

PLASMA ELECTROLYTIC POLISHING TECHNOLOGY PROGRESS DEVELOPMENT FOR Nb AND Cu SUBSTRATES PREPARATION*

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Abstract

Superconducting radio frequency (SRF) cavity performance is highly dependent on surface preparation. Conventionally, electropolishing (EP) is used to achieve a clean surface and low roughness for both Nb and Cu substrates (in thin films SRF cavities), but it requires harsh and corrosive solutions like concentrated acids. Plasma Electrolytic Polishing (PEP) is a promising alternative that uses only diluted salt solutions and has several advantages over EP. PEP can replace intermediate steps like mechanical or chemical polishing, thanks to its superior removal rate of up to 2-8 $\mu\text{m}/\text{min}$ of Nb and 3-30 $\mu\text{m}/\text{min}$ of Cu. It achieves Ra roughness of 100 nm for both substrates and has a higher smoothing effect than EP. PEP is also suitable for normal conducting cavities and other accelerator components, including couplers. We demonstrate the effectiveness of PEP on SRF substrates and analyse substrate defect evaluation. We demonstrate the application of PEP onto SRF substrates: Cu QPR sample and 6 GHz cavity.

INTRODUCTION

The PEP process is a non-conventional method used to treat various types of metal and alloy surfaces. It is a powerful and fast process that does not require any preparation of the treated surface. However, ensuring scalability and application of PEP can be a complex endeavour. The application of PEP onto Cu and Nb surfaces for SRF has already been discussed and published [1]. In this study, we discuss further advancements in scalability and present a new setup designed for treating larger samples.

THE NEW SET-UP

All experiments were conducted in the chemical laboratory of the Superconductivity and Surface Treatment Service at Legnaro National Laboratories (LNL) of INFN. Two DC power supplies were connected in series to deliver a high voltage (300 V) and high currents (up to 150 A) output. Various samples with different geometries and dimensions were subjected to treatment. The experiments conducted on the 18 cm^2 samples demonstrated a current density ranging from 0.2 to 0.8 A/cm^2 . The process for these samples was carried out using a 3 L solution.

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Considering the constant value of the experimented current density, the larger samples treated in subsequent experiments could easily reach currents approaching 150 A. Consequently, an increase in heat production is expected. The high temperatures generated during the process may decrease the stability of the treatment and potentially lead to oxidation or corrosion effects. During the initial stages of the process, current spikes were observed, reaching values 2-5 times higher than the working currents. These current values exceed the maximum sustainable limits of the currently employed power supplies, indicating the need for improvements to the setup.

Design and Production

A new facility was designed and developed specifically for the treatment process of larger area samples such as QPRs [1], and 6 GHz cavities. The design of the facility took into consideration several fundamental characteristics, including:

- The ratio of bath volume to anode area, which needed to be greater than 0.2 L/cm^2 .
- The material of the bath had to be an insulator.
- The capability to accommodate a large surface cathode, with an anode to cathode ratio of 10:1.

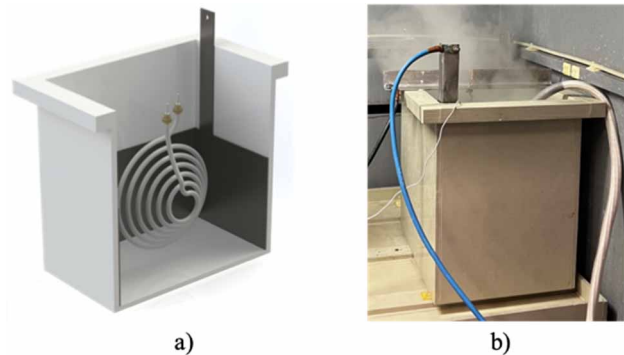


Figure 1: a) A schematic render of the plastic bath used for PEP; b) Photo view during PEP process.

Figure 1a illustrates the polymeric bath made of PVC that was designed and fabricated for this purpose. The experimental setup consisted of an Nb cathode, a resistance element, and a thermocouple to ensure precise temperature control. The treated sample (anode) was connected positively and suspended in the bath, as shown in Fig. 1b. The bath had a capacity of approximately 30 L of solution, with a total volume of 50 L. Such system provided better temperature control and a more stable polishing process.

The larger solution volume/anode area ratio compared with the previous set-up using 3 L beaker resulted in a reduction in vapor production and a less vigorous reaction, thereby enhancing the stability and controllability of the process.

