OXYGEN DIFFUSION IN RRR NIOBIUM DURING HIGH TEMPERATURE BAKING*

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Abstract

Past oxygen diffusion measurements were mostly conducted with commercial grade niobium. RRR measurement of furnace treated niobium samples showed the oxygen diffusion rate in high purity niobium can be much different from past measurements. Samples were baked in furnace at various conditions and subsequently etched incrementally before RRR measurement. Compared to the oxygen concentration of reference niobium sample, a new O diffusion constant can be obtained by the RRR method.

INTRODUCTION

The hydrogen concentration in SRF cavities can be elevated during the chemical processing. Such hydrogen concentration can cause dramatic degradation for RF performance during horizontal operation. High temperature baking in ultra high vacuum can release the hydrogen from bulk niobium. Typical baking takes 10 hour soaking at 600 °C or 2 hour soaking at 800 °C. Such baking requires high vacuum furnace. During the evaluation of Fermilab furnaces, the high background vacuum pressure caused niobium samples to have significantly degraded residual resistivity ratio (RRR). Calculation showed the RRR degradation is very high and inconsistent compared to previously measured oxygen diffusion constant in niobium [1,2]. Niobium RRR improvement after progressive acid etching can be one way to measure niobium oxygen diffusion in baking temperature (600°C). In a separate experiment, titanium shield was used to reduce the oxygen partial pressure while RRR niobium sample was baked. The change of niobium RRR indicated the oxygen diffusion constant is consistent with that of niobium sample without titanium shield.

EXPERIMENTAL METHOD

RRR of Niobium samples (1/8 x 1/8 x 3 in^3) were measured before the baking. Niobium samples were all etched by BCP for 15 minutes with niobium wires attached. Samples were rinsed in de-ionized water in an ultrasonic container. Niobium wires were used to suspend the niobium samples in the furnace without the sample contacting any surfaces. Their RRR were measured again after the baking. In the case of Titanium shield, samples were also analyzed with SEM/EDS. No other elements were detected within SEM/EDS sensitivity.

Table 1 lists the RRR results of niobium samples baked in the furnace without titanium shield. The oxygen partial pressure was at 9x10^{-8} Torr during the baking. The RRR degraded dramatically. BCP etching removed 80 μm from sample P. It recovered its RRR to 183. All BCP etching was conducted under cold solution (10-12 °C) to avoid hydrogen migration.

Table 1: RRR Measured for Samples Baked Without Titanium Shield, RRR = R(300K)/R(10K). 50nV noise corresponds to ±30 in RRR error bar.

Sample	Before bake	Baked 650 °C 10 h	BCP removal of 80 μm
Sample P	400	165	183

For the second test, a small titanium tube was used as shield as shown in Figure 1. RRR degradation shown in Table 2 was less significant compared to those in Table 1. The oxygen partial pressure decreased to 2.6x10^{-8} Torr during the 600 C soaking as shown in Figure 2. Yet the RRR still degrades as shown in Table 2. Most likely it would be due to the overwhelming size of the furnace (φ36"x150") compared to the smaller Ti tube (φ6"x8"). The open port of the tube can not be fully effective to prevent residual oxygen to travel to the sample.

The third test in a series was conducted using mostly enclosed large Ti tube (φ10"x20"). Its vacuum was shown in Figure 3. The oxygen partial pressure was decreased further to minimum 1.1x10^{-8} Torr. The samples showed smallest RRR degradation as shown in table 3.
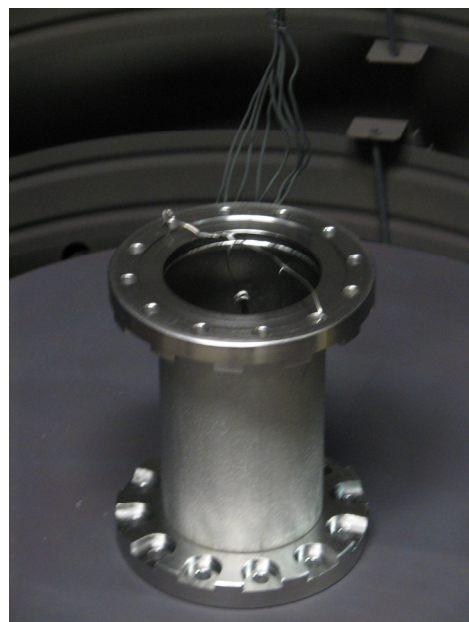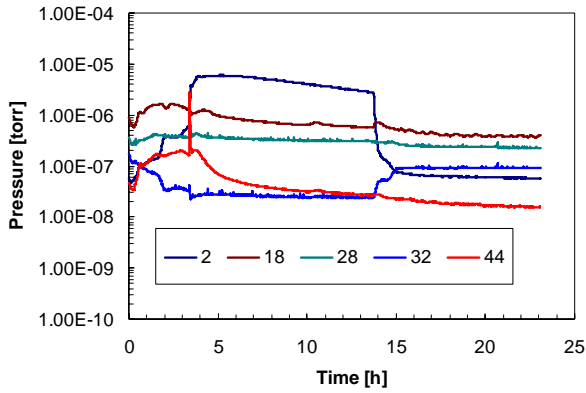

Figure 1: Sample suspended into the Ti tube.

