

Study of the Use of Vacuum Baking in the Reduction of Surface Oxide in Niobium and a Method to Maintain It

J. Kaufman, H. Padamsee, R. Kirby (SLAC)

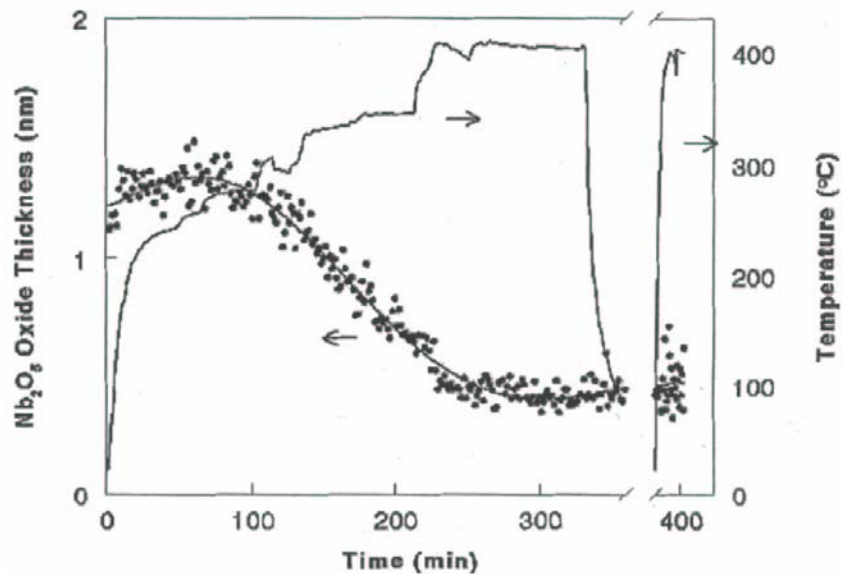
Vacuum Baking in the Reduction of Surface Oxide in Niobium

With niobium cavities being an integral part of present and future accelerator science, understanding the properties of the inner surface is an important aspect in the production of high gradient cavities. Current methods in the preparation of niobium cavities allow a major portion of the cavities to reach around 30-40 MV/m without a drop in the quality factor if the cavities are prepared by Electro Polish and baked. Without baking most cavities have been limited to this amount by what is called high field Q-slope which is a sharp degrading in the quality factor above 20MV/m.

One method to overcome some high field Q-slope problems has been baking of the cavity at 100 degrees Celsius. An increase in cavity performance has been seen with this baking but the physics and chemistry behind this process is not well understood. Many of the theories on the cause/effect relationship of baking of the cavity and increased performance are based on the effects of oxygen (oxide) on this inner surface. None of these theories have been proved or disproved by experimental means.

One of the methods to experimentally study these theories involving oxygen and the inner surface of the cavity would be to produce a niobium cavity with a surface significantly reduced of oxide or even a cavity with an oxide free inner surface. With this in mind and with the premise that with niobium the oxide is dissolved into the bulk at elevated temperatures, we have undertaken a study of the effects of 300 – 500 C vacuum baking of niobium samples in-situ in an XPS and studying the effects on the surface of the niobium. This is with the hope of removing or greatly reducing the oxide on the surface, which could in turn lead to the production of a niobium cavity with a oxide free inner surface.

Cornell Nb Coupon Heating Two Heatings

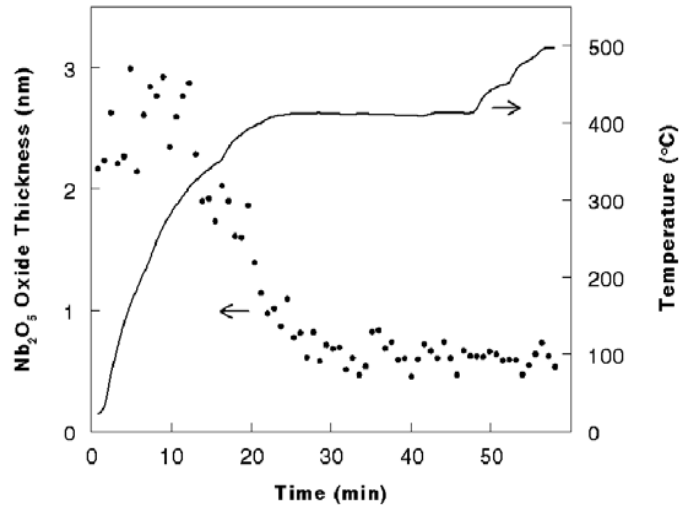


The first experiment Robert Kirby ran involved heating the high RRR niobium coupon to 400 C and tracking the pentoxide peak as a function of time and temperature. It is seen from the graph at the left that upon reaching 400 C after heating for 300 minutes the oxide thickness is 30% of its original value.

