

# ANALYSIS OF NIOBIUM SURFACE AND GENERATED PARTICLES IN VERTICAL ELECTROPOLISHING OF SINGLE-CELL COUPON CAVITY

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## Abstract

In our previous studies, we have reported parameter investigation for vertical electropolishing (VEP) of one-cell niobium (Nb) Tesla/ILC type cavities using a Ninja cathode. A one-cell coupon cavity containing six Nb disk coupons at its different positions was found effective to reduce time and cost to establish an optimized VEP recipe. In this work, we present surface analyses of VEPed Nb coupon surfaces using scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDX) and x-ray photoelectron spectroscopy (XPS). Surfaces contained micro- and nano-sized particles which were found with random distributions and different number densities on the beam pipe and iris coupons. Surfaces of equator coupons were found to have relatively less number of particles or almost clean. To analyze particles, a few particles were picked-up from a coupon surface using a tungsten tip under SEM and analyzed with EDX, while the coupon was moved out from the SEM chamber to avoid its effect in EDX spectra. The particles were confirmed as oxygen-rich niobium and contained fluorine and carbon also. XPS analysis of the coupon surfaces was also performed for further study of surface chemistry.

## INTRODUCTION

Niobium (Nb) superconducting radio-frequency cavities are used in the accelerator facilities worldwide. Performance of the Nb cavities depends on the inner surface morphologies and the contaminants present at the cavity surface. The contaminants present on a cavity surface enhance the risk of field emission which limits the cavity performance. The surfaces of Nb samples after being treated with the electropolishing (EP) process, which is used as the final surface treatment of Nb cavities, were widely studied. The previous studies reported sulfur (S) and fluorine (F) contaminants on the EPed surfaces [1–3]. Some studies have found Nb particles on the cavity surface [2, 3]. However, generation mechanism of such Nb particles is still unclear and elemental information of such particles is not enough. Therefore, further study to ascertain the conditions in which such particles are formed and detailed elemental study of such particles should be performed. We have already reported a surface treatment process of single-cell cavities with the vertical electropolishing (VEP) performed using a unique cathode named Ninja cathode [4–7]. In this study, we present the particle distribution at different positions of the single-cell coupon cavity by analyzing the Nb coupons, which were

set to the cavity in the VEP process. The study also shows surface analysis of Nb samples EPed in a beaker at laboratory scale, and was aimed to determine the process in which particle formation occurs on the EPed surface.

## EXPERIMENT

### Vertical EP

VEP experiments of a single cell Nb coupon cavity were carried out using a setup as reported elsewhere [4]. The cavity was designed to have six Nb disk type coupons at beam pipe, iris and equator positions as illustrated in Ref. [4]. A VEP experiment was performed with a special cathode named Ninja cathode which contains retractable blades. The blades were made of insulator, whereas Al cathode parts were set on the insulating blades [5, 6]. VEP were performed with the standard electrolyte (98wt% sulfuric acid and 55wt% hydrofluoric acid in a volumetric ratio of 9:1) used for EP of Nb cavities. VEP was performed with Ninja cathode's rotation speed of 30 rpm, acid circulation in the cavity from the bottom to top direction with a flow rate of ~5 l/min, a cavity temperature below 25°C, and at an applied voltage of ~12 V. The VEP experiment lasted for 80 min to remove Nb with a thickness of ~50 μm. The EP acid was circulated in the cavity for ~15 min after the voltage was turned-off. The cavity was rinsed with pure water after the acid was drained-out.

### Laboratory EP

Lab EP experiments were performed for Nb samples prepared in a size of 20 x 14 mm<sup>2</sup> from the same Nb sheet that was used to make Nb coupons for VEP experiments. Therefore, all the samples and coupons had the same initial surface with rolling marks and an average roughness Rz of ~4.5 μm. Nb samples used as an anode were set in an EP bath while an Al plate was set as a counter electrode. The EP of the samples were performed at stirring speeds of 0, 80 and 170 rpm for a removal thickness of ~50 μm. In each experiments, two samples were EPed at the same time. EP bath temperature was maintained at ~20°C.

