ANALYSIS AND FIELD EMISSION CHARACTERISTIC OF NIOBIUM SURFACE TREATED WITH ELECTROPOLISHING PROCESS

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Abstract

Niobium (Nb) coupons in-situ-electropolished (EPed) with an Nb SRF coupon cavity and laboratory EPed Nb samples were analyzed with XPS, SEM, EDX for chemical, morphological and elemental information of their surfaces. The coupons EPed simultaneously showed different peak intensity ratios of Nb^0 to Nb^{5+}, different concentrations of O, C and other elements on their top surfaces. The results were related to the number density of particle clusters, which were present on the surface and confirmed to be Nb_2O_5 by XPS and EDX analyses. Both XPS and EDX analyses revealed that the particles contained C, F, and Cu impurities. Field emission characteristics were measured for the EPed coupon surfaces with two different field emission measurement systems. The surface having particles showed a significantly higher emission current at a lower electric field compared to a relatively clean surface. This article also describes a mechanism of particle formation on the surface and necessary optimized post-EP processes that removed the undesired synthesized particles from the cavity surface.

INTRODUCTION

Particle accelerator machines use niobium (Nb) superconducting cavities for acceleration of electrons and other particles. The cavity's performance is evaluated in terms of its accelerating gradient and quality factor. The nine-cell 1.3 GHz cavities generally reaches an accelerating gradient of 35–40 MV/m. To reach a high gradient, an electropolishing process is applied to the cavity to smoothen its surface and reduce the contaminants which might act as a field emitter at a high accelerating field and limit the cavity performance.

In this work, we show how the post-EP process affects the chemical state and field emission property of the surface. This paper includes a study on the chemical analysis and field emission characteristics of the electropolished niobium surface with different surface analytical tools and emission measurement systems.

EXPERIMENTAL SETUP

A 1.3 GHz single-cell Nb coupon cavity with six Nb coupons in a size of ø8 was electropolished with a vertical electropolishing system. The coupon cavity is shown in Fig. 1. Detail of the coupon cavity and VEP systems were reported in ref. [1]. In the post-EP process, the cavity was rinsed with water for ~10 min to washout the EP acid (a mixture of H_2SO_4 and HF) from the surface.

The coupon surfaces after the EP process were analyzed with x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and energy dispersive x-ray spectroscopy (EDX). Field emission study was conducted with a triode system to measure an emission current from a surface area lying under the accelerating grid having size of ø6. The triode system was reported elsewhere [2]. The gap between the grid and sample was kept to be 100 µm. A negative voltage (0–10 kV) was applied to the sample, the grid was kept grounded, and the fluorescent screen was set at a positive voltage of 200 V. An emission measurement from a localized position was performed with a scanning tungsten (W) tip of field emission scanner (FES). The detail of the FES has been given in ref. [3]. The gap between the tip and Nb surface was set to be 20 µm. The tip was set at positive voltage ranging from 0 to 3.5 kV and the Nb surface was grounded. In emission current measurement with the FES, a femtoammeter was used. An electric noise restricted the measurement of an emission current lower than 10 pA.

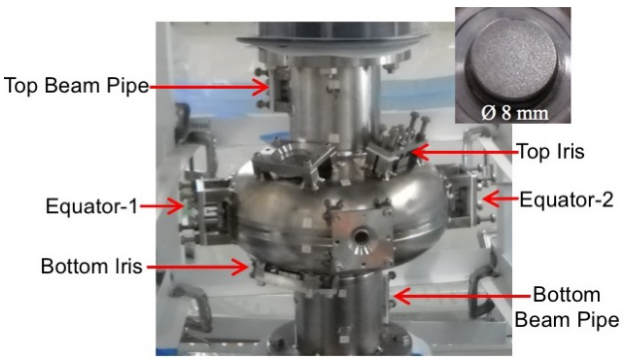

Figure 1: Schematic of the 1.3 GHz Nb coupon cavity with the coupon positions. The inset shows a coupon having a diameter of ø8.

