ELECTROPOLISHING OF NIOBIUM TO OBTAIN DEFECT FREE SURFACES*

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Abstract

Viscous film formation on an electropolished surface is critical to obtain a good surface finish. Evidence for the formation of this film on niobium was found in electrochemical experiment results and optical observations. The film plays a critical role in the electropolishing mechanism as it was found that the surface is pitted where a stable viscous film cannot be formed. The depth of the surface material removed is also critical to the degree of surface finish obtained. Roughness and profile evolution over polishing time was used to characterize the degree of finish.

INTRODUCTION

Superconducting Radio Frequency (SRF) cavities need to have a good surface finish to achieve a maximum electric field gradient. The set goal for the elliptical shaped TESLA SRF cavities is 35 MVm^{-1}. However, the gradient practically achieved is around 30 MVm^{-1} [1]. The surface condition of the niobium cavities is one major reason preventing the achievement of the target accelerating gradient.

Electropolishing (EP) is so far the most efficient technique to get a good surface finish and is now a standard step in cavity processing sequence. It is very superior to mechanical polishing. Niobium is electropolished by applying a positive potential with respect to a pure aluminium counter electrode in a polishing mixture containing 1 volume hydrofluoric acid (48%) and 9 volume sulfuric acid (96%). The reactions taking place at the electrode are [2]:

At working electrode:
$$2Nb + 5SO_4^{2-} + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 5SO_4^{2-} + 10e^-$$
$$Nb_2O_5 + HF \rightarrow H_2NbOF_5 + HNbF_6 + NbF_5 + 3 H_2O$$
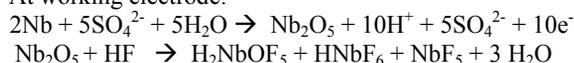
At counter electrode:
$$2 H^+ + 2e^- \rightarrow H_2$$
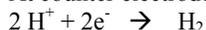
Niobium gets oxidized to form niobium pentoxide which is then dissolved in the presence of hydrofluoric acid and sulphuric acid to form niobium fluoride and oxofluoride species.

The mechanism of electropolishing is related to current distribution on the surface of the sample. EP of a metal is usually carried out in the plateau region of the polarization curve [3] (Fig. 1). This plateau is obtained because of mass transport limitation. Tian et al. suggested the formation of a compact film of probably niobium oxide on the surface of the niobium. The authors also suggested that the limiting current density region on the polarization curve in the case of niobium is probably due

to diffusion of fluoride ions through the compact film [4]. This film is however water soluble and difficult to analyze by ex-situ techniques. A bluish green layer (Fig. 2) is seen to flow slowly down a vertical electrode at the end of electropolishing when the current is switched off. It has not been possible to analyze this film because of this limitation.
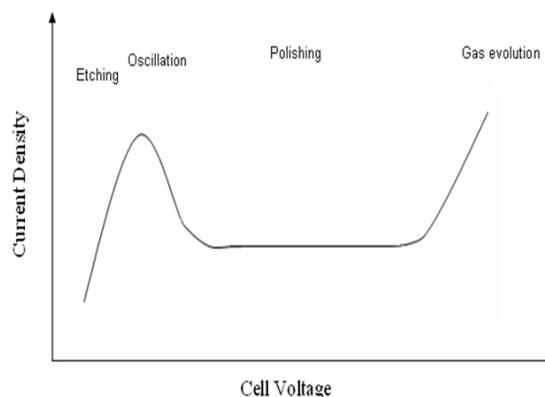
Fig. 1: A typical polarization curve for electropolishing.
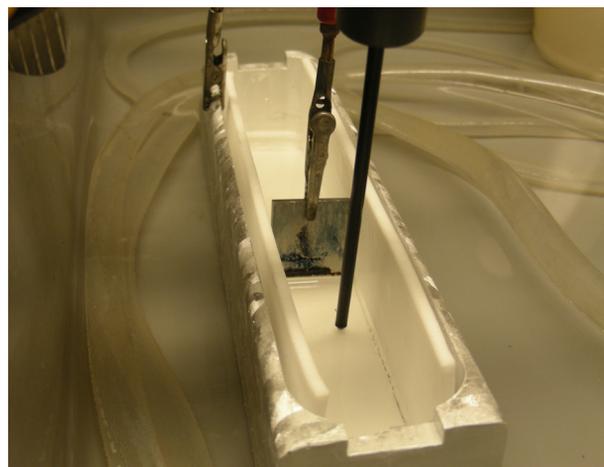
Fig. 2: Bluish green viscous film seen on the surface while electropolishing.