### Surface Analysis

The coupons and sample surfaces were observed with a scanning electron microscope (SEM). The SEM chamber maintained at ultrahigh vacuum was equipped with energy dispersive x-ray spectroscopy (EDX) and a field emission scanner (FES). The FES was designed with a scanning anode tungsten (W) needle with a sharp tip. The needle can be moved in xyz directions with a precision of

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0.25  $\mu\text{m}$  [8, 9]. The purpose of the installation of the FES in the SEM chamber was to obtain a field emission map of an Nb surface. In this work, the W-tip of the FES was used to pick-up contaminant particles from an Nb surface for their analysis with EDX. The coupon surfaces were also analyzed with x-ray photoelectron spectroscopy (XPS). High-resolution spectra for Nb, oxygen (O) and carbon (C) were recorded with an analysis area of  $700 \times 300 \mu\text{m}^2$  at 20 eV pass-energy of the analyzer. XPS data for elements found with low concentrations were recorded at a pass-energy of 160 eV to get their intense peaks.

## RESULTS

### Surface Analysis of VEPed Coupons

**SEM Images** Nb coupon surfaces after several VEP experiments were observed with SEM. Beam pipe and iris coupon surfaces were found to have particles with random distributions while the equator surface was always clean or contained the less number density of particles. Typical SEM images of one set of the coupons including beam pipe, iris and equator coupons after the VEP experiment performed with the Ninja cathode rotating at 30 rpm are shown in Fig. 1. The images of these coupons are shown here because the beam pipe and iris surfaces contained the higher number densities of particles and show a clear difference from the equator coupons.

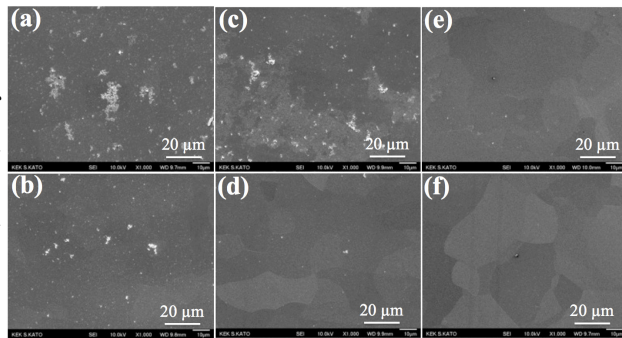


Figure 1: SEM images of six Nb coupons at (a) top beam pipe, (b) bottom beam pipe, (c) top iris, (d) bottom iris, and (e-f) equator.

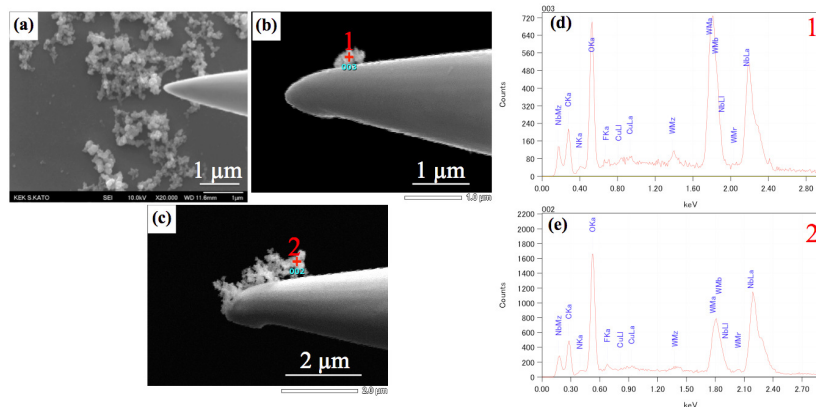


Figure 3: SEM images of the W-needle (a) without particle cluster, with (b) particle cluster-1, and (c) particle cluster-2. EDX spectra of (d) particle cluster-1, and (e) particle cluster-2.

