

# SURFACE STUDY ON NIOBIUM STAIN AFTER ELECTRO-POLISHING FOR SUPER-CONDUCTING RF CAVITY

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## Abstract

In development of superconducting radio-frequency niobium cavities, there are problems in low performances of electro-polished (EP) cavities with a fresh EP solution due to stains on the surfaces with discoloration. Although the stain problems have been known from the past researches, the detailed study with surface analysis has not been carried out. In this study, the stains on the niobium surfaces were observed with x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy and scanning electron microscope. According to results of XPS, there are some differences in atomic components at the stained and non-stained surfaces, ex, a little amount of fluorine and no metal oxide were found only at the stained surface. In this article, we will describe the detail of the XPS results.

## INTRODUCTION

For ILC project, various experimental studies are ongoing to produce high performance superconducting niobium radio-frequency cavities in STF in KEK [1]. To achieve high gradient which is larger than 35 MV/m in a 9-cell cavity, electro-polishing (EP) method has been adopted as surface treatment for niobium cavities. Recently some 9-cell cavities after EP showed limited performance in vertical tests [2]. According to optical inspection for inside of cavities, there were stains with discoloration on the surfaces [3]. Those stains would cause heavy field emissions in vertical tests. Authors had made an effort to produce the brown stains on niobium samples with an EP in a laboratory (lab-EP) with vary acid conditions. We found that a fresh EP solution can cause the brown stains on the niobium surfaces [3]. In this study, we will report observation results with x-ray spectroscopy (XPS) and scanning electron microscope (SEM) for the stains on the niobium sample surfaces that were produced by the lab-EP setup.

## STAIN GENERATION IN LAB-EP

Niobium samples with stain were prepared by using the lab-EP setup as shown in Fig. 1(a). The EP solution was fresh that means less niobium concentration ( $< 0.4$  g/l) in the solution. We prepared niobium sample pieces that were the size of  $20 \times 15 \times 2.8$  mm. Some sample pieces were treated at once with a holder plate made of niobium shown in Fig. 1(b). Two cathode plates made of aluminum were set at both edges of a bucket. The holder plate with samples was rotating during EP process. In this study, the stained samples were prepared by following recipe;

- EP for 20  $\mu$ m of removal depth with a fresh solution ( $< 0.4$  g/l for niobium).
- Exposure to the air for 70 min. without any rinsing.
- Light pure-water (P.W.) rinsing for a few tens seconds.
- Exposure to the air again.

In this procedure, no stains appeared before light P.W. rinsing. However, after the rinsing, stains with discoloration appeared within a minute in the dried area on the surface. Fig. 2 shows the appearance of stains in the upper side of the samples. One can see that no stains appeared in the bottom area of each sample covered with P.W. The size of stains was several mm in a width and the colour of stains was brown. These stains were similar to the stains in 9-cell cavities revealed after EP. These stains were observed with XPS and SEM to find the compositions of the stains and the solution to avoid.

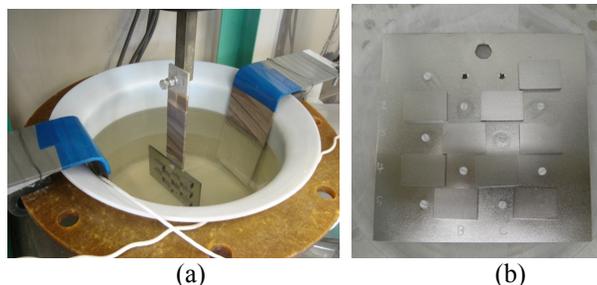


Figure 1: Outline of lab-EP setup (a) and samples on holder plate before lab-EP (b). The plate with samples was rotating during EP process.

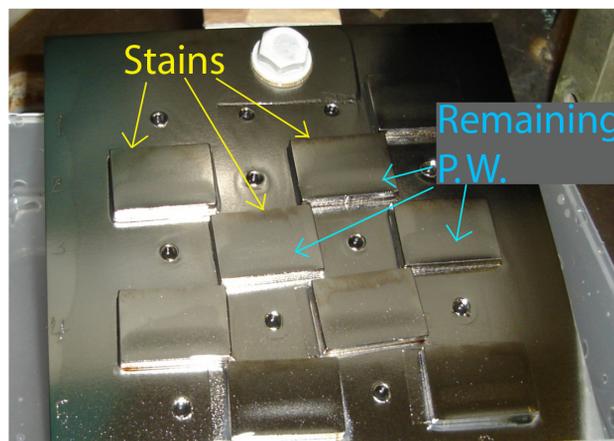


Figure 2: EPed niobium samples after light P.W. rinsing. On the upper dried area of each sample, brown stains appeared.

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## SURFACE OBSERVATION

### XPS Analyses

We have developed an extremely high vacuum (XHV) surface analysis system (Fig. 3) which is capable of performing XPS with argon ion etching [4]. The probing area of XPS analysis was less than 2 mm in a diameter. After baking, the base pressure in the analysis chamber is on the order of  $10^{-9}$  Pa.