RESULTS AND DISCUSSION

Surface Analysis

The six coupon surfaces were analyzed with XPS. High resolution Nb 3d peaks for the six coupon surfaces are shown in Fig. 2. The peaks showed different intensities for Nb^{5+} and Nb^0 peaks. The intensity ratios of Nb^{5+} to Nb^0 varied for the coupons and were higher for the top beam pipe and top iris coupon surfaces. The ratios for all the coupons are shown in Fig. 3 (a). The atomic concentrations of the present elements on the top surfaces of the coupons are shown in Fig. 3. Both top beam pipe and top iris coupon

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surfaces showed higher C, F, and traces of Cu compared to that on the other coupon surfaces.

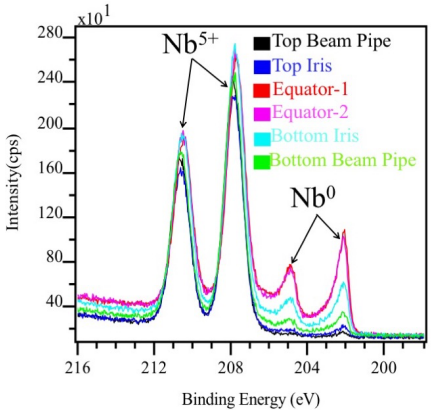

Figure 2: High resolution Nb 3d peaks measured for the coupon surfaces with XPS.

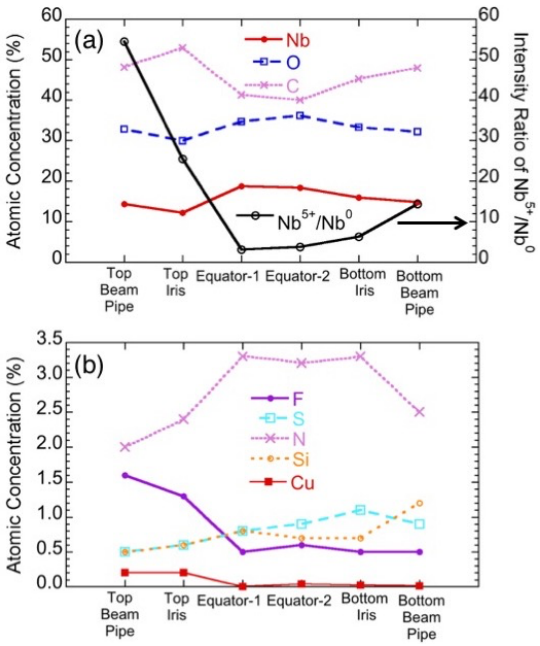

Figure 3: (a) Peak intensity ratios of Nb^{5+} to Nb^0 for all the coupon surfaces. Atomic composition of (a) Nb, O, and C and (b) F, S, N, Si, and Cu elements present on the top surfaces of the electropolished coupons.

The surfaces were observed with SEM to investigate for any difference in morphology and present contaminants on the surfaces. Mainly the top beam pipe and top iris coupons were found to have many particle clusters on their surfaces. A correlation was found in the SEM images and XPS results. The surfaces having the higher number density of particles showed a higher peak intensity ratio of Nb^{5+} to Nb^0 in the XPS analysis.

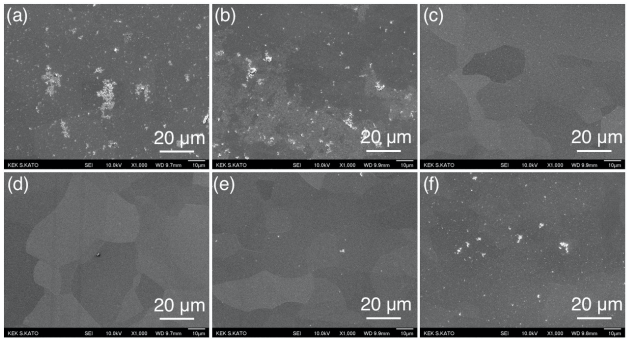

Figure 4: SEM images of the surfaces of coupons positioned at (a) top beam pipe, (b) top iris, (c) equator-1, (d) equator-2, (e) bottom iris, and (f) bottom beam pipe of the cavity.

