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ELECTROPOLISHING STUDY ON NITROGEN-DOPED NIOBIUM SURFACE*

V. Chouhan†, T. Ring, E. Viklund, G. Wu, Fermi National Accelerator Laboratory, Batavia, IL, USA

Abstract

The nitrogen doping (N-doping) process is applied to niobium (Nb) superconducting cavities to enhance their quality factors. The N-doping is followed by an electropolishing process that provides the final surface of the cavities. A controlled EP process is necessary to get the benefit of N-doping and achieve a high accelerating gradient. We have performed electropolishing of N-doped Nb surface under various conditions to understand their impact on the surface. A modified EP process was developed to obtain a smooth pit-free surface.

INTRODUCTION

Niobium (Nb) made superconducting RF (SRF) cavities are used in particle accelerators. The performance of the accelerator machine obviously depends on the performance of individual cavity used to make the accelerator machine. The field gradient (E_{acc}) and quality factor (Q_0) of the cavity determines its performance. Higher Q_0 value reduces cryogenic power to run the machine. To improve Q_0 value of the cavities, nitrogen-doping (N-doping) was invented at Fermilab [1] and successfully implemented to prepare 1.3 GHz 9-cell cavities for Linac Coherent Light Source-II (LCLS-II) and LCLS-II HE. High-β (0.92) elliptical cavities for Proton Improvement Plan-II (PIP-II) are also processed with N-doping process [2].

The initial Nb surface is processed with electropolishing (EP) method to prepare a desired smooth surface. Optimum EP conditions are required to attain a smooth surface specially for 650 MHz cavities which have a large surface area, and EP parameters for these cavities deferred from the standard EP parameters applied to 1.3 GHz cavities. The surface is doped with nitrogen at a temperature of 800 °C. The N-doped surface is processed again with EP to remove the top 5–10 µm material. The top layer of the N-doped surface usually contains an undesired nitride layer. To reduce BCS resistance for Q_0 improvement, an adequate concentration of interstitial nitrogen atoms in the RF penetration depth without any nitride phase is required [3].

The N-doped surface in the EP process might show pitting. The pitting was attributed to a high temperature in the EP process [4]. Premature quench of the cavity at low field is attributed to the pit on the N-doped cavity surface. Cold EP, which was conducted at comparatively lower cavity temperature, improved the quench field of the cavities as confirmed with LCLS-II cavities.

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† vchouhan@fnal.gov

This study aims to improve understanding on how different EP conditions impact the N-doped surface. This paper also proposes an EP process that reduces the risk of pit formation on the N-doped surface.

EXPERIMENT

EP Setup

The setup used for EP of the samples was a two-electrode system which employed an Nb sample as anode and aluminum as a counter electrode. The surface area of the aluminum cathode was chosen to be approximately 10% of the Nb surface area, similar to the cathode surface area used in cavity EP. Figure 1 shows a schematic of the setup. A power supply (40 V×12 A) was used for EP and an *I-V* measurement. To measure the *I-V* curve, the voltage was scanned from 0 to 20 V, and the corresponding current values were recorded. The temperature of samples during EP was regulated by a heat-sink coil immersed in the acid bath. Two thermocouples were used to measure acid and Nb sample temperatures. A LabView program was used to control the power supply and record a sample current, sample temperature, and acid temperature.

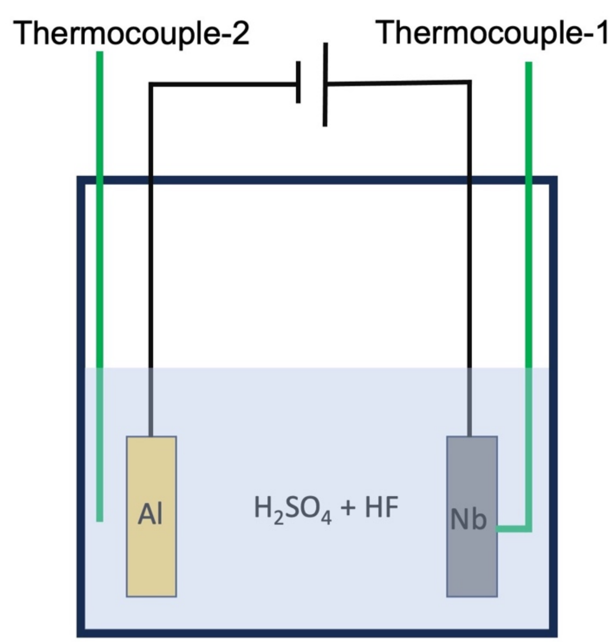

Figure 1: Schematic of the EP setup. Thermocouple-1 and -2 used to measure temperature of Nb sample and acid, respectively.

