EFFECT OF CURRENT DENSITIES ON SULFUR GENERATION AT ELECTROPOLISHED NIOBIUM SURFACE

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Abstract

We conducted a series of electropolishing (EP) experiments in aged EP acid with high (≈50 mA/cm^2) and low (≈30 mA/cm^2) current densities on Nb surfaces. The experiments were carried out both for laboratory coupons and a real Nb single cell cavity with six witness samples located at three typical positions (equator, iris and beam pipe). All the samples surface were investigated by XPS (x-ray photoelectron spectroscopy), SEM (scanning electron microscope) and EDX (energy dispersive x-ray spectroscopy). The surface analysis showed the EP with a high current density produced a huge amount sulfate particles at Nb surface whereas the EP with a low current density is very helpful to mitigate sulfate at Nb surface in both the experiments.

INTRODUCTION

Electropolishing (EP) is the commonly used surface treatment for Nb SRF cavities [1,2]. The functioning of EP greatly depends on its I-V characteristics and electrolytic conditions. The EP electrolyte for Nb surface is composed of hydrofluoric acid (HF, 40 wt %) and sulfuric acid (H_2SO_4, 96 wt %) in a volumetric ratio of 1:9. At STF (KEK), the EP electrolyte has been used for about 1 year hence electrolyte is aged after every EP. Prior experimental results [3] confirmed a large amount of contaminants (sulfur and fluorine) at Nb surface after the EP in aged acid with the high current density. Therefore it would be very interesting to demonstrate the effect of low current density with aged EP acid. In this article, we present a systematic study on contaminant generation based on different current densities during EP in aged acid. The surface analytical tools were employed in order to characterize the Nb surfaces.

EXPERIMENTAL DETAILS

Laboratory EP

We conducted two laboratory EP in aged EP acid with the high (experiment 1) and low (experiment 2) current densities. Table 1 summarizes the laboratory EP experimental conditions. For the experiments, rectangular type Nb samples (20×14×2.8 mm^3) were used and fixed on a Nb base plate (100×100×2.8 mm^3). This Nb plate along with samples was then EPed at a laboratory EP facility at KEK. Fig. 1 shows the laboratory EP set-up with three electrode scheme.

During EP, the Nb plate worked as anode and two aluminium plates were used as a cathode. The Nb plate was twisted up to 180^0 with a speed of 5-6 rpm to agitate the EP process. After EP, the Nb plate was rinsed in ultra pure water and all the samples were detached.

Table 1: Laboratory EP Experimental Conditions

	Average Current Density (mA/cm^2)	EP Acid Temperature (^{0}C)	Nb conc. in EP Acid (g/l)	Removal Depth (µm)
Experiment 1	50	30	7.6	20
Experiment 2	33	27	7.3	20

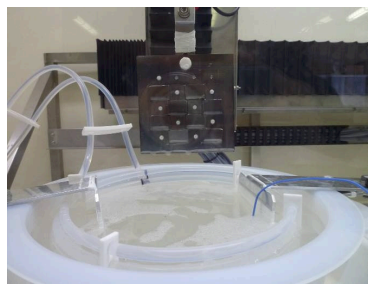

Figure 1: A three electrode laboratory EP set-up at KEK.

Cavity EP

In order to confirm the laboratory EP experimental results with a real Nb cavity, we also conducted EP experiments in aged acid on a real Nb single cell test cavity with the high (experiment 1) and low (experiment 2) current densities. Table 2 describes the experimental conditions of cavity EP. The cavity was drilled with six holes at three typical positions namely equator, iris and beam pipe. The six disc type Nb samples of the diameter of 8 mm same as cavity holes were prepared and fixed at cavity holes (see Fig. 2). This cavity assembled with six samples was electropolished (EPed) at EP bed [1,3,4] in STF, KEK in the routine manner as ILC cavities are EPed. During EP, the cavity acted as anode which was rotating with a speed of 1-2 rpm and a cylindrical aluminium rod inside the cavity worked as a cathode. The flow rate of EP electrolyte was maintained at 5 l/min.

After EP, the cavity was rinsed with ultra pure water and moved to a clean room. All the samples were carefully detached and kept in a multiholder carousel and in an UHV suitcase [4].

Table 2: Cavity EP Experimental Conditions

	Average Current Density (mA/cm^2)	EP Acid Temperature (^{0}C)	Nb conc. in EP Acid (g/l)	Removal Depth (µm)
Experiment 1	48	25	7.8	50
Experiment 2	30	25	6	20

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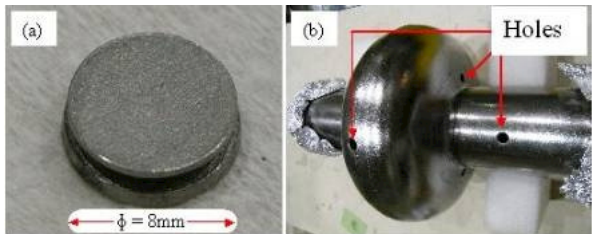


Figure 2: (a) Nb disc type sample (b) Nb cavity drilled with six holes.

