Solid State Gettering and RRR
by Dan Kapner

Introduction

In particle accelerators, particles are subjected to an electric field to supply them with energy. This electric field is applied with RF cavities. RF cavities are shells of conducting metal that generate electric fields when alternating current flows through them at a certain frequency. Many cavities in use currently are made from normal conducting material. These normal conducting RF cavities are limited by the amount of power they use. By using superconducting materials for the RF cavities, power use becomes less of a concern since superconductors have virtually no resistance. The switch to superconducting RF cavities will allow greater electric fields to be generated, thus supplying greater energy to the particles, while using less power.

There are several factors that can inhibit the performance of a cavity. One of these factors is the presence of impurities in the material itself. To get niobium to superconduct, we must chill it with liquid helium. If impurities are present within the niobium, its performance as a superconductor will be hindered. Our goal is to remove these impurities using solid state gettering techniques.

Solid state gettering is the evaporation of a substance, or gettering agent, onto a desired surface, from which the agent may withdraw impurities. In our case we use titanium as a gettering agent. A sample of Niobium is wrapped in Titanium foil and placed in a furnace. As the temperature rises, enough Titanium vaporizes and settles on the surface of the sample, so that, with continued heating for several hours, impurities, mainly Oxygen, diffuse out towards the Titanium layer. At the end of the furnace run, what remains is a purified Niobium sample with a layer of titanium and oxygen on the surface. The layer of impurities is removed from the Niobium sample by etching it in a 1:1:2 ratio of nitric, fluoric, and phosphoric acids, also called BCP.

After being etched, the samples' purifies are measured. A sample's purity is reflected in what's known as the residual resistivity ratio, or RRR. This RRR is a ratio of the voltage across a superconductor at room temperature and the same voltage across that superconductor at 4.2 Kelvin, the temperature of liquid Helium. For a normal conducting material, the resistivity is proportional to temperature. At higher temperatures, resistivity is proportional to T^3, a result of the scattering of conduction electrons off of vibrating elements in the metallic lattice. At low temperatures, resistivity is proportional to T^5. Resistivity also receives a contribution from residual resistivity, that is a result of imperfections in the lattice of the material. These imperfections result from the presence of different sized molecules in the lattice, i.e. impurities. At room temperature, the residual resistivity is negligible with respect to the temperature-dependent resistivity. In a superconducting state, there is no resistivity. But, a superconductor can be driven out of a superconducting state by the application of a magnetic field. When this magnetic field, termed the critical field, is imposed, the sample becomes normal conducting. At this low temperature, the residual resistivity is no longer negligible. The voltage across the sample is measured, and thus provides a means by which to measure the purity of the sample in the RRR.

The ultimate goal of RRR research is to find ways to purify niobium so that there might be a consistent method for producing superconducting RF cavities. For this project, there are several goals. At the time of this report, there were fluted beam tubes being produced. To insure that the chemical etching would not reduce the thickness of these flutes too much, I measured the etching rates of 1:1:2 nitric, fluoric, and phosphoric acids, or BCP, on a niobium sample of comparable quality to the flutes. This sample was 192A-3. Previously, Marcela Arana did research on whether or not using Hafnium and Zirconium as gettering agents in addition to Titanium would increase the purity of the Niobium samples. With samples 162-E, 162-F, and 162-K, I set out to test and confirm her findings. The final goal of this project is to determine whether or not prolonged heating of samples in the presence of Titanium effects a significant increase to their purity.

RRR Setup Description

To measure the RRR of a sample, we must cool it down to 4.2 K. In the interest of keeping the liquid helium from evaporating more quickly, the sample is cooled down in liquid nitrogen before inserted into the dewar with the helium. Once the sample is cooled, a signal is sent through it. This signal starts at the function generator of the RRR setup. The signal is a sinusoidal wave with a frequency somewhere between 30 and 40 hertz. This signal goes to the power supply where it is turned into an amplified current signal. The generated signal also goes to the lock-in amplifier where it serves as an external reference for the signal returning from the sample.

The current signal from the power supply goes into the current leads on the sample. The current running through the sample is read by an ammeter connected to the "to ammeter" leads on the sample. The peak to peak voltage of the signal being sent to the sample is read by a multimeter connected to the current programming unit of the power supply. The current from the power supply runs through the sample and through the ammeter and generates a very small voltage, because of the temperature, across the sample.