EDX analysis was conducted to get elemental information of the particle clusters. EDX spectra of particles lying on the surface provided information of particles but it might also include the information for the Nb surface as EDX provides information for a depth down to 1–2 µm. Therefore, elemental information obtained from the EDX spectra of particles lying on the surface might not be accurate. To analyze an individual particle cluster with EDX, a particle cluster was detached from the surface using a sharp W-tip of the FES. The particle cluster on the surface and on the tip is shown in Fig. 5 (a) and (b), respectively. The sample was moved to the loadlock chamber of the SEM before analysis of the particle so as to avoid the influence of the Nb sample surface in the EDX spectrum of the particle. The EDX spectrum of the particle is shown in Fig. 5 (c). The spectrum revealed that the particle was made of niobium oxide and contained C, Fe, and Cu impurities. The result corroborated with the XPS result which also showed C, F, and Cu contaminants on the surfaces having particle clusters.

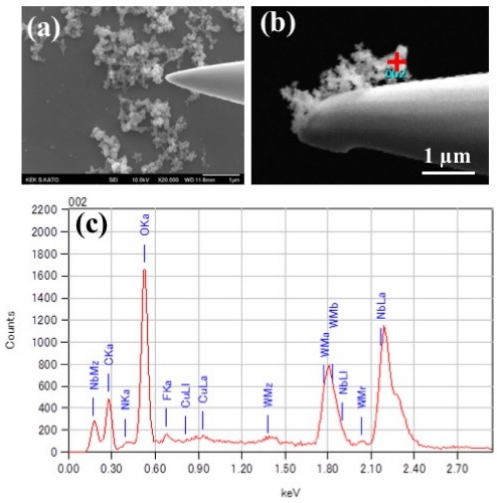

Figure 5: (a) Particle cluster on the coupon surface. (b) Particle cluster picked-up by the W-tip. The dark background shows absence of the sample and sample holder underneath the particle. (c) An EDX spectrum of the particle located on the tip.

The combined surface study with XPS, SEM, and EDX suggested that the Nb in the particles might remain in the oxide form. Since Nb peaks for the different coupon surfaces in XPS showed no difference except the peak intensities, it seems that Nb in the particles was in the Nb^{5+} state. The presence of the niobium oxide particle clusters with high concentration of C might be responsible for lowering the intensity of Nb^0 peak and yielded the different peak intensity ratios for the different coupons. The F and Cu impurities came from the EP acid and water, where water contained traces of Cu.

The particles might synthesize in the post-EP water rinsing process. In the post-EP water rinsing, niobium fluoride species remained in the acid viscous layer on the surface might react with water to form Nb_2O_5 particle clusters. In the case of insufficient post-EP water rinsing, the particles might remain adhered on the surface.

