

SURFACE STUDIES OF CONTAMINANTS GENERATED DURING ELECTROPOLISHING*

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Abstract

Electropolishing is now the preferred method for chemical treatment of niobium cavities. It provides a very smooth surface and, after baking, accelerating fields between 35 - 40 MV/m [1]. However, the reproducibility of performance needs to be improved substantially. Some of the leading causes are related to contaminant residues after electropolishing, such as sulfur particles. We have carried out studies to enhance the deposition of such particles so that we can isolate and study the residues. We will present analysis of these studies using optical microscopy and SEM. In an attempt to dissolve these contaminants, we have also conducted studies on the effectiveness of various rinsing agents, such as degreasing agents and dilute HF.

INTRODUCTION

The performance of niobium cavities prepared by electropolishing is strongly affected by contamination on the surface of the cavities, which are responsible for field emission and possibly quench. The studies presented here were designed to investigate sulfur contamination from the sulfuric acid used in the surface treatment of electropolishing and to test different ways of removing this contamination.

COLLECTION AND IDENTIFICATION OF CONTAMINATION FROM A 9-CELL CAVITY

This first attempts were to analyze contamination directly from a 9-Cell cavity electropolished at Cornell University in the vertical electropolishing set-up. After the cavity was electropolished, a lint-free cloth was used to gently wipe the inside of the cavity beam tube and collect particles deposited on the surface. To examine the particles in the scanning electron microscope (SEM), a carbon tape mount was used to pick up the particles from the cloth. In the SEM, many small spot scans were conducted on individual particles to analyze their elemental composition using energy dispersive X-ray analysis (EDX). Particles were found to contain either sulfur or niobium/oxygen. Figure 1 shows a S particle and Figure 2 a niobium-oxide particle. The weight percent of niobium and oxygen in the oxide particles indicated that the majority of them were likely niobium pentoxide particles. The sulfur particles were expected to appear from electropolishing; this was a good verification that electropolishing does in fact produce the S contaminant. However, niobium pentoxide particles were a surprise because the presence of HF in the electrolyte. HF is known to quickly dissolve pentoxide. Although a

niobium pentoxide layer does form on the surface during electropolishing.

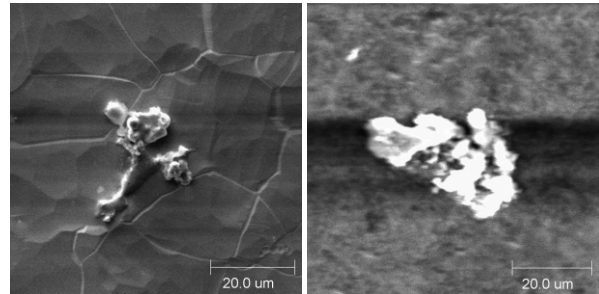


Figure 1: (Left) Typical S particle found on beam tube of 9-cell cavity extracted by wiping with a clean, lint-free cloth. (Right) Typical niobium-oxide particle found.

PRECIPITATION AND EXAMINATION OF SULFUR FROM A TEST EP CELL

To further study sulfur deposits, sulfur was precipitated on small niobium samples that could be examined under a microscope without removing the particles from the niobium. For the first tests, a closed cylindrical niobium vessel was made by welding a niobium plate to the bottom of an old beam tube. The resulting can was 4 3/8" in height and 2 3/4" in diameter. See Figure 2. It had a surface area of 27,635 square millimeters and could hold approximately 400 milliliters of electrolyte. The electropolishing set-up was similar to the method used for electropolishing half and single cell cavities. The power supply anode clamp was attached to a metal hose clamp secured around the can, and the cathode was made from a 1/4" strip of 1100 aluminum. Flexible arms were created from a Teflon rod at the top of the tube in order to increase the stirring vortex.

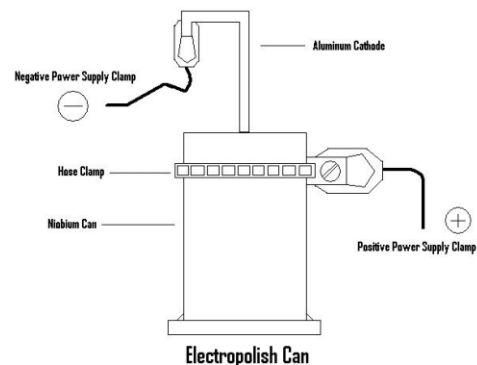


Figure 2: Test cell for electropolishing.

A four hour electropolish was carried out using the normal electropolish solution of nine parts sulfuric acid to one part hydrofluoric acid. Current oscillations were strong, but weakened as time progressed. Two precipitates adhered to the can: a yellow powder forming in clumps and a white film. See Figure 2. The can was then electropolished for an additional two hours with the same electrolyte, which greatly increased the amount of precipitate. This was repeated again for another two hours with the same electrolyte. The current oscillations were small and disappeared after an hour and a half. Additional precipitation of contaminants was minimal.



