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PRELIMINARY RESULTS ON "POLARIZED" BUFFERED CHEMICAL POLISHING OF A LARGE GRAIN NIOBIUM CAVITY*

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Abstract

In order to further understand the relation between the high-field Q-drop and the native oxide layer on the surface of SRF niobium cavities, we tried to alter the oxidation of niobium by applying a small voltage between a large-grain niobium cavity and a niobium rod inserted in the center, during buffered chemical polishing (BCP). The cavity RF test results at 1.7 K and 2.0 K did not show any major difference in the Q-drop behavior, compared to a standard BCP treatment. In one case, dark gray regions were visible inside the cavity and were responsible for additional losses, as seen with temperature maps. In order to better understand the electrochemical process occurring during the "polarized" BCP treatment, measurements of the polarization curve have been made on a cylindrical niobium sample, with a cylindrical niobium rod in the center.

INTRODUCTION

The oxidation of the niobium surface of superconducting radio-frequency (SRF) cavities is an important subject which has been studied since a long time [1]. Recently, the discovery of anomalous losses occurring at high RF fields ("Q-drop") has brought back much attention on the role of the oxide layer and on the process of the oxidation of niobium. It is well known that the oxidation of niobium is a field assisted process (Cabrera-Mott model), where oxygen ions are attracted to the metal by a negative contact potential (Mott potential $V_M \sim$ -0.6 V), yielding the Nb_2O_5 growth. In the early stage of growth, the oxide growth rate is limited by the diffusion of ions aided by the Mott potential, while in the later stage it is limited by the tunneling of electrons through the oxide aided by a positive ionic diffusion potential ($V_D \sim 0.17$ V) dying out with Nb_2O_5 thickness at about 2 – 3 nm [1].

During the standard buffered chemical polishing (BCP) of niobium surfaces, the niobium is oxidized by the nitric acid and the oxide layer is removed by the hydrofluoric acid, resulting in etching of the surface. In this contribution we report the RF test results on a large-grain single cell where positive and negative voltages were applied between the cavity and a rod inserted in the center during BCP and the following rinse with ultra-pure water. The aim was to try to alter the oxidation by changing the

niobium potential: by applying a negative polarity to the cavity, the oxidation should be slowed, but pick-up of hydrogen ions may be favored. Reversing the polarity, oxidation should be enforced and hydrogen pick-up should be reduced. The experiments done on the cavity were followed up by measurements of the polarization curve using a niobium cylinder with the same diameter as the cavity beam tube, to try to better understand the process.

CAVITY PREPARATION AND RESULTS

A 1.47 GHz single-cell cavity of the CEBAF shape made of large grain high purity (RRR > 200) niobium from Ningxia was used for this investigation. A schematic of the cavity etching setup is shown in Fig. 1.
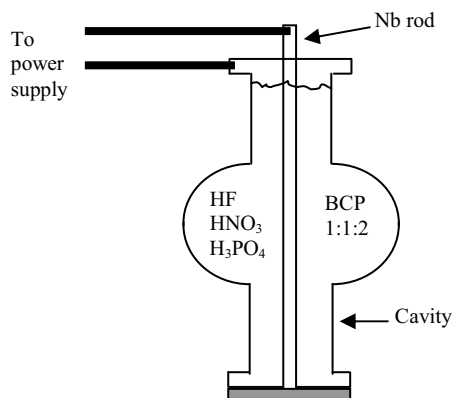

Figure 1: Schematic of the setup for the cavity etching.

In the first surface preparation, the power supply was set to operate at a constant voltage of -1 V (the cavity is negative, i.e. the cathode) to retard the oxidation and the current was limited to 1 A. After filling the cavity with a solution of HF, HNO_3 and H_3PO_4 in 1:1:2 ratio by volume, the voltage settled to -0.83 V. Etching was done for about 2 min, removing approximately 5 μm of material. The cavity then followed the standard preparation consisting of high-pressure water rinse for 1 h without potential control, drying in a class 10 clean room for 3 h, assembly of beam tube flanges with RF probes, evacuation on a vertical stand to about 10^{-7} mbar. The high power RF tests at 2.0 K and 1.7 K were limited by Q-drop, starting at a peak surface magnetic field $B_p \sim 103$ mT, without field emission. The residual resistance R_{res} was quite low (~ 3nΩ). The cavity was parked at 90-150 K for 30 h to check whether enough hydrogen was introduced in the Nb during BCP but the result was negative.