The experimental results presented in this study were obtained by treating three different samples with the newly designed plant:

- Bulk Cu QPR;
- Cu cylinder with a 2.3 cm diameter and 10 cm length;
- Cu 6 GHz cavity.

To treat the bulk Cu QPR (Fig. 2a), a PVDF cap was designed (Fig. 2b). The purpose of the cap was to prevent the solution from entering the sample, thereby avoiding plasma activation on the inner surface. This approach allowed the reduction of the working currents and focused the polishing solely on the external surface, which is the target region of interest.

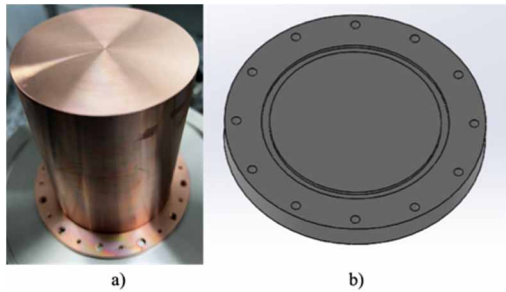


Figure 2: a) Bulk Cu QPR; b) PVDF cap.

To securely attach the cap to the flange, eight M4 screws were used to fix the sample in place.

For the Cu cylinder and the 6 GHz Cu cavity, the main goal was to treat their internal surfaces. Previous tests revealed that without proper shielding, the process primarily occurred externally. To address this issue and concentrate the plasma treatment internally, heat shrink tubing was applied, as depicted in Fig. 3.



Figure 3: Heat shrink tubing applied on cylinder Cu sample (on the left) and on the 047 cavity (on the right).

Performing internal polishing on cylindrical samples and 6 GHz cavities poses a significant challenge. Electro-polishing of internal surfaces typically requires an internal cathode that closely resembles the surface being treated. However, in the case of PEP treatments, employing only an internal cathode is particularly challenging due to the required anode-to-cathode ratio of 10:1. Therefore, the use of an internal cathode can be considered within a double cath-

ode. The final objective of the research is to achieve the polishing of internal surfaces using only an external cathode.

RESULTS

The newly developed PEP setup facilitated the conduction of multiple tests on Nb and Cu samples of various geometries, with the objective of investigating the scalability of the PEP process to elliptical shapes.

Temperature Factor

Temperature plays a crucial role in determining the quality of surfaces treated with the PEP process. Typically, working temperatures for PEP processes are within the range of 60 – 90 °C.

A systematic study of the PEP process, particularly regarding temperature behaviour, is essential. Figure 4 shows the relationship between working current density and bath temperature, demonstrating an inverse proportion.

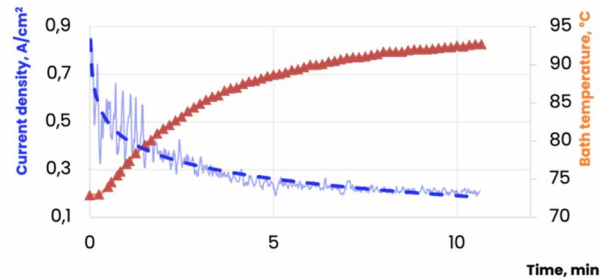


Figure 4: Current density vs bath temperature (70-90 °C) curves in time for a Nb PEP treatment of 10.5 min [2].

During the PEP process, it was observed that the current density decreases proportionally as the temperature increases. This phenomenon leads to a decrease in the polishing rate.

For Nb surfaces, the PEP treatment was conducted using a water solution consisting of 3% NH₄F and 1% NaF, with an applied voltage of 300 V and a working temperature ranging from 78 °C to 85 °C [3].

In comparison to traditional treatment methods, the Nb PEP process demonstrates lower Ra values (surface roughness) when the same amount of thickness is removed. This indicates that the PEP process can achieve a smoother surface finish for Nb samples [2].

It is worth noting that temperature has a significant impact on the uniformity of the final surface. Figure 5 displays the results of three separate tests conducted at different starting and average working temperatures, highlighting the variations in surface quality achieved.

It is evident from the results that the PEP process for Nb surfaces exhibits better uniformity when using a temperature range of 85 °C to 90 °C. Data indicates that both the average temperature and the starting temperature are crucial factors for achieving a uniform polishing outcome.

