

## NIOBIUM SAMPLE SURFACE TREATMENT BY BUFFERED ELECTROPOLISHING

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### Abstract

The electrolyte of buffered electropolishing (BEP) is consisted of hydrofluoric, sulfuric and lactic acids. In the present work, the process of BEP has been familiarized and the main parameters were investigated. It was demonstrated that the polishing rate of BEP had a linear relationship with current density; therefore the polishing rate can be controlled via current density, which make the control of BEP easier. Through inspection using a metallographic optical microscope (MOM) and an Atomic Force Microscope (AFM), it is proved that Nb surfaces treated by BEP were much smoother than those treated by the electropolishing (EP) process widely used in the superconducting radio frequency community.

### INTRODUCTION

The surface condition of Nb superconducting radio frequency (SRF) cavities used in particle accelerators is thought to be one of the important factors in determining their performance. So in the past several years, most the laboratories and universities involved in R&D programs for RF cavities studied on it. Due to the advantages that electro-polishing have shown, it has become an established procedure for smoothening of metallic surfaces. But with the development of Nb surface treatment, a new method called BEP (Buffered Electro-Polishing) has been reported [1, 2]. It is on the basis of EP and has more advantages than it [2]. So, to improve the performance of our lab's Nb cavities further, as part of our R&D effort we have initiated a study on it.

The electrolyte of BEP was first described by Monti for corrosion protection [3] which was consisted of hydrofluoric, sulphuric and lactic acids. To the study of Niobium samples, our goal is to understand the relevant parameters involved in BEP, to understand the technological problems and the familiarization with the process itself. Performing the EP on multi-cell cavities or even on the dumbbells is a complicated task and requires expensive infrastructure [4]. So, for understanding the process and evaluate the influence of each parameters as well as their relationship, the small Nb samples experiment is necessary. Furthermore, because the smaller amount of acid involved and the limited amount of hydrogen generated during the BEP process of small sample, it can safely performed in a fume hood of laboratory environment. Otherwise, because the sample was not so much costly, relatively easy to isolate the conditions that affect the surface finish during BEP and we can use its result to instruct the polishing process of niobium cavity. We have tried many ratios of the acid

mixture and found a better one according to the I-V curve and the surface smoothness. Besides, we also changed various conditions to controlling the polishing process. In this paper, we will describe the result of the investigations on the parameters that control the polishing process, the relationships of them and the surface smoothness in different conditions observed by metallographic optical microscope (MOM) and Atomic Force Microscope (AFM).

### EXPERIMENT

#### *The flat sample setup*

The setup of sample treatment experiment is schematically shown in Fig.1. It consists of an electrolytic cell composed of an aluminium cathode [1][5] and a niobium anode (sample) immersed in a hydrofluoric (48%), sulphuric (98%) and lactic acids (85%) mixture. The temperature was measured by a thermometer which immersed in the acid. A water or ice bath in the secondary containment was used to keep the temperature of the acid mixture according to the different condition. A stir bar is needed for the acid mixture and the velocity of acid mixture was calculated through data simulation. The Nb anode and the pure aluminium cathode of the same area are connected to the electrical circuit through two alligator clamps which also serve as mechanical support by fixing the electrodes to a PTFE bar which is suspended on top of a PTFE beaker. Then the BEP process can be performed when there is a voltage.

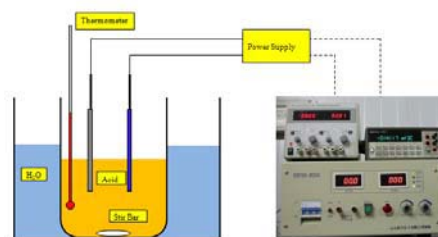


Fig.1. Schematic set-up of BEP for small samples

#### *The fundamental of buffered electropolishing*

The mechanism for BEP is similar as EP. It can be proposed by Jacquet theory [6]. A viscous layer of anodic dissolution products is formed. Respect to the bulk of the electrolyte, this layer has higher viscosity and greater electrical resistivity. The thickness of the liquid insulating layer is greater in crevices than on projections. The current density on projections it is higher than in crevices. For this reason, projections dissolve more rapidly than crevices, and this produces a surface-leveling effect.

