

SURFACE CHARACTERIZATION OF NIOBIUM SAMPLES ELECTRO-POLISHED TOGETHER WITH REAL CAVITIES*

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Abstract

We report the results of surface characterizations of niobium samples electropolished together with a single cell cavity. These witness samples were located in three regions of the cavity, namely at the equator, the iris and the beam-pipe. Auger electron spectroscopy (AES) was utilized to probe the chemical composition of the topmost four atomic layers. Scanning electron microscopy with energy dispersive x-ray for elemental analysis (SEM/EDX) was used to observe the surface topography and chemical composition at the micrometer scale. A few atomic layers of sulphur (S) were found covering the samples non-uniformly. Niobium oxide granules with a sharp geometry were observed on every sample. Some Nb-O granules appeared to also contain sulphur.

INTRODUCTION

Electropolishing techniques are the state-of-the-art for finishing SRF accelerator cavities made of bulk niobium in order to gain a high field gradient. We are interested to investigate the surface state of a real cavity after EP. The motivation of this study is to search for possible impurities left by electropolishing process [1-3], which may enhance field emission and degrade a cavity's field gradient limit.

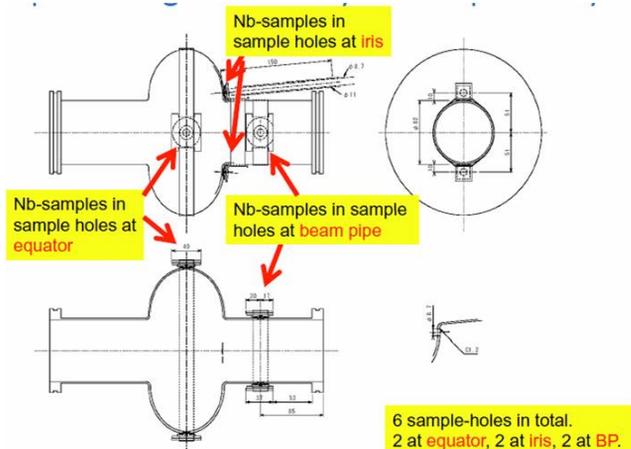


Figure 1: Three witness samples were located in a single cell SRF cavity and electro-polished in-situ.

Specifically, this study was initiated to search for any sulphur residues on the cavity surface immediately after EP. Large amount of yellow sulphur crystalline powders were found at the outlet of the used EP electrolyte. In this study three small witness samples have been processed *in-situ* with a single cell SRF cavity (Figure 1). The samples are round disks of 10mm in diameter. They experienced the same EP (50µm removal) as the real cavity. They were rinsed by ultra-pure water (UPW) but without ultra-sonic rinsing. The samples were located at iris, equator and beam pipe respectively. The entire EP-related experiment was conducted at KEK, Japan.

EXPERIMENT RESULTS

Auger electron spectroscopy was applied to study chemical composition of the samples' topmost atomic layers. AES (*PHI 660* system made by *Physical Electronics*TM) is only sensitive to the first four atomic layers. Its best sensitivity on atomic concentration is 0.2%. This instrument has an absorption current imaging system (ABS), which roughly shows surface morphology and elemental mass. The ABS imaging system was used to identify the primary electron beam spot and the Ar⁺ depth profiling ion beam spot. Figure 2 shows the AES "finger print" spectra of niobium and sulphur. Their peak profile and peak energies were both used to identify S in empirical spectrum. One should note that the S peak (153eV) is in the middle of two Nb peaks (146eV and 170eV).

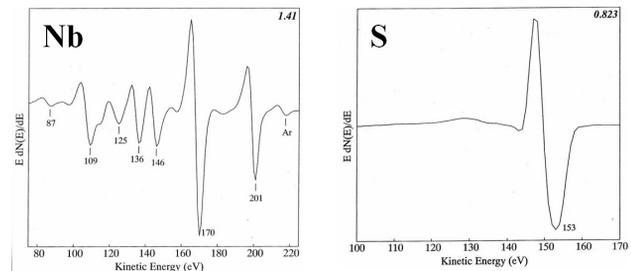


Figure 2: AES "Finger print" spectrum of Nb and S.

