

STUDY OF SURFACE TREATMENT OF 1.3 GHz SINGLE-CELL COPPER CAVITY FOR NIOBIUM SPUTTERING

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Abstract

A R&D program on niobium sputtering on copper cavities has started at IHEP in 2017. Single-cell 1.3 GHz copper cavity has been chosen as a substrate. A chemical polishing system has subsequently developed and commissioned recently to accommodate the etching of both copper samples and a cavity. Different polishing agents have been tested on copper samples and later characterized. The results of these surface treatment tests are presented.

INTRODUCTION

For the last few decades, superconducting RF (SRF) cavities were generally made from high purity bulk niobium. After decades of development, RF cavity performance has approached the theoretical limit for bulk Nb [1]. Consequently, how to improve cavity performance and reduce the fabrication costs of SRF cavities is always among the top concerns in SRF field. A R&D program on niobium-coated copper cavities has recently been funded by the PAPS (Platform for Advanced Photon Source Technology) project [2] and started at IHEP.

Surface quality of copper substrates prior Nb sputtering plays a vital role in cavity superconducting performance and is the focus of this paper. The testing of several surface treatment agents, sample characterization and the real copper cavity surface treatment system are described.

SURFACE TREATMENT AGENTS OF COPPER SUBSTRATE

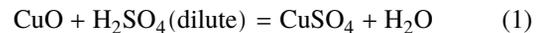
Three kinds of chemical etching agents were attempted to obtain a high-quality surface of copper substrates. We cut the oxygen-free copper sheet by wire-cutting to obtain copper samples of 30 mm in length, 10 mm in width and 1 mm in thickness, shown in Fig. 1(a). Copper samples of this size are processed in order to facilitate subsequent characterization analysis.

The sample surface to bath volume ratio will affect chemical etching rate, so the control variable method should be adopted in the chemical etching experiments of all agents. The experimental scheme is designed to ensure that there are two copper samples (a superficial area of 5.6 cm² per sample) with an mixed acid volume of 500 ml for each chemical polishing.

Dilute Sulfuric Acid Etching

Copper surfaces are easily oxidized in the air. The primary aim is to remove the oxide layer on the surface of

OFHC copper samples. Copper ions can be formed by the chemical reaction of dilute sulfuric acid with copper oxide. The chemical reaction involved is as follows:



On the basis of this chemical reaction, dilute sulfuric acid was taken into consideration as an agent. Therefore, we conducted the experiments of copper samples with dilute sulfuric acid. The primary parameters that we focus on are chemical etching rate, surface roughness R_a and surface morphology, which would serve as the important basis for judging the feasibility of this agent.

Three sulfuric acid concentrations were tried, 10%, 15% and 20% respectively. In addition, the chemical polishing temperature of each concentration was kept at room temperature. In this experiment, the acid solution did not turn blue with the elapsed time. The surface of the copper samples soaked in the sulfuric acid was not significantly improved by visual inspection. Conversely, the surface of the copper sample after chemical polishing became darker and dirtier. Samples after chemical polishing were photographed as shown in Fig. 1(c). In terms of the surface roughness, the roughness before chemical polishing is 0.587 μm , and the roughness after chemical polishing is 0.533 μm . Obviously, there is no improvement in the surface roughness of the copper sample.

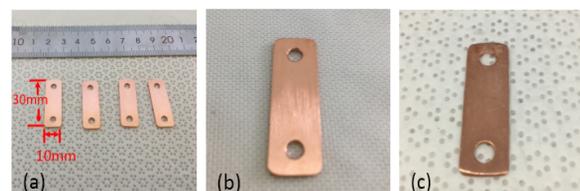


Figure 1: Dimension of copper samples (a), copper samples before chemical polishing (10% sulfuric acid) (b) and copper samples after chemical polishing (10% sulfuric acid) (c).

