

STUDY OF BUFFERED ELECTROPOLISHING ON NIOBIUM SHEET

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Abstract

In this paper, research on applying buffered electropolishing (BEP) technology to treat the surface of Nb sheet was reported. Through optimization study, much faster polish rate and smoother surface comparing with conventional electropolishing treatment were got. The maximum mass rate could reach $4.66\mu\text{m}/\text{min}$ in our experiments. It was over 10 times higher than traditional EP. Meanwhile, the best surface mean square root (RMS) roughness could approach nearly 21nm . This study shows BEP has a great potential to replace the traditional EP process and become a new generation of technology for treating SRF cavity.

INTRODUCTION

Surface condition plays a critical role on superconducting radio frequency (SRF) cavity performance [1]. Since SRF cavity was born, researches on niobium surface treatment have not stopped to improve their performance. In recent years, with the buffered chemical polishing and then electropolishing gradually becoming chief means for SRF cavity treatment [2-4], the performances of multi-cell cavities have great improvement. Cavities treated by BCP could reach more than $25\text{MV}/\text{m}$, and the others treated by EP could reach a reproducible accelerating field of about $30\text{ MV}/\text{m}$. However, the accelerating field still cannot reach the request ($35\text{MV}/\text{m}$) of International Linear Collider (ILC) [5]. And on the other hand, polishing rate of traditional EP was another problem. It was only about $0.38\mu\text{m}/\text{min}$ [6]. So if a cavity treated by EP, more than 6 hours will cost on it. With the long treatment period and very expensive equipment, the technology of EP made the cost of SRF cavities added greatly. Thus, a new method for SRF cavity treatment called buffered electropolishing (BEP) was firstly proposed by Thomas Jefferson National Accelerator Facility (Jefferson Lab) [7, 8].

As part of cooperation with Jefferson Lab and the study on the fabrication of multi-cell niobium cavity, the research on BEP was also carried on at Peking University [9, 10]. The electrolyte of BEP was consisted of hydrofluoric, sulphuric and lactic acids. Niobium samples were used in the present stage of study for the purpose of decreasing the cost, safety and convenience to isolated parameters. The goal was to evaluate the influence of parameters to this process, as well as the technological problems involved in it. In this paper, effects of parameters on I-V characteristic, polishing rate and smoothness of surface were described. With more than hundred optimization experiments, the maximum of polishing rate $4.66\mu\text{m}/\text{min}$ was got in our experiment, which was more than 10 times faster than conventional EP. On the other hand, with over a $200\times 200\mu\text{m}$ area

measurement by high resolution 3D profilometer at Jefferson Lab, the surface RMS roughness of BEP treated samples could repetitively reach around 50 nanometres. All of above shows this new technology had a great potential to become a new niobium treatment technology to instead of conventional EP.

EXPERIMENTAL

Experimental Installation

The installation of sample BEP experiment is schematically shown in Fig.1. It consisted of an electrolytic cell composed of an aluminum cathode and a niobium anode (sample) immersed in a hydrofluoric, sulphuric and lactic acid mixture. The Nb anode and the pure aluminum cathode at the same area were connected to the electrical circuit through two alligator clamps which also serve as mechanical support by fixing the electrodes to suspend on top of a PTFE container. The circulating water or ice bath in the secondary containment was used to keep the temperature of the acid mixture according to different conditions. And a platinum resistance temperature needle protected by PTFE was immersed in the acid to monitor the temper during the reaction. Then a magnetic stirring apparatus was used under the secondary containment to control the velocity of acid mixture flow. The monitor for the rotational velocity of the stir bar was a self-made apparatus according to the principle of electromagnetic induction. It mainly consisted of an induction coil and an oscilloscope. In additional, another oscilloscope was used to measure I-V characteristics with appropriate electric circuit. Then, the BEP process can be performed after sample preparation.

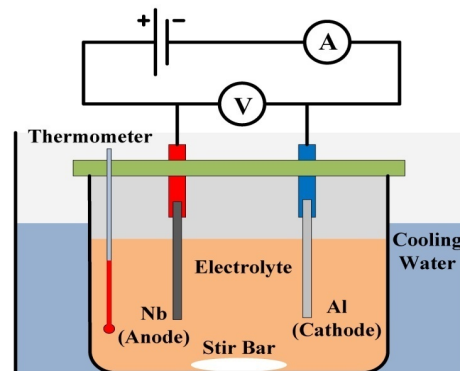


Figure 1: Schematic installation of BEP for small samples.