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A typical measured I-V curve for the samples was shown in Fig. 2. Four regions corresponding to etching, periodic oscillation of anode current density, polishing, and gas evolution on the anode surface were identified [1]. The detailed shape of the curve depends on not only the surface area ratio of cathode and anode, but also on the initial surface roughness and other conditions [8]. In the etching region a relatively strong oxide layer is built up on the surface. At higher voltage this layer is removed and the polishing process begins. In the range of polishing the current is nearly independent of the applied voltage. The width of this plateau depends sensitively on the temperature of the electrolyte. For even higher voltages gaseous oxygen is set free at the anode, i.e. the surface to be polished. The oxygen bubbles result in discontinuities on the surface. With Niobium (and also Tantalum) one observes oscillations of the current in this region while the voltage is kept fixed. The oscillation are probably caused by the cyclic build-up and removed of oxygen layers on the surface. The surface look was given under a MOM for samples from each region after electropolishing for 1800 s [2]. Therefore, the optimal polishing conditions were found at the transition point between the polishing plateau area and the rapid increase of I as indicated in Fig. 3.

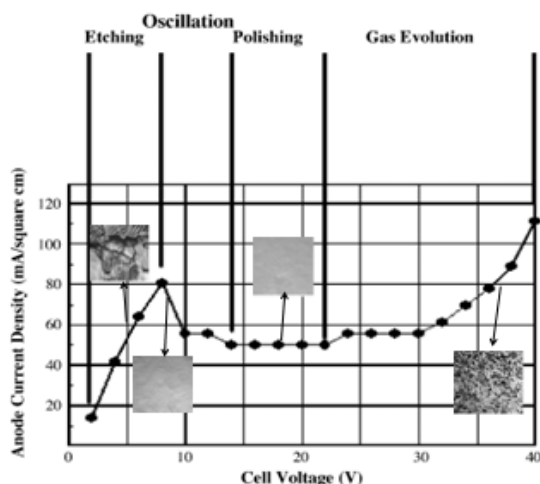


Fig.2. Anode current density measured as a function of applied voltage for the polishing system shown in Fig. 1. Four areas are identified as discussed in detail in reference [1] [2]

## RESULTS AND DISCUSSION

In the process of BEP, there are several parameters with controlled it. We need to know mainly the following parameters and their relationships such as: limiting current density, stirring speed, working temperature, and so on. They are not isolated and moreover all of them maybe bring effect to the surface smooth of niobium sample.

### The current voltage characteristic

Due to the high number of variables involved in the fabrication and conditioning of the cavities, it is not obvious how to establish a correlation between surface

finish and cavity performance; in general the smoother the surface the higher is the probability to obtain a high performing cavity. The electrochemical process must be tweaked to the optimal I-V combination in order to obtain the best surface finish in the electropolishing range. So obtaining an optimal current voltage curve is necessary.

### I-V curve with time and temperature

During the BEP process, the I-V curve is the function of temperature or time. Just as shown in the Fig.3, they are similar, but the trend is reverse. For the temperature, in the theory of chemical reactions the increasing of temperature results in an increase of the ion mobility. This implies a descent of the electrical resistance. Besides, due to the electro-chemical process and out gassing of HF, the HF-concentration of the acid decreases with the time past. So the I-V curve is changing with time like the Fig.3. And the current is becoming smaller quickly and then changing slowly as shown in Fig.4.

This phenomenon is very useful to us. If we chose a working condition, it will be changed with time and temperature. So it requires us make the working place near the start of polishing region to avoid the I-V curve changing along with time.

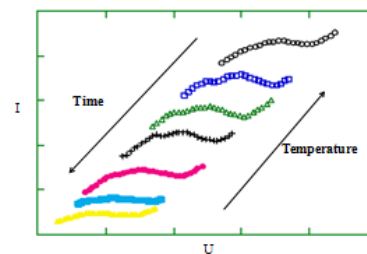


Fig.3. The schematic illustration of I-V characteristic evolving with time and temperature [7]