We did a new treatment, this time setting the voltage on the power supply to +1 V (the cavity is the anode) and limiting the current to 1 A. After filling the cavity with the acids, the voltage settled to 0.76 V and after 2min about 6 μm of material was removed. Fig. 2 shows the current flow as a function of time, showing current spikes when the cavity was filled with acids and during the rinses with ultra-pure water. The RF tests at 2.0 K and 1.7 K were limited by Q-drop, starting at a peak surface magnetic field B_p ~ 100 mT, without field emission. The residual resistance was 10 nΩ.
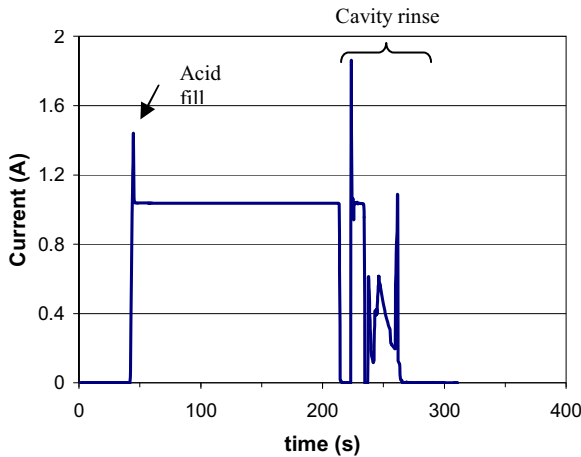

Figure 2: Current flow during the "polarized" BCP experiment, showing peaks during the filling with acids and rinsing with ultra-pure water.

In a third test we set the power supply voltage to +1.5 V and limited the current to 3 A. After filling the cavity with the BCP mixture, the voltage settled to 0.33 V and after 2 min about 6 μm was removed. After rinsing the cavity with ultra-pure water, two "gray stripes" connecting the beam pipe with the equator were visible inside the cavity. Also some areas appeared "discolored" blue likely caused by a thicker oxide layer being connected to the voltage settled at 0.33 V. Several pits distributed on the cavity surface were also noticed. These features are shown in Fig. 3.

The RF tests at 2.0 K and 1.7 K were limited by Q-drop, starting at a peak surface magnetic field B_p ~ 100 mT, without field emission. The residual resistance was 6 nΩ. Temperature maps showed stronger heating in areas of the "gray stripes" (Fig. 4). The "gray stripes" were eliminated after 10 μm removal by standard BCP 1:1:2, heat treatment in a vacuum furnace at 600 °C for 10 h and additional 20 μm BCP 1:1:2. A plot summarizing the RF test results at 1.7 K for the three "polarized" BCP experiments is shown in Fig. 5. A $Q_0(B_p)$ curve for an earlier test on the cavity after standard BCP 1:1:1 is added for comparison.
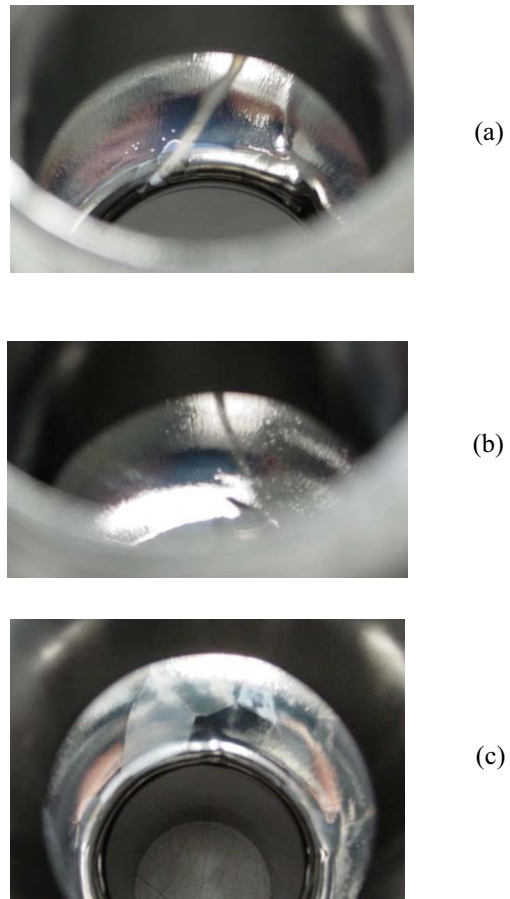