Surface Analysis

The samples surface were characterised by XPS (x-ray photoelectron spectroscopy), SEM (scanning electron microscope) and EDX (energy dispersive x-ray spectroscopy). The three loadlock systems are also attached with our XPS system to transfer the samples from UHV suitcase without exposing them to atmosphere [4].

EXPERIMENTAL RESULTS

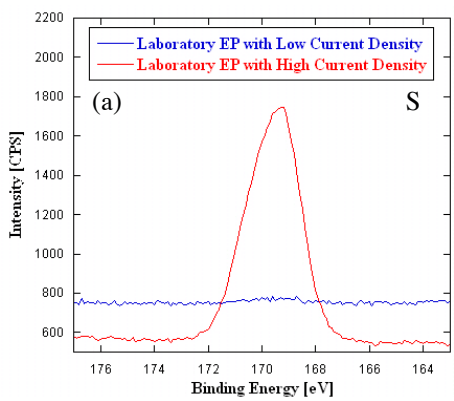
Table 3 and 4 describe the atomic composition present at top surface in laboratory EP and cavity EP experiments respectively. The XPS analysis of samples surface showed a huge amount of sulfur present after the EP with the high current density.

Table 3: Atomic Composition (at. %) Present at Top Surface of the Samples Treated in Laboratory EP

Elements	Experiment 1 (at. %)	Experiment 2 (at. %)
F	<0.1	<0.1
S	10.3	0.3

Table 4: Atomic Composition (at. %) Present at Top Surface of the Samples Treated in Cavity EP

Elements	Experiment 1 (at. %)			Experiment 2 (at. %)		
	Equator	Iris	Beam Pipe	Equator	Iris	Beam Pipe
F	3	3	4	0.9	0.2	0.4
S	4	7	2	0.5	<0.1	0.2



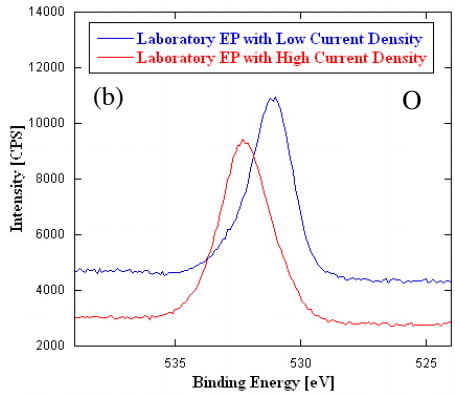


Figure 3: XPS spectra of samples surface treated in laboratory EP (a) Sulfur and (b) Oxygen.

According to XPS results, sulfur was reduced drastically on the samples surface EPed with low current density. A XPS chemical shift in sulfur (at ≈170 eV) and oxygen (at ≈533 eV) spectra (See Fig. 3 and 4) was observed in both the experiments with high current density which confirms the sulfur presence at top surface in oxidation form as sulfate (SO_4^{--}) [5]. The original binding energy of sulfur and oxygen is 164.4 eV and 531.7 eV respectively. No XPS chemical shift was observed in oxygen spectrum where sulfur was found quite less at Nb surface (See Fig. 3 and 5).

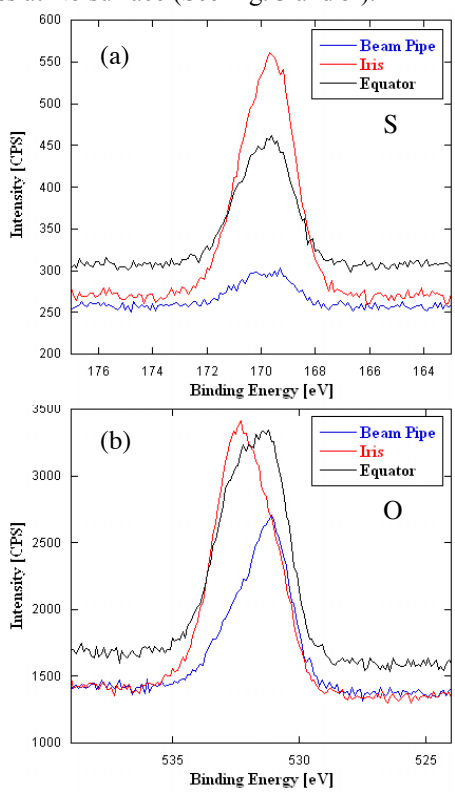


Figure 4: XPS spectra of samples surface treated in cavity EP with high current density (a) Sulfur and (b) Oxygen.

