

INITIAL RESULTS FROM INVESTIGATIONS INTO DIFFERENT SURFACE PREPARATION TECHNIQUES OF OFHC COPPER FOR SRF APPLICATIONS

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Abstract

As part of efforts to improve the performance of thin film coated accelerating cavities, improvement of the topography of the surface of copper is being pursued. This is known to strongly affect the properties of the deposited superconducting thin film. This study focuses on determining the optimal procedure to enhance homogeneity and smoothness of the copper surface. OFHC copper substrates have been processed using mechanical polishing (MP), chemical polishing (CP) and electrochemical polishing (EP) procedures as well as a combination thereof.

The parameters of each of the procedures have been tested and optimised to produce the smoothest surface possible. The resulting samples have been analysed using a scanning electron microscope (SEM), a laser profilometer (LP) and a confocal laser scanning microscope (CLSM).

Results indicate the superior performance of electropolishing over chemical polishing in terms of planarization efficiency, while a combination of mechanical polishing followed by electropolishing provides the most homogeneous and smooth surface when utilising the critical current density of the electrolyte.

INTRODUCTION

This study forms part of a larger study looking at the optimisation of Nb and NbN thin films deposited onto copper substrates, to be used in superconducting radio frequency (SRF) accelerating cavities. In order to assist with the production of higher quality films, an improved copper surface preparation procedure was investigated.

When depositing a thin film onto a copper substrate/cavity, it is well known that the thin film will replicate the morphology of the copper substrate [1]. As such, any changes in the surface of the copper substrate will be evident in the deposited Nb film and therefore influence the properties of the film as well. This is evidenced by the reduction of defect density in thin films, where a reduction in the surface roughness of the substrate onto which it was deposited, is seen [2]. The effect of the substrate on the deposited film allows one to optimize the copper surface prior to the deposition of the thin film so as to enhance the performance of the film.

There has been considerable research into the effects of different surface treatments for thin films deposited onto copper however, they are not as clear as for bulk Nb and considerable research is still required to fully comprehend how the thin film is affected. The overarching conclusion is that a reduction in surface roughness leads to improved

cavity performance [2]. The roughness of the copper surface can also lead to contact issues at the interface between the copper cavity and the deposited thin film, resulting in decreased superconducting performance [3]

During cavity forming processes or as a by-product of mechanical polishing, a damaged surface layer is understood to form on the copper surface. This has been reported to lead to a decrease in thin film performance [4]. The thickness of this layer is reported to be between 50-150 μm and should be removed for optimum superconducting performance [5].

With this in mind, studies were completed which utilised different copper surface preparation techniques, including mechanical polishing (MP), chemical polishing (CP) and electropolishing (EP), in order to optimise the copper surface preparation process for future thin film deposition.

EXPERIMENTS

A single Cu sheet was cut into 25x25 mm samples which were then subjected to the different surface preparation procedures. Prior to CP or EP, samples were first degreased in an ultrasonic bath with acetone (15 min), followed by ethanol (15 min), then rinsed with distilled water and blow dried with N_2 gas.

Chemical Polishing

In this study, the chemical solution SUBU5, initially developed at CERN for the LEP-II cavities [6], was used for all CP processes. The exact procedure used for the chemical polishing process was adapted from that used in the ARIES research project [7]. SUBU5 is comprised of sulfamic acid ($\text{H}_3\text{NO}_3\text{S}$) (5 g/l), hydrogen peroxide (H_2O_2) 35 % (50 ml/l), n-butanol 99 % (50 ml/l) and ammonium citrate ($\text{C}_6\text{H}_{14}\text{N}_2\text{O}_7$) (1 g/l). During polishing, the mixture is maintained at a working temperature of 72°C. Bath agitation is utilised during polishing to decrease the likelihood of pitting, a common issue with SUBU5.

The SUBU5 process is preceded and followed by immersion in sulfamic acid in order to increase wettability (before) and passivate the copper surface (after). The passivation of the sample following the chemical polishing needs to be completed as fast as possible, to avoid oxidation of the chemically active surface.

Samples were chemically polished in SUBU5 without mechanical polishing for 30 min, 60 min, 90 min and 120 min. Further samples were chemically polished for 30 min following mechanical polishing with 2000 grade, 3000 grade, 4000 grade and 4000 grade + 1 μm polishing fluid with a polishing disk.