A high resolution scanning electron microscope, *Hitachi-4700*, was used to observe surface morphology. It has an accessory of energy dispersive X-ray (EDX) detector made by *EDAX*TM. Unlike AES, which uses emitted Auger electrons to identify elements, the EDX system utilizes characteristic x-ray photons produced by the primary electron beam to probe chemical elements. It explores ~2µm deep and atomic sensitivity ~2%. In

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contrast to AES (4 atomic layers), EDX is a more “bulk-like” elemental analysis technique.

Sample 2 Results

Sample 2 was located on the equator. Five spots were surveyed by AES (4 of them are presented here in Figure 3). The spots are evenly distributed and separated by 1~2mm away. No sulphur was found in the entire spectrum. Under SEM, granules (Figure 4) were observed sparsely located on the largely smooth surface. EDX

study (spectrum not shown here) on the granules found oxygen and Nb element only. The granules’ morphology looks like sintered crystallites. Because the probing depth of EDX is 1 μ m, it is speculated that the granules are made of niobium oxide. It is noticed the granules in Figure 4 reside on a very smooth surface. It is not yet known if the granules drifted to surface by the etchant or were formed in-situ.

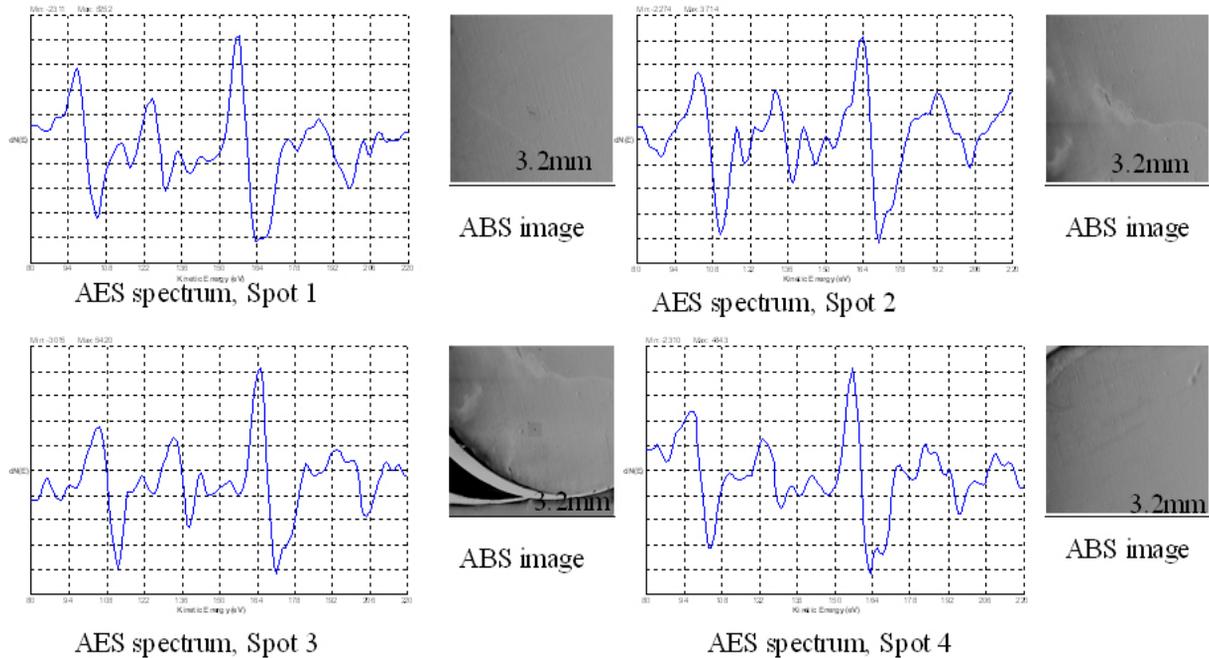


Figure 3: Empirical AES data elected from 4 spots. They have no S peak. The spectrums are collected from the ABS imaging area (right on each spectrum).