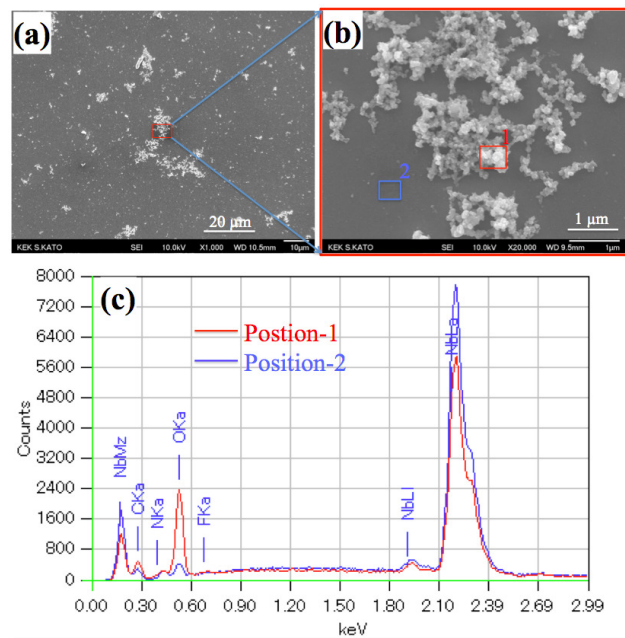


Figure 2: (a) SEM image 1000 $\times$  (b) Zoomed-in view of a particle with highlighted positions of EDX analyses and (c) the EDX spectra at these positions.

**EDX Analyses** Several coupons were analysed with EDX after being treated in VEP processes. The beam pipe coupon (in Fig. 1(a)) that contained the higher number density of particles was chosen for detailed EDX analysis. EDX spectrum was obtained on a particle cluster present on the top beam pipe coupon surface. A SEM image of the particle and analyzed positions are shown in Fig. 2. The spectrum is compared with an EDX spectrum of the clean Nb surface near the particle. The EDX spectrum revealed that the particle contained a higher concentration of oxygen and carbon, whereas the intensity of the Nb peak was reduced. Since an EDX analysis depth is around 1–2  $\mu\text{m}$ , the Nb surface influenced the spectrum of the particle. Hence the analyses of particles on the coupon surface cannot provide the enough elemental information of the particles.

Particle clusters were picked up from the coupon surface using the W-needle tip under the SEM observation. SEM images in Fig. 3 show the tip before and after picking-up the particle clusters from the surface. The coupon was moved to the load-lock chamber of the SEM before the particles were analyzed with EDX. The EDX spectra at the particles are shown in Fig. 3 (d) and (e). EDX mapping was also performed for one of the cluster particles as shown in Fig. 4. The EDX spectra and maps clearly revealed that the clusters were oxygen-rich Nb particles that also contained C, F, and copper (Cu) impurities.

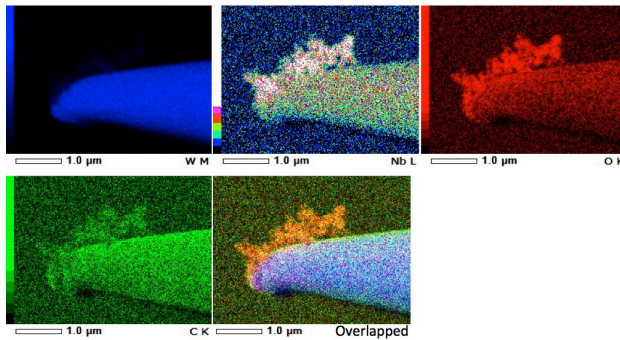


Figure 4: EDX maps for W, Nb, O, and C elements and overlapped map.

**XPS Analyses** The Nb coupons after the VEP experiment were analyzed with XPS. Nb, O, C, and F peaks for the six coupons are shown in Fig. 5. Nb<sup>0</sup> peak intensities were found to be different for different coupons and are supposed to depend on the number density of particles. The highest peak intensity ratio of Nb<sup>0</sup> to Nb<sup>5+</sup> was calculated for the equator surfaces which were clean or contained the lowest number density of particles. Atomic concentrations of elements present at the top surfaces of the coupons and the peak intensity ratios of Nb<sup>0</sup> to Nb<sup>5+</sup> are shown in Fig. 6. The top beam pipe and top iris surfaces, which contained the larger number of particles, showed lower atomic concentrations of Nb, and O while higher atomic concentrations of C were found on the surfaces. The clean equator coupon surfaces contained a lower concentration of C. Since Nb peak structures except their intensities for the surfaces covered with many particles were similar to that for the clean surfaces, the particles supposed to be clusters of Nb<sub>2</sub>O<sub>5</sub>, which contained C. The coverage of the surfaces with Nb<sub>2</sub>O<sub>5</sub> particles and C might reduce the peak intensity ratio of Nb<sup>0</sup> to Nb<sup>5+</sup>.