Figure 3: White and yellow deposit accumulated on the can after heavy electropolish.

The can was sectioned into coupons for analysis. The white film formed an adhesive bond to the yellow precipitate. The next step was to try to remove this adhesive film from the niobium surface. First, a coupon was treated with HPR for ten minutes. This seemed to remove the white film, but under the optical microscope there was still a trace or imprint of the film. Next, a coupon was ultrasonic cleaned with a solution of DI water and ivory dish soap for fifteen minutes. It was left to air-dry overnight. This removal technique had little effect on the film. Lastly, the coupon was immersed in a 1:1 solution of 49% hydrofluoric acid (HF) and water. This removed the film in less than thirty seconds. A more dilute one to ten solution of HF and DI water provided a less aggressive approach to cleaning the coupon, and the film was removed after a ten minute soak.

Some of the white film was filtered out of the water from a DI water rinse of a coupon, and examined in the SEM. EDX showed mostly niobium and oxygen along with traces of sulfur and fluorine. This supports the previous discovery of particles of niobium and oxygen on the inner surface of the 9-cell cavity.

In another study of sulfur precipitation and removal, small flat niobium coupons were electropolished in a special electropolishing set-up. The coupons were placed in an electrolyte bath overflow tank during the electropolishing of ACCEL_5, a 1.3 GHz 9-Cell cavity.

This electrolyte consisted of ten parts sulfuric acid to one part hydrofluoric acid plus an additional 10cc of nitric acid per four liters of electrolyte[2]. The deposits on these coupons were examined under the SEM (see Figures 4 and 5). EDX confirmed that the deposits were indeed sulfur. Ethanol was then tested as a possible way to dissolve the sulfur particles. The coupons were soaked in ethanol for 20 minutes and left to dry. They were again examined in the SEM, and pictures were taken of the places where the sulfur deposits had been (see Figures 4 and 5). The locations of the original deposits before ethanol soak were found by using a combination of the grain boundaries in the original pictures and a coordinate system scribed on to the sample.

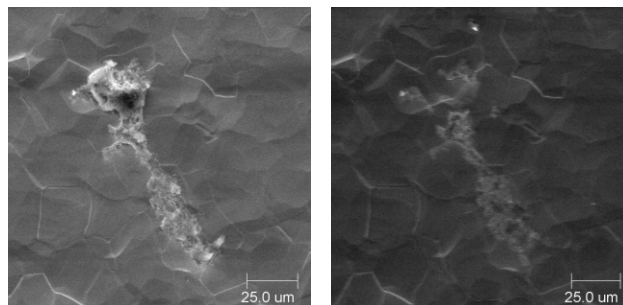


Figure 4 (Left): Sulfur deposit on niobium after electropolishing. (Right): Sulfur deposit after soaking in ethanol for 20 minutes.

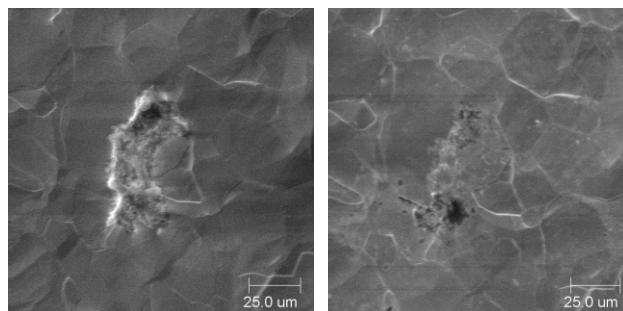


Figure 5: (Left): Sulfur deposit on niobium after electropolishing. (right): Sulfur deposit after soaking in ethanol for 20 minutes.

The ethanol succeeded in dissolving most of the sulfur particles; however, Figures 4 and 5 show that some residue or imprint was left after the ethanol soak. EDX showed only niobium. If there was a residue, it was too thin to appear in the analysis. Auger analysis, which is more surface sensitive than EDX, was attempted on the residues, but switching between SEM and Auger instruments made it hard for the areas to be located again.

CONCLUSIONS

This study was designed to collect and analyze contamination that arises from electropolishing. Different methods of removing the contamination were also tested. An adhesive layer under the sulfur deposits was found and analyzed, and it is likely that it is mostly niobium pentoxide. Dilute HF and ethanol were the two most successful methods of removal. However, these should also be studied using Auger analysis to examine the niobium surfaces more closely after the removal of the contamination. The possibility that niobium oxide provides the adhesive layer for the sulfur should be investigated further, including the white film's failure to change color on heating. Understanding how the contamination becomes attached to the surface will be a step toward being able to remove or prevent it.

REFERENCES

- [1] L. Lilje, et al, "Achievement of 35 MV/m in the Superconducting Nine-Cell Cavities for TESLA", Nucl. Instrum. Methods A 524, p. 1 (2004).
- [2] T. Higuchi and K. Saito, "Development of Hydrogen-Free EP and Hydrogen Absorption Phenomena", <http://srf.desy.de/fap/paper/WeO15.pdf>