Because this voltage is so small, we use a four-lead connection to the sample. Two leads serve to send the current through the sample. The other two are for the lock-in amplifier. If we tried to measure the voltage across the sample on the same loop as the ammeter, the voltage would include that across the ammeter. So, we place two leads between the current leads and connect these to the lock-in amplifier. The lock-in amplifier has a very high internal resistance, so that it may read very small signals and also so that it will not draw much current from the ammeter loop. The voltage leads from the sample run to the input of the lock-in amplifier which then displays the voltage on its own scale and on the digital multimeter to which it is connected.

A magnetic field is used to drive a sample out of superconductivity. To achieve this magnetic field, a superconducting magnet is immersed in the helium along with the sample.

The strength of the magnetic field is proportional to the current that runs through the magnet. This current can be controlled with the second power supply at the base of the RRR setup. The current is measured from the output above the second power supply. The output is a voltage, but through the magnet there is one millivolt per ampere. Thus reading the output in millivolts on a multimeter is essentially reading the amps going thorough the magnet.

Etch Rates

The sample 192A-3 was etched at fifteen minute intervals in BCP. Before and after each etch, its thickness was measured with a micrometer. All etching on this sample was done between ten and fifteen degrees centigrade, mimicking the process the flutes needed to undergo.

Table 1 : Etch Rate of 1:1:2 BCP on Niobium Sample 192A-3 :

time etched (min)	thickness (in)	total etch rate (inches/min)
0	0.1279	n/a
15	0.1260	1.27E-04
30	0.1241	1.27E-04
45	0.1219	1.33E-04
60	0.1154	2.08E-04

The rate is fairly constant until the last fifteen minute interval. The thicknesses of other samples from the same sheet, i.e with approximately identical starting thicknesses, were checked and provide additional data for the etch rate. These samples were not held in any temperature range. The etch rate is measured with respect to the starting thickness of sample 192A-3.

Table 2 : Etch Rate of 1:1:2 BCP on Niobium Samples 192B-3, 192A-2, 192B-2 :

sample	time etched	thickness (in)	total etch rate (in/min)
192A-3	0	0.1279	n/a
192B-3	30	0.1239	1.33E-04
192A-2	45	0.1218	1.36E-04
192B-2	60	0.1199	1.33E-04