Sample Preparation

The samples, measuring 10×10 mm and 20×20 mm, were prepared from the same sheet of high RRR (relative resistivity ratio) Nb material. The samples experienced bulk EP of 100 µm to prepare the initial surface. Bulk EP was performed at 18 V while maintaining the sample temperature between 25–30 °C. Subsequently, the samples were subjected to 2/0 N-doping that was performed by introducing nitrogen gas in the furnace operated at a high temperature. In the 2/0 N-doping process, the sample was heat-treated at 800 °C for 3 h followed by introduction of nitrogen gas at a pressure of 25 mTorr for 2 min [5].

The final light EP, which was a crucial step to keep the surface smooth and defect-free, was performed for 5–7 µm. To understand the impact of EP on the N-doped surface, EP was performed at different sample temperatures and voltages. Electrolyte used for EP was a mixture of sulfuric acid (96wt%) and hydrofluoric acid (70wt%) in a volumetric ratio of 10:1 [6].

RESULTS

I-V Curve

An *I-V* curve represents the chemistry on the Nb surface. The onset voltage for the current plateau in the *I-V* curve represents the minimum required voltage for EP to attain a smooth Nb surface. EP performed below onset voltage yields an etched rough surface of Nb. The EP voltage should be kept well above the onset for EP of Nb cavities [7–9]. Typical *I-V* curves measured for undoped and N-doped Nb surfaces are shown in Fig. 2. *I-V* curves were found identical in both cases. The onset voltage in both cases was ~7 V.

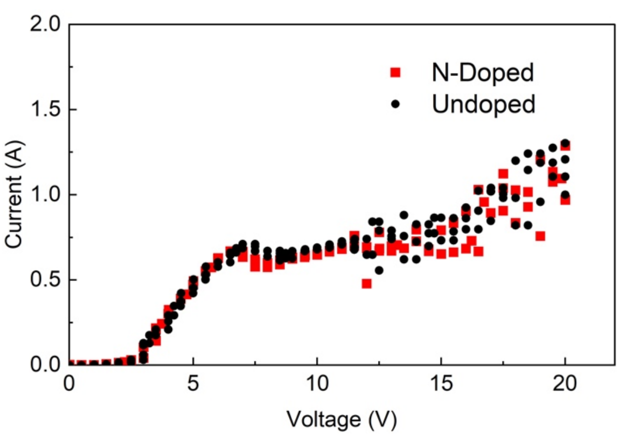

Figure 2: Current versus voltage (*I-V*) curves measured for N-doped and undoped Nb surfaces.

Effect of Temperature

EP of N-doped surface was performed at different sam-ple temperatures ranging from 0 to 40 °C. A constant volt-age (18 V) was applied to perform EP for 5 µm removal. The applied voltage is the standard voltage that is usually applied to EP the 1.3 GHz cavities. The current density var-ied with sample temperature and the highest current den-sity measured at temperature range of 40 °C was ~50 mA/cm2.

The sample surfaces were observed with an opti-cal microscope. The images of the sample surfaces are shown in Fig. 3.

The images revealed that the sample surfaces were hav-ing pits formed during the EP process. A higher tempera-ture enhanced the number of pits on the surface. The depth of pits and diameter also increased at higher temperatures. This suggested that cold-EP reduces the risk of pitting on the N-doped Nb surface. No pitting was found on an un-doped surface electropolished at 40 °C. This revealed that the presence of niobium nitride layer on the N-doped sur-face might be responsible for pitting.

Effect of Voltage

N-doped samples were electropolished at different volt-ages ranging from 8 to 22 V. The sample temperature dur-ing EP was kept being ~40 °C. A higher temperature was selected to see a pronounced impact of the applied voltages on the surface. The current density was measured to be 45±5 mA/cm^2 for the applied voltages from 8 to 22 V.