Fig. 4 shows XPS energy spectra of the non-stained and stained area on a niobium sample surface. In the stained area, a clear fluorine peak (Fig. 5 (b)) was found and the

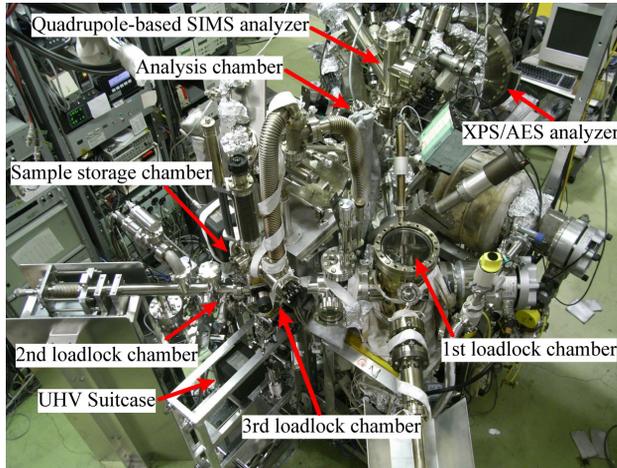


Figure 3: Overview of the XHV surface analysis system. The system equipped with XPS/AES/SIMS analyzers. The base pressure in the analysis chamber is on the order of  $10^{-9}$  Pa.

atomic composition was around 1 atomic %. Sulfur and aluminum for both areas and fluorine for the non-stained area were lower than detection limits in our XPS condition that were around 0.1 – 0.3 atomic %. Atomic compositions for both areas are shown in Table 1. In Fig. 5 (a), spectra for niobium of both areas are shown. Both areas were found to be covered with niobium oxide, mainly  $Nb_2O_5$ , as the same as other EPed niobium surfaces. However the peaks for metallic niobium were not found in the stained area. We can suppose that a thickness of oxide layer of the stained area would be thicker than one of the non-stained area. The difference of the peak energy of  $Nb_2O_5$  between two spectra would be due to charge up of the thicker oxide layer.

XPS depth profiles with argon ion etching for the non-stained and stained areas are shown in Fig. 6 (a) (b). Ion beam with 5 keV was raster scanning and normal incidence to the surface. The thickness of oxide layer which is defined by a full width half maximum (FWHM) of oxygen intensity, of the stained area was around 7 nm and more than twice of one of the non-stained area. This result is consistent with the result of XPS observation mentioned above. There were no differences between the depth profiles of the non-stained area and the other usual EPed samples.

Table 1: XPS Atomic Compositions in atomic % for Stained and Non-stained Area.

