests on K-15 and K-16 also an improvement in Qo vs. Eacc from Eacc ~ 25 MV/m to Eacc > 30 MV/m was observed. This improvement remained after an additional HPR treatment. The Oo values at 2K remained nearly the same before and after baking because of a rather large residual surface resistance ( ~ 16 n $\Omega$ ) which masked the improvements in  $R_{BCS}$ . Typically, the electropolished KEK cavities exhibit " processing" (multipacting) levels around Eacc ~ 16 MV/m and Eacc ~ 27 MV/m. It should be emphasized that after the 140°C baking the processing times to overcome these barriers have become much shorter, an effect, which can easily be understood in terms of removal of residual adsorbates from the surface.

# 3 DATA ANALYSIS WITH Halbritter's COMPUTER PROGRAM

# 3.1 Halbritter's BCS Surface Resistance Program [5]

Halbritter's BCS surface resistance program calculates the BCS surface resistance using 7 parameters : frequency f, temperature T, critical temperature T<sub>c</sub>, energy gap  $\alpha = \Delta / k_B T_c$ , London penetration depth  $\lambda_L$ , coherence length  $\xi_0$  and mean free path  $\Lambda$ . Using this code, C. Liang and L.Doolittle [7] developed the fit program BCSFIT to estimate the material parameters  $T_c$ ,  $\alpha$ ,  $\lambda_L$ ,  $\xi_0$  and  $\Lambda$  from the measured temperature dependence of the surface resistance. From our past experiences BCSFIT gives good fitting, when  $\alpha$  and  $\Lambda$  were used as free parameters and critical temperature, London penetration depth and coherence length were fixed at  $T_c = 9.25K$ ,  $\lambda_L =$ 360Å, and  $\xi_0 = 640$ Å. Typically in such a fit, gap values were around  $\alpha$ =1.86 and the mean free paths were around 1000Å for chemically polished surface and 230Å for electropolished surfaces. So far we have considered that the often observed higher Q-value at 4.2K for electropolished cavities is caused by the smaller value of mean free path, which happens to be close to the BCS surface resistance minimum. As shown from this new analysis described following, however, this consideration is has to be changed.

### 3.2 Three parameter fitting

In using our standard two parameter fitting routine for the experimental results after the baking at 140°C we realized that no satisfactory fit could be obtained; especially the fitted surface resistance was too large around 4K and too small around 2K. This tendency is already seen in the two parameter fitting when we carefully look. In order to find out which of the material parameters is impacting the most on the 140°C baked BCS surface resistance, we carried out a set of calculation with only one parameter as a fitting parameter and all others fixed at the typical numbers as mentioned above. This exercise is demonstrated in Figure 4. It became obvious that the London penetration depth is an as sensitive material parameter as the mean free path and has to be taken into account as a free parameter in our data analysis of the results after baking.

Another problem was to determine an initial value for the mean free path  $\Lambda$ . As shown in figure 5, R<sub>BCS</sub> has a minimum as a function of  $\Lambda$ , leaving some ambiguity about the value of  $\Lambda$ . Often for the data after baking, best fits are obtained in two cases, namely for large values of  $\Lambda$  (~ 5000Å) and for very small values (~10 Å). Using the resulting parameter sets from the fits, we then calculated with Halbritter's program the penetration depth and we chose the set , which gave a longer penetration depth after baking than before baking. This judgment took into account the experimental observation that after the baking the resonance frequency of the cavities always changed to slightly lower values indicating an increase in volume.

In summary, the criteria used for judging the BCSFIT valid were;

- 1) a three parameter fit with  $\alpha$ ,  $\Lambda$ , and  $\lambda_L$  as free parameters,
- 2) the smallest chsquare value for the fit,
- 3) the fit parameter set has to result in a longer penetration depth.

An example of BCSFIT for the baked data (K-15) is presented in Figure 4. In the graph two parameter fitting result is also shown for a comparison. Table 1 summarizes the analyzed results from the experiments on K-15 and K-16. Some more information are added on KEK cavities K-11 and JL-1 to see the  $85^{\circ}$ C baking effect in the chemical polished or electropolished surfaces. One result of the chemically polished cavity (P-6) also presented as a comparison with electropolishing. The other fit result of P - 3 cavity manufacture out of reactor grade niobium material also added to discuss the relationship in the mean free path between the surface and the bulk.