Since F and Cu concentrations were also found to be higher on the top beam pipe and top iris surfaces, the particles of Nb<sub>2</sub>O<sub>5</sub> contain F, and Cu impurities as well. Two F peaks were observed at the binding energies of 685.8 and 690.6 eV. Intensities of the F peaks at 690 eV were higher for the coupon surfaces which contained the higher number of Nb clusters. The F peaks at the binding energy of 685.8 eV might represent niobium pentafluoride [10] whereas the peak at 690.5 eV might be the result of a compound of F and hydrocarbon [11, 12]. Nitrogen (N) was usually not found on coupon surfaces after other VEP processes. S concentration had not found relation

with the number density of particles. The source of silicon (Si) is unknown.

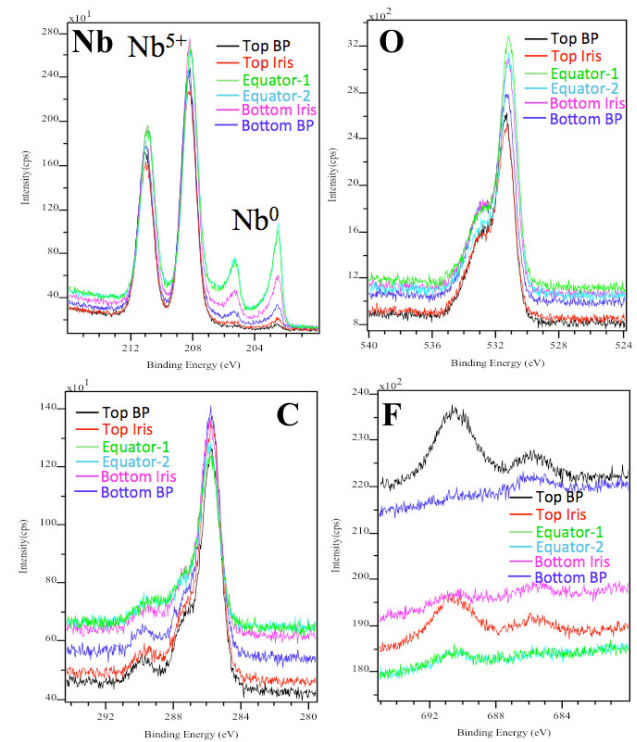


Figure 5: XPS peaks for Nb, O, C and F elements on Nb coupon surfaces after VEP.

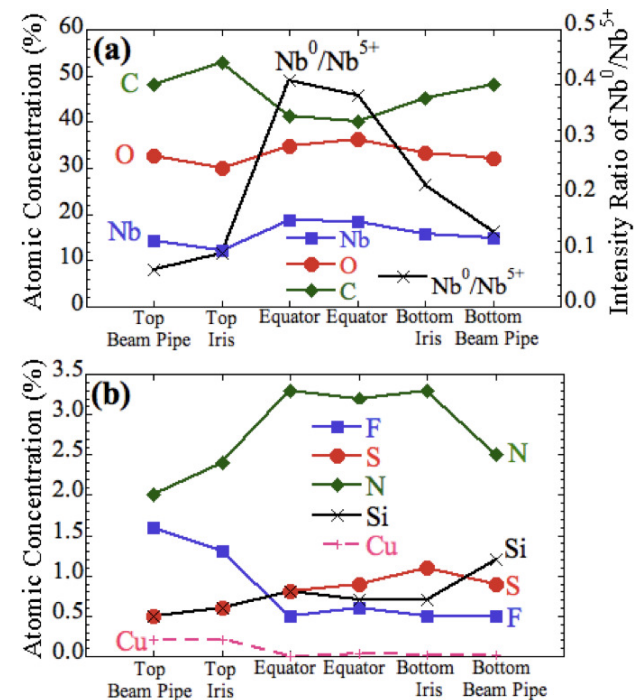


Figure 6: Atomic concentrations for present elements on the top surface of the top beam pipe coupon and peak intensity ratio of Nb<sup>0</sup> to Nb<sup>5+</sup>.