Elements	Nb	O	C	S	F
Non-stained	19	59	22	<0.1	<0.3
Stained	13	48	38	<0.1	1

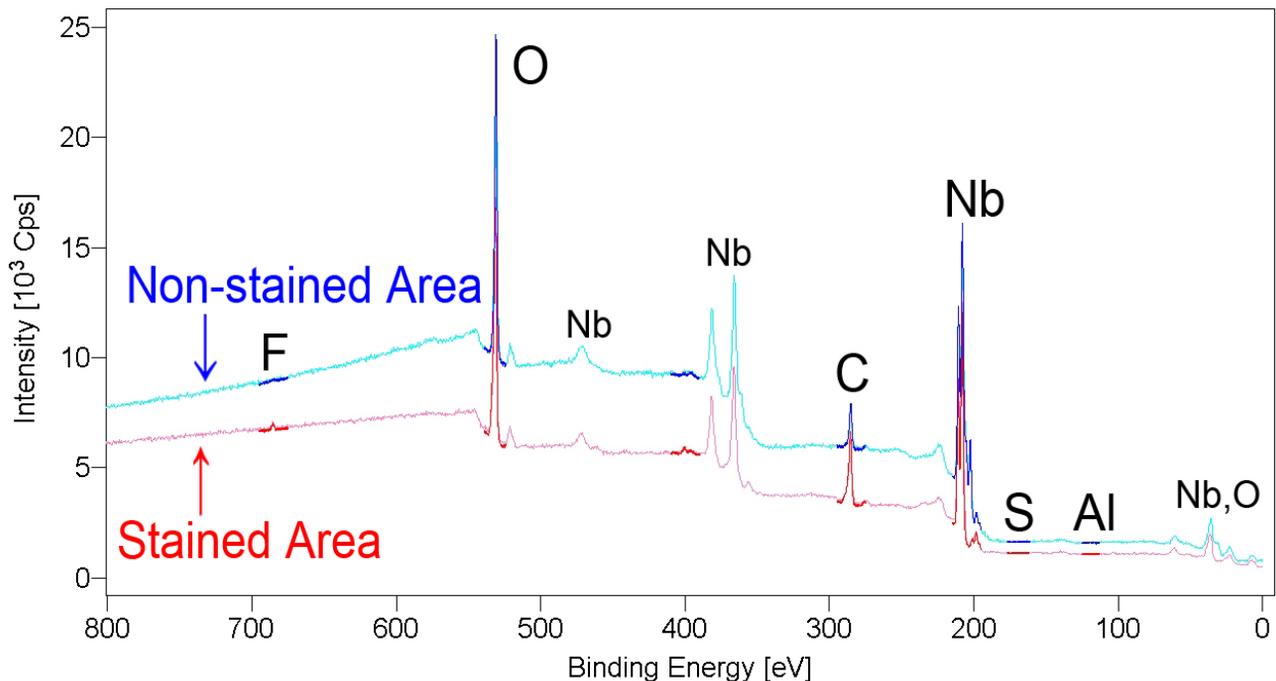


Figure 4: XPS energy spectra of the non-stained area and stained area on a sample. No sulfur and aluminum were found. Fluorine was found only on the stained area.

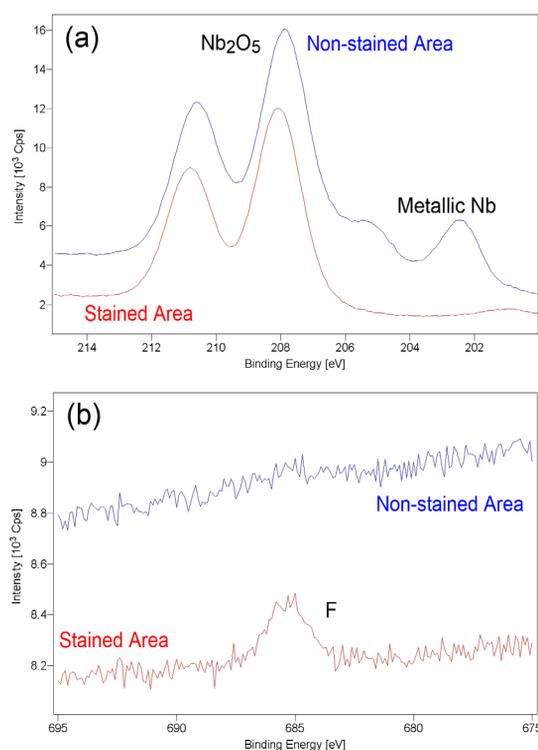


Figure 5: XPS spectra for niobium (a) and fluorine (b) in the stained and non-stained area.

### SEM Observation

The sample was observed with SEM and energy dispersive X-ray spectroscopy (EDXS) for the stained and non-stained area. For example, Fig. 7 shows the SEM image of the stained area. We can find many dots with the size of sub micro meter in both areas on the surface. The size of the dots was too small to analyze with XPS. In EDXS analyses, the compositions of the dots were not identified because of less sensitivity for lower-Z element contamination on higher-Z material for EDXS. According to surface observation of the other EPed niobium sample, the similar dots were found to be sulfur with a ToF-SIMS image analysis [4]. We can consider that the dots were sulfur came from EP solution.

### CONCLUSION

The lab-EPed niobium sample was analyzed with XPS for the non-stained and stained areas. Component of metallic niobium was not found at the stained area. It is consistent with the depth profile result which revealed thicker niobium oxide layer at the stained area. Fluorine was only found at the stained area. It might suggest that the mechanism of the brown stain appearance has some relation with an insoluble compound of fluorine from the EP solution. In SEM observation, many dots which would be considered sulfur contaminants were found in both areas. Further researches to find better rinsing methods and/or polishing techniques and to understand mechanism of production of the stain are necessary.

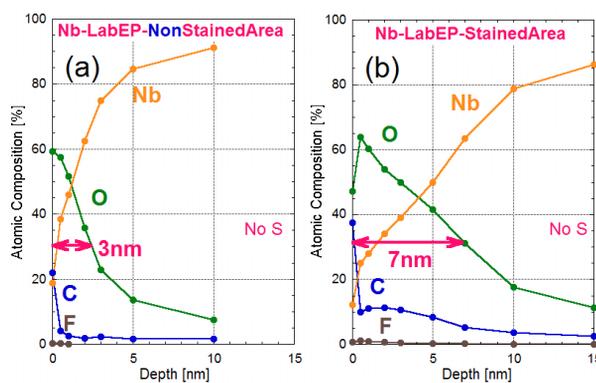


Figure 6: Depth profile with argon ion etching for the non-stained (a) and stained area (b). The thickness of oxide layer (FWHM) for the stained area was around 7 nm that was more than twice of one of the non-stained area.



Figure 7: SEM image of the stained area of the niobium sample. Many dots were found in both of the non-stained and stained area.

### ACKNOWLEDGEMENTS

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