Figure 3: Gray stripes [(a), (b)] and discoloration (c) observed after the "polarized" BCP experiment at 0.33 V/3 A. One is looking through the beam pipe into the cavity and see a segment of the lower half cell from equator to lower beam pipe.
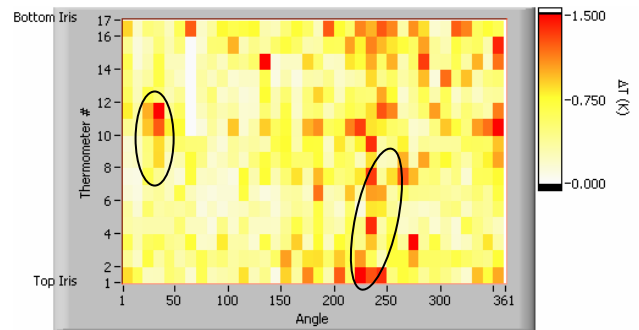

Figure 4: Temperature map at 1.7 K and B_p = 120 mT measured during the RF test after 0.33 V/3 A "polarized" BCP. The ovals show the location of the "gray stripes" of Fig. 3a and 3b.
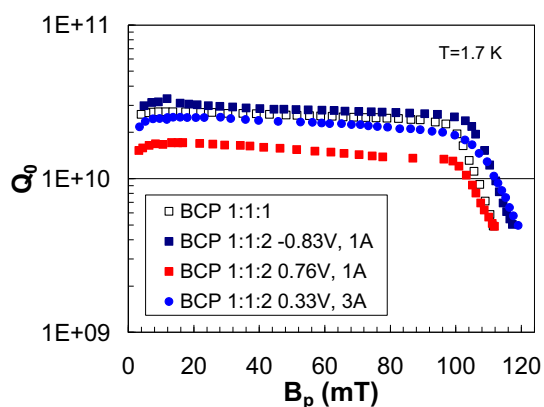
Figure 5: Summary of the RF tests at 1.7 K for three "polarized" BCP experiments. An earlier measurement after standard BCP is included for comparison. All the tests are limited by Q-drop.

SAMPLE MEASUREMENTS

In order to better characterize the "polarized" BCP process, we measure the polarization curve for a Nb cylinder 70 mm diameter (same as the cavity beam tube). The same Nb rod used for the cavity experiments (9.4 mm diameter) was used as the other electrode. The active surface areas of the cylinder sample and of the rod are 200 cm^2 and 27 cm^2 respectively. A mercury-mercurous sulfate reference electrode in a bridge tube was used to measure the potential of the cylinder sample. A schematic of the test setup is shown in Fig. 6 and a picture is given in Fig. 7.
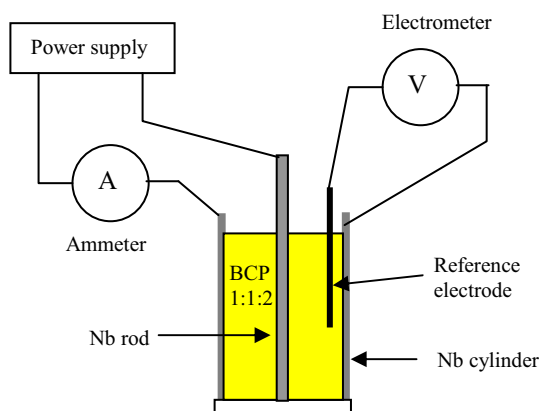

Figure 6: Schematic of the test setup for the "polarized" BCP experiment on a Nb cylinder sample.

A plot of the power supply and reference electrode voltages as a function of the current I is shown in Fig. 8. The temperature of the acid is about 27 °C. With anodic polarization of the cylinder, significant hydrogen evolution was observed near the rod for increasing voltage. It was found that when cathodic polarization was applied to the cylinder, there is a range of voltages (~ -1.5 V to ~ -1.8 V, measured from the power supply) where current oscillations occur. The frequency of the oscillations seems to decrease for more negative voltage up to the point where $I(t)$ becomes non-periodic. Some

