

STUDIES ON THE FUNDAMENTAL MECHANISMS OF NIOBIUM ELECTROPOLISHING

E. Viklund*, D. Seidman, Northwestern University, Chicago, IL
 T. Ring, L. Grasselino, S. Posen, Fermi National Lab, Batavia, IL

Abstract

To improve the superconducting performance of niobium SRF cavities, electropolishing (EP) with a sulfuric and hydrofluoric acid mixture is used. The chemistry of this reaction is complex due to the interactions between diffusion mechanisms, surface oxide structure, and multiple chemical species. Past studies on the EP process have produced a certain set of optimum parameters that have been used successfully for a long time. However, two recent developments have called the efficacy of the existing EP process into question. Since the introduction of nitrogen doping the surface quality of some cavities has been very poor. Also, EP performed at colder than standard temperatures leads to an increase in the cavity performance. To understand these questions, we perform a multivariate study on the EP process using niobium test samples electropolished at different temperatures and potentials. We find that electropolishing at lower potentials leads to rough surface features such as pitting and grain etching. Some of the surface features show similarities to features seen in niobium cavities. The effect of electropolishing temperature is not clear based on the results of this study.

INTRODUCTION

Electropolishing is a well-established process for smoothing the inside surface of niobium SRF cavities. Despite this, the scientific knowledge regarding this process is lacking in many areas. This is because the chemistry of the electropolishing reaction is highly complex due to the interactions between diffusion mechanisms, surface oxide structure, and multiple chemical species. Electropolished cavities sometimes end up with a rough surface finish or surface defects without any explanation. To improve the quality and repeatability of the electropolishing process we polish niobium samples at different potentials and temperatures.

BACKGROUND AND MOTIVATION

Niobium is a passivating metal, meaning that when an electric potential is applied, a protective oxide layer is formed on the surface preventing the metal from being dissolved. In HF containing solutions, the oxide is chemically dissolved by the HF allowing more of the metal to be oxidized. The metal is dissolved through this two step reaction. The mechanism for how this reaction occurs is dependent on many variables such as the electrode potential, the temperature, and the amount of electrolyte mixing. The dissolution mechanisms can be broken down into two main types: active dissolution and diffusion limited dissolution. In the active region, the reaction rate is limited by the elec-

trode potential dependent kinetics of the niobium dissolution reaction. In this region the current increases with the potential, since the reaction is driven by the electric potential. In the diffusion limited region, the current is limited by the diffusion of HF to the surface of the Niobium. The current remains constant even with increasing potential in this region, since diffusion is not affected by the electrode potential. Separating these two regions is a region of instability where the current spontaneously oscillates (see Fig. 1).

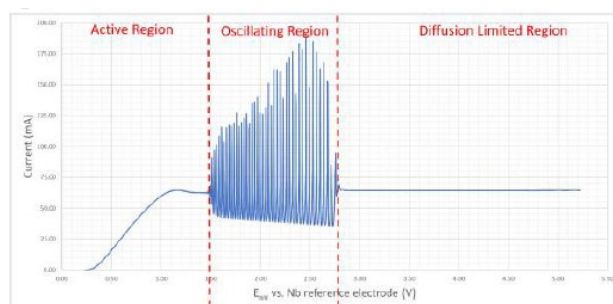


Figure 1: The etching current as a function of the electrode potential of niobium electropolished in an HF containing electrolyte. The current response is divided into the active, oscillating, and diffusion limited regions.

EXPERIMENTAL

Samples were polished two at a time in a 1:9 mixture of 48% hydrofluoric acid and 99% sulfuric acid. The electropolishing potential is applied between the niobium working electrode and an aluminum counter electrode. The electrolyte is circulated by a pump and cooled by a heat exchanger to control sample temperature. The surface temperature of the niobium samples is monitored by a thermocouple attached directly to the surface. The sample surface temperature is controlled by changing the acid temperature using a chiller.