Hafnium and Zirconium as Gettering Agents

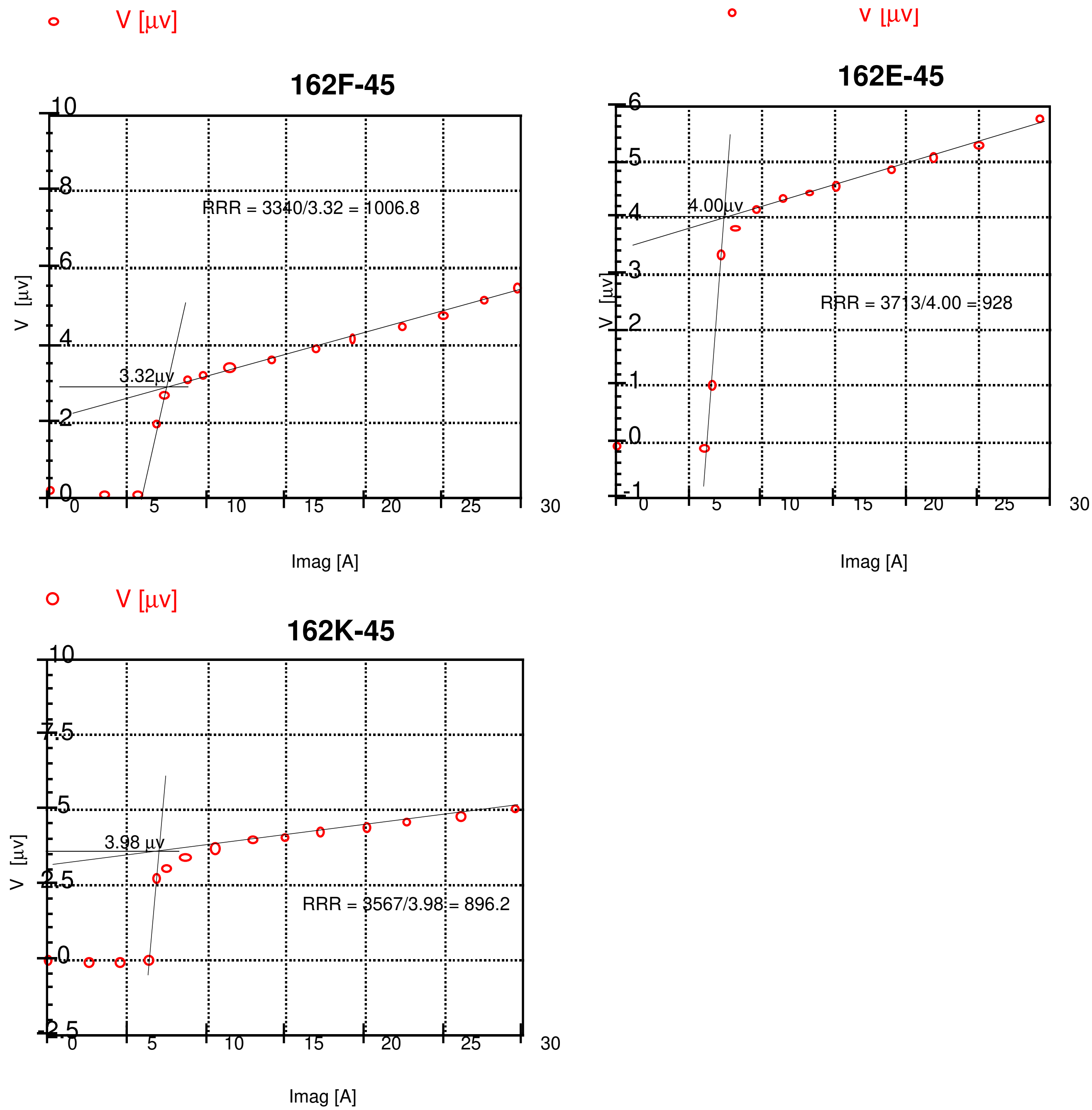
In her report, “Purification of Nb Using Solid State Gettering Methods,” Marcela Arana attempted to remove Nitrogen and Carbon impurities from Niobium using Hafnium and Zirconium as gettering agents, while still using Titanium. She concludes that “the Niobium coated with Zirconium and Hafnium showed a lower RRR than the sample given the titanium wrapping alone [a fact which] indicates that instead of removing impurities from the Niobium, the Hafnium and Zirconium seem to block the diffusion of the atoms towards the Titanium and limit its effect.”

Sample 162-F was used as a control, having only been treated with Titanium. Sample 162-E was sputtered with 1.2 μm of Zirconium, and sample 162-K was sputtered with 1.2 μm of Hafnium. Each of these samples received these treatments for Marcela Arana’s project, but were never tested. Each were etched in 1:1:2 BCP for 45 minutes and had their RRR’s measured.

Table 3 : Effects of Hafnium and Zirconium as Gettering Agents on RRR

sample	treatment received	RRR before treatment	RRR after treatment
162-F	Ti only	620	1006.8
162-E	Ti, Zr	672	928.2
162-K	Ti, Hf	886	896

Titanium alone was the most effective in purifying the samples. Zirconium and Titanium were more effective than Hafnium and Titanium.



Graphs 1-3 : RRR measurements of Samples 162-F (Ti treated), 162-E (Ti, Zr treated), 162-K (Ti, Hf treated)

Furnace Time's Effect on RRR

When a sample is purified by solid state gettering methods, it is placed in a furnace that is kept at a high vacuum. The furnace reaches about 1400 degrees centigrade and stays at this peak temperature for four to eight hours. When Zirconium and Hafnium are used as gettering agents, they must first be applied to the surface of the Niobium after evaporation.

But, when Titanium is used, the sample need only be wrapped in Titanium foil. When the furnace heats up, enough Titanium condenses onto the Niobium surface so that Oxygen impurities may diffuse outwards towards this layer. The question arises as to whether the purity of the Niobium will increase with increased furnace time. To address this question, six samples were prepared, each sample receiving one more furnace run than the preceding sample.

