

ANALYSIS OF HIGH FIELD Q-SLOPE (HFQS) CAUSES AND DEVELOPMENT OF NEW CHEMICAL POLISHING ACID*

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Abstract

In our previous studies of High Field Q-slope (HFQS) we have concluded that nitrogen contamination from the nitric acid is the main cause of the degradation of the Q in buffered chemical polished cavities. Our conclusion is made based on previously unresolved phenomena which are found from huge amount of published cavity test data, including fine grain, large grain and single crystal cavities treated with EP and BCP. According to this analysis, we have started developing new nitrogen-free chemical polishing acid. Hydrogen peroxide with HF mixture was reported able to react with Nb, and there's no extra element contamination in it, so we replace the conventional BCP with this mixture to start our study. In this paper, some Nb coupon sample results with new acid will be reported. We completed the first step of developing the new acid and we got the Nb finish roughness no worse than conventional BCP.

INTRODUCTION

Demand for New Acid

For superconducting Nb cavities, chemical polishing or electropolishing (EP) is required to remove defects and the contaminated surface layer. It is an important process that leads to much better performance. One commonly used method – Buffered Chemical Polishing (BCP) – always suffers from cavity High Field Q-slope (HFQS) which seriously limits the cavity performance at high operating field. The other method – EP [1] – can recover the cavity HFQS by an extra 120 °C low temperature baking (LTB) post EP [2]. However, EP is not always applicable to low/medium β cavities because of their complicated shapes. Therefore, a new chemical polishing process is in demand, especially for low/medium β cavities which are used in heavy ion accelerators.

HFQS is the phenomenon where Q_0 (unloaded Q) performance of the SRF cavity begins to drop exponentially when the magnetic field increases beyond 80 - 100 mT (corresponding to an accelerating gradient E_{acc} of 20 - 25 MV/m for ILC elliptical shape cavity [3]). The Q_0 drop is caused by pure heating at RF high magnetic field region (equator area) on the SRF surface [4–6], and it ultimately limits the

magnetic field to below 130 mT (E_{acc} is 30 MV/m for ILC elliptical shape cavity).

Low to medium β cavities evolved in many areas and are becoming one of the most widespread types in LINACs. FRIB is an example of a heavy ion accelerator project whose cavities suffer from HFQS. All FRIB cavities are treated with BCP. Statistically, the performance of ~ 35% of the cavities at FRIB is limited by pure HFQS (HFQS without X-rays) [7]. An example is shown in Fig. 1, the FRIB cavities experience Q_0 drop starting from $B_p \sim 85$ mT in $\beta = 0.041$ Quarter Wave Resonators (QWRs).

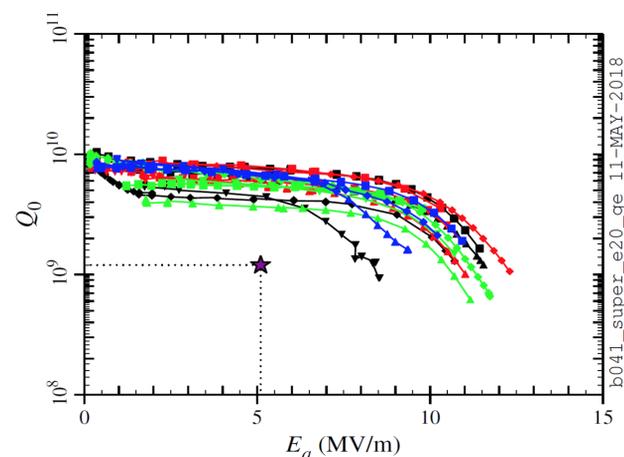


Figure 1: FRIB cavity performance at 2 K in Vertical Test, $\beta = 0.041$ QWRs, $B_p/E_{acc} = 10.71$ [mT/(MV/m)].