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Electropolishing

For the EP process, a well-known copper electrolyte of phosphoric acid (85 %) (H_3PO_4) and n-butanol was utilised in a ratio of 3:2 with a copper counter electrode. A current density of 6 A/dm² was used for initial EP experiments, based on work completed at CERN [4]. The electrolyte was not agitated during polishing.

As with the CP experiments, samples were subjected to EP with and without previous MP. Those without MP, were electropolished at a temperature of 30°C and 50°C for 20 min and 40 min respectively. Further samples were initially mechanically polished, and then electropolished at 40°C for 40 min. The MP used for these experiments was the same as that described for the CP samples above. The copper cathode used for polishing was roughly 5 x the size of the anode in order to facilitate higher polishing rates as determined during pre-testing.

Following the implementation of the electrochemical characterisation process, further samples were subjected to EP using the newly found critical current density of 18.5 A/dm².

Electropolishing and Chemical Polishing

A series of samples were also polished with a combination of EP and CP. the CP was employed for a shorter time frame, to try and avoid pitting observed during the initial CP experiments. These samples were subjected to EP at 40°C for 20 and 40 min, followed by a CP for 5 and 10 min respectively.

Electrochemical Characterization

After initial electropolishing experiments, electrochemical characterisation, using a saturated calomel reference electrode (SCE) and a copper counter electrode, were employed in a three-electrode cell. This cell was utilized to complete an electrodynamic sweep of the copper-electrolyte combination. This determination is based on the work performed by Jacquet [8].

To monitor the effectiveness of the surface preparation procedure, the surface roughness is measured following each step of the process using an UBM laser profilometer with a scan size of 1 x 1 mm. Additionally, surface images are captured using an Olympus LEXT OLS 4000 confocal laser scanning microscope (CLSM), as well as a Zeiss Ultra 55 Scanning Electron Microscope (SEM). To monitor the loss of material after the specific treatments, the samples were weighed with a microscale.

RESULTS AND DISCUSSION

The as-received copper sheet has an RMS surface roughness of $S_q = 526 \pm 90$ nm as measured by CLSM. Initial copper substrates were prepared using a MP followed by a nitric acid etch prior to thin film deposition. This resulted in a surface as shown in Figure 1, with an RMS surface roughness $S_q = 844 \pm 14$ nm as measured by CLSM. Due to the fact, that defect sites on the substrate's surface, like grain boundaries, lead to a higher nucleation rate on these sites, these defect sites are extremely visible on the films'

surface, see Figure 1 (Inset). This phenomenon is known as surface decoration.

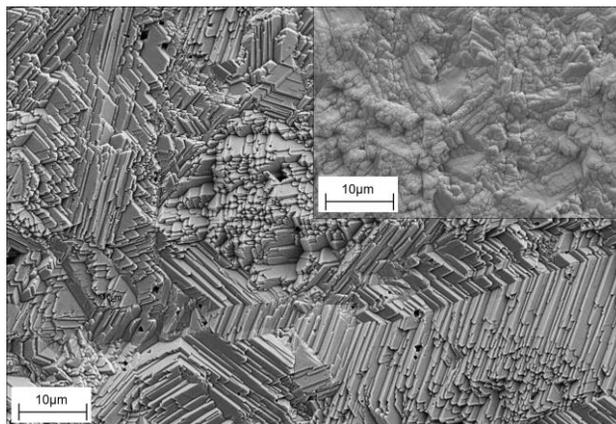


Figure 1: (Main) Copper sample following Nitric acid etch. (Inset) NbN thin film deposited onto nitric acid etched copper sample.

The CP results, displayed in Figure 3, indicate that without MP, the smoothest surface is reached after 60 min of CP. Thereafter, the surface roughness increases again due to increased pitting. Samples treated with CP following MP display relatively equal surface roughness values in the region of $S_q \approx 110$ nm, regardless of MP grade. It is also evident that the CP etches more prominently at the grain boundaries, as indicated in Figure 2.

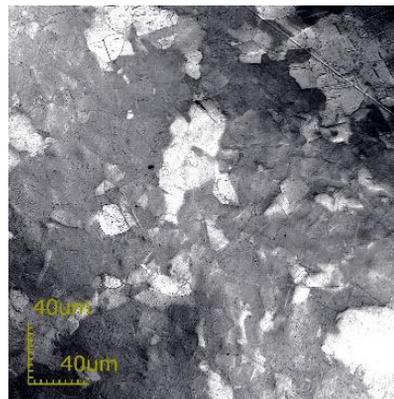


Figure 2: CLSM image of the polished copper surface following 30 mins of CP. Enhanced grain boundary etching is visible.