Farther into the graph you will see an area where the temperature of the niobium coupon was lowered to 100 C. During this lowered temperature the oxide thickness remained low.

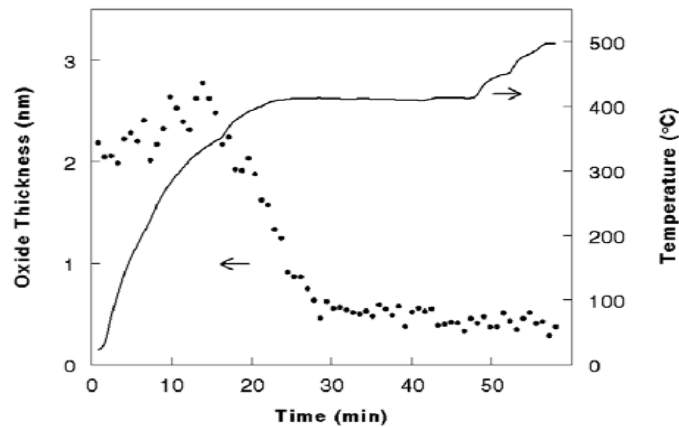
Cornell Nb Coupon Heating

Sample #3, Nb⁵⁺ Valence (pentoxide)



Cornell Nb Coupon Heating

Sample #3, O²⁺ Valence



A second analysis was undertaken with changes to the testing criteria.. The final temperature was raised from 400 C to 500 C. The heating time was decreased from greater than 400 minutes to 60 minutes. Also both the O²⁺ valance and the Nb⁵⁺ valance signals were tracked as a function of time and temperature.

Results of this experiment indicated that again the surface oxide after heating was 30% of what the initial level was. It was also shown that the dissolution/diffusion of the oxide from the surface can happen in a much shorter time frame than shown by the previous experiment. Increasing the temperature from 400 C to 500 C did not have a significant effect on the surface oxide, at least in the time constraints of this experiment.

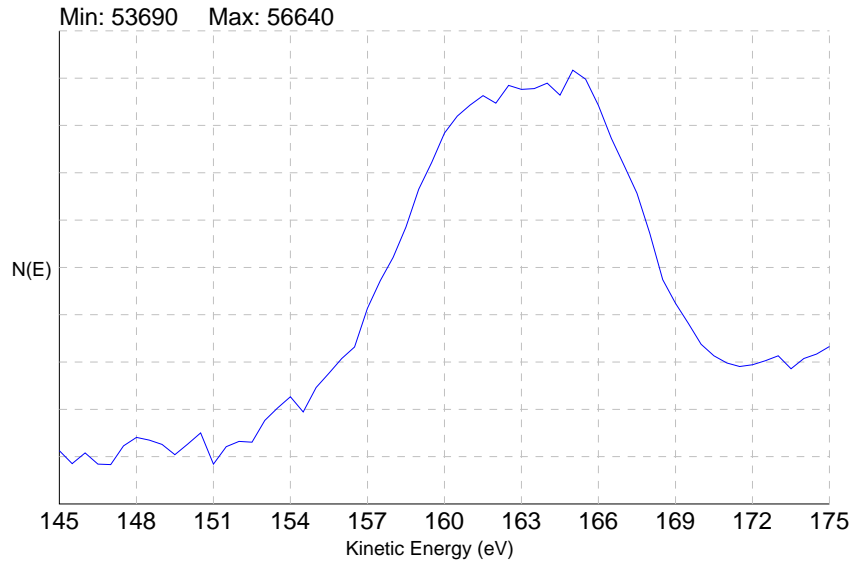
This series of experiments have shown promise in producing a niobium cavity which has been altered to have a much reduced oxide, inner surface. With the new installation of a hot stage on the Cornell, Auger/SIMS instrument further experimentation will be undertaken. This will include extended bakes at lower temperatures to study the effects the now standard 100 C bake on the niobium surface along with determining the minimal temperature and time that substantial oxide reduction takes place. Also studied will be the regrowth of the oxide layer as a function of time and temperature.