In the case of Cu PEP, a similar relationship between current density and temperature exists. However, the uniformity issues observed with low starting temperatures are specific to Nb surfaces and not observed with Cu. This sug-

gests that the impact of starting temperature on uniformity differs between the two materials.

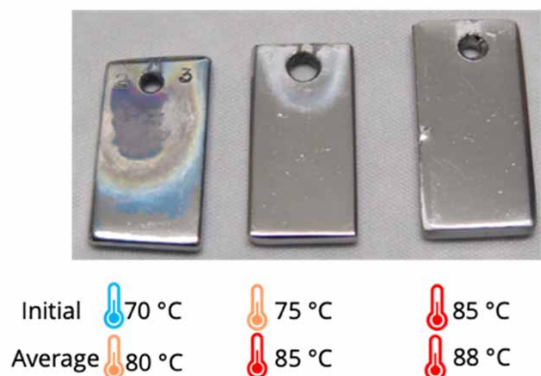


Figure 5: Three Nb samples treated with PEP at different temperature.

Process Scalability

The PEP process for Cu samples is carried out in SUBU5 solution applying a voltage of 300 V with a working temperature in the range of 70 – 97 °C [2, 4]. It is worth to mention that after the treatments with SUBU5 solution, it is necessary to do a passivation step in sulfamic acid (10 g/L water solution). Two samples were selected to evaluate the effectiveness and suitability of the PEP process for treating Cu surfaces of different geometries and applications: bulk Cu QPR and 6 GHz cavity.

Bulk Cu QPR

The QPR sample was treated using a voltage of 300 V for a duration of 10 min. During the treatment, peak currents reached up to 150 A, while the working currents, once the process stabilized, ranged around 80-100 A.

The surface of the treated sample appeared reflective and smooth (as shown in Fig. 6).

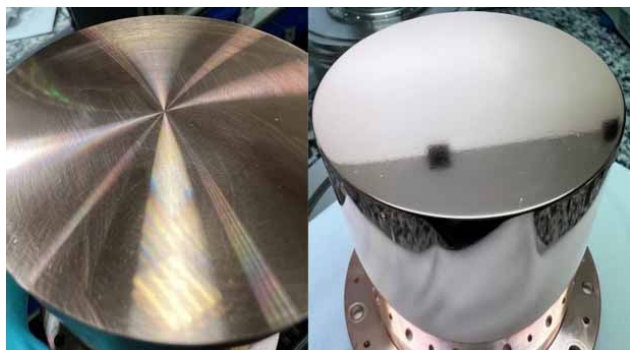


Figure 6: Cu bulk QPR before (on the left) and after (on the right) 10 minutes PEP process.

6 GHz Cavity – Internal Surface Treatment

As a preliminary test prior to treating the 6 GHz cavity, the cylindrical sample was subjected to a PEP treatment using a voltage of 300 V for 8 min. The average passing current during the treatment was around 25 A, with an initial

peak ranging from 30 A to 35 A. External heat shrink was applied to the sample to facilitate the process.

The sample was inserted vertically into the bath and connected to the anodic polarisation distribution holder.

After the 8-minute PEP process, a total of 4.06 g of material was removed from the sample, corresponding to a thickness reduction of approximately 73 μm. Since a chemical polishing solution (SUBU5) was used for the PEP process, it is necessary to establish that the resulting polishing was primarily due to the PEP treatment. To demonstrate this, certain calculations were conducted.

The material removal rate due to electrochemical dissolution can be estimated using the Faraday’s law as follows:

$$\Delta m = kIt.$$

Where k is the electrochemical constant for Cu, I is the current during the process and t is the time.

The calculated removed mass of 3 g aligns with the experimental mass removal, confirming the occurrence of PEP, as the current efficiency exceeds 100 %. The removal rate during the process was 10.5 μm/min, which is seven times higher than the removal rate achieved with SUBU5 etching. The heat shrink tubing successfully withstood the high voltage and working temperature applied during the PEP process. The surface of the sample has been uniformly polished, except for the top part of the tube where etching occurred (as depicted in Fig. 7).



Figure 7: Surface of the cylindrical sample treated with PEP after 7 minutes of processing.

The presence of etching on the upper edge of the sample is likely attributed to the intense boiling phenomena occurring in that region. This violent boiling can lead to a lack of plasma ignition and subsequent different mechanism in that specific area.

The test results demonstrate that PEP process can be successfully achieved internally without the need for a double-cathode setup.