RESULTS AND DISCUSSION

I-V Characteristic of BEP for Niobium Samples

Fig. 2 shows an I-V curve for BEP of niobium sample. Like typical electropolishing I-V characteristic, four

regions corresponding to etching, periodic oscillation of anode current density, polishing, and gas evolution on the anode surface were identified depending on the potential applied. Initially, the current density increased linearly with the voltage until reaching the maximum value. At this region, the behaviour was dominated by ohm resistance in the electrolyte. Then current began to decrease with the oscillation until reach a steady plateau. In this region, a relatively strong oxide layer is built up on the surface, which could be realized as a capacitance. Thus the current began to oscillate. Over a horizontal range, the current density was nearly independent of the applied voltage and the surface to be polished. For even higher voltages, gaseous oxygen is set free at the anode and the oxygen bubbles result in discontinuities on the surface.

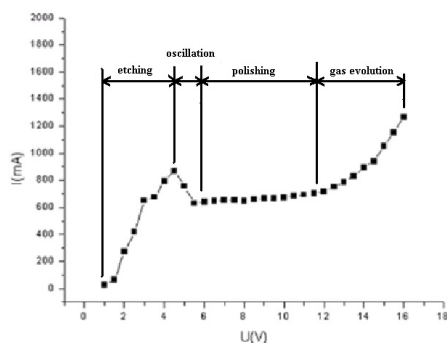


Figure 2: The typical I-V curve for buffered electropolishing.

However, not all the I-V curves have the same shape. The detailed shape of the curve was various with the different conditions. It depends not only on the electrolyte flowing speed, but also on, temperature and other conditions.

Figure 3 was the development of I-V curve with different flowing speed of electrolyte. They were measured at different electrolyte flowing speeds while other experiment conditions were the same. This investigation was necessary because acid agitation was an indispensable means in electrochemical polishing to keep a stable material removal in time, especially in the high viscosity of the acid mixes in BEP and for the irregular cavity geometry later. It would become an important parameter to get an optimal polishing rate and smooth Nb surface. In Fig. 3, we could see the I-V curves have greatly difference with the different flowing speeds of electrolyte which were indicated by the rotation rates of the magnetic stirring bar. With the static electrolyte, the I-V curve had a long polishing plateau. But the limiting current density was smallest of all. With the flowing speed of electrolyte becoming faster, the width of polishing plateau changed little, but the limiting current density continued to increase. Then, when the rotational speed of the magnetic bar was above a special value, about 15Hz in Fig. 3 which was determined by other experimental conditions, the horizontal parts of curves began to become a slanted curve toward up. As to this phenomenon, we thought it was not a symbol of the

maximum electrolyte flowing speed we could use, although the polishing plateau was not as clear as those at the lower flowing speed. Oppositely, we thought it represented the flowing speed of electrolyte was just fast enough to bring the complex compound of niobium oxide layer around the niobium sample surface away. That fast flowing speed was necessary especially to the high viscosity BEP acid solution because it would make the anodic films [12, 13, 14] occupy more voltage comparing common acid solution. So, the faster electrolyte flowed, the more external complex composition of the film could be brought away, and the electric field strength in the compact lay near the niobium surface would be enhanced. Just due to the stronger electric field, a higher polishing rate could be achieved during the BEP.

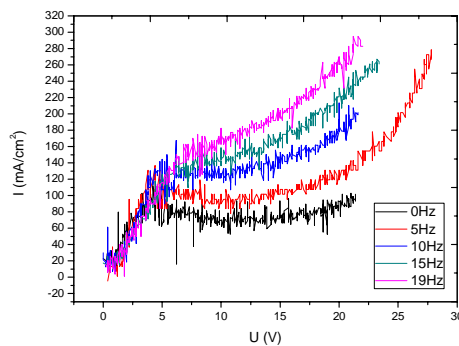


Figure 3: Development of I-V curve with different rotational speed of the stirring bar.