Moreover, Figure 2 shows the comparison among different concentrations of dilute sulfuric acid. Among three concentrations, the higher the concentration, the higher the thickness and rate of etching. However, the removal thickness of all concentrations does not exceed 3 μm , and the chemical etching rate does not exceed 0.2 $\mu\text{m}/\text{min}$. In summary, all the above analysis results show that the surfaces after dilute sulfuric acid etching do not meet the subsequent coating requirements.

$\text{H}_2\text{O}_2 - \text{H}_2\text{SO}_4$ Mixed Acid Solution

In the chemical polishing process of the above agent, the acid does not turn blue. Considering the presence of

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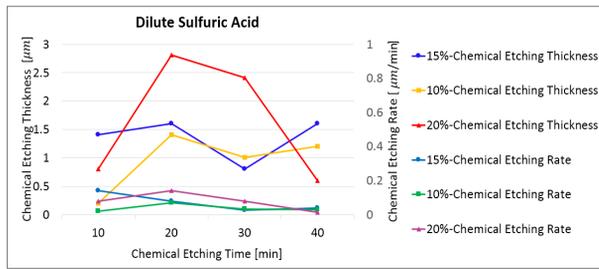
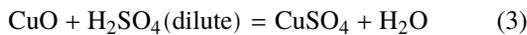
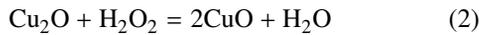


Figure 2: Variation curve of the chemical etching thickness and rate with elapsed time for the dilute sulfuric acid.

Cu₂O [3], hydrogen peroxide needs to be added to dilute sulfuric acid as an oxidant. We referred to H₂O₂ – H₂SO₄ – CH₃CH₂OH – CH₃COOH mixed acid agent [3]. According to this agent, ethanol (CH₃CH₂OH) can alleviate the decomposition of hydrogen peroxide (H₂O₂), and the added acetic acid (CH₃COOH) is able to further improve the surface of samples. The main chemical reactions are as follows:



Several compositions and contents of this mixed solution are listed in Table 1. Its temperature was also kept at the room temperature when it worked. The time range of 1-12 min was concerned during this experiment. As soon as the copper samples was put into the mixed solution, the reaction occurred violently, and the acid solution immediately turned blue. As shown in Fig. 3, the etching rate is very high, and 80 µm thickness can be removed in just 12 min.

Table 1: The Compositions and Contents of the Mixed Acid Agent

Composition	Content
H ₂ SO ₄	200 g/l
H ₂ O ₂	70 ml/l
CH ₃ CH ₂ OH	40 ml/l
CH ₃ COOH	40 ml/l

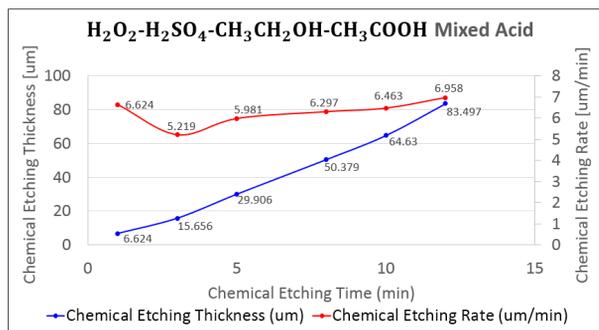


Figure 3: Variation curve of the chemical etching thickness and rate with elapsed time for H₂O₂ – H₂SO₄ mixed acid solution.

Samples after chemical polishing were photographed as shown in Fig. 4. It can be seen from Fig. 4 that the surfaces are not bright enough and begin to grow the convex morphology with the elapsed time. SEM pictures (Fig. 5) show that the copper surfaces are uneven and generate much pitting corrosion. The surface roughness is aggravated by the protrusions produced on the surface, and the surface roughness of the copper instrument is beyond the range of the roughness measuring instrument (Model number: TR200, R_a measurement range: 0.005 µm-16 µm). Based on the analysis, the copper surfaces which are chemical polished by this mixed acid fail to meet the requirements of subsequent coating.