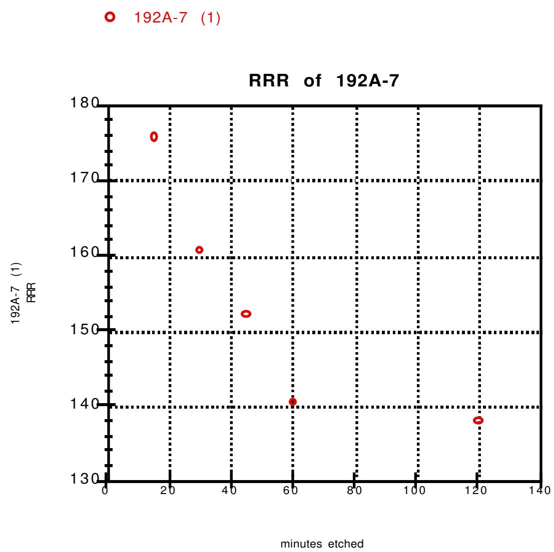
Table 4 : Identification of Samples and Furnace Times

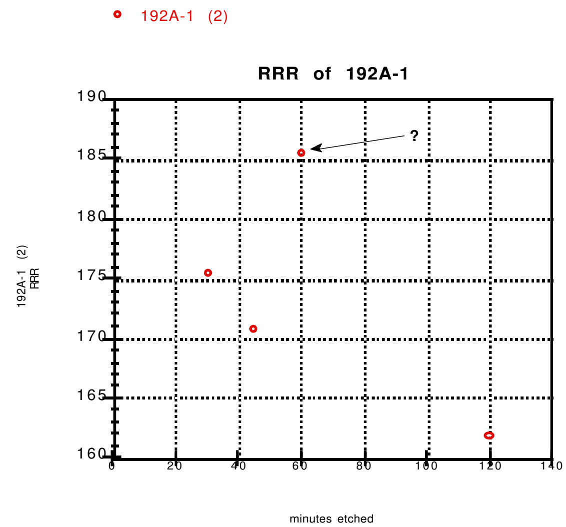
sample	# of furnace runs
192A-7	1
192A-1	2
192A-9	3
192A-8	4
192A-6	5
192A-10	6

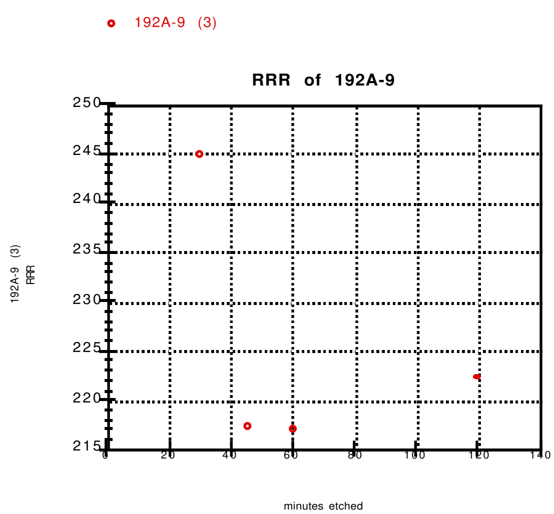
Each sample was etched at fifteen minute intervals four times and then given a final sixty minute etch. This was done to get an idea of whether the depth of titanium diffusion depended on the time spent in the furnace.

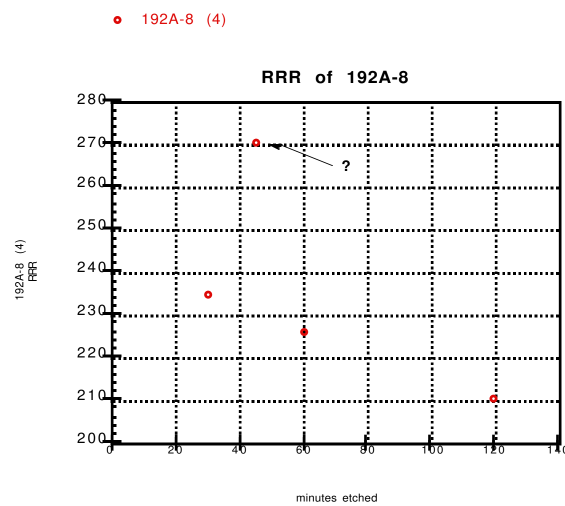
After fifteen minutes of etching, only sample 192A-7 showed a transition. Failure to show a transition indicates that too many impurities, i.e. Titanium, are still present in the sample. After thirty minutes, only sample 192A-10 still showed no transition. These are both indications that the furnace time does affect the diffusion depth of the Titanium.