In case of cavity EP experiments with the high current density, maximum sulfur/sulfate was found at the iris sample surface (up to 7 at. %) and minimum at the beam pipe sample surface (up to 2 at. %).

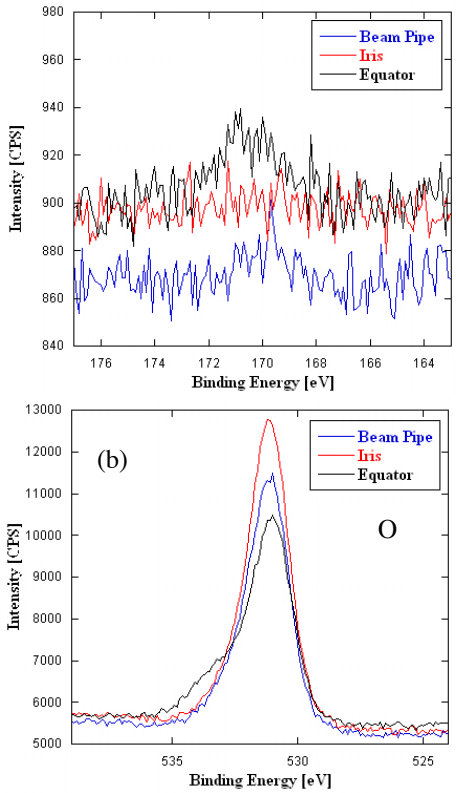
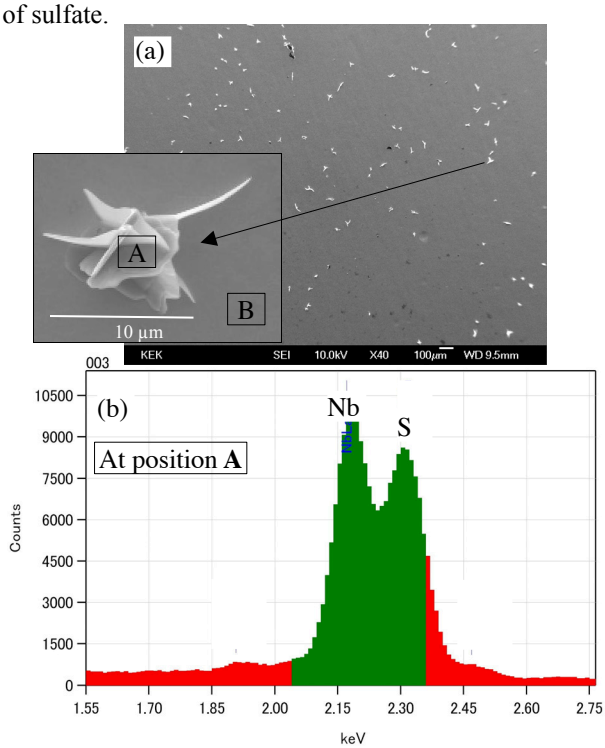


Figure 5: XPS spectra of samples surface treated in cavity EP with low current density (a) Sulfur and (b) Oxygen.

SEM observations (see Fig. 6 (a)) of the samples EPed with the high current density showed a high number density of particles of more than 10 micron size at the surface. EDX analysis (see Fig. 6 (a) and (b)) of the particles confirmed that the particles are composed of sulfur and oxygen. A collective information from XPS and EDX results reveal the fact that the particles consist of sulfate.



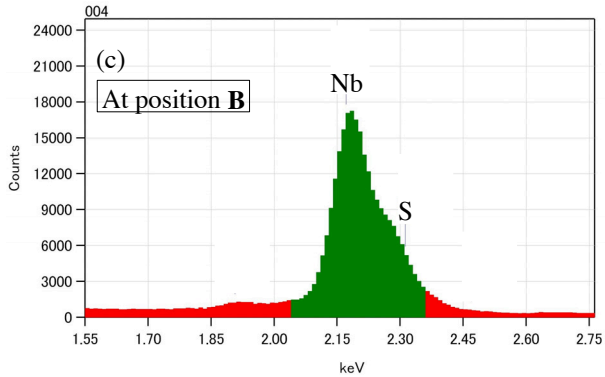


Figure 6: (a) SEM images of the sample surface EPed with high current density (b) EDX spectrum at particle (position A) and (c) EDX spectrum at non-particle area (position B).

CONCLUSIONS

We carried out a series of EP experiments in aged EP acid with the low (≈30 mA/cm^2) and high (≈50 mA/cm^2) current densities. According to the XPS, SEM and EDX results, a huge amount of sulfate particles were found at the surface EPed with the high current density whereas the EP with the low current density was very effective to mitigate sulfur at Nb surface. Therefore, it can be concluded that EP in aged electrolyte should be carried out with a low current density in order to assure the lowest possible sulfate at Nb surface.

Further investigations of surface roughness and oxide layer formation by EP with the low current density is necessary to be explored.

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