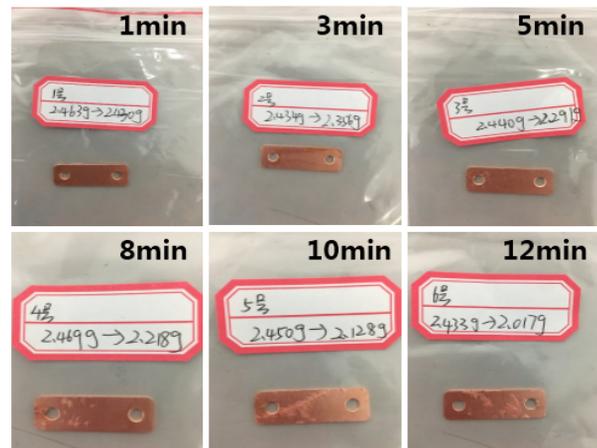


Figure 4: Copper samples after the chemical polishing (H₂O₂ – H₂SO₄ – CH₃CH₂OH – CH₃COOH mixed acid agent).

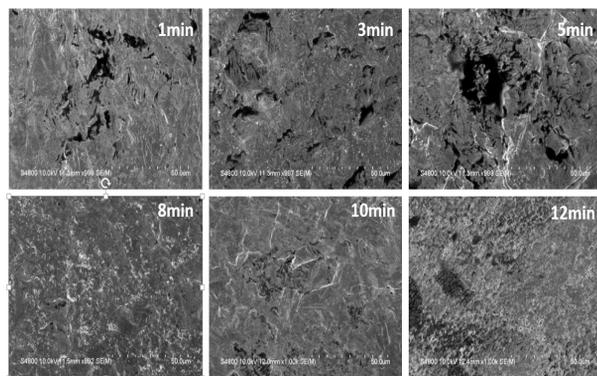


Figure 5: The SEM surface pictures of copper samples after the chemical polishing at different time.

SUBU5 Chemical Etching

Generally, the surface treatment of copper substrate cavity is carried out by SUBU5 chemical polishing developed for LEP2 at CERN. This agent contains four components of sulfamic acid, ammonium citrate, hydrogen peroxide and n-butanol [4]. Different concentration of these four components were studied in CERN, and the agent for SUBU5 was

finalized [5]. SUBU5 is an acid solution mixed with 5 g/l sulfamic acid, 1 g/l ammonium citrate, 50 ml/l hydrogen peroxide, 50 ml/l n-butanol and ultrapure water and working temperature is 72 °C [5]. Samples need to be activated before SUBU5 bath and passivated after SUBU5. Both the activation and passivation solution are dilute sulfamic acid (5 g/l) [6].

Chemical or electrochemical corrosion process involved in SUBU5 with the oxygen free copper is shown in Fig. 6 [5]. In a bath containing sulfamic acid and hydrogen peroxide, hydrogen peroxide in contact with copper samples produces intensively bubbles. n-Butanol can inhibit the decomposition of hydrogen peroxide at high temperatures (72 °C). As shown in Fig. 6, in the hydrolytic reaction of copper sulfamate, copper hydroxide precipitation will be one of the products. Ammonium citrate is added as the complexant to prevent precipitation on the sample surface [5].

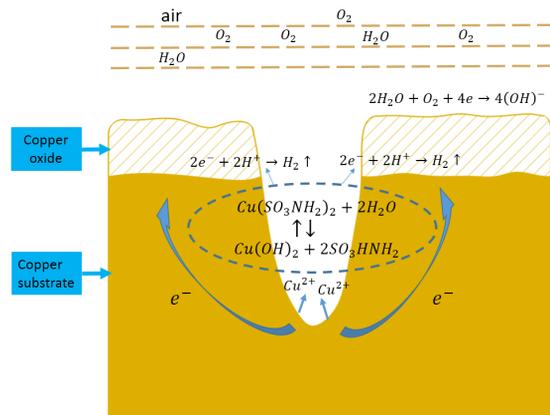


Figure 6: Chemical and electrochemical processes in the reaction of oxygen-free copper with SUBU5 acid [5].