Optical microscope images of the sample surfaces are shown in Fig. 4. The sample electropolished at 8 V that was ~1 V above the onset voltage showed a smooth surface without any noticeable pit on the surface, although the sur-face had some submicron features. The features reflected as a different color contrast on different grains. A few pits were seen on the surface in an area of 10×10 mm elec-tropolished at 10 V. The number of pits increased with in-crease in the applied voltage. At a higher voltage the pits were wide and deep. The results revealed that the applied voltage also affects the formation of pits on the surface.

Effect of Low Voltage EP or I-V Measurement

The effect of low-voltage EP was also investigated. The low-voltage EP performed at 3 V that fall in the etching regime in the *I-V* curve removed a dark gray-colored film from the N-doped surface. The film leaving the sample sur-face was visually observed. The phenomenon was ob-served when an *I-V* test was conducted. This phenomenon was not observed when the voltage was above the onset voltage in EP. The removed film found in the rinsing water and acid was collected to perform its microscopic and chemical study.

The microscopic study was performed with a scanning electron microscope (SEM). The SEM image of the film is shown in Fig. 5. The morphology of the film appeared as the N-doped surface which showed nitride precipitates on the surface [10]. Moreover, in the chemical analysis per-formed with energy dispersive x-ray spectroscopy (EDS), the intensity of nitrogen element was significantly high suggesting that the film contained nitrogen atoms. The re-sults suggested that a low-voltage EP could peel-off the top thin nitride layer from the surface.

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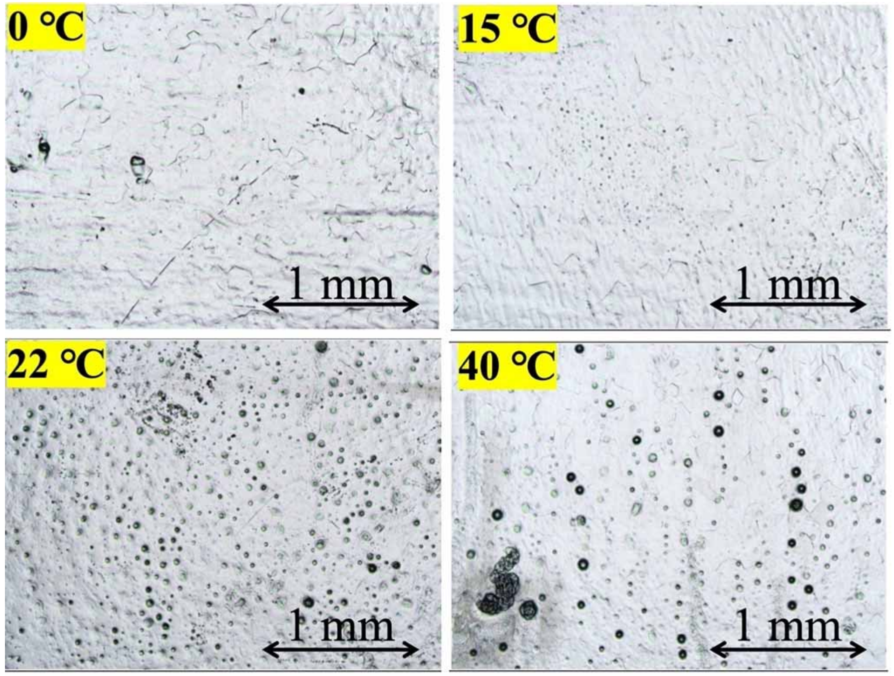

Figure 3: N-doped surfaces after 5 µm removal in EP performed at 18 V and various sample temperatures ranging from 0 to 40 °C.