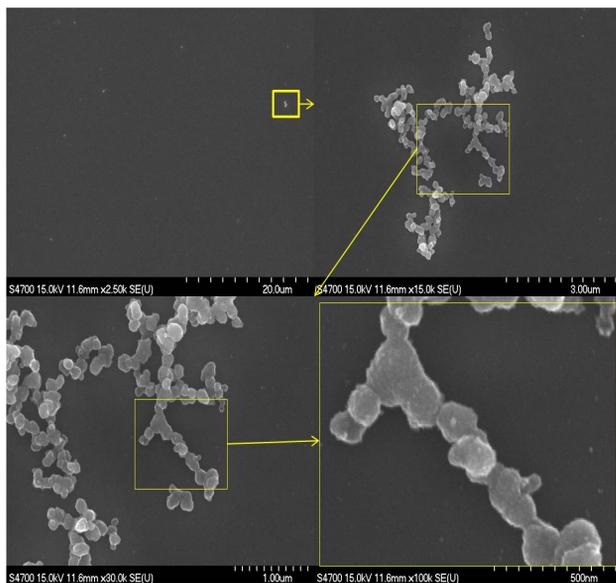


Figure 4: Granules made of Nb-O were observed on the samples surface. They reside on clear ambient surface, and their density is low.

Sample 4 Results

Sample 4 was located at the iris area. Three spots were surveyed by AES. Figure 5 is the spectrum from spot 1. It has an obvious sulphur peak (label in red). The atomic concentration ratio of Nb to S is close to 3:1. The spectra that were collected from other spots are not shown here. The S atomic compositions are different on different spots, and their S peak intensities are less than that on spot 1 (but larger than zero). AES sampling area is 2*2 μ m² on each spot. It suggests that S forms an atomic-thin layer on the outmost surface of the sample. The coverage is not uniform however.

An Argon ion beam was used to slightly sputter the surface. The beam current is 10nA, beam spot 27mm² and beam accelerating voltage 2kV. The sputtering rate (or depth) was not empirically calibrated, but it was evaluated theoretically that the profiling depth is smaller than 10 atomic layers. Before the sputtering (Figure 6), the S peak has an obvious profile (Nb/S ~3:1). After the sputtering, S peak intensity becomes much smaller (Nb/S ~8:1). Figure 7 is the ABS image on the same spot before and after sputtering. It seems that the sputtering cleared a surface oxide layer (thus reduced the charging effect).

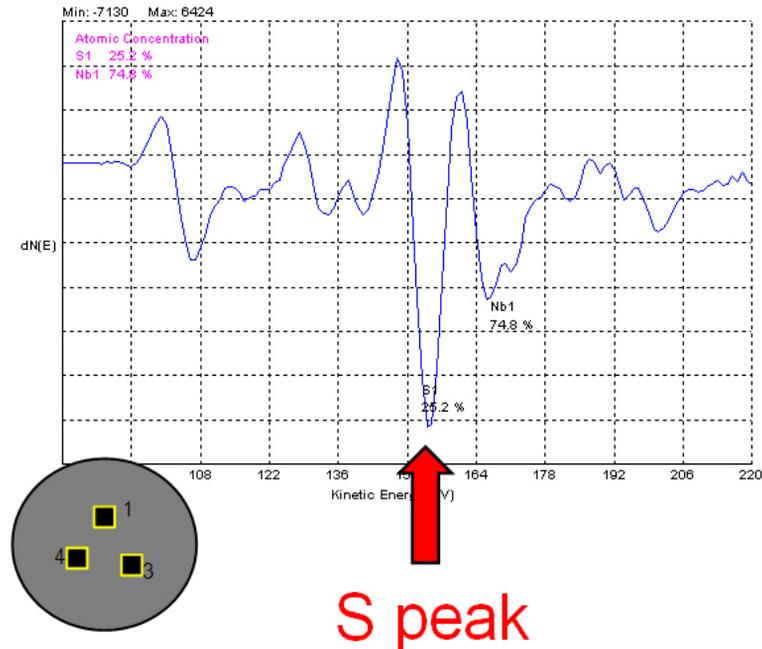


Figure 5: AES spectrum collected on spot1. The S peak is labelled in red. This spectrum shows the Nb:S atomic ratio is ~ 3:1.