In the mean time, the electric field difference between protrusions and well is also enlarged which would make the surface much smoother. The following experiment result would confirm it. As to the trend of limiting current density increasing with the faster electrolyte flowing speed, it was also consistent with our beginning judgment. Because the sticky layer on the surface of the sample would take lot of voltage, the faster the electrolyte flowed, the less sticky layer would be left and the smaller voltage it would be take. And the curve would move up.

Besides acid agitation, we found the I-V curve was also sensitive with the temperature in the BEP process. Fig. 4 showed the I-V curves with different temperature. They were measured at the temperature of 12.5, 16.5, and 22 degree Celsius, and also in the same other conditions. In the part of polishing plateau regions, it was similar as those with different flowing speed of electrolyte above. With the higher of temperature, the limiting current density also increased. It could be understood by the theory that the higher temperature could increase the mobility of the ions which made the reaction faster. And as to the sharper of the curve in etching region, it may be related to the properties of the BEP electrolyte. However, as to the part of etching region, we could see the different effects of those two parameters on I-V characteristic. With different electrolyte flowing speed, the slopes of I-V curve of this part were nearly the same; while different temperature, they were different. With higher temperature,

the slope of I-V curve of this region became much sharper. We thought it was because agitation could not change the property of the mixed acid, while the higher temperature maybe could make it changed, no matter in physic or chemical. The simplest explanation for this phenomenon was that, within certain range, the higher temperature could lower the viscosity of BEP electrolyte in physical. So the resistance of the electrolyte decreased, and the curve in etching region would be sharper. However, detailed mechanism might be not so simple, and needed to further study. But here the result of the trend of limiting current density development with temperature in BEP was the thing we were main concerned and it represented the polishing rate of this technology, which will be showed in the following part of this paper.

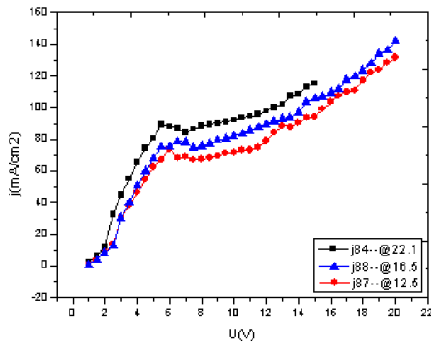


Figure 4: Development of I-V curve with different temperature.

Effect of Parameters on Polishing Rate

In the process of niobium cavity treatment, polishing rate is one of the most important parameters. The high polishing rate could greatly reduce the time of cavity fabrication and further decrease the cost of SRF cavity. What was more, the high demand of more than twenty thousands 9-cell cavities by ILC [5] also required fasting process of niobium cavities' fabrication. After optimization, in our BEP experiment, the maximum polishing rate could reach 4.66µm/min.

Fig. 5 showed the effect of temperature on polishing rate. As shown, the whole region could roughly divide to three regions by temperature according to the polishing rate. In the first region, the temperature was below 23 degree Celsius. In this part, the maximum polishing rate was only about 1.5µm/min. Between 23 C and 26 C was the second region. In this region, the polishing rates were distributed from about 1.0µm/min to 2.7µm/min. And in the last region, the temperature was above 26 C. As seen in the figure, except one data point, all the other polishing rates were more than 2.3µm/min, and the polishing rate didn't increased obviously with temperature increasing. So it showed us that if we would like to get high polishing rate, the temperature over 23 degree Celsius was needed. And if the temperature we chose was between 23 C and 26 C, the other conditions like agitation, voltage and so on needed to be considered to improve polishing rate. And if the temperature above 26 C was chose for polishing, polishing rate seemed not to be a problem. But

the high temperature, especially above 35 C, will make the reaction hard to control [11] and more impurities include oxides may be brought into the surface because of it.

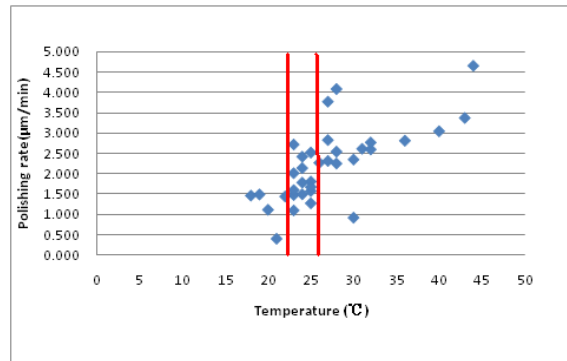


Figure 5: The effect of temperature on polishing rate.