examples are shown in Fig. 9. The cylinder had a smooth surface finish after the experiment.
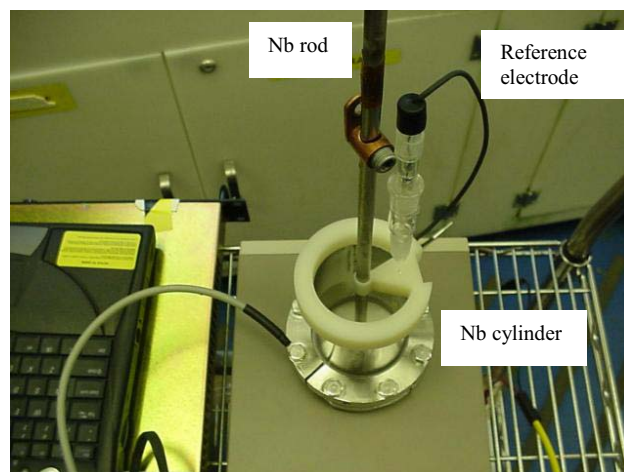

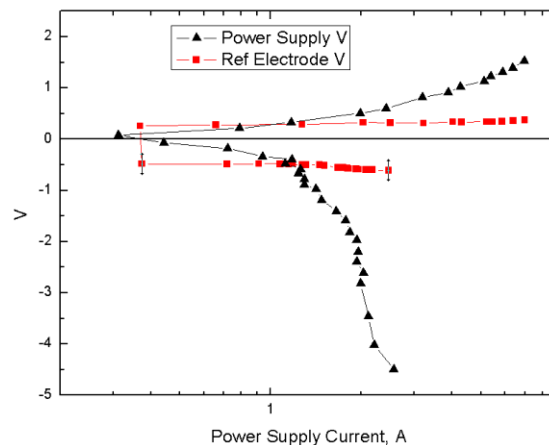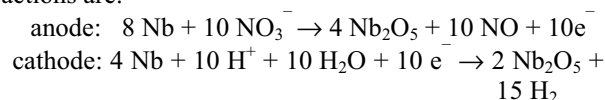Figure 7: Picture of the electrochemical cell used for the "polarized" BCP experiment on a Nb cylinder sample.


Figure 8: Polarization curve for the "polarized" BCP experiment with the Nb cylinder. 1:1:2 solution was used.

DISCUSSION

Nitric acid is the one that has the lowest dissociation constant in the BCP solution and therefore may provide most of the ionic current. It is likely that the electrode reactions are:

anode: $8\,Nb + 10\,NO_3^- \rightarrow 4\,Nb_2O_5 + 10\,NO + 10e^-$
cathode: $4\,Nb + 10\,H^+ + 10\,H_2O + 10\,e^- \rightarrow 2\,Nb_2O_5 + 15\,H_2$

The reaction causing the dissolution of the niobium oxide should be unchanged

$$Nb_2O_5 + 10\,HF \rightarrow 2\,NbF_5 + 5\,H_2O$$
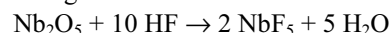
The current oscillations observed in a certain range of the applied voltage are most likely associated with the diffusion of ionic species through a viscous layer at the metal/solution interface and the build-up and dissolution of the Nb_2O_5. This process may be similar to the occurrence of current oscillation during electropolishing [2].
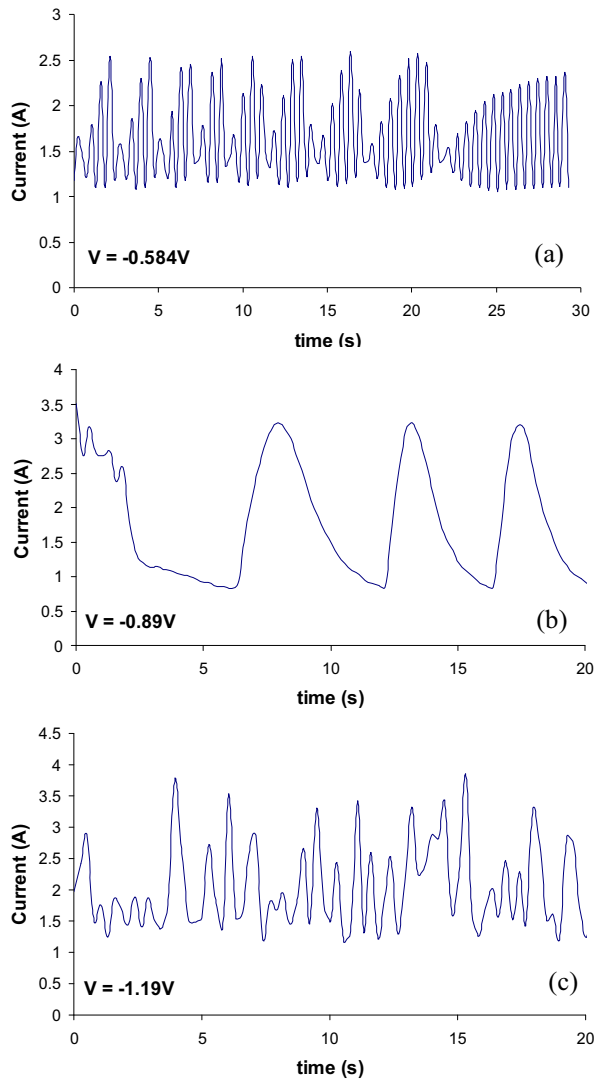
Figure 9: Current vs. time measured for different power supply voltages. A fast-Fourier transform of the signals, show peaks at 0.41 Hz, 1.657 Hz, 2.13 Hz and 3.31 Hz for (a), 0.236 Hz and 3.551 Hz for (b).