The EP surface roughness results, which are shown in Figure 4, indicate a level of reliance on electrolyte temperature. Following 20 min of EP, the sample polished in 50°C electrolyte possesses the smoothest surface, followed by the 40°C and then the 30°C samples. This does however change after 40 min of EP, where the sample polished in 40°C electrolyte possesses the smoothest surface. This result requires further investigation. The material removal rate is found to drastically change with electrolyte temperature, increasing from 0.5 µm/min at 30°C to 2.08 µm/min at 50°C.

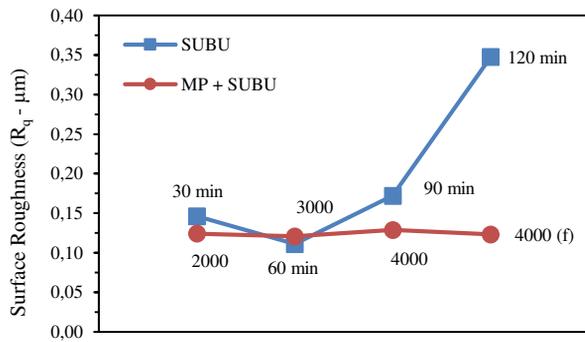


Figure 3: CP result overview. Blue data indicates results for CP only while red data is for MP + CP. The (f) specifies the use of 1 μm polishing fluid after 4000 grade MP.

The surface roughness of samples treated with MP + EP can be seen to steadily decrease as the fineness of MP increases. The smoothest surface was obtained using a combination of MP, with 4000 grade paper + 1 μm fluid, and EP at 40°C for 40 min, with a resultant $R_q = 43 \pm 1 \text{ nm}$. The copper surface following MP + EP also displays a more homogeneous finish than samples only treated with EP. Multiple samples polished at lower current densities displayed surface striations following polishing, most likely due to the passage of bubbles along the copper surface.

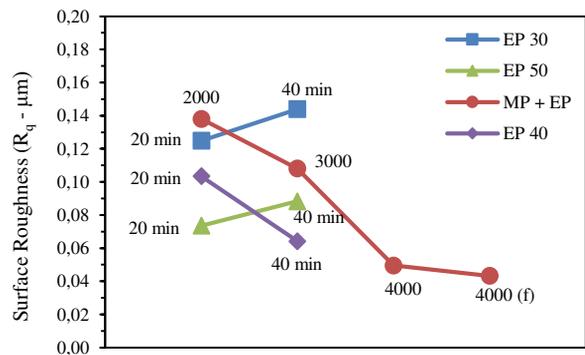


Figure 4: EP result overview. Blue data details 30°C electrolyte EP. Purple data details 40°C electrolyte EP. Green data points detail 50°C electrolyte EP results and red data points detail MP + 40°C (40 min) EP data. The (f) indicates the use of polishing fluid after 4000 grade MP.

The introduction of the electrodynamic sweep investigation, which resulted in the polarization curve shown in Figure 5, was based on trying to find the optimum polishing setting for our anode-cathode-electrolyte combination. From this, the optimum current density to be used during the electropolishing process was determined and was found to be equal to 18.5 A/dm^2 . The copper samples polished at this setting displayed a surface roughness of $R_q = 59 \pm 2 \text{ nm}$, which is a vast improvement over the nitric acid etched surface. Samples also showed a much reduced presence of surface striations following EP.

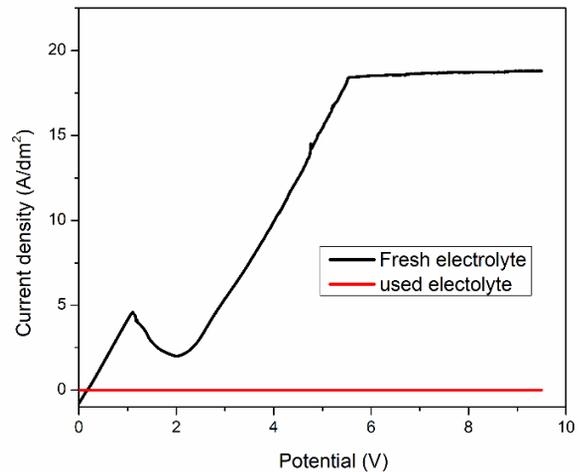


Figure 5: Polarization curve showing current density vs. voltage of the new and used (3 cycles) phosphoric acid + butanol electrolyte.