To obtain a more smooth and brighter surface, SUBU5 chemical polishing experiments were carried out. In order to ensure that the copper samples were in a stable temperature system and prevented the metal temperature probe from reacting with SUBU5, the water bath heating was adopted (shown in Fig. 7(b)). There are two copper samples with SUBU5 volume of 500 ml. The specific processing steps are as follows [6]:

- Mechanical polishing.
- Degreasing.
- Activation pretreatment with dilute sulfamic acid (5 g/l, about 5 min).
- Chemical polishing (SUBU5) with bath agitation.
- Passivation with dilute sulfamic acid (5 g/l, about 5 min).
- Ultrapure water cleaning.
- Soaked in absolute ethyl alcohol.
- Drying with high purity nitrogen and packing in plastic bag under high purity nitrogen.

According to SUBU5 polishing steps, it was found that samples were rapidly oxidized when they were taken out from SUBU5 bath (shown in Fig. 8 right). Several experi-

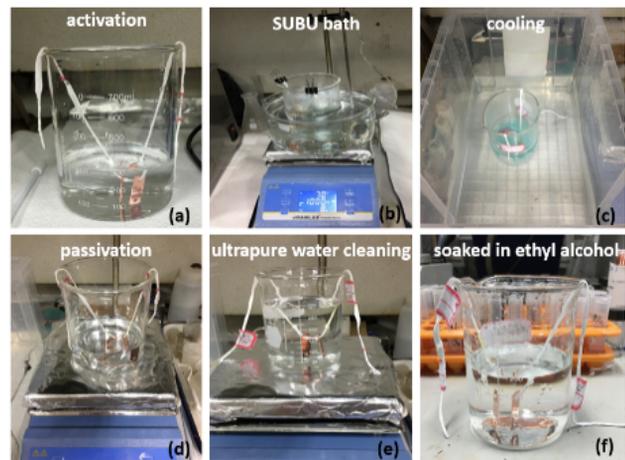


Figure 7: Adjusted SUBU5 chemical polishing steps.

ments were repeated. It was found that no matter how fast two steps were conducted, copper samples would still oxidize rapidly. When the copper samples were immersed in SUBU5 bath, the copper samples were bright and there was no tendency to oxidize according to our visual observation (shown in Fig. 8 left). As shown in Fig. 8 (right), there is only a small part of the smooth surface in the middle. And the oxidized area is widely distributed around the sample. As we know, the copper material is easily oxidized at the high temperature (72 °C). When the copper samples are removed from bath at 72 °C, there is great possibility that the copper samples which are exposed to oxygen will oxidize immediately. Therefore, we consider that copper samples need to be cooled to the room temperature (around 25 °C) before getting removed from bath. The specific steps are adjusted shown in Fig. 7. The oxidation of copper samples disappears following adjusted steps, as shown in Fig. 9.

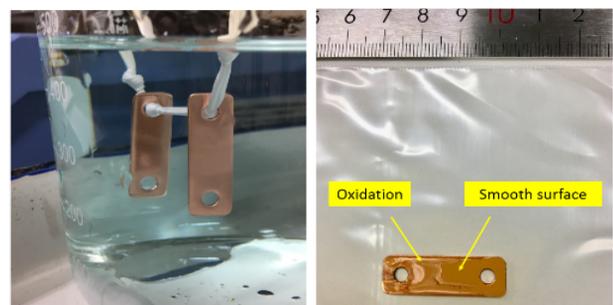


Figure 8: Bright copper samples soaked in SUBU5 bath (left) and oxidized copper samples taken out from SUBU5 bath (right).