Maintaining The Reduced Oxide Surface

With the above plan of building a niobium cavity with a reduced oxide inner surface we have begun preliminary studies into maintaining this altered surface over time to thinner oxide levels. This will be critical in our ability to first process this low oxide inner surface and then retain this surface through the installation and testing of the cavity.

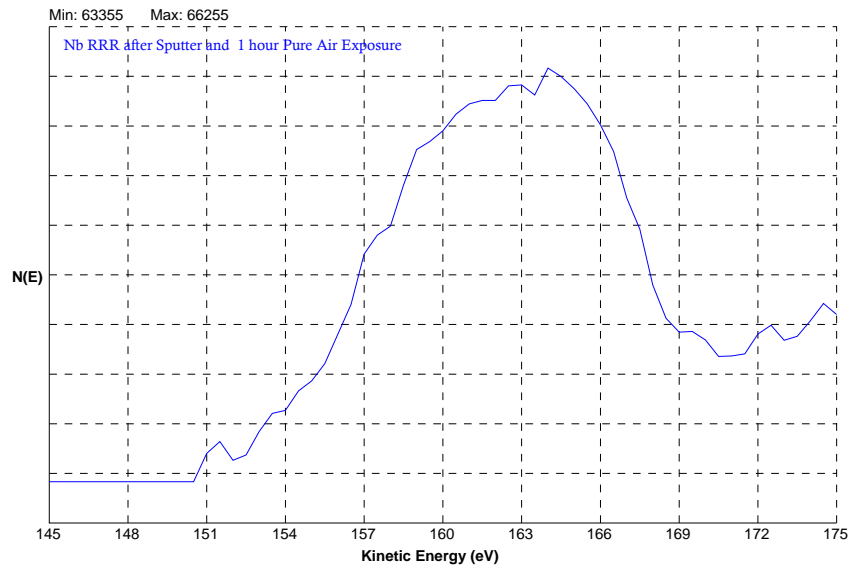
In preliminary studies we ion beam sputtered niobium samples in the Cornell Auger/SIMS instrument until all oxide was removed as indicated by Auger analysis. We then exposed these oxide “clean” surfaces to different controlled environments in the Auger/SIMS intro chamber. The samples were then reanalyzed with Auger analysis. By looking at peak shapes and binding energies of the niobium peak spectra we were able to obtain some initial concepts into oxide regrowth on oxide free niobium surfaces. Being that it was Auger analysis and not XPS analysis we could only develop some preliminary indications as peak shifts and binding energies for chemical bonding is not as straight forward as XPS.

Nb As Is (Unspattered)



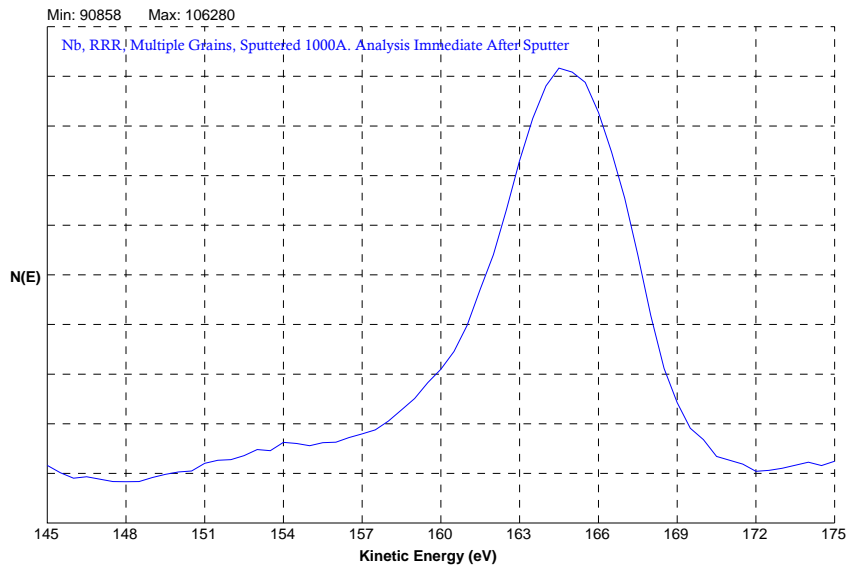
To get a baseline for our Auger peak shape an “as is” sample of high RRR niobium that was BCP 1:1:2 processed was analyzed. The Auger spectra gave a broad peak which we feel was indicative of the oxide state of the surface of a unaltered niobium cavity.