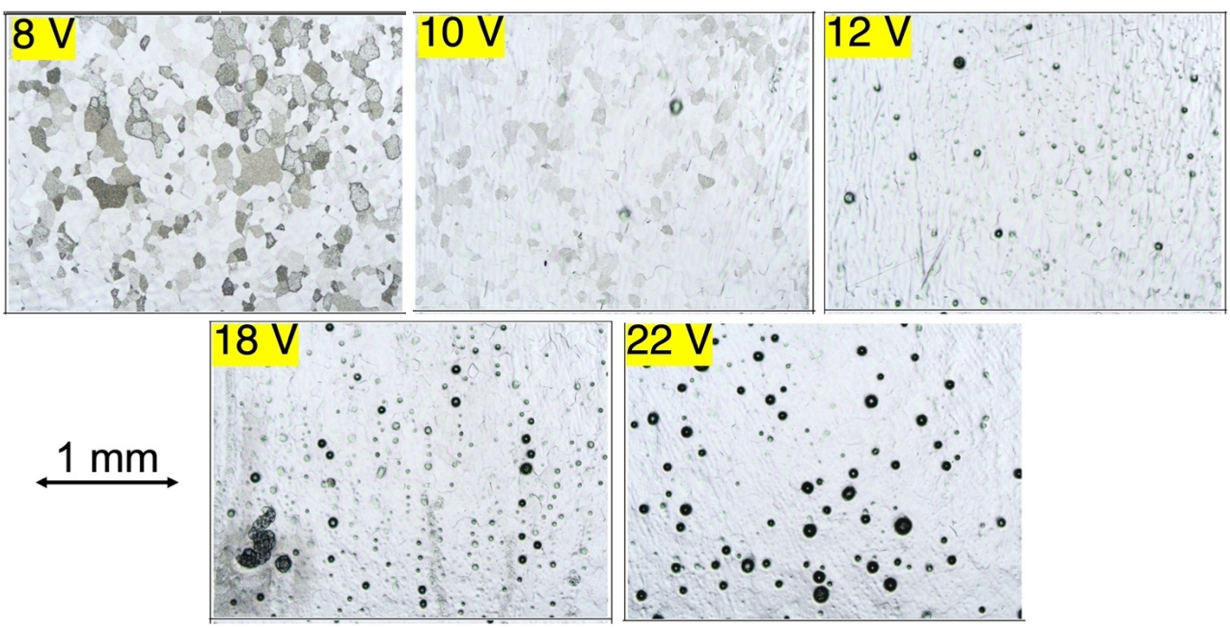

Figure 4: N-doped surfaces after 5 µm removal in EP performed at 40 °C and various voltages ranging from 8 to 22 V.

Two-Step EP

The two-step EP process, as the name suggests, was conducted in two distinct stages to complete a desired material removal. In the first step, an *I-V* test was conducted. The voltage was increased in a step of 1 V in every 12 s. The *I-V* was performed from 0–20 V as shown in Fig. 2. The second step included EP at the standard voltage of 18 V to complete total target removal. Two N-doped samples were processed with two-step EP at sample temperatures of 11 and 40 °C. The removal thickness in both cases was ~7 µm.

Optical images of the samples are shown in Fig. 6. Both samples regardless of temperatures in EP showed no noticeable pits on their surfaces. The marks appeared as black dots on the surfaces were merely the foreign contaminant particles. The results confirmed that the two-step EP process could avoid pit formation on the N-doped surface.

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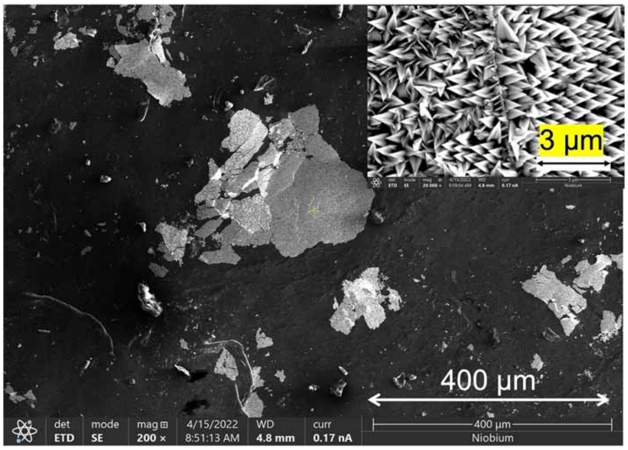

Figure 5: SEM image of the removed film in the low-voltage EP process. Inset: Zoom-in image of the film.