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### Analyses of Lab EPed Samples

**SEM Images** The Nb samples after EP at stirring speeds of 0, 80 and 170 rpm were observed with SEM and analyzed with XPS. The SEM images are shown in Fig. 7. The sample surfaces EPed at the higher speeds contained the less number of Nb particle clusters as found on the equator coupons.

Atomic concentrations for the top surface of the samples are given in Fig. 8. The atomic concentration of Nb was higher for the samples EPed at the higher speeds as also observed with another set of three samples EPed with these samples. C concentration was higher on the surface EPed without stirring. The difference in the peak intensity ratios of Nb<sup>0</sup> to Nb<sup>5+</sup> on the surfaces was not significant because C was already less on the lab EPed surfaces. F on the surface EPed at 0 rpm was less than 0.5% that seemed to be higher compared to that on the other surfaces EPed with stirring. S and Si on all the surfaces were found to be less than 0.2%. The results show that a higher acid flow rate on the Nb surface during EP might reduce the number density of the particles.

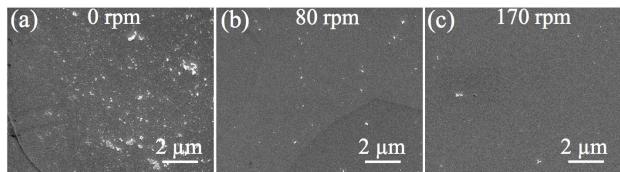


Figure 7: SEM images of Nb samples EPed with stirring at (a) 0, (b) 80, and (c) 170 rpm.

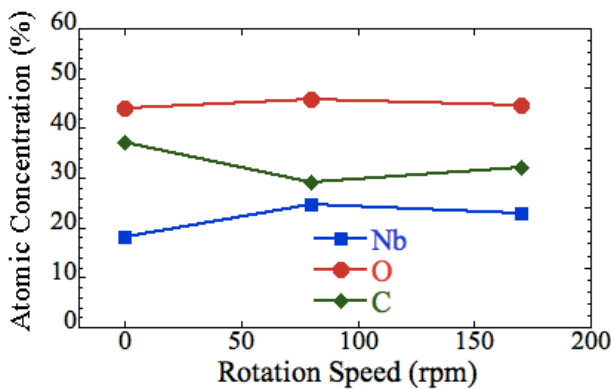


Figure 8: Atomic concentrations for the top surfaces of the lab EPed samples.

### Removal of Particles

The lab EPed samples were dipped in the EP acid for 5 min and then rinsed well with ultrapure water. The sample surfaces were again examined with SEM and XPS. SEM images and atomic concentrations for the top surfaces of the rinsed samples are shown in Figs. 9 and 10, respectively. The images show similar and clean surfaces of the samples. The Nb<sub>2</sub>O<sub>5</sub> particles dissolved in the acid within 5 min. XPS analyses of the surfaces revealed that the surfaces have similar properties in terms of atomic

concentrations. C concentration on the surface EPed at 0 rpm reduced while the Nb concentration increased.

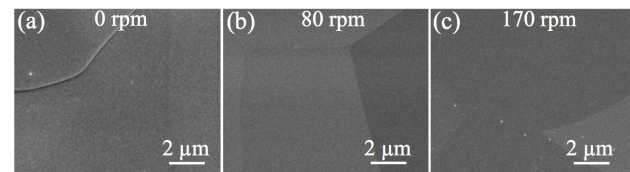


Figure 9: SEM images of lab EPed samples after dipping in the EP acid.