### 4 INTERPRETATION OF THE BAKING EFFECT RESULTS BY THE TWO FLUID MODEL

# 4.1 RF surface resistance by the two fluid model

BCS theory accompanies very complicated calculation and results in a difficulty to intuitively understand its physics. Two fluid model is very helpful to interpret these experimental results. It becomes a wordy expression but we present its some important formulas, which are used in our consideration.

In the Two fluid model the superconducting state is described by the presence of normal electrons (density nn) and superconducting electrons (ns). RF field interacts with the normal conducting electrons causing a RF surface resistance. All conduction electrons ( $n_c$ ) in the material are the sum of both species:



Figure 3: BCSFIT one parameter fitting for the baked data







Figure 5 : Surface resistance calculated by the two fluid model and BCS theory Used parameters are Tc=9.25K,  $\alpha$ =1.86,  $\lambda_L$ =360Å,  $\xi_o$ =640Å, frequency =1300 MHz

 $\label{eq:nc} \begin{array}{l} n_c = n_n + n_s \eqno(2). \end{array}$  Here,  $n_c$  is related to the normal electrical conductivity  $\sigma_n$ :

$$\sigma_n = \frac{n_c e^2 \Lambda}{m v_F} \tag{3},$$

where e is the electron charge, m is the electron mass and  $v_F$  is the Fermi velocity. The surface resistance is only proportional to  $n_n$  and is calculated from  $n_c$  and  $\Delta$ :

$$n_n = n_c \cdot \exp(-\frac{\Delta}{k_B T}) \tag{4}.$$

The temperature dependent part ( $R_{BCS}$ ) of the RF surface resistance Rs for an angular frequency  $\omega$  and a temperature T is given by this model as [8]:

$$R_{BCS} = c \cdot \lambda eff^3 \cdot \sigma_n \cdot \frac{\omega^2}{T} \cdot \exp(-\frac{\Delta}{k_B T}) \quad (5).$$

c is a constant not depending on materials,  $\lambda$ eff is an effective RF penetration depth related to the London penetration depth  $\lambda_L$  and the effective coherence length  $\xi$ :

$$\lambda eff = \lambda_L \cdot \sqrt{\frac{\xi_O}{\xi}}$$
(6).

 $\xi_0$  is the coherence length for pure material ( $\Lambda = \infty$ ):  $\xi_0 = (h/2\pi) \cdot v_F / 2\Delta$  (7).

Table 1 : BCSFIT Results

The effective coherence length however depends on mean free path:

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{\Lambda} \tag{8}.$$

The London penetration depth is described in SI units as following:

$$\lambda_L = \sqrt{\varepsilon_o \frac{mc^2}{4\pi n_s e^2}} \tag{9}.$$

 $R_{BCS}$  contains the electric conductivity, as a result the mean free dependence on  $R_{BCS}$  is given as following:

$$R_{BCS}(\Lambda) \propto (1 + \frac{\xi_0}{\Lambda})^{3/2} \cdot \Lambda$$
 (10).

 $R_{BCS}$  increases proportionally to  $\Lambda$  with larger mean free path; for shorter mean free path it also increases but with decreasing mean free path. Therefore,  $R_{BCS}$  has a minimum in its dependence on  $\Lambda$ . In Figure 5 the mean free path dependencies of the surface resistance as given by the two fluid model and the BCS theory are shown. The two fluid model gives a rather good explanation at the mean free path less than 5000 Å.

Cavity	f	Tc	α	$\lambda_{\mathbf{L}}$	ξo	$\Lambda$	CHISQ	$\lambda_{eff}$	κ
treatment	[MHz]	[K]		[A]	[A]			[A]	
K-15	1298 751	9.25	2.01	360	640	4520	4 970E2	/3/	0.78
CP	1290.751	9.25	2.01	500	040	4320	4.970112	-5-	0.70
K-15	1298.233	9.25	1.73	206	640	3670	1.960E2	270	0.50
EP									
K-15									
EP, 140 <sup>0</sup> C baking	1297.124	9.25	1.96	197	640	42	3.058E2	690	4.18
K-16	1298.894	9.25	1.81	333	640	850	3.709E2	465	1.3
СР									
K-16	1298.37	9.25	1.68	182	640	5170	2.181E2	243	0.41
EP									
K-16									
EP,140 <sup>o</sup> C baking	1298.16	9.25	1.71	156	640	100	1.421E2	390	4.5
JL-1									
CP,85 <sup>0</sup> C baking	1298.3	9.25	1.87	338	640	800	5.047E2	474	1.3
JL-1									
EP,85 <sup>0</sup> C baking	1292.081	9.25	1.80	175	640	1850	7.896E1	254	0.73
K-11									
CP,85 <sup>0</sup> C baking	1300.2	9.25	1.82	298	640	240	1.835E2	547	1.8
K-11									
EP,85 <sup>0</sup> C baking	1296.106	9.25	1.79	182	640	5550	2.632E2	239	0.42
P-6	1488.43	9.25	1.76	360	640	825	1.115E2	505	1.4
СР									
P-6									
CP,140 <sup>o</sup> C baking	1488.34	9.25	1.83	194	640	42	1.165E2	680	17.4
P-3									
R-grade, CP	1496.3	9.25	1.79	280	640	248	9.438E1	510	2.8