Figure 2: Partial pressure during the 600 C 10 hour baking with open titanium tube.

Table 2: RRR Measured for Samples Baked Inside an Open Ti Tube, RRR = R (300K) /R (10K). 50 nV noise corresponds to ±30 in RRR error bar

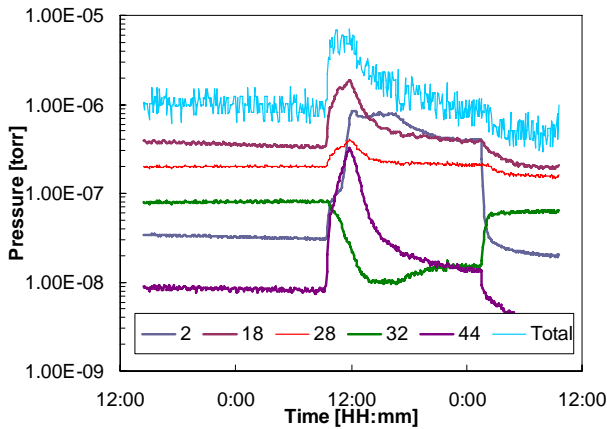| Sample	Before bake	Baked 650 °C 10 h
Sample 1	370	271
Sample 2	301	227

Figure 3: Partial pressure during the 600 C 10 hour baking with large enclosed Titanium tube.

Table 3: RRR Measured for Samples Baked with Single Cell Titanium Shield, RRR = R (300K) /R (10K). 50 nV noise corresponds to ±30 in RRR error bar

Sample	Before bake	Baked 650 C 10 h
Sample D	401	387
Sample F	314*	313

*Sample F was previously baked in different furnace.

OXYGEN DIFFUSION CONSTANT

For samples that see high oxygen content in furnace, the bulk oxygen density variation was negligible compared to the oxygen diffused into the polluted layer. This simplifies the calculation, for one does not need to consider the initial oxygen density distribution in diffusion process other than assuming an initial constant ϕ_0. Deep in the bulk, when the oxygen density is close to the initial amount, the RRR should remain high, so the error would be minimal. Certainly this initial O density will be considered in future effort.

Thus the density should be

$$\frac{\phi(x,t) - \phi_0}{\phi_0(0) - \phi_0} = erfc(\frac{x}{\sqrt{4Dt}})$$

To calculate $\phi_0(0)$, the starting density at the niobium boundary [3] at time of zero, one assumes the certain ratio (S) of O_2 molecules that impact the niobium surface will be absorbed and diffuse into the first polluted layer. The ratio S is usually called sticking coefficient, which we will assume it is 0.5. The influx of O_2 molecules can be expressed as:

$$F = \frac{P}{\sqrt{2\pi mkT}},$$

where P is O_2 partial pressure, m is O_2 mass, k is boltzman constant and T is temperature.

So the initial boundary density $\phi_0(0)$, after baking time period t_0 can be obtained as:

$$\phi_0(0) = \frac{SFt_0}{2\sqrt{Dt_0}},$$

where $2\sqrt{Dt_0}$ is the diffusion distance. It is assumed to be constant during the baking. In the following calculation the D was arbitrarily assumed to be 3.34×10^{-12} m^2/s. Later we will see this number closely matched the experimentally measured data.

In a typical high oxygen pressure of 1×10^{-7} Torr, Figure 4 shows the polluted layer is around 100 µm with highest O concentration at 1300 ppm. Most of the niobium sample maintains low O concentration after the polluted layer.

Total resistivity of niobium at 10 K would be [4]

$$R_T(r,t) = R(10) + C_o(r,t)\frac{dR}{dC_o} + R(other),$$

where $C_o(r,t) = \phi(x,t)$, R(10) is resistivity at 10 K,

C_o is O weight ppm, dR/dC_0 is the resistivity coefficient for O impurities and R(other) is resistivity caused by all other impurities at 10 K.
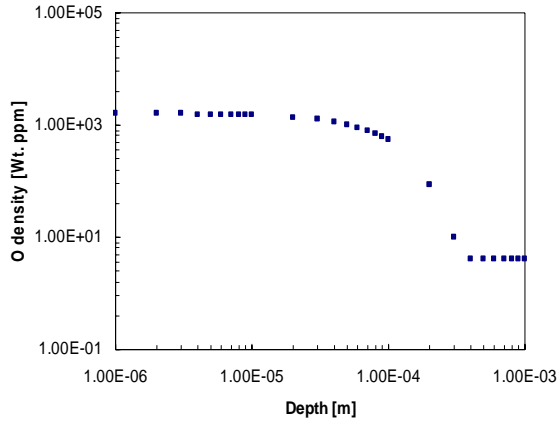
Figure 4: The polluted layer is around 100 µm with O concentration around 1300 weight ppm. 4 ppm initial O concentration is assumed and sticking coefficient is at 0.5.