The EP process for processing SRF cavities, however, does not result in defect free surfaces. Pitting is commonly found near the heat affected zone of the electron beam welded region [5]. Pits can be due to a

multitude of reasons. Therefore, it is essential to understand the basic mechanism behind EP of niobium. The first step is to understand the viscous layer formed on the niobium surface during EP.

EXPERIMENTAL

High purity polycrystalline Nb was studied and two configurations were used for the working electrode. One was a freely exposed niobium surface in a flag electrode configuration and the other configuration was that of a masked sample. The masking was done using a teflon sample holder leaving a flat circular exposed area of 1.075cm^2. The samples were mechanically polished to 600 grit for reproducible starting conditions. They were then cleaned using acetone and then ultrasonically cleaned in distilled water. The electrolytic cell body is made up of 99.9999% aluminium which also serves as the counter electrode. The cell is kept in a water bath to maintain the temperature of the electrolyte which is very critical to the electropolishing process. The electrolyte used is a 1:9 volume mixture of HF(48%) and H$_2$SO$_4$(96%), the standard composition used for cavity electropolishing developed at KEK. A Sorensen XDL 35-5P power supply and Fluke 8845A digital multimeter were used for applying a current and measuring the surface potential of niobium. The data collection was automated using a customized Labview program. The schematic of the experimental setup is shown in Fig. 3.
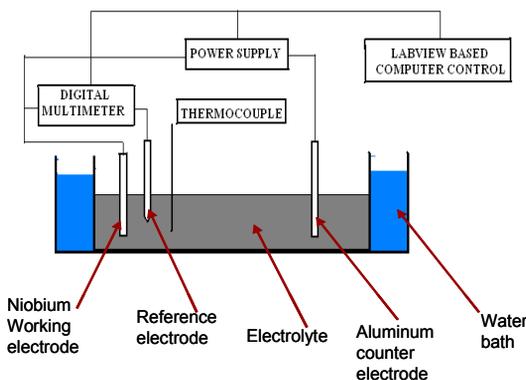
Fig. 3: Schematic of the experimental setup.

Surface profile measurements were carried out using Veeco's Contour GT-K1 optical profilometer.

RESULTS AND DISCUSSIONS

Viscous Film Formation During EP

As mentioned, the viscous film is visually evident on the niobium surface during EP (Fig. 2). There is also other evidence. A vertical electropolished sample clearly shows a profile in the depth of material removed from top to bottom of the sample. Figure 4 shows an optical profilometer measurement of the depth of material removed. There is more niobium removed from the top

part of the vertical sample compared to the bottom part. Gravity seems to affect the viscous film in that it is thinner at the top part of the exposed surface in Fig. 4 compared to the lower part because of hydrodynamic conditions. This result in a higher dissolution current at the top of the sample and 17 um of more material removed during the same polishing time.
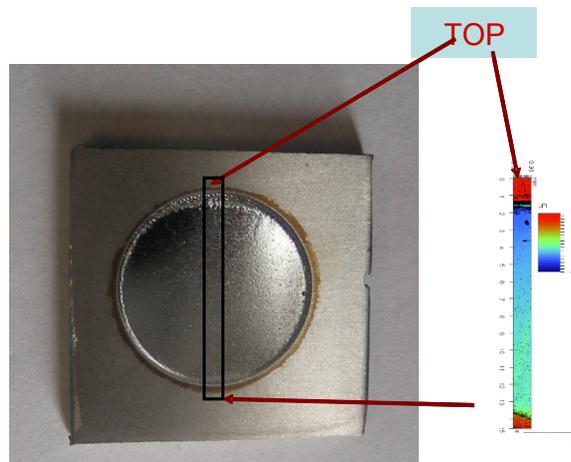
Fig. 4: Height gradient from top to bottom of an electropolished sample.

Ridges were observed at the bottom edge of electropolished sample (Fig 5) which is also likely related to the downward flow of the viscous film under the effect of gravity.
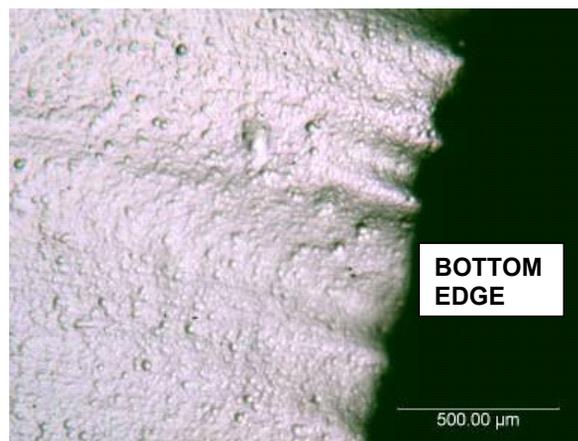
Fig 5: Ridges observed due to film sliding.