The used electrolyte (electrolyte solution following polishing of three samples) indicated in Figure 5, was tested in the electrodynamic sweep setup to determine its usability. It was found to display a much reduced performance (essentially zero) compared to the new electrolyte. This was verified on multiple occasions. A decrease in performance was also noticed after a single cycle.

The polishing rate (rate of thickness reduction) showed a marked reliance on the current density, increasing steadily with increasing current density. This is displayed in Figure 6. The outlier at $\sim 2.5 \text{ A}/\text{dm}^2$ in Figure 6, is believed to represent a second optimum polishing setting with superior polishing dynamics. This is supported by the polarization curve which shows a trough at this current density. Based on this, samples polished at 2.5 A/dm^2 will result in different surfaces depending on the voltage applied. This does however require further testing and verification.

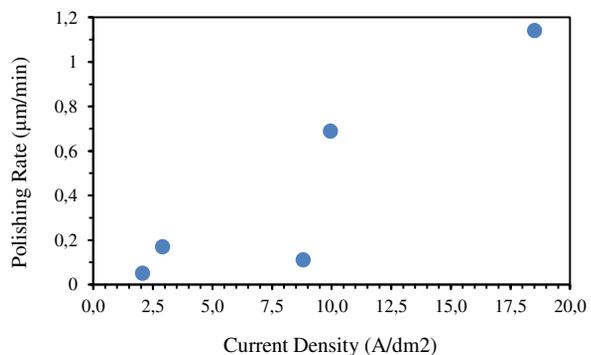


Figure 6: Electropolishing experiment results detailing the effect of current density on the polishing rate.

The use of both EP and CP resulted in a surface similar to that obtained for the CP samples themselves. This despite the reduced time of the CP process. The surfaces became rougher following the CP and pitting was evident in the 10 min samples.

The resultant copper surface following both EP and CP procedures, enjoys a vast improvement over nitric acid etched copper surface in terms of surface roughness and topographic homogeneity. This is carried over to the deposited thin film as shown in Figure 7. A NbN thin film was deposited onto an EP copper sample. The thin film is once more seen to mimic the surface onto which it was deposited. This thin film also has a far shinier surface than the films deposited onto nitric acid etched copper.

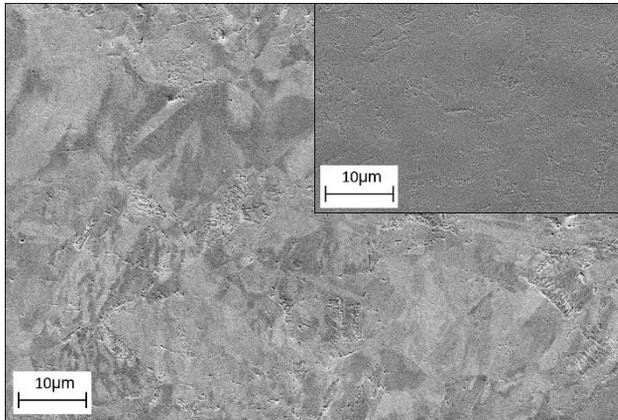


Figure 7: (Main) Copper sample following EP. (Inset) NbN thin film deposited onto EP copper sample.

CONCLUSIONS

From the testing completed so far, it is evident that the use of a combination of MP and EP results in the most homogeneous and smooth surface. The MP creates a more uniform surface to start the polishing from, as it removes any irregular surface abrasions present when received. Sufficient material must be removed following MP to ensure the removal of any possible inclusions of abrasive material, caused by the MP procedure.

The use of the optimal current density, as determined through an electrodynamic sweep, allows for a superior surface finish while minimising the presence of striations on the surface of the sample. In order to remove the damaged surface layer present following MP, a 2 hour EP is recommended for all samples prior to thin film deposition. In order to ensure consistent results and polishing rates, the electrolyte should be renewed for each sample.

The introduction of CP post EP is found to enhance the presence of grain boundaries which leads to these being detectable in the thin film as well (surface decoration). IF CP is to be used it should be for a short duration (≤ 5 min) to avoid possible pitting of the surface.

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