Assuming other major impurities are N (2 ppm), C (1 ppm) and Ta (50 ppm), Niobium RRR can be calculated [2] shown in Figure 5.
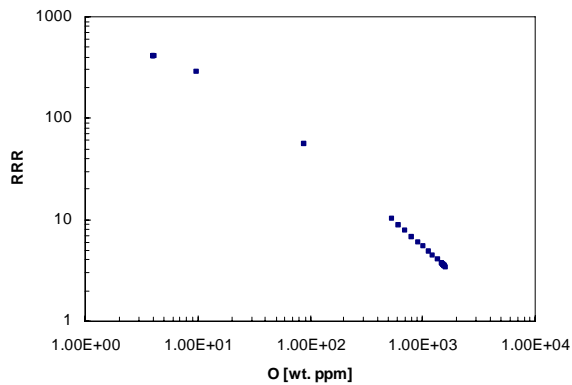

Figure 5: Niobium RRR decreases with increased uniform O concentration.

Since the O concentration is not uniform as shown in Figure 4, the RRR will depend on the sample size and its dimensions of polluted layer.

Through a simplified geometry of niobium RRR samples (Figure 6), if voltage drop in an L meter long niobium stick is V, the current flow through the entire section of niobium sample is:

$$I = \int \frac{V}{R_T(r,t)L} 2\pi r dr$$

Sample resistivity by effectiveness is:

$$R_e = \frac{\pi R^2}{\int_0^R \frac{2\pi r dr}{R_T(r,t)}},$$

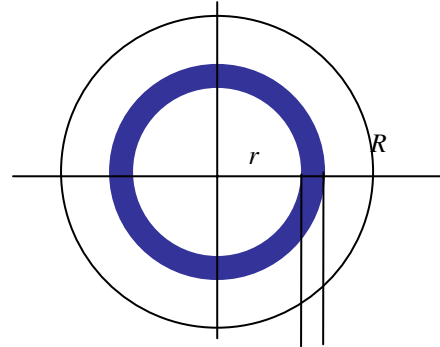where $t=t_0$ and R is sample size.

Figure 6: A simplified round wire to represent the square pieces of Niobium samples.

RRR calculation can be expressed as

$$RRR = \frac{R(300)}{R_e},$$

where $R(300)$ is resistivity at 300 K.

Assuming the general parameters discussed previously, one obtains the RRR degradation as seen in Figure 7.

Table 4 listed those RRR measured after exposed to different oxygen partial pressure during baking. Those data were plotted together with the calculated RRR.
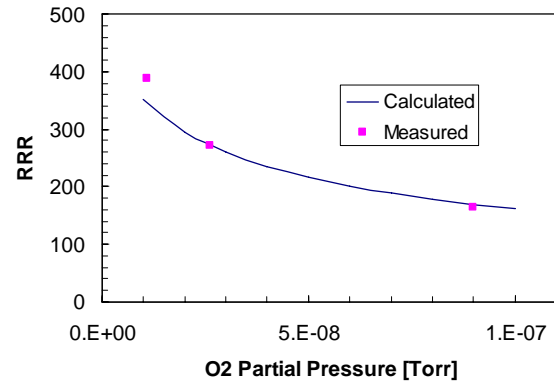

Figure 7: RRR degradation as function of O_2 partial pressure (Torr).

06 Material studies

Table 4: RRR After Baking and Their Dependence on O_2 Partial Pressure

Sample	Before bake	Baked 650 °C 10 h	O_2 partial pressure [Torr]
Sample P	400	165	9.0×10^{-8}
Sample 1	370	271	2.6×10^{-8}
Sample D	401	387	$\sim 1.1 \times 10^{-8}$

Further calculation using this set of parameters predicted the material removal of 80 μm will recover the RRR of niobium sample P from 165 to 181, which closely matched the measured data listed in Table 1.

DISCUSSION AND CONCLUSION

Niobium RRR depends on various interstitial impurities. The set of impurity levels were referenced from modern day niobium material for SRF applications [5]. From the residual gas analyzer data, it is believed that the partial pressure of oxygen was the single variable affected by the titanium shield. During the sample baking process, Hydrogen and Oxygen would be the two elements that will change their concentration greatly in niobium. There is reason to believe the further deceasing of already low initial hydrogen concentration in niobium sample does not affect the overall RRR very much. It is safe to conclude the RRR degradation was dominantly due to the Oxygen diffusion in niobium.

The matching of calculated RRR and measurement data suggested the oxygen diffusion constant for niobium at 650 °C would be around 3.34×10^{-12} m^2/s. which is in between the previous measured data.

Future work will continue the progressive etching of the niobium sample and conduct the surface elemental analysis to improve the knowledge of the interstitial impurities for more accurate diffusion constant measurement.

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