Before the experiment, the samples were prepared by removing 100 microns of material from the surface at 18 volts to ensure an equal starting point. During the experiment five microns of material was removed with the experimental electropolishing conditions. The amount of material removal is measured through three separate methods: integrating the etching current, measuring the change in sample thickness with a gauge, and measuring the change in weight of the sample. All three methods show good agreement.

After the EP, the surface roughness of the samples is measured using an interferometric white light optical microscope and the surface is imaged using scanning electron microscopy.

*viklunderic@gmail.com

MEASUREMENTS AND RESULTS

Sample EP Analysis

The resulting surface finish of a sample after electropolishing is dependant on the potential applied to it during the process. We see that at lower potential, the surface becomes very rough.

At one volt, certain grains on the surface of the niobium are etched faster than others resulting in a stepped surface. There are also facets and other rough features present on certain grains while other grains are smooth. This shows that certain grains have a higher surface energy when exposed to the electropolishing electrolyte.

When three to five volts are applied to the samples the grain etching is less common, but we instead see a large amount of small pits. These pits are only present on certain grains and grain boundaries indicating that the cause of the pitting may be related to the surface energy of these grains when exposed to the electrolyte (see Fig. 2).

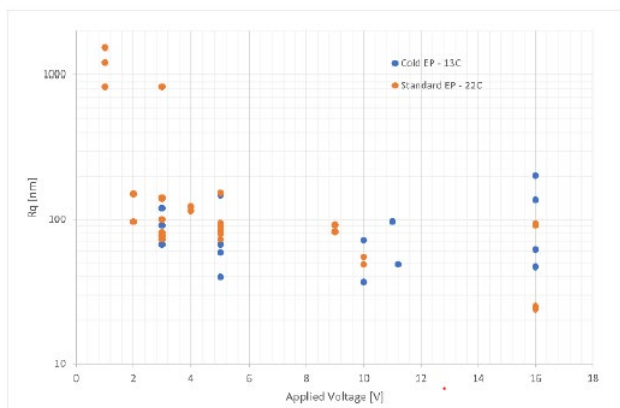


Figure 2: The measured surface roughness of various niobium samples electropolished at different voltages and temperatures.

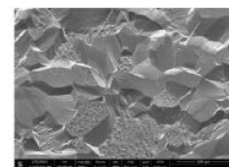
Samples polished at higher voltage are very smooth in comparison. The samples electropolished at potentials above five volts show only small steps at the grain boundaries and the main source of surface roughness is large scale undulations.

The temperature dependance of the surface roughness is not clear from the samples in this study. From the scanning electron micrographs we do not see any significant difference in the surface morphology between the standard and cold electropolished samples (see Fig. 3). The surface roughness measurement show that the cold electropolishing matches or slightly outperforms the standard electropolishing at low voltages. However, at higher voltages the standard temperature electropolishing produces the smoother surface.

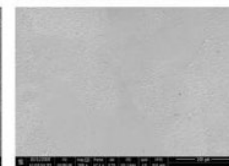
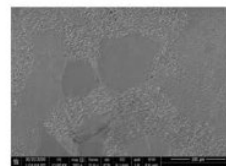
Cold EP - 13C

Standard EP - 22C

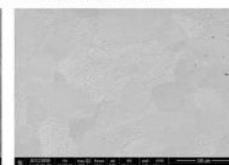
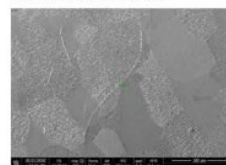
1 Volt EP



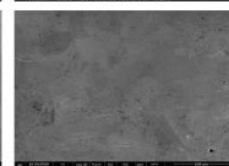
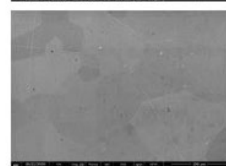
3 Volt EP



5 Volt EP



10 Volt EP



16 Volt EP

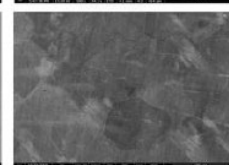
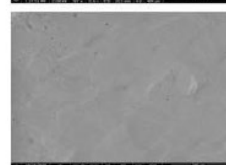


Figure 3: Scanning electron micrographs of samples electropolished at different potentials and temperatures.