Nb Exposed to Ultra Pure/Ultra Dry Air in Intro Chamber for 1 Hour After Sputter to Remove Oxide



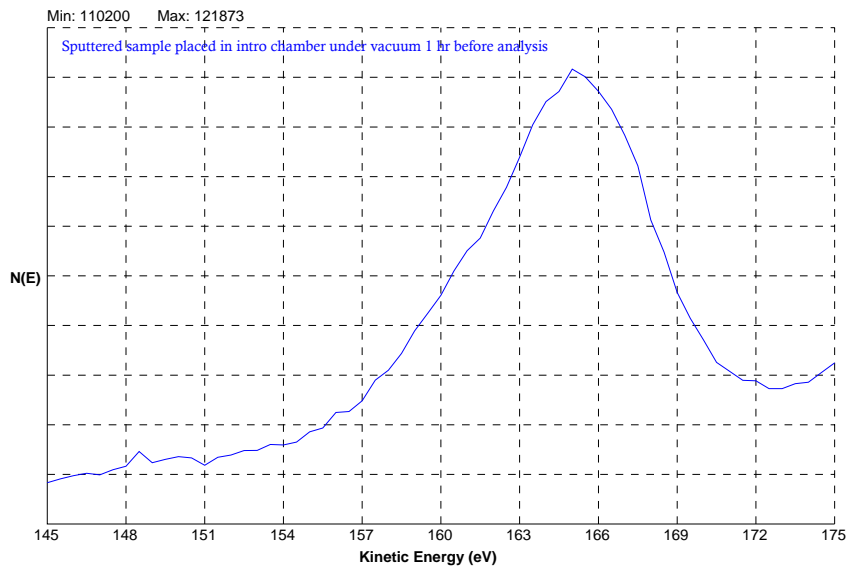
To check our assumption that the shape of our Auger peak was due to the oxide layer, we ion sputtered the sample to a “clean” oxide free niobium. We then immediately exposed the sample to an ultra pure/ultra dry air mixture in the instrument intro chamber for one hour. This was done under the premise that the pure oxygen was the only reactive component of the (nitrogen, argon, oxygen) air mixture. The sample was then immediately reanalyzed and peak shapes appeared similar to the as is sample, giving us an indication that the peak shape we were observing was that of highly oxidized niobium.

Nb Sputtered “Clean” with Ion Beam While Under Auger/SIMS Instrument Vacuum



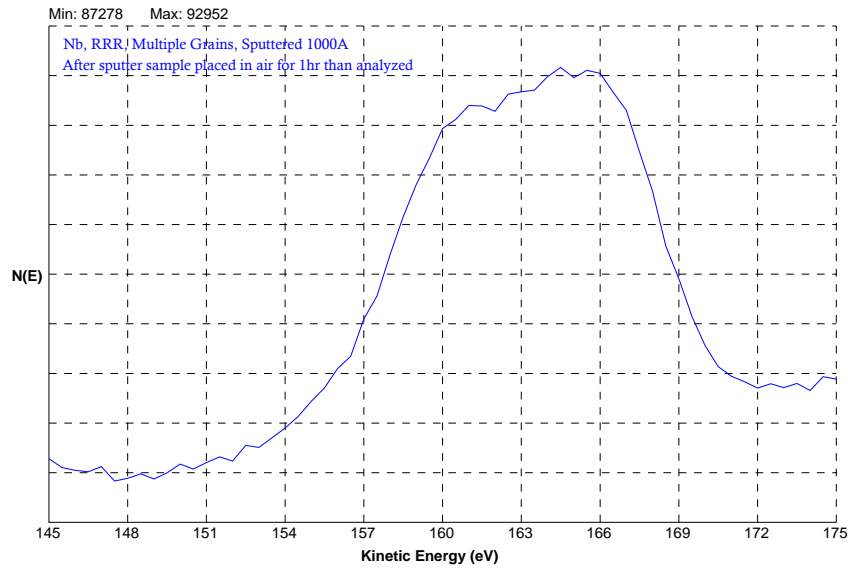
An ion sputtered “clean” oxide free niobium sample was then analyzed to give us a niobium peak shape indicative of pure oxide free niobium. As seen this peak is distinctly less broad than the peaks of the samples that contained the oxide. Using this distinct difference in peak shapes we could do some preliminary studies on maintaining a oxide free niobium surface.