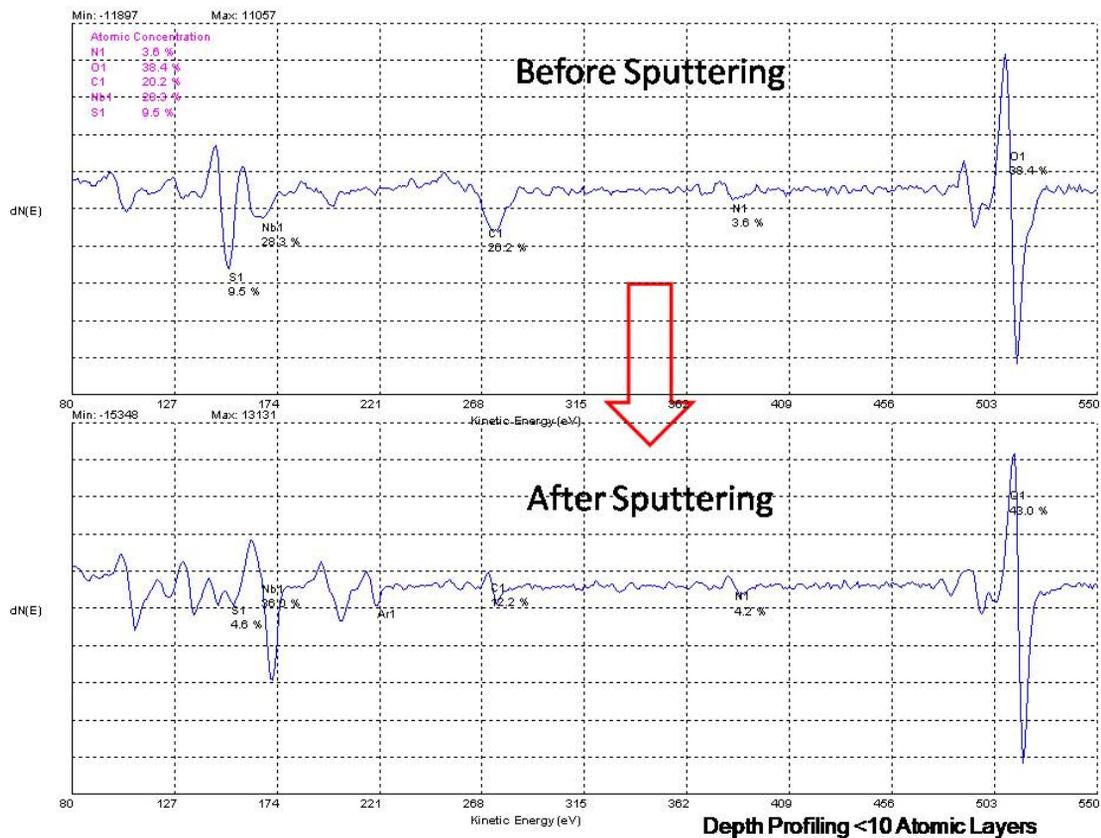


Figure 6: AES spectra of a spot before and after a slight sputtering. Fewer than 10 atomic layers were removed by the Ar⁺ beam. The S peak was greatly reduced after sputtering indicated that the coverage of S is ultra-thin.

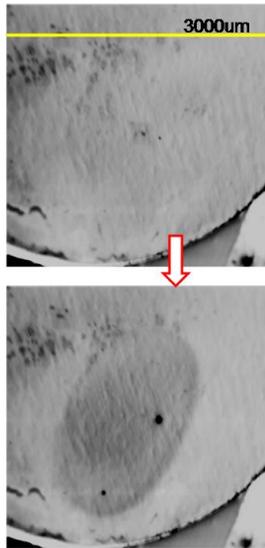


Figure 7: ABS images of the sputtered spot. It seems the Ar^+ beam cleaned the surface charging layer.