GRAIN ETCHING AND FACETING AFTER LOW

Voltage EP

Samples polished at very low voltages show a large variance in the etching rate between different crystallographic grains on the surface of the Niobium. Some grains also show faceting or rough surface morphology, presumably due to the high surface energy of these grains. This type of surface morphology has also been seen on certain areas in 9-cell cavities polished at higher voltages. Nitrogen doped 9-cell cavities in particular have shown poor performance after the standard electropolishing procedure. A surface analysis study on one of these poorly performing cavities found that the surface shows similar grain etching features and faceting that was found in this study [1]. The results of our study indicate that these surface features are caused by a low electropolishing voltage, which may seem to be contradictory to the previous findings, since the cavity was electropolished at high voltage. However, even though the cavity was electropolished at high voltage the potential distribution in the cavity may be non-uniform due to potential losses in the aluminum electrode and losses in the electrolyte, so the potential at the niobium surface may be much lower in certain areas (see Fig. 4).

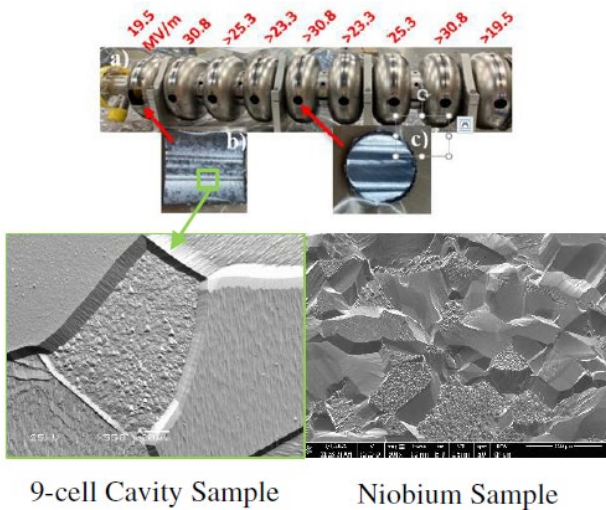


Figure 4: Image of CAV018 after samples have been cut from each cell. The quench field is displayed above each cell (top) [1]. Scanning electron micrographs of the cut-out from the first cell of the cavity (left) [2], and of a niobium sample electropolished at one volt (right).

CONCLUSION

We have compared the surface quality of niobium samples electropolished at different potentials and temperatures. We found that the surface roughness is strongly dependent on the potential and less dependent on the temperature. We find that the surface becomes drastically different at lower potentials due to pitting and grain etching. The grain etching features have been seen in electropolished cavities as well, which may indicate that the reason for the poor surface quality in these cavities is due to insufficient potential.

We find that the cold electropolishing does not significantly affect the surface roughness of the samples, and may even make the surface rougher at the potentials used in cavity electropolishing. This finding combined with the finding that grain etching occurs in cavity electropolishing suggests that the reason why the cold EP process leads to better cavity performance is because it prevents grain etching rather than through reducing the surface roughness directly. Further studies will need to be performed to explore the effects of temperature on grain etching.

REFERENCES

- [1] D. Bafia *et al.*, “New Insights in the Quench Mechanisms in Nitrogen Doped Cavities”, in *Proc. 19th Int. Conf. RF Superconductivity (SRF’19)*, Dresden, Germany, Jun.-Jul. 2019, pp. 592-596. doi:10.18429/JACoW-SRF2019-TUP062
- [2] A. Cano *et al.*, “New insights on the SRF Nb cavities performance from spectroscopic data. An XPS study,” TTC 2020.