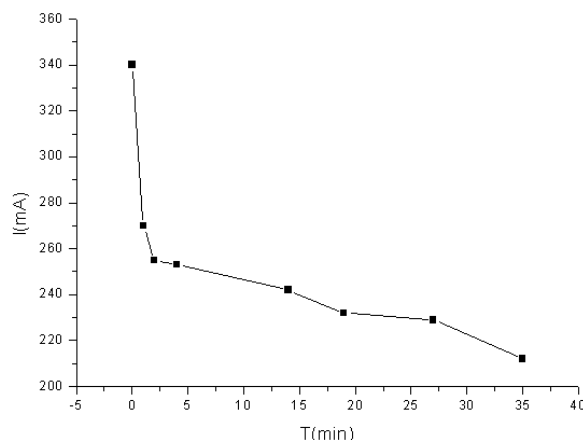


Fig.4. The change of current with time when it is in the polishing process

### I-V curve with stirring speed

Acid agitation is necessary during both EP and BEP to keep a stable material removal in time, but the high viscosity of the acid mixes used in both processes raises the problem of differential etching in different areas due to the cavity geometry. So it is necessary to do some investigation about it. In the study of this process, we found the I-V curve also changes with different stirring speed as shown in Fig.5. That is consistent with our beginning judgment. According to the polishing theory,

there will be sticky layer on the surface of the sample and it takes most of voltage. If stirring fast, it will make the sticky layer become thin and its electrical resistance become smaller. And the curve will move up. So the stirring speed is an important parameter to get an optimal polishing rate and smooth Nb surface.

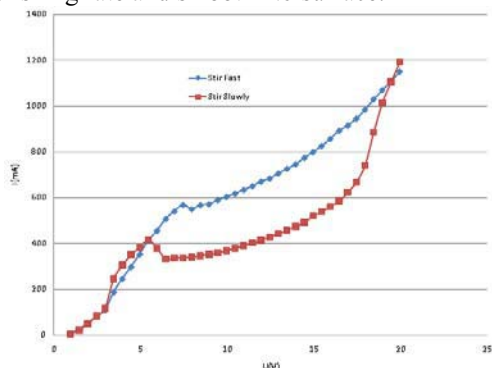


Fig.5. I-V curve with different stirring speeds

· The affection of cathode area to I-V curve

In the process of buffered electropolishing, the material, geometrical shape and surface area of the cathode is very important. The influence of the cathode area to I-V curve was shown in Fig.6. It shows that the area of cathode must be large enough compared with anode for this process. If it is too small, there will be no characteristic I-V curve for us to choose the best working point and didn't know which voltage is in the polishing region. We think the reason of this phenomenon is due to if the chemical reaction enough. If the area is too small, the cathode cannot provide enough material to reaction. And it became a bottle-neck of the whole polishing process. The result is that the reaction is always in the etching region and cannot give a good surface finish.

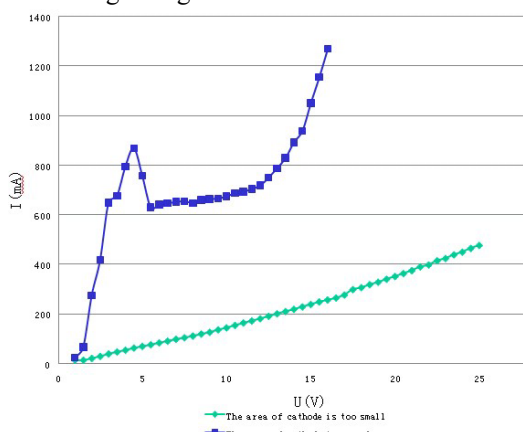


Fig.6. I-V curves with different cathode areas

*Relationship between Polishing rate and current density*

Based on an amount of experiment data, we found the polishing rate is the function of polishing current density and they have a linear relationship. The result of linear simulation by least square method is  $v=0.014J$  as shown in Fig.7;  $v$  is the polishing rate,  $J$  is the current density.

For prove whether it is reasonable, we first assumed the niobium is 5+. If polishing time is 1 second, polishing area is  $1\text{ cm}^2$ , and the polishing current density is  $1\text{ A/cm}^2$ , there will be 1 coulomb charge take part in reaction. If the chemical prices of niobium is 5 just as we assumed, the mass of niobium will be  $(1/6.02 \times 10^{23}) \times (6.28 \times 10^{18}/5) \times 93 = 19.4 \times 10^{-5}\text{ g}$  and the thickness will be  $19.4 \times 10^{-5}\text{ g} / (8.66\text{ g/cm}^3 \times 1\text{ cm}^2) = 2.24 \times 10^{-5}\text{ cm}$  according to assumed area. So we can get the theory relationship is  $v=0.0134J$ . It is very close to the relationship from the experiment. And it also can be explained by Faraday's law of electrolysis. This is important to guide us to control the polishing rate.