Besides temperature, the electrolyte flowing speed also had the effect for polishing rate. Although it was not as obvious as the effect of temperature on polishing rate, it also could be divided into two regions by the flowing speed of electrolyte as shown in Fig. 6. Similar as above, the flowing speed of electrolyte was represented by rotational frequency of the magnet stirring bar. In the left region of the red line, the rotational frequency of stirring bar was below 15Hz, and most of the polishing rates were concentrated from about 0.5 to 2.2µm/min. And in the right region, where the rotational frequency was above 15Hz (include 15Hz), the minimum polishing rate was about 1.5µm/min and the maximum polishing rate could reach about 4.7µm/min. Although the data point were a little diffusion, it still could be concluded that if the high polishing rate needed to be got, the rotational frequency of magnetic stirring bar should be above 15Hz, which was also identical with the analysis in the frontal part of I-V characteristic. In addition, the thinner film generated by faster electrolyte flowing speed also allowed easy transport of ions through the compact oxide film by diffusion [15, 16], which also will speed up the polishing rate.

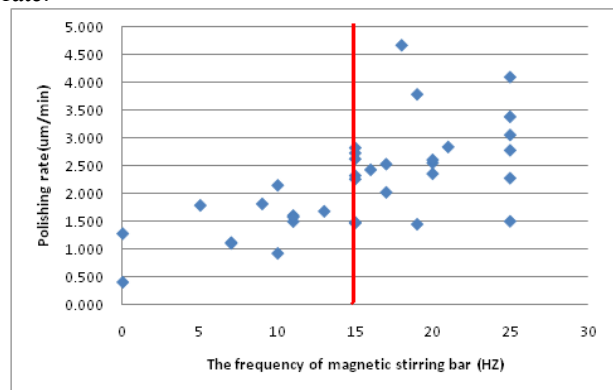


Figure 6: The effect of flowing speed of electrolyte on polishing rate.

Effect of Removed Thickness on Surface Roughness in BEP

Due to high number of variables involved in the fabrication and conditioning of the cavities, it is not very obvious how to establish a correlation between surface finish and cavity performance. However, in general, the smoother the surface is, the higher the probability will be to obtain a high performing cavity. To achieve the optimum RF performance, the surface of the cavity must be as close as possible to ideal [1]. In our BEP experiment, the best surface RMS roughness could be close to 21nm which measured in an over 200×200μm area at Jefferson Lab

Fig. 7 showed the relationship between roughness and removed thickness in BEP process. Initially, when the removed thickness was about 25μm, the RMS roughness was only about 270nm. Then, before 75μm, with increase of removed thickness, the value of RMS roughness decreased rapidly. After that, when the roughness was above 75, a long nearly horizontal region with the RMS roughness around 50nm was appeared. It provided very useful information for us to the further study on cavity BEP. If we would like to get a smoother surface repetitively, the minimum removed thickness about 75μm was needed. It could be understood by the basically theory of electropolishing proposed by Jacquet theory [12]. A viscous layer of anodic dissolution products will be formed during the EP process. 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 is higher than in crevices, thus projections dissolve more rapidly than crevices. So, it produces the altitude difference between projects and crevices less and less with the increase of average removed thickness.

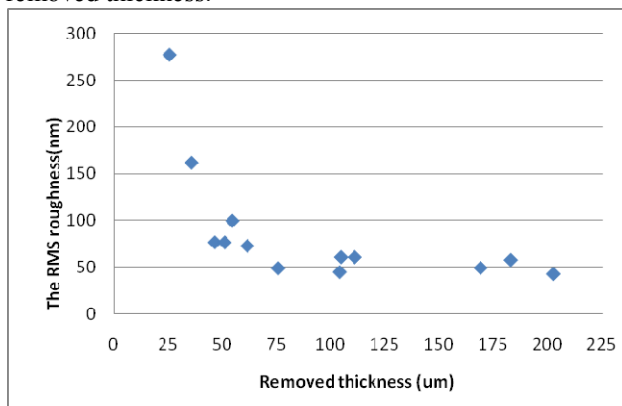


Figure 7: Relationship between the roughness and removed thickness.