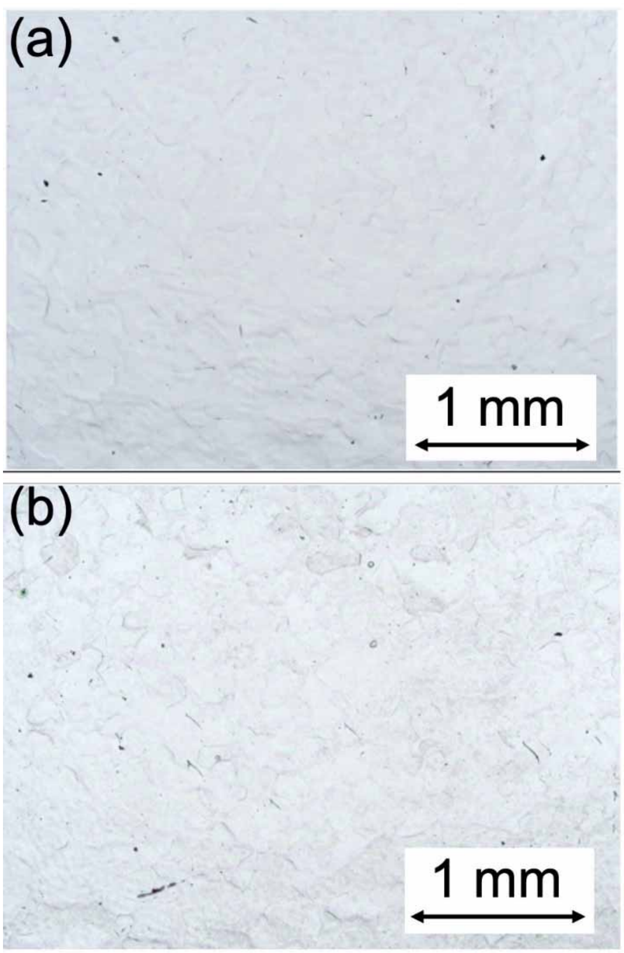

Figure 6: N-doped surface after two-step EP performed at 18 V and sample temperatures of (a) 11 °C and (b) 40 °C.

DISCUSSION

The surface after EP at different temperatures and voltages clearly showed that the presence of the top nitride layer seems responsible for pit formation. This was also confirmed by performing EP of undoped surface under the same conditions. The undoped surface was free from pits. Gas evolution from the nitride layer might be responsible for pitting on the surface. The gas evolution was observed for first two minutes when voltage higher than the onset voltage was turned-on for EP. The formed bubbles on the surface may impair the diffusion layer to enhance removal locally.

The results also suggested that temperature and voltage both were responsible for pit formation. The pit formation might be related to the total electrical power in the EP process. A higher temperature enhances chemical reaction and current that contributed to enhance the total power. This was confirmed with the samples treated at different voltages. Although the samples temperature was 40 °C, pits were not formed in EP performed at a lower voltage between 8–10 V. A higher voltage obviously enhanced the total power while the current was almost remained similar for all the samples. Due to a higher power, pits grew with a significantly larger depth.

The two-step EP process presented here peeled-off the top nitride layer, leaving the surface with interstitial nitrogen atoms. A low-voltage in EP was found necessary to peel-off the layer. However, a voltage lower than the onset voltage makes the surface rough, it cannot be adopted removing total target removal. Instead, it should be applied to remove only the top nitride layer that is usually found with a thickness of a few hundreds of nanometers. The layer can be removed in the *I-V* scan also since *I-V* includes a low voltage region. This explains why the N-doped surface provided the *I-V* trend similar to that for the undoped sample. The nitride layer was already removed in the etching region (0–7 V) and have no impact on the onset voltage and the *I-V* trend.

An *I-V* was preferred to peel-off the layer in the two-step EP. After *I-V* scan was over, the surface had no nitride layer present to form pits on the surface as evident from the sample surfaces experienced the two-step EP process.

CONCLUSION

The study was conducted to investigate the impact of surface temperature and voltage during EP on the N-doped surfaces. N-doped surface processed with EP at a higher temperature or voltage produced a significantly greater number of pits on the surface, with larger depths. The pit-formation was supposed to be caused by the niobium nitride layer present on the N-doped surface.

To address this issue, a two-step EP approach was proposed. It involved conducting an appropriate I-V measurement followed by EP at the standard voltage. This two-step process effectively removed the nitride layer from the surface during the *I-V* measurement, resulting in a pit-free surface after the second step is completed. Notably even at a high temperature of 40 °C, the two-step EP method yielded a surface free from pits.

Based on the results, it was concluded that the implementation of the two-step EP technique might be advantageous for N-doped cavities, as it mitigated the risk of pit formation on the surface.

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