Sample 6 Results

Sample 6 was located on the beam pipe. Three spots were surveyed by AES (data not shown here). Similar to the testing results of sample 4, they are also covered non-uniformly by a thin layer of S. Various micro-granules were investigated by SEM/EDX, and the granules morphology is similar to that observed in sample 2 and sample 4. However, on one granule, EDX detected S (Figure 10). Figure 8 is this granule's SEM images. Like a generic one, it lays on a smooth surface stand-alone and it is far away from the other particles. The first EDX detection window (a yellow box) is shown at the upper-left corner. The EDX spectrum (Figure 9) shows only Nb and O (Nb:O = 1:5). The Nb/O ratio is much lower than a naturally oxidized Nb surface. Had S existed here, its characteristic x-ray energy should be 2.3keV. A vertical green line is labelled at that position (Fig 8b). It shows that no S was found. The profile of the primary Nb peak (2.0-2.4keV) is literally the same as that obtained from pure bulk Nb sample (the Nb fingerprint spectrum was not shown here). The "shoulder" and the "spike" on the green line's left side stem from an Nb peak. The second EDX detection window is shown at the bottom-right corner. The S peak at 2.3keV can be easily identified. Atomic percentage of S is about 8%. Considering the EDX profiling depth is 1-2 μm , the S concentration is significant.

On one area of sample 6, besides the omnipresent Nb granules, there exist crystal-like particles (see Figure 9a). Because of their sharp geometry (see Figure 9b), they might be potential electron field emitters. EDX survey found N, O, Fe, S, Nb on it (Figure 9c). The elemental ratio of N, O, Fe, and S is 18:65:11:6. Similar crystallites features have not yet been observed on other EP'ed samples. Nevertheless, we found rectangle-shape particles on another EP studies. In that study, it was speculated that the crystal-like particles are alien impurities caused by a

defective DI water filtering system. The source of formation of the "micro-flower" particles on sample 6 is unknown.

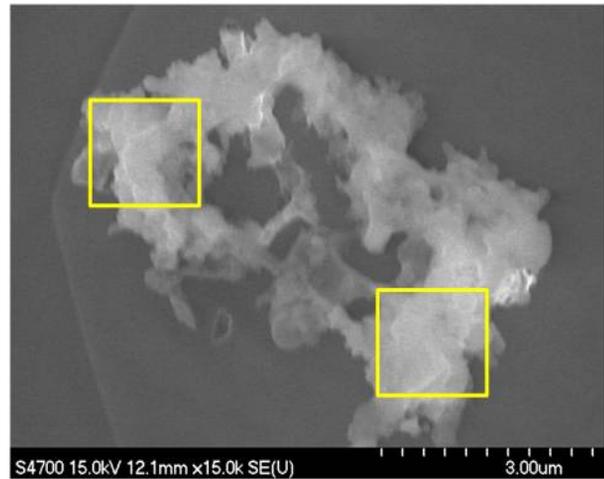


Figure 8: A sulphur-embedded granule observed on sample 6. S is enriched on one area but not all suggesting that the S coverage is not uniform.

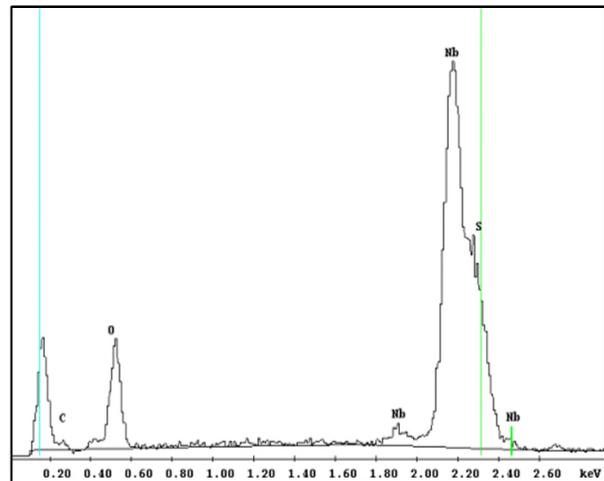


Figure 9: EDX spectrum collected from the upper-left window showing the granule only has Nb and O. O level is higher than a naturally formed Nb_2O_5 .