The Cu 047 6 GHz cavity was treated vertically applying 300 V for two cycles of 5 min each. The average passing current ranged from 30 A to 35 A and the total removed thickness achieved was 67 μm.

Similarly, to the cylindrical sample, the etching phenomenon was observed on the top cut-off of the internal surface of the treated cavity, see Fig. 8.



Figure 8: Top cut-off of the 6 GHz cavity after 10 min of PEP treatment. The yellow circles highlight the etched part.

Before the process, the internal surface showed evident scratches due to the forming, particularly in the cell part. A comprehensive characterization of the internal surface before and after the polishing has been done with LNL visual inspection system, see Fig. 9.

The polishing left the copper surface highly reflective, and the prior visible scratches were effectively smoothed out.

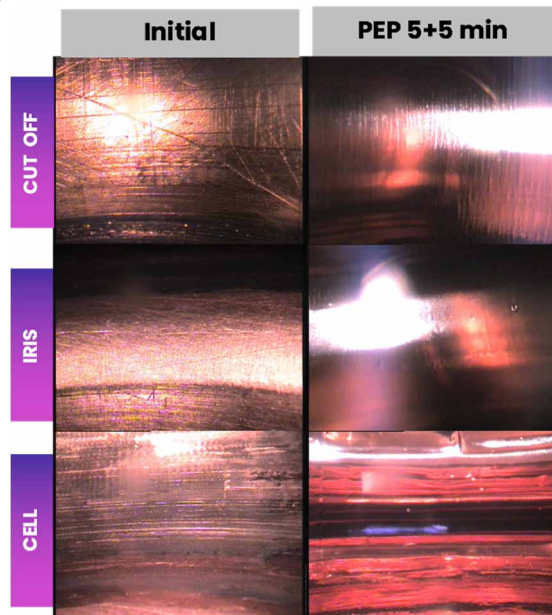


Figure 9: Internal surface inspection of the cavity before (on the left) and after (on the right) the PEP treatment.

Current Efficiency

The current efficiency parameter determined as follows:

$$CE = \frac{\Delta m}{kIt} \times 100\%.$$

The CE was evaluated by comparing the experimental weight difference (Δm) and the hypothetical mass that would be removed if the process followed the Faraday's law, where all the current is used for metal dissolution.

In the case of Cu, all of 3 conducted tests exceeded a CE above 100%. Specifically, the CE for the cylindrical sample was approximately 116%, while 047 6 GHz cavity, was 101%.

These results align with previous tests conducted at LNL. Additional investigations conducted have demon-

strated a synergic effect between the electrochemical process and the SUBU5 solution, which can result in a current efficiency reaching 150% [2]. The synergic effect can be explained by the presence of electrochemical dissolution reaction, plasma etching and SUBU chemical polishing. The contribution of the SUBU chemical reaction does not exceed more than 1 - 2% and cannot explain such high values for CE.

For the bulk Cu QPR, the weight loss after 5 min of PEP processing was 11.69 g. In contrast, the theoretical mass that would be removed, considering an average passing current of 50 A, was calculated to be only 4.67 g. This suggested a CE of approximately 250%.

This unexpectedly high CE value indicates that besides the SUBU5 and anodic dissolution effects, other factors are likely contributing to erosion rates.

CONCLUSIONS

This study demonstrated the feasibility of PEP application for 6 GHz elliptical cavities and bulk Cu QPR samples. Scaling up the PEP process to these complex geometries presented challenges due to factors such as high passing currents, large anode/cathode ratio, and rapid temperature increase. However, through a series of tests and systematic research, successful polishing of both Cu bulk QPR and 6 GHz cavity was achieved.

In this work, a plant to treat the target samples was developed. The possibility to polish internally the hollow structures without the usage of an internal cathode was firstly demonstrated, although further improvements and studies are still necessary.

The influence of temperature on surface quality was examined, revealing a correlation between bath temperature and the final appearance of the surface. The calculation of current efficiency showed a synergistic effect between the PEP process and the chemical polishing solution.

In conclusion, this study provides valuable insights into the adaptability and effectiveness of the PEP process for complex geometric structures. The developed and patented solutions at Legnaro National Laboratories will be used to further improve the scalability of Plasma Electrolytic Polishing. Future plans include conducting uniformity studies of the internal PEP process, while the primary focus remains on upgrading the current facility to treat 1.3 GHz cavities.

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