Once adjusted SUBU5 steps are determined, it is necessary to explore the relationship between the chemical polishing rate and time. There are two copper samples (shown in Fig. 1, an area of 2.8 cm²) with the SUBU5 volume of 500 ml for each polishing. As shown in Fig. 10, when the chemical etching time is 10 min, the corresponding rate is the highest. With the elapsed time, the rate gradually decreases.

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Figure 9: Polished copper samples following the steps described in Figure 8.

And when time reaches 30 min, the chemical etching rate tends to be stable. Samples begin to oxidize in SUBU5 bath when samples are etched to 40 min (shown in Fig. 10), because SUBU5 solution with 2 samples reaches saturation. For the ratio of SUBU5 volume to 2 copper samples (ratio: 44.6 cm), the whole chemical etching time should be controlled within 40 min. When SUBU5 bath solution is used to its limit, it is necessary to offer the new SUBU5 solution. And copper samples continue to be chemical polished to obtain the thickness (at least 140 μm [7]) we need to remove.

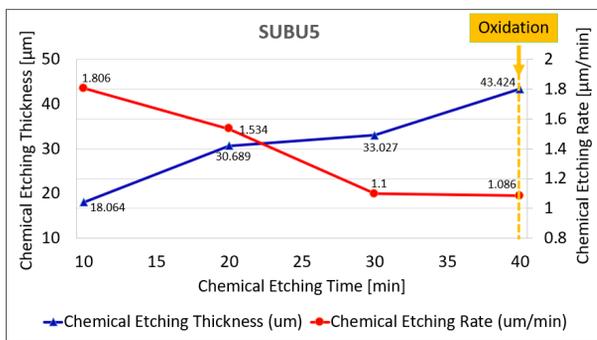


Figure 10: Variation curve of chemical etching thickness and rate with elapsed time for SUBU5 agent.

In terms of the background roughness of copper samples (before SUBU5) is around 0.5 μm . Then the surface after SUBU5 bath polishing presents an average roughness R_a of 0.1 μm . It is an acceptable value according to the experience at CERN [5]. The oxygen-free copper samples that are successfully chemical polished can be able to get a surface close to that of a mirror. Therefore, the reflectivity measurement of copper samples was conducted (shown in Fig. 11). It can be seen from the Fig. 11 that the reflectivity of copper samples which got SUBU5 surface treatment has been improved obviously within the visible light band. SEM images are shown in Fig. 12. There are some pitting and slight scratches on the sample surface. Figure 12 shows the surface morphology of samples that are removed 40 μm layer. There is possibility that SUBU5 polishing time is increased (to remove surface layer around 140 μm) to remove pitting [7]. Slight scratches are likely to have been introduced during other steps and not from SUBU5 chemical polishing itself,

which should be avoided as much as possible during the whole surface treatment.

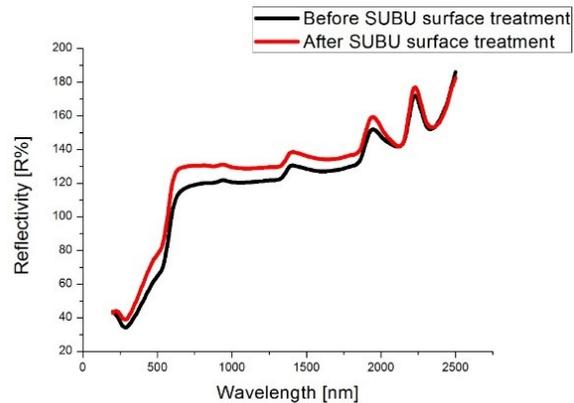


Figure 11: Reflectivity measurement of copper samples.

Above all, SEM images show that the sample surface is generally smooth. Results of the reflectivity measurement show that the surface by SUBU5 is brighter compared with previous two agents. And the average roughness R_a of 0.1 μm is an acceptable value for the subsequent coating. In order to find a higher quality substrate, we will explore the electropolishing next.