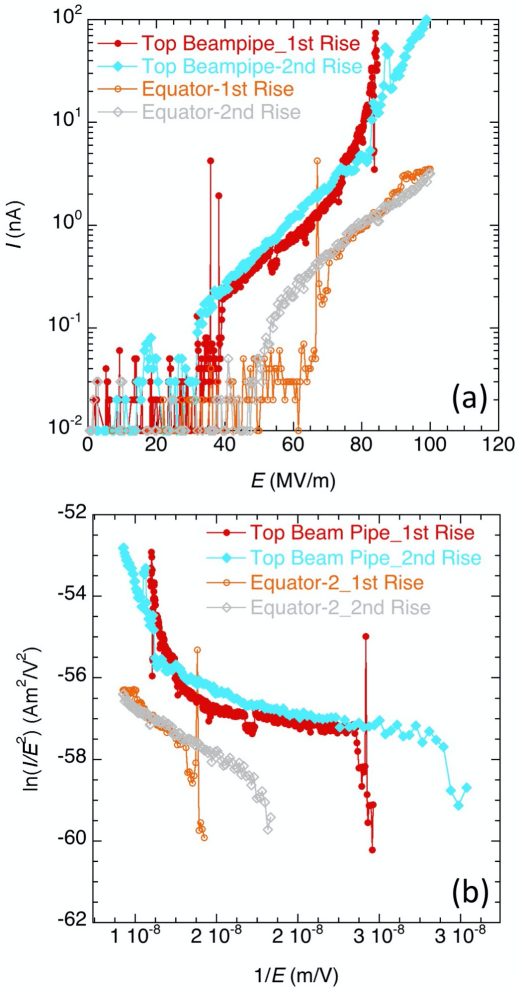

Figure 6: Field emission from the top beam pipe and equator coupon surface. The emission measured with a triode system. (a) Emission current against applied electric field between the coupon surface and the graphite grid with a diameter of ø6. (b) The corresponding FN plots.

Field Emission Study

Field emission measurement was performed for the top beam pipe and equator coupon surfaces. The emission was repeated for both samples. The field emission characteristics of the surfaces and corresponding FN plots are shown in Fig. 6. The electron emission suddenly started at a high field in the first voltage rise. In the second voltage rise, the turn-on field, at which the emission current started, decreased. The phenomenon was observed for both coupons. The comparison of the emission currents for both coupons showed that the top beam pipe coupon surface yielded a higher a higher emission current at a lower field. This might be due to the presence of the higher number density of particle clusters on the top beam pipe coupon surface. It appeared that the particles might act as electron emitters.

To confirm this, emission measurements were performed for particles with a spherical W-tip having a diameter of ~55 µm. An emission characteristic of a particle is shown in Fig. 7. The emission characteristic in Fig. 7 showed that the particle emits at a higher field in the first rise. In the second rise, the emission started at much lower field and the current intensity was significantly higher than that in the first voltage rise. A clean position on the coupon surface was also measured for emission up to the field of 175 MV/m. No emission current from the clean position was detected by the current meter. The emission result was consistent with that obtained with the triode system. The measurements conducted with both methods suggested that particle cluster acted as electron emitters at a high electric field.

The field emission in the first voltage rise was attributed to the formation of conducting channels in the clusters at a high field [4,5]. The channels might remain active in the second voltage rise. This might result in emission at a lower turn-on field in the second voltage rise.

Removal of Particles

Ultrasonic rinsing was applied to the cavity for 15 min after another VEP experiment and post-EP water rinsing conducted for a longer time of 30 min. A SEM image in Fig. 8 (a) shows the surface after VEP, post-EP water rinsing for 30 min, and ultrasonic rinsing for 15 min. The ultrasonic rinsing was conducted with an average ultrasonic power of 20 W/L. The particle clusters with the lower number density were found on the surface. The coupons were set back to the cavity for a prolonged ultrasonic rinsing with FM-20 detergent and pure water. Fig 8 (b) shows the surface after the prolonged ultrasonic rinsing for more than 1 h. The particle and other contaminants disappeared from the surface in the long ultrasonic rinsing of the cavity.

An electropolished surface containing particle clusters was also soaked in the EP acid for 5 min. The acid soaking removed almost all the particles and other contaminants from the surface as confirmed in a SEM observation.

The post-EP water rinsing performed even for 1 h, the particle cluster, although in less number, were found on the surface. A short-time ultrasonic rinsing was found to be not enough for removal of all the particles from the surface. To remove almost all particle clusters and other contaminants, a prolonged ultrasonic rinsing or surface rinsing with HF acid seems to be required.