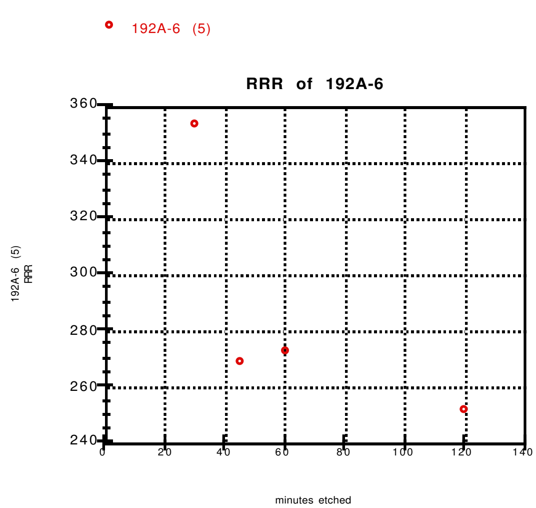
The samples were given a final one hour etch, giving them each a total of two hours etching time. After 120 minutes, all of the titanium should have been etched off the surface of each of the samples, leaving only the purified Niobium. As expected, the longer a sample had been in the furnace, the higher its RRR, except for a deviation between three and four furnace runs.

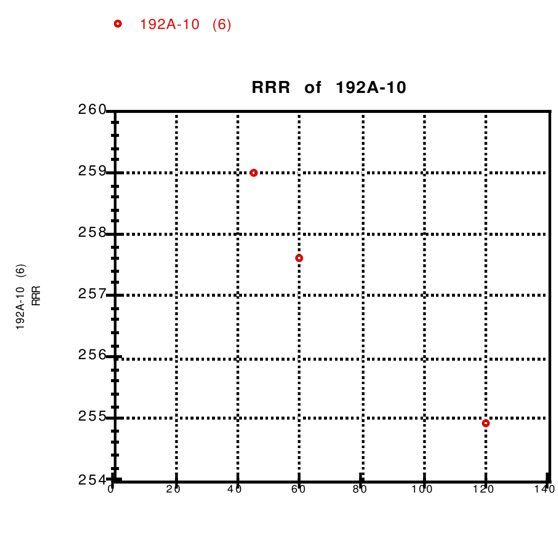




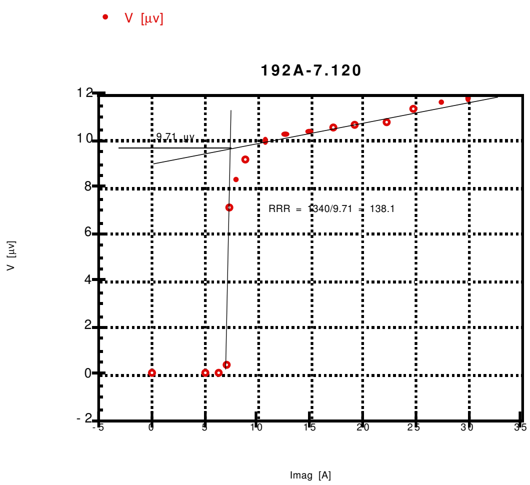


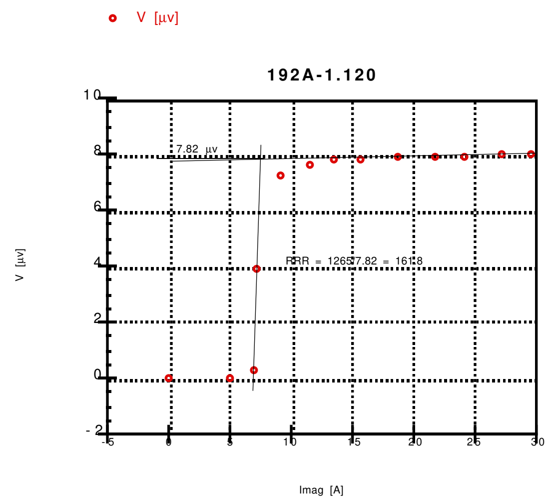


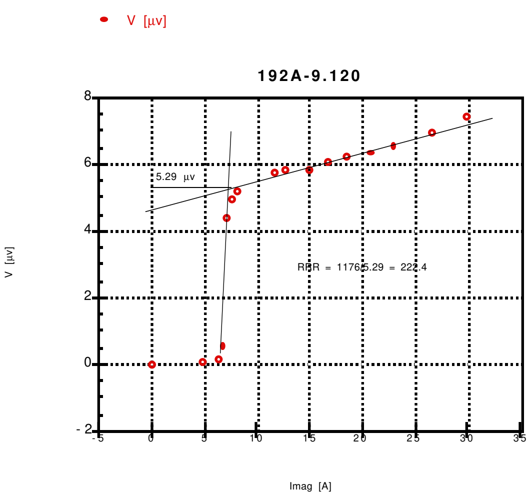


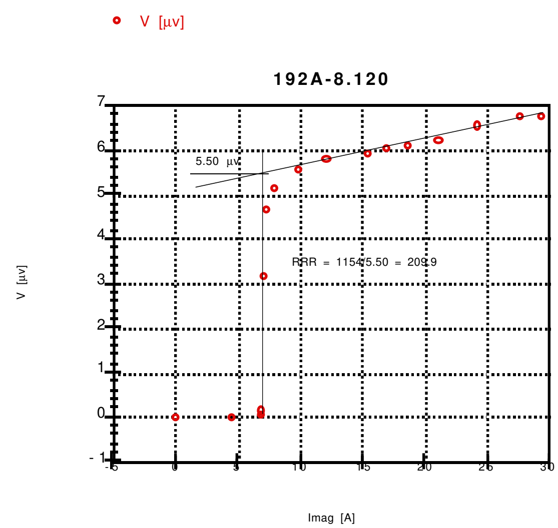


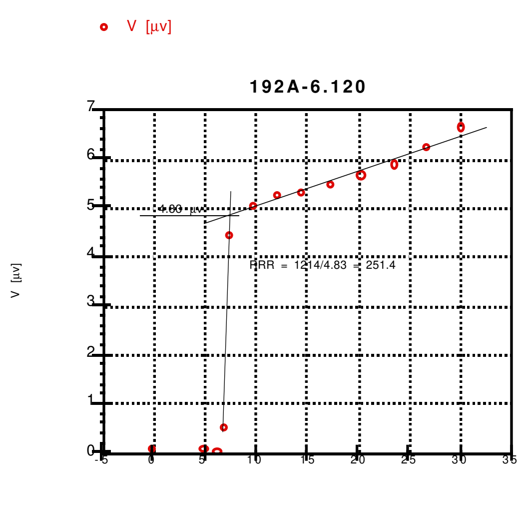
Graphs 4-9 : RRR vs. Time Etched for the Samples

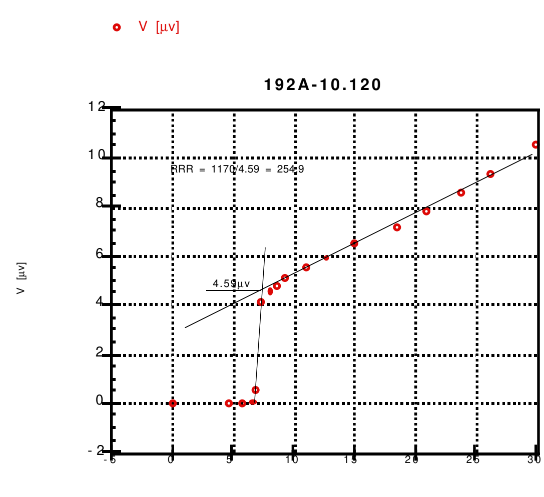












Graphs 10-15 : Final RRR Measurements for the Samples

Table 5 : RRR's After 2 Hours of Etching

sample	# of furnace runs	RRR after 120 min
192A-7	1	138.1
192A-1	2	161.8
192A-9	3	222.4
192A-8	4	209.9
192A-6	5	251.4
192A-10	6	254.9

Conclusions

In this project, the etch rate of 1:1:2 BCP was measured to be 1.7*10^-4 inches per minute. Also, using Hafnium or Zirconium as gettering agents in conjunction with Titanium was not as successful as using Titanium alone. These gettering agents were supposed to have removed additional impurities than the oxygen for which the Titanium is used. In fact, the addition of either of these gettering agents into the Niobium sample seems to inhibit the diffusion of the oxygen outwards. Finally, the RRR of a sample was determined to be dependent on furnace time. That is, the more time a sample spent in the furnace, the more pure it became. The increased furnace time allowed the Titanium to seep deeper into the sample, and also allowed the Oxygen more time to seep outwards. Both of these processes helped to gather more Oxygen close to the surface from which it could be etched.