# 4.2 Interpretation of the 140°C baking effect

We try to explain the observed changes in material parameters after the 140°C baking by diffusion of adsorbates or surface oxides into the niobium material. Among several candidates such as hydrogen, carbon dioxide, water is most plausible. One can calculate from the known diffusion constant Do, the activation energy Ea, the temperature T and the baking time to the mobility r of the various gas species:

$$r \sim \sqrt{D \cdot t}_{O} \tag{11},$$

$$D = Do \cdot \exp(-\frac{Ea}{k_B T}) \tag{12}.$$

Niobium is nearly transparent for hydrogen at  $140^{\circ}$ C and a baking time of ~ 40hrs (mobility 21mm): for nitrogen the mobility is only 1.6 Å under those conditions, whereas for oxygen it is in the order of the penetration depth (~1300 Å). An experiment, during which after baking material was in successive steps removed from surface and the surface resistance was measured each time, confirmed that the effect of the baking disappears after removal of several thousand Å [1].

Oxygen from e.g. the interface [9] diffusing from the surface into the penetration depth shortens the mean free path. A shorter mean free path in turn shortens the coherence length (equation 8), which increases the effective RF penetration depth (equation 6), hence causing a lowering of the resonance frequency of the cavity. This interpretation dependent on only the mean free path change with the baking effect seems to right qualitatively but can not explain quantitatively the amount of the R<sub>BCS</sub> deduction (dR<sub>BCS</sub>/R<sub>BCS</sub> ~ - 0.5) especially on the chemical polished surface. Considersing the two fluid model, we has to calculate the total derivative of equation (5) with  $\alpha$ ,  $\Lambda$  and  $\lambda_{\rm L}$  in order to evaluate the real reduction rate as following;

$$\frac{dR_{BCS}}{R_{BCS}} = -\frac{17.2}{T} \frac{d\alpha}{\alpha} + 3 \frac{d\lambda_L}{\lambda_L} + (1 - \frac{3}{2} \frac{\xi}{\Lambda}) \frac{d\Lambda}{\Lambda}$$
(13),

$$\frac{d\lambda_{eff}}{\lambda_{eff}} = \frac{d\lambda_L}{\lambda L} - \frac{1}{2} \cdot \frac{d\xi}{\xi}$$
(14).

Here, for the first term of (13) we used the relationship

$$\frac{\Delta}{k_{BT_c}} = 1.86 , \text{ Tc} = 9.25 \text{ K for niobium}$$
(15).

These equations make rather clear individual contributions from three parameter changes by the baking. Examples are calculated for 4.2K in Table 2 with K-15(EP) and P-6(CP) used the number in Table 1. Here,  $\xi/\Lambda$  in the 3rd term in eq. (13) was calculated using the values after baking. The evaluated reduction factor dR/R is an under estimate by a factor 2 for the electropolished surface and an over estimate for the chemically polished surface. Such the under or over estimating comes from the harder  $\Lambda$ dependence of R<sub>BCS</sub> in the two fluid model, which is seen in Figure 4. However, eq. (13) is very suggestive. It shows that the sign changes at  $\xi/\Lambda=2/3$ . Namely the mean free path becomes smaller and results in  $\xi/\Lambda<2/3$ , the contribution to R<sub>BCS</sub> from  $\Lambda$  starts to increase. This is due to the longer RF penetration. However, even at such a small mean free path, other two parameters cancel the increase in  $R_{BCS}$ . Especially chemically polished surface has a shorter London penetration after the baking. It much cancels the mean free path part. Thus even the mean free path becomes very short by the baking, a net reduction of a nearly 0.5 in  $R_{BCS}$  appears.