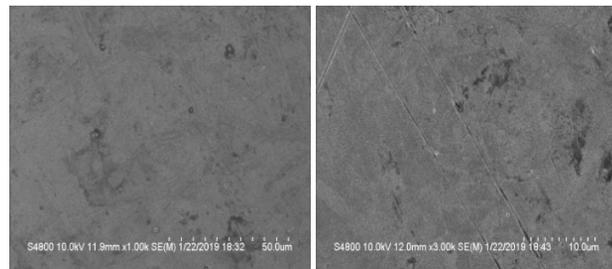


Figure 12: SEM images of copper samples magnified 1000 times (left) and 3000 times (right).

CHEMICAL POLISHING CIRCULATION SYSTEM

Once we have confirmed the chemical polishing agent and steps, we will start the study of chemical polishing for 1.3 GHz copper cavity substrate.

A closed cycle system was established for the copper cavity substrate (shown in Fig. 13). In this system, ultra-pure water tank is located at the top of this setup (shown in Fig. 13). And two tanks in line for SUBU5 and passivation respectively are located behind the setup, shown in Fig. 14 (left). The SUBU and passivation solution are pumped out by two pneumatic pumps respectively from tanks and into the pipeline to participate in the circulating. The self-circulating pipe volume is 6 liters, and the volume occupied by 1.3 GHz copper cavity is 4 liters. The self-circulating direction is indicated by the red arrow in Fig. 13. And the magnetic

pump controls the entire self-circulating. SUBU5, passivation solution and ultrapure water enter from the bottom of the copper cavity and eventually flow out from the top of it, which will bring the liquid into full contact with the inner wall of the cavity. The heater heats SUBU5 to ensure working temperature 72 °C. However, it takes 15 minutes for the heater from room temperature to working temperature due to power supply constraints. The waste liquid is discharged into the waste tank as shown in Fig. 13. A sample holder is installed and fixed at the pipe, shown in Fig. 14 (right). The chemical polished copper samples will be characterized to obtain relevant parameters that are not easily detected in the copper cavity, such as surface roughness, reflectivity, surface morphology, etc.



Figure 15: Chemical polished copper cavity substrate.

for the copper cavity substrate has been built and commissioned. It has been planned to expand the volume of the circulation pipe in order to increase the copper removal.

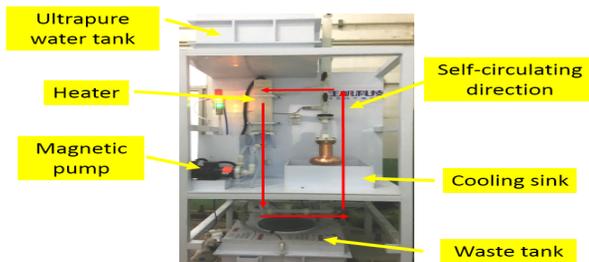


Figure 13: Chemical polishing cycle system for the copper cavity substrate.

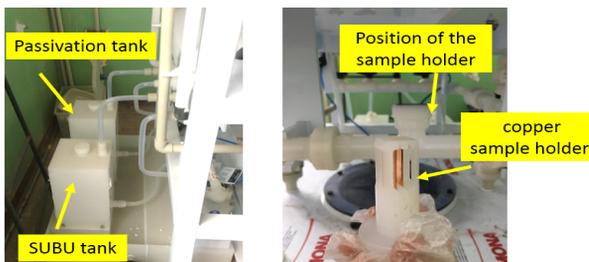


Figure 14: Two tanks in line for SUBU solution and passivation solution respectively (left) and copper sample holder in circulation pipe (right).

The chemical polished copper cavity substrate following the procedure above is shown in Fig. 15. The inner surface of the copper cavity is smooth and shiny and the average roughness is close to 0.2 μm. However, the removal thickness per cycle is limited due to the pipe volume limitation. We are now adjusting the setup of the chemical polishing system to obtain a larger volume of pipe.

CONCLUSIONS

The chemical polishing agent and specific procedure have been determined. Meanwhile, the chemical polishing system

ACKNOWLEDGEMENT

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