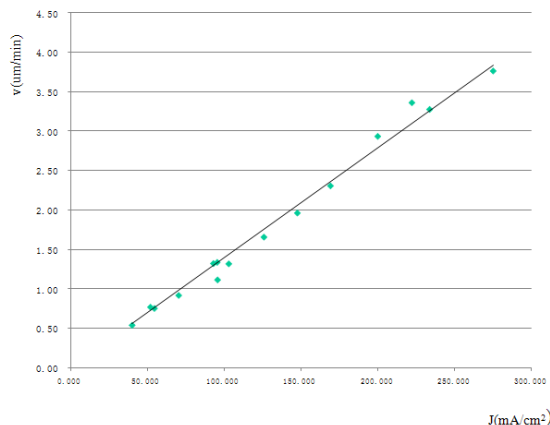


Fig.7. Polishing rates vs. current densities

*Nb sample surface under MOM and AFM*

The process of buffered electropolishing and how the main parameters control the polishing were discussed above. Through adjustment of parameters such as temperature, stirring speed, polishing time, and the choosing of polishing voltage, we could get the optimal conditions for polishing the niobium samples. We found that the parameters are not isolated, and we could through the mathematic method get what we want, both polishing rate and the surface finish. Fig. 8 shows typical optical images of the surfaces and their MOM photos in 1000 times of Nb sample surface were presented in Fig.9. The left picture is the sample polished by mechanic method contrasting the right one which was polished by BEP. Just like we see, it is very smooth. The Fig.10 gave us the roughness data using AFM. The RMS is around 5nm and the distance between the highest and the lowest place is about 20nm.



Fig.9. The picture of polished Nb samples

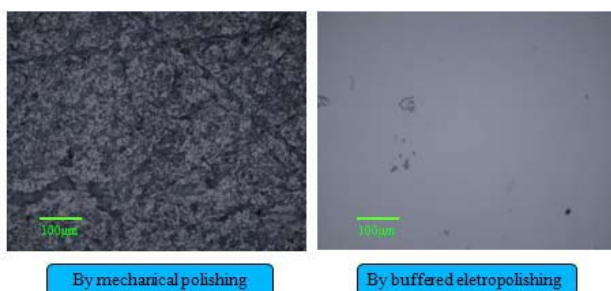


Fig.9. MOM photos in 1000 times of Nb sample surface

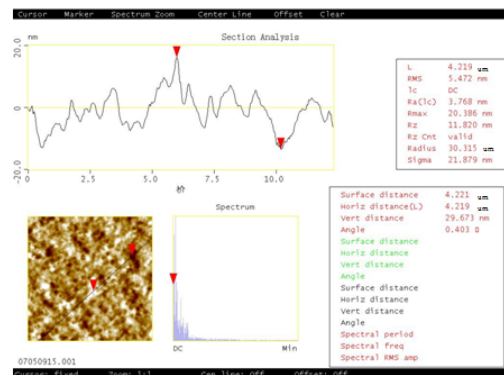


Fig.10. Nb sample surface profiles using AFM

## CONCLUSION

With the new electrolyte, we have systematically studied the process of BEP for small niobium sample. The main parameters that control the BEP process were discussed, which helped us choose a much better condition for treatment of the niobium surface. Through the help of surface observation using MOM and AFM, we found that Nb surfaces treated by BEP were much smoother than those treated by the conventional EP process. It is the basis for further study of niobium dumbbell BEP.

## ACKNOWLEDGMENTS

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## REFERENCES

- [1] Jean R. Delayen et al. ALTERNATE ELECTROLYTE COMPOSITION FOR ELECTROPOLISHING OF NIOBIUM SURFACES. 2001 SRF Workshop, KEK, Tsukuba City, Japan, September 6-11, 2001
- [2] Andy. T. Wu et al. Smooth Nb surfaces fabricated by buffered electropolishing. Applied Surface Science 253 (2007) 3041–3052
- [3] H. Monti, Me'taux Corros. Ind. 33 (1958) 481.
- [4] N. Steinhau-Kuehl et al. Electropolishing at DESY, SRF 2003 workshop, Lubeck Sept. 2003.
- [5] A.T.Wu, in: Proceedings of the 11th Workshop on RF Superconductivity, ThP13, Germany, 2003.
- [6] Jacquet, P.A. Trans. Electrochem Soc, 69, 629, (1936)