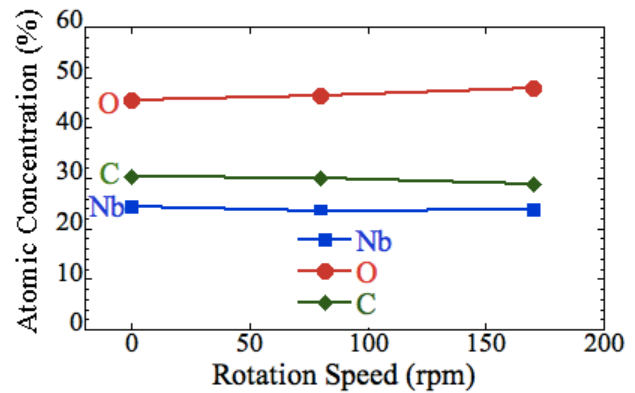


Figure 10: Atomic concentrations for the top surfaces of the lab EPed samples after dipping in the EP acid.

## DISCUSSION

The particle clusters presented on the lab EPed samples dissolved in the EP acid while they were dipped in the acid only for 5 min. The dissolution of particles in the acid indicates that the Nb particle clusters were supposed to be not formed in the VEP process because the EP acid was circulated in the cavity for 15 min after turning-off the voltage. The acid circulation time of 15 min after VEP was long enough to dissolve such particles from the cavity surface.

These particle clusters might be nucleated in the process of cavity rinsing with water. Rinsing parameters including water flow rate, and rinsing time and concentration of dissolved O<sub>2</sub>, and CO<sub>2</sub> in water might be responsible for generation and the number density of the particles. Although the particles were not formed in the EP process, the number density of particles might depend on the stirring speed in the lab EP or VEP process. It can be explained as follows. In the case of stagnant or slow acid flow at the surface during EP, the removed Nb atoms in EP might stay on the EPed surface after the acid was drained-out. The Nb atoms which remain on the surface might form clusters of Nb<sub>2</sub>O<sub>5</sub> as a result of reaction with water containing O and CO<sub>2</sub> or with dilute acid present on the surface in a slow rinsing process. The level of acid dilution that depends on the water flow rate might be different at different positions inside the cavity. As a result of this the number density of particle might be different at the different positions. The high stirring speed that enhances flow speed of the acid on the surface in the

EP process might reduce the number of Nb atoms on the surface. The effect of higher stirring speeds was observed on the lab EPed sample surfaces. The equator surface might experience a higher acid flow on its surface when the Ninja cathode was rotating. The higher flow at equator might reduce the number density of particles on the equator. However, the iris surfaces might also experience a higher acid flow than that on the beam pipes. The particle clusters might move from the beam pipe surface to the iris coupons in the rinsing process. Cu impurity in the particle clusters was possibly from water. Higher F concentration at the surface containing particles indicates that the particle clusters might be formed in the presence of dilute acid on the surface in the rinsing process.

In the further study we will examine the effect of dissolved O<sub>2</sub>, and CO<sub>2</sub> in water and the presence of dilute acid on EPed surface in the rinsing process to understand the nucleation mechanism clearly.

## CONCLUSION

Nb coupons set at the Nb single-cell cavity in the VEP process were observed with SEM and analyzed with EDX and XPS. The particle clusters were found on the iris and beam pipe surfaces randomly with different number densities. The equator coupons were found relatively clean as confirmed after several VEP experiments. The particles clusters were picked-up using the W-needle tip of the FES and analyzed with EDX while the coupon was moved out of the analysis chamber. The EDX spectra and map revealed that the particles are Nb-rich particles containing F, C and Cu impurities. The XPS analysis showed that the surfaces, which contained the higher number density of particles, were found to have lower Nb concentration and higher C, F, and Cu concentrations. The analysis results confirmed the EDX results and indicated that the particles were clusters of Nb<sub>2</sub>O<sub>5</sub>.

The lab EP experiments at the different stirring speeds and dissolution of particles in the EP acid indicated that (1) the higher acid flow rate on Nb surface during EP might reduce the number density of the particles on the EPed surface, and (2) the particles were supposed to be formed in the cavity rinsing process with water. The particle nucleation might depend on dissolved O<sub>2</sub> and CO<sub>2</sub> in water, and the rinsing conditions including rinsing time, and water flow rate which control the level of acid dilution and residence time of the dilute acid on the surface.

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