Alternative Acid Treatment

It is highly probable from our recent analysis that the HFQS under BCP arises from nitrogen contamination, which is introduced by nitric acid in the commonly used BCP acid. Thus, the replacement of the nitric acid by an alternative is a promising way to mitigate this issue. For this purpose, past experiment results that are relevant to this study are summarized as follows [8]:

1. If nitric acid (1500ppm) is added to EP, subsequent LTB can no longer always eliminate the HFQS [9].
2. BCP HFQS has a deep memory effect which cannot be explained only by surface smoothness changes [1, 8].
3. Large grain/single crystal cavities have very smooth surface after etching by BCP ($R_z \sim 0.2 \mu\text{m}$), but their

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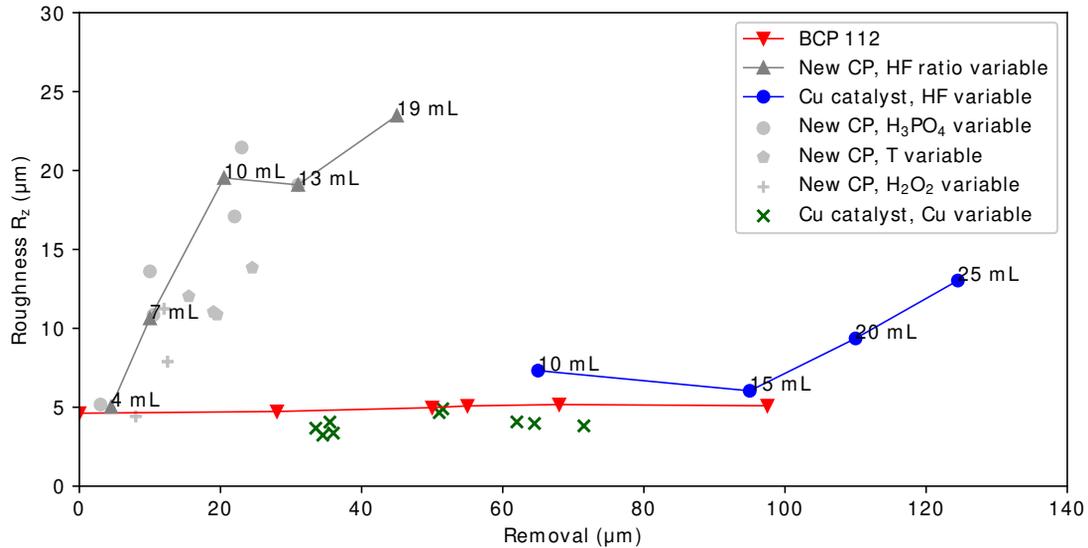


Figure 2: Optimization of new acid process and BCP baseline data with surface roughness Vs material removal.

highest achievable gradients before quenching occurs are still lower than those of EP'ed fine grain cavities (40 MV/m in case of ILC shape) [10–13].

- Nitrogen doping technique shows that the Nb-N phase generated on the SRF top surface has very harmful impact on cavity performance. This layer has to be removed by EP ~ 5 µm [14].
- No grain boundary heating observed for BCP'ed large grain cavity, while the grain boundary areas are the only places have high roughness [15].

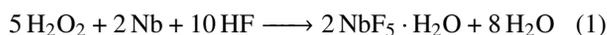
Based on these experiments, we formulated three criteria on the alternative acid:

First, the acid need enough oxidization capability to make the etching possible.

Second, surface roughness after polishing should be similar to conventional BCP result. It has been reported that high surface roughness will lead to magnetic field enhancement [16, 17], and result in flux trapping [18]. A previous simulation of EP'ed cavities suggests field enhancement will start from a surface roughness of ~ 3 µm [19].

Finally, the alternative acid should be nitrogen-free to prevent nitrogen contamination.

Based on these conditions, hydrogen peroxide (H₂O₂) becomes the first candidate that comes to our mind for replacing the nitric acid as a new oxidizer, since it does not introduce any extra element contamination and is itself a strong oxidizer. An extra benefit is that the reaction will not generate any hazardous NO_x gas. The reaction of the H₂O₂ plus HF with Nb is:



Similar works were reported long ago, but both got high roughness [20, 21].

NEW ACID EXPERIMENT

To maintain consistency with previous published data sets, we take R_z as a measure of surface roughness defined by:

$$R_z = \frac{1}{5} \sum_{i=1}^5 (R_{p,i} - R_{v,i}) \quad (2)$$

where $R_{p,i}$ and $R_{v,i}$ denote the i^{th} highest peak and i^{th} lowest valley within the evaluation length respectively [22]. R_z is directly measured by the stylus (roughness tester).

Experimental Setup

Prior to the experiments, niobium samples (fine grain, RRR = 250 - 300, 50 mm × 15 mm × 4 mm) were mechanically polished by emery paper (#320) to adjust the initial surface roughness to ~ 4.5 µm. The surface roughness after etching was measured at no fewer than 5 points near the initial measurement points and the results were averaged.

