Linear Collider Collaboration Tech Notes

SLAC EDX/Auger of Cornell Nb Breakdown Test Plate B2†

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[‡]Abstract

Residues located in the breakdown craters of a Nb cathode plate used for DC breakdown tests were successfully identified by energy-dispersive x-ray spectrometry. These residues were from deliberately seeded particles of nickel as well as adventitious silica debris. In addition, splashes of tantalum were found, apparently generated from the anode.

1 Introduction

At the SLAC Structure Breakdown Workshop last summer, Hasan Padamsee of Cornell University gave a very nice review of the current knowledge on breakdown phenomena in niobium (Nb) superconducting cavities. In particular, he pointed out that the breakdown-arc craters almost always have a material impurity associated with them and that the impurity residue, in the crater, is detectable by Auger electron spectroscopy (AES) and generally not by energy-dispersive x-ray spectrometry (EDX). The area immediately surrounding the crater is known as a “starburst” (SB), observable only in the secondary electron microscope (SEM) and is due to plasma-etching of the surface by pre-breakdown ionized gas activity. The SB is observable in the SEM because the plasma etches away the fluorine residue, from the HF-HNO₃ chemical etch process, left on the Nb surface. This results in an area (the SB) having a secondary electron image contrast different from the rest of the Nb surface.

To investigate the impurity breakdown-generating process under defined conditions, Cornell has created an archetype Nb “cavity” plate which is seeded with a known impurity, nickel (Ni), and subjected to DC fields capable of generating breakdowns. Again, these craters show that the seeded impurity residue, leftover after the breakdown, is detectable by AES and not by EDX. Hasan and his colleague, Gregory Werner, have graciously supplied one of their experimental plates to SLAC for examination with our in-house AES and EDX techniques. The plate was previously analyzed by a

contract lab, for Cornell, and Greg has provided photos and details about locations of SBs and analyses of them.

Examinations at SLAC have shown that most craters on copper do not have detectable residues (except for carbon) in them. A significant difference between copper (Cu) accelerator cells and Nb cavities is that there are only a few, easily definable, craters on Nb cavity surfaces. Many are single arcs because the first arc leads to an immediate quench of the superconducting state and no further damage ensues. Room temperature copper accelerator cells, on the other hand, suffer many hits in the same spot with hundreds of surrounding arcs of various sizes, making it difficult to even identify where the first arc took place. Under the most carefully controlled conditions, Lisa Laurent’s rf nose tests, the few arcs which have locatable causes are due to gas discharge at grain boundaries or melting and gassing of carbonaceous debris. Non-carbonaceous debris tends to be silicate or alumino-silicate, i.e., concrete dust.

The results on Nb and Cu, therefore, may not be inconsistent but due to a difference in operational parameters. To rationalize the two sets of results, we need to show that SLAC’s analytical capability for residue detection is of the same order of sensitivity as Cornell’s. Specifically:

- 1) Are the crater residues on the Cornell Nb plate detectable by SLAC’s EDX,
- 2) Can they also be detected by SLAC’s AES,
- 3) Can the SLAC analysis add new information to the Nb plate results, and
- 4) Why has SLAC not observed SB’s on Cu?

Unfortunately, the SLAC AES system’s SEM imaging capability was not functioning properly at the time of this work. As a result, of the four SB’s post-breakdown analyzed by Cornell, only SB 18’s crater could be located for AES analysis. The main emphasis, then, is on SLAC EDX identification of residues in all the SB’s for which Cornell provided photos.

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2 Experimental Details