Surface Topography

Fig. 8 showed the surface topography of niobium samples with different instruments. Fig. 8a) was the picture of BEP treated samples [9]. Each sample could obviously be divided into two parts by eyes. The shining

parts were treated by BEP, while the other parts of samples were the original surface. We could see the reflection of the other sample clearly in the shining part like in a mirror. Fig. 8b) and c) were the surface topographies observed by metallographic optical microscope (MOM) respectively corresponding to original surface and the BEP treated surface [9]. They were the images which magnified to 1000 times. It could be found that the roughness of surface was greatly improved after BEP. In addition, in the process of taking pictures of them with MOM, it was nearly hard to focus because of the smoothness of the surface sometimes. Fig. 10d) was a picture scanned by high resolution 3D profilometer on the BEP treated sample over a 200×200μm area at Jefferson Lab. With the RMS roughness of 21nm, it was hard to see any heave on it. Comparing with the RMS roughness 250nm of traditional EP, it was nearly decreased by 10 times.

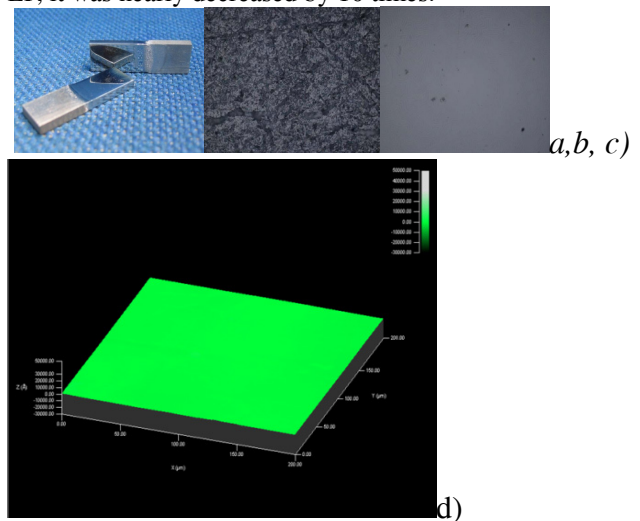


Figure 8: Surface topography of samples by different instruments.

Preliminary Result of BEP on Demountable Cavity

Because of the irregular shape of the SRF cavity, current density distribution in the cavity becomes complex during the BEP process, especially in the much more viscous BEP electrolyte. So, as to make clear the different current distribution in different area of the cavity, a demountable cavity was fabricated at JLab. It consisted of two half cavities and each of them has a flange at the position of equator to make them together, which was showed in the Fig. 9. So, it became easily to demount for observation the effects in different region after each BEP experiment. Moreover, three samples according to the different distance to the equator were designed in one of the two half cavities. Thus, the difference of the I-V characteristic and the BEP effect could be easily measured with the help of the three samples.

At part of coordination between JLab and Peking University, the preliminary experiment of the demountable cavity was carried on at Peking University. Fig. 10 was the picture of demountable cavity after

treated by BEP. The right part was the upward cup during BEP, which was polished, while the left part was the downward cup which only showed the etched surface. We thought the difference between the upward and downward was brought by the high viscous of BEP electrolyte. Under the effect of the gravity, the high viscous film which formed in the BEP process in the downward would be more the upward part. Together with the voltage it occupied, the downward surface cannot get enough voltage. That is, this part couldn't reach the polishing region and stayed in the etching region. So it showed etched surface. And the further study will be carried out in next period.



Figure 9: Picture of demountable cavity.



Figure 10: The picture of demountable cavity after BEP.

CONCLUSION

In this paper, BEP process was systematically studied. Through discussion of effects of parameters on I-V characteristic, polishing rate and surface roughness, the optimum results were got. The polishing rate could repetitively reach around $2.5\mu\text{m}/\text{min}$, while the surface RMS roughness could repetitively get to around 50nm which measured in an over $200\times 200\mu\text{m}$ area at Jefferson Lab. Comparing with conventional EP, the BEP polishing rate was over 7 times faster, and the surface RMS roughness was decreased more than 5 times. And the result of the maximum polishing rate $4.7\mu\text{m}/\text{min}$ and the best roughness of 21nm also indicated this technology still has potential to improve. All above shows BEP technology has a great potential to replace conventional EP and become a new generation of technology to treat niobium SRF cavities.

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