Acid Ratio Controlling

The first group of experiment is done to study the acid ratio influence on the finishing surface roughness. We set all trials the same reaction time, so the removal for each case is different, as shown in Fig. 2 grey triangle marks. This mixture resulted in $R_z = 20 - 25 \mu\text{m}$, while the conventional BCP acid can attain a roughness of ~ 5 µm (red inverted triangle marks in Fig. 2). The total volume of acid is fixed at 55 mL, and the acid ratio is changed. No optimum point could be obtained when the volume of 50% H₂O₂ was varied from 51 mL to 36 mL correspondingly. 24 mL HF + 31 mL H₂O₂

and 27 mL HF + 28 mL H₂O₂ experiments were also done, but the roughness were beyond the roughness tester's measurement range (25.2 μm). The acid bath temperature was not actively controlled, the initial temperature was 18 °C and the final temperature ranged from 35 to 60 °C. This is the same in other experiments.

Other Trials

Figure 2 (different marks in grey) also shows trials for studying other parameters: H₃PO₄ amount (to adjust viscosity [23–25]), initial temperature and H₂O₂ concentration. None of these parameter variation changes the effect that the new acid lead to very high roughness.

Several other parameters were also investigated but not shown on the graph: H₂O₂ decomposition, agitation effect, and replace the H₃PO₄ to H₂SO₄ (increase both viscosity and oxidation capability). However, the surface roughness remained very rough.

Large grain niobium samples were used to investigate the reason. The samples were composed of two large crystalline with sizes ~ 3 cm × 1 cm. These two crystalline had different crystal orientation. We observed a big difference in surface roughness after ~ 20 μm etched in these crystalline. One had $R_z = 6.8 \pm 2.5 \mu\text{m}$ and another had $R_z = 16.6 \pm 3.6 \mu\text{m}$. This provided evidence to suggest that preferential etching depends on the crystal orientation. In the mean time, $R_z = 6.8 \pm 2.5 \mu\text{m}$ is still much higher than BCP large grain (~ 0.3 μm), so the high roughness is not only due to grain difference but also have a erosion effect on each grain.

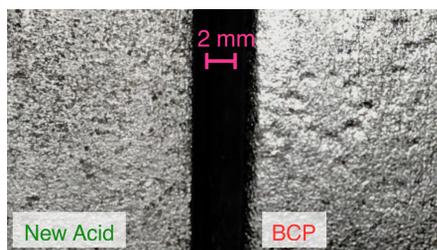


Figure 3: Comparison of new CP plus Cu catalyst with BCP processed Nb sample. The removal for both cases are ~ 95 μm.

OPTIMIZATION FOR ACID WITH COPPER CATALYST

We made several tests and found that the addition of a small amount of Cu to the acid prior to immersing Nb can lead to much improved results. The reaction was much faster and the finishing surface was much better than all the cases that were done without Cu. Further more, the Nb sample treated with this acid has no “orange skin” (Fig. 3) texture, unlike the BCP case.

Acid Ratio Controlling

The optimization of HF concentration was conducted again (Fig. 2, blue dot marks). We fixed the total amount of acid mixture (55 mL), the amount of 29 mL 50% H₂O₂, and the amount of Cu (300 ppm). The concentration of HF was adjusted to 26 mL by adding water to the 50% HF. For instance, 15 mL HF means 15 mL of 50% HF acid and 11 mL of water. The reaction speed increased rapidly with HF concentration, and so did the finishing surface roughness. We found the HF amount at 15 mL gave the best surface roughness, and then we chose it for subsequent experiments.

Initial R_z Improving & Cu Amount Controlling

We polished niobium samples mechanically with emery paper of #600 to get a more standard initial surface roughness ~ 2.5 μm. Also, previous copper catalyst experiments were done by copper powder, which posed difficulties in weight control because electrostatic force made the powder easily spill out of the container. We then replaced it with thin copper wire for increasing the accuracy of copper concentration. We then did the Cu amount controlling experiment.

This effect is shown in Fig. 2 (green x marks). Based on the results with copper concentration in the range of 250 - 600 ppm, a finishing roughness of 3 μm can be achieved, and it does not increase with the removal amount. In this trial, no obvious copper amount dependence was observed.

CONCLUSION

We concluded N contamination is one of the reasons for BCP'ed cavity HFQS problem based on several phenomena, so we tried a new hydrogen peroxide with hydrofluoric acid mixture. We adjusted different parameters but all cases of the experiments resulted in high roughness. Lastly, we found that adding copper catalyst to the new acid can reduce the Nb sample roughness to a similar level as conventional BCP.

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