Eq. (14) also leads to an interesting prediction which a frequency shift should be smaller in chemically polished cavities than electroplated cavities. Due to oxygen diffusion the effective coherence becomes shorter and the RF penetration increases. However, the London penetration is shortened (see Table 1) though we do not yet know why, and it cancels somehow the contribution from the longer RF penetration . This effect is very large in chemically polished cavities because the London penetration depth varies largely in such cavities (see Table 1, P - 6). On the other hand in electropolished cavities, the London penetration depth is already short and is little changed by the baking. In Table 3 calculated examples are shown using the results in Table 1 for K-15 and P-6. The chemically polished cavity, the frequency shift is much smaller than the electropolished cavity.

Table 2: Example of an evaluation for the individual contribution to the RBCs reduction by the baking with the three parameters for K-15( electropolished surface) and P-6 (chemically polished surface)

	dα/α	$d\lambda_L/\lambda_L$	$d\Lambda/\Lambda$	1st	2nd	3rd	dR/R
K-15 EP	-0.13	-0.044	-0.989	-0.52	-0.13	+0.40	-0.25
P-6 CP	-0.04	-0.46	-0.46	-0.16	-1.38	+0.39	-1.15

Table 3 : RF penetration change by the baking

	dξ/ξ	$d\lambda_L/\lambda_L$	$d\lambda_{eff}/\lambda_{eff}$
K-15 EP+140 <sup>0</sup> C baking	-0.93	-0.044	+0.42
P-6 CP+140 <sup>0</sup> C baking	-0.93	-0.46	+0.005

#### **5 DISCUSSION**

### 5.1 Mean free path in the penetration depth

The analysis as outlined above is just a parameter fitting and the results are phenomenological. It still has to be explained why the London penetration depth becomes smaller by the baking (see Table 1). The two fluid model only answers that the density of superconducting electron  $n_s$  increases by the baking. The microscopic explanation should be done in the future. It has been suggested [10] that the diffusion of oxygen into the penetration depth causes a smearing of the density of states [11] and might lead to a reduction in RF absorption.

As for now we assume that this analysis has - after all - a physical meaning. One of the interpretations of the fit

parameter set concerns the mean free path in the penetration depth. The mean free path in the matrix is given by [8]

$$\Lambda [Å) = 27 \cdot RRR \tag{16}.$$

With a RRR value of 200, a mean free path of 5400Å results. This value is close to the fitted value for the mean free path after electropolishing, indicating that the electropolished surface is as pure and clean as the bulk material. However, that is not the case of chemically polished surface. Applying equation (16) to the parameters from Table 1, one calculates a RRR value in the surface layer of RRR~30. In the case of the reactor grade cavity P - 3 this value reduces to ~ 10, which was manufactured out of reactor grade niobium material.

Through this data analysis, we have to reconsider the explanation for the higher Q-value at 4.2K in electropolished cavities. This effect is due to not the BCS minimum in the mean free path, but the shorter RF penetration depth effect by the shorter  $\lambda_L$  and the very longer  $\Lambda$  in the electropolished surfaces.

### 5.2 Ginzburg-Landau Parameter $\kappa$

The Ginzburg-Landau parameter  $\kappa$  is given by

$$\kappa = \lambda_{\rm eff} / \xi \tag{17}.$$

The  $\kappa$  value separates superconductor into two types : Type-I ( $\kappa$ <1) and Type-II ( $\kappa$ >1). Niobium is known as a Type-II superconductor, but for a pure material it is close to a Type-I. From Table 1 we can take the following information : The electropolished surfaces have a κ-value of 0.4 - 0.7, suggesting a Type-I behavior. After baking, the  $\kappa$ -value becomes much larger and changes the surface to a Type-II is suggested. This is not too surprising if one accepts the oxygen diffusion explanation : it is well known that a Type-I superconductor can be changed to a Type-II as a result of increased impurity. κ-values of chemically treated surfaces range from 0.8 - 2.8 and show not always Type-II characteristics. On the 85°C baking has been done at KEK, the baking effect is already started if one look carefully at the results in Table 1. Especially the chemically polished surface has much sensitive even at the lower baking temperature.

# **6 SUMMARY**

In this investigation we have confirmed that a baking of electropolished cavities at 140°C for longer period of time lowers the BCS surface resistance by nearly a factor of 2, an effect, which was also observed on chemically polished surfaces. We analyzed this effect by using Halbritter's surface resistance program and it can be well explained by diffusion of oxygen into the penetration depth. However, one has to allow a change of the London penetration depth - solely a shortening of the mean free path does not " do the trick". Experimentally it needs to be confirmed in future experiments that the penetration depth is actually increasing after "in-situ" baking. The analysis also seems to indicate that electropolished cavity surface shows a clean Type-I behavior. After baking the material changes to a Type-II superconductor.

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