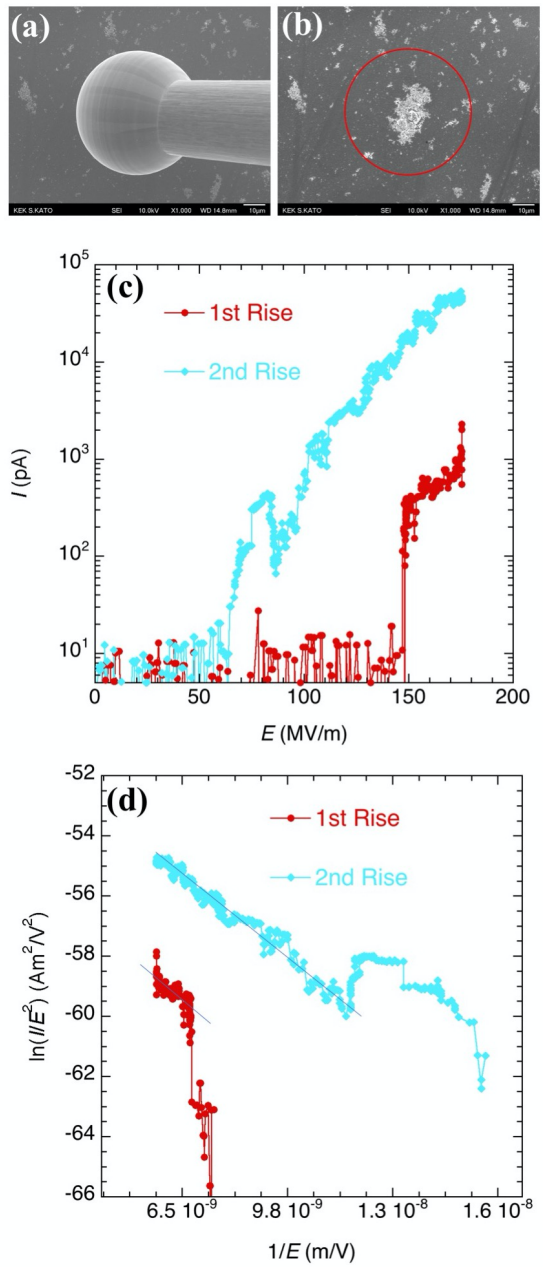

Figure 7: SEM images of W-tip (a) set over the particle (b) with a gap of ~20 µm. Field emission characteristics of the particle in the first and second voltage rise (c), and corresponding FN plots (d).

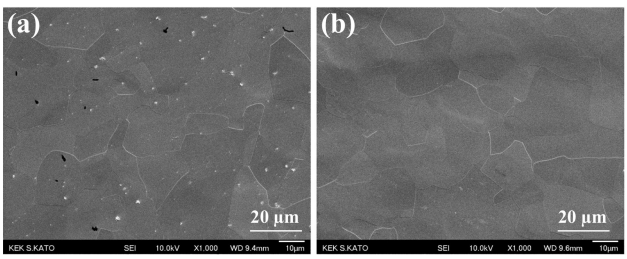

Figure 8: SEM images of a coupon surface after VEP, post EP water rinsing, and ultrasonic rinsing of 15 min. (b) Surface after additional ultrasonic rinsing for more than 1 h.

CONCLUSION

Surface analysis and field emission measurements of the Nb coupon surfaces, which were in-situ electropolished with the coupon cavity, were conducted. XPS analysis of the coupon surfaces showed different atomic concentrations and different peak intensity ratios of Nb^{5+} to Nb^{0}. The SEM and EDX study of the surfaces showed that niobium oxide particle clusters adhered on mainly the top beam pipe and top iris coupon surfaces. These surfaces showed higher peak intensity ratios of Nb^{5+} to Nb^{0}. It appeared that the particles were responsible for the different peak intensity ratios. The particle clusters might synthesize in the post-EP water rinsing in which niobium fluoride species might react with water to form Nb_2O_5 particle clusters. In the case of insufficient rinsing and water flow, the particles might remain adhered on the cavity surface. Field emission study conducted for the surface containing many particles and relatively clean surface. The emission results showed that a turn-on field was lower and emission current was higher for the surface with many particles. The localised emission measurement for the particle clusters confirmed that the particles emit at a high electric field. The number density of particle reduced significantly when the post-EP water rinsing was performed for a longer time followed by an ultrasonic rinsing for 15 min. However, to remove almost all particles and other contaminants, prolonged ultrasonic rinsing with FM-20 detergent and pure water was found to be effective. Alternatively, the particle cluster could be removed by soaking the Nb surface in the EP acid or dilute HF acid.

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