Nb Exposed to 10^{-6} Torr Vacuum in Auger/SIMS Intro Chamber for 1 Hour After Sputter to Remove Oxide



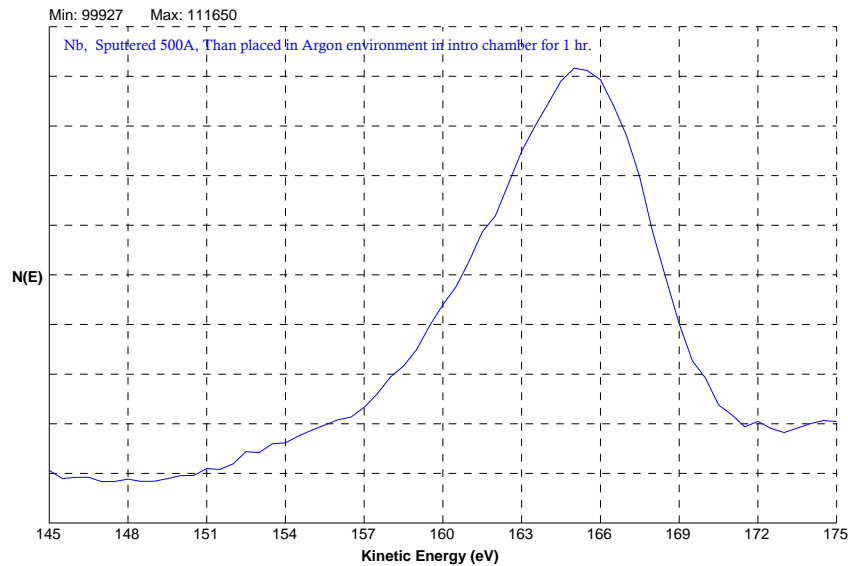
Since we were using the sample intro chamber on the Auger/SIMS instrument to do our experiments we needed to determine the effects of the chamber on our samples tested. We exposed a niobium sample in which the surface had been ion sputtered free of oxide in the Auger/SIMS, to the intro chamber vacuum for one hour. After the one hour exposure the sample was reanalyzed. The Auger spectra showed a slight broadening of the niobium peak indicating a small amount of oxide had reformed. This was expected as oxide formation on niobium has been seen at much higher vacuums than the 10^{-6} torr intro chamber. The upside of this is that the peak shape indicates that oxide levels are still greatly decreased from a “normal” niobium cavity surface.

Nb Exposed to Room Air for 1 Hour After Sputter to Remove Oxide



To test the effects of standard atmospheric conditions or “room air” on an oxide free niobium surface we exposed an ion sputtered oxide free niobium sample to room air in the intro chamber for one hour. After the exposure the sample was analyzed with the Auger. The spectra of the niobium peak was broad and similar in shape to both the “as is” niobium sample and the sample exposed to the pure air. This indicates that if a niobium cavity that has been processed to have an oxide free or reduced oxide surface, is allowed to have contact with room air the processed surface will be compromised.

Nb Exposed to Argon in Intro Chamber for 1 Hour After Sputter to Remove Oxide



As mentioned earlier one of the complications of testing a reduced or oxide free cavity surface, is maintaining this altered surface from the processing of the surface, through the assembly of the cavity test set up, to the start of testing. One of the techniques being explored to accomplish this is keeping the cavity surface exposed to an inert gas at positive pressure. For our testing we exposed a niobium sample, ion sputtered oxide free, to a steady stream of 3 psig ultra pure argon gas for one hour in the instrument intro chamber. Auger analysis after the exposure indicated only a slight broadening of the Auger peak over the oxide free peak. This preliminary indication suggests that maintaining an altered cavity surface by blanketing it with an inert gas is possible.