The effect of film formation can also be related to current oscillations observed at the end of polarization curve for the case of flag electrode as shown in Fig. 6. The film thickness increased with potential until it started to flow under its own weight. The current oscillations at higher potential were a result of the formation and re-dissolution of the film formed. The start of oscillation occurred at a higher potential when the electrolyte was stirred. This may be because the film in this case was not as thick as the one formed in static conditions for the

same potential values. Because it was thinner, it was able to support its own weight until a higher potential value. When it was no longer able to do so and started to flow, the current oscillation set in. No such oscillation was found in the case of polarization curve conducted on a masked sample. This is probably due to controlled hydrodynamic conditions on the surface of the niobium.
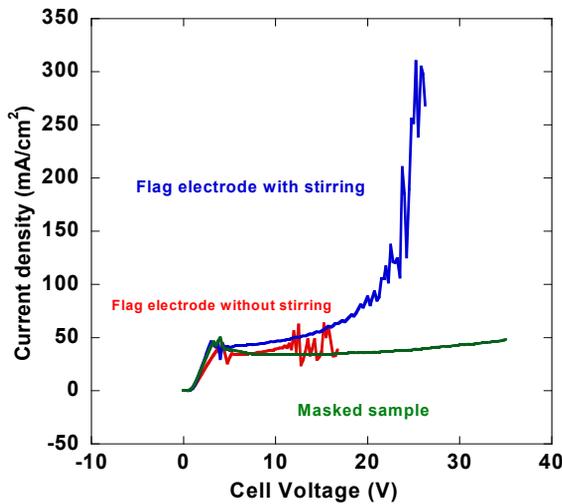
Fig 6: Polarization curve emphasizing the effect of stirring and electrode masking scheme.

Extensive pitting was found on the bottom surface of an electropolished flag electrode sample under the same conditions that resulted in a polished appearance with no pits on the flat vertical surface. This clearly indicates the importance of a stable viscous film formation for the electropolishing process to take place. The bottom of the flag electrode could not support the film because of gravity, which resulted in extensive pitting of the surface as is evident in fig 7.

Fig. 7: Pits formed at the downward facing surface of a flag electrode.

EP of a niobium sample with its face exposed upwards was carried out to compare the results with a vertically exposed surface. The current density vs. time plot (Fig. 8) clearly shows the film thickness dependence on gravity. The polishing film formed on the surface of the electrode with face up configuration was thicker than the one formed on the vertical electrode for the same experimental parameters. As a result, the current density for the face up configuration was lower than that of vertical electrode configuration. This comparison points to the importance of the role of hydrodynamics in electropolishing. The hydrodynamic conditions prevailing at the surface of the face up electrode is much different from that prevailing at the vertical electrode surface.
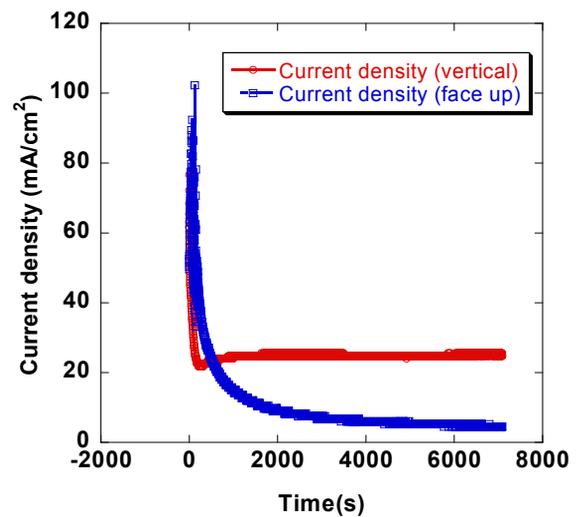
Fig. 8: Current transient showing effect of electrode configuration in electrolyte.