In order to interpret the results on the cylinder sample, let's consider the voltage vs. current density curve for a Nb electrode. When cathodic polarization is applied, the voltage decreases at high enough current densities when hydrogen gas evolution occurs ($2H^+ + 2e^- \rightarrow H_2$). When anodic polarization is applied a plateau region is expected at a current density corresponding to the Nb_2O_5 dissolution. The same kind of processes occurs both at the rod and cylinder, but they will happen at higher current for the cylinder due to the larger surface area. This is shown schematically in Fig. 10. Therefore, the plateau and current oscillations observed with cathodic polarization of the cylinder would be due to the anodic reaction occurring at the rod. The plateau for the anodic polarization of the cylinder should occur at about 10.5 A (same current density as for the rod), which is above the maximum value we measured during the experiments.
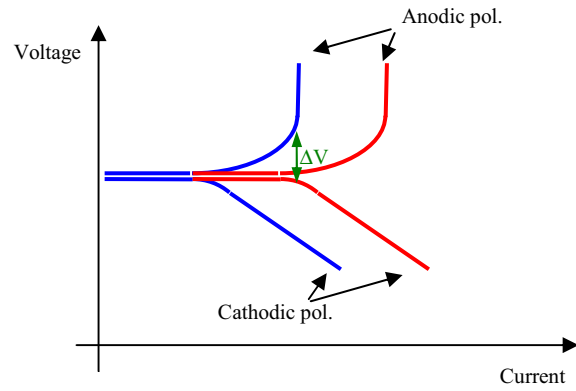

Figure 10: Schematic representation of the voltage, corrected for the potential drop in the electrolyte, as a function of the current for the rod (blue) and the cylinder (red). The curve for the cylinder is shifted to higher current because of the larger surface area. ΔV is the power supply voltage with cathodic polarization of the cylinder, at the plateau region for the rod.

We think that the "gray" stripes maybe due to the formation of the so-called "gray oxide" [3], which is a crystalline form of Nb_2O_5 which could nucleate while holding the Nb surface at a potential during the fill-and-dump water rinses.

CONCLUSIONS

A control of the niobium oxidation process during BCP was attempted by holding a Nb cavity to a fixed potential during chemical etching. Both anodic and cathodic polarizations were applied in separate tests. The cavity RF test results did not show any significant difference from a standard BCP-type cavity and, in particular, no significant changes in the Q-drop behavior were found. In one case where the current was limited to a higher value, "gray" stripes were visible inside the cavity and were responsible of additional RF losses, as observed with temperature mapping. We attribute these features to crystalline niobium pentoxide.

Further investigation of the "polarized" BCP process was done on a cylindrical Nb sample and showed the presence of current oscillations, which are interpreted as due to the anodic reaction at the other electrode (rod). It would be interesting to repeat the experiment with a larger diameter rod to verify the presence of a plateau in the anodic polarization of the cylinder and whether the operation in such plateau region would give similar polishing results as obtained by electropolishing. These conditions may then be tried for the polishing of a niobium cavity.

REFERENCES

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[3] P. Kneisel, Proc. 1st SRF Workshop, Karlsruhe, 1980 KFK report 3019, p.27.