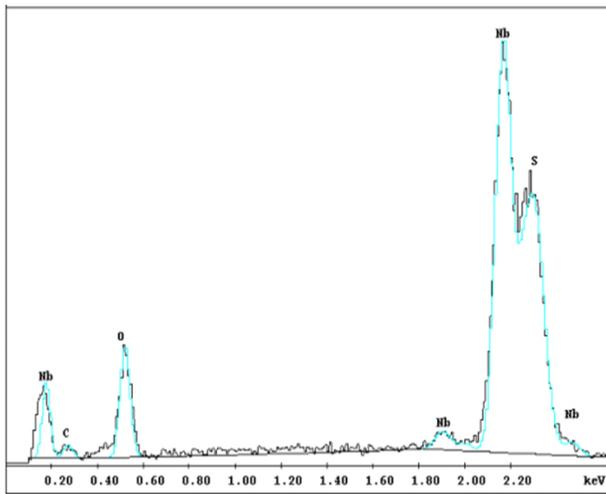


Figure 10: EDX spectrum collected from the bottom-right window. It shows a high concentration level of S (8 at %).

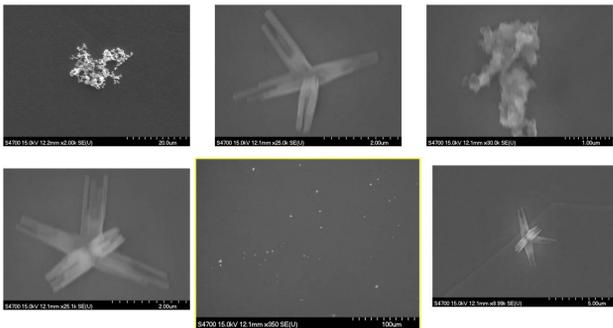


Figure 11: Nb-O granules and crystal-like particles are found on one area of sample 6 (center figure in row 2).

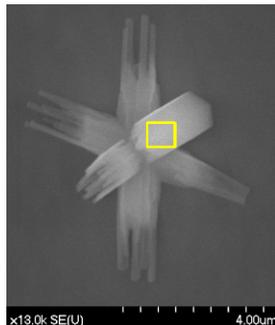


Figure 12: SEM micrograph of one typical crystal-like particle. A yellow box labels the area surveyed by EDX (see Figure 13).

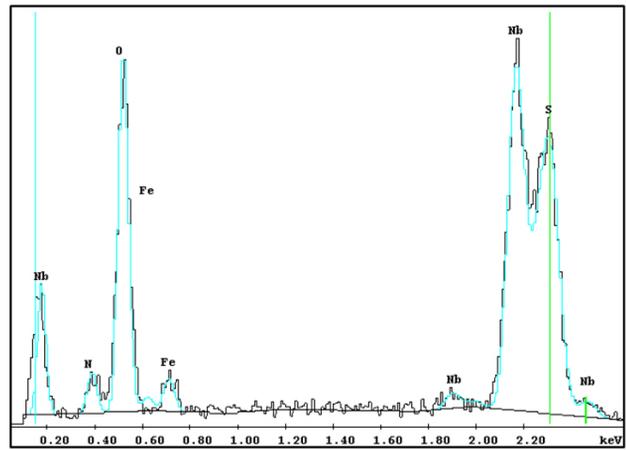


Figure 13: EDX spectrum collected from the yellow box (Figure 12). It contains S, Fe, N element besides Nb and O. The origin of Fe and N are unknown.

SUMMARY

Three samples, which were treated in a SRF single cell as a witness of EP process, have been surveyed by AES and SEM/EDX. Oxygen enriched Nb granules (like sintered powder) have been observed on all samples. Their crystal structure and formation mechanism are unknown. A few atomic layers of S were observed covering the Nb samples surface non-uniformly. Some areas of the micro-granules could be a place to harbour S (see Figure 8). Crystallite particles containing unexpected impurities were found on one samples.

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