Evolution of Surface Roughness with Electro-polishing Time

100-150um of damaged layer has to be removed from the niobium surface to prepare a surface good enough to achieve maximum accelerating gradients. The evolution of the surface with EP time and hence the depth of material removed was compared using rms surface roughness (R_q) and average surface roughness (R_a) as statistical parameters (Table 1). Three samples were electropolished for 2, 4 and 6 hours respectively and their surfaces characterized using an optical profilometer over a scan area of 238 μm by 318 μm. The depth of material removed was calculated using the average current density over the polishing period by using the given formula based on Faraday's law.

$$dl/dt = iM/nF\rho \qquad (1)$$

dl/dt = rate of thinning of niobium
F = Faraday constant
i = current density
M = Atomic weight of niobium
n = valence
ρ = density of niobium
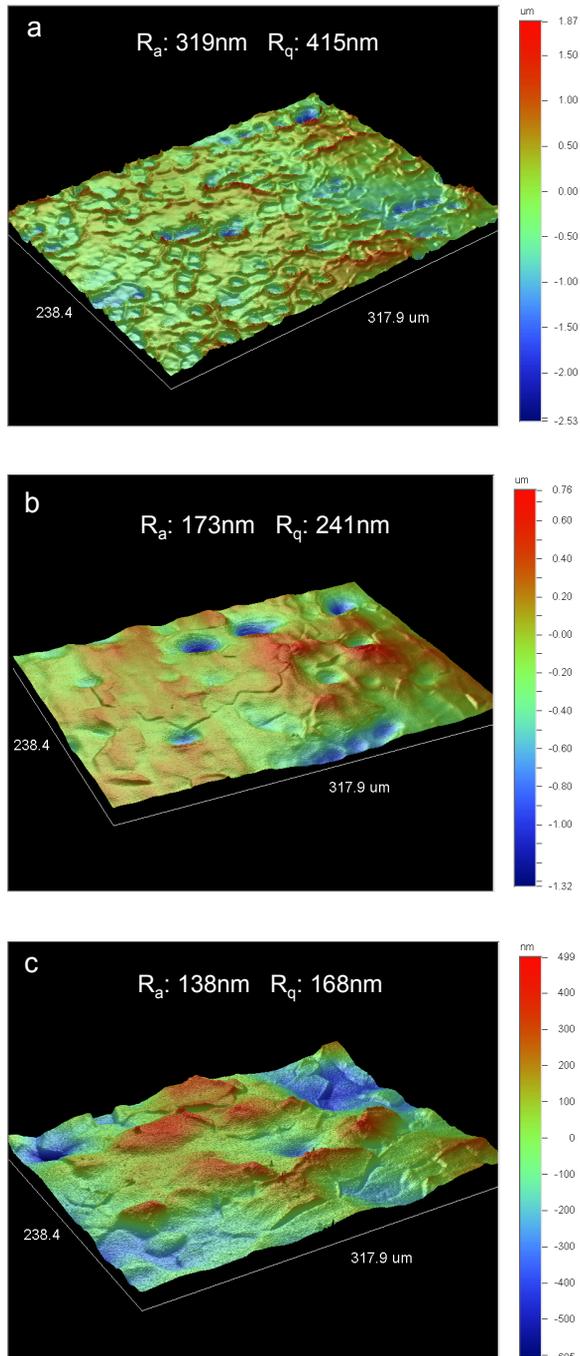
The surface roughness improved with EP time and the depth of material removed. A typical scalloped surface appeared after 2 hours of EP which gradually flattened out as more material was removed. The grain boundaries are still visible even after 6 hours of electropolishing. It has been found that buffered electropolishing helps remove the steps at the grain boundary better [6].

Table 1: Roughness values extracted from optical profilometer images and thickness removal calculation using equation 1.

Polishing time (Hrs)	Ra (nm)	Rq (nm)	Thickness removed (um)
2	319	415	50.1
4	173	241	108.6
6	138	168	156.8

CONCLUSION

The formation of a viscous film is essential for the electropolishing process to take place. The exact nature and composition of the film formed on niobium is still unknown because of its solubility in the electrolyte. Extensive pitting may take place at surface where a stable film cannot form. This has to be taken into consideration while determining the speed with which the SRF cavities are rotated while EP. Hydrodynamic aspects must be taken into consideration while optimizing the polishing parameters. There is improvement in surface finish with polishing time. There is a huge change in surface quality when the EP time is increased from 2 hours to 4 hours but not much change takes place when the time is further increased to 6 hours. So keeping the economic points in view, about 100 um defect layer removal may be sufficient to get the desired performance.

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Fig. 9: Evolution of surface topography with electropolishing time: (a) 2 hrs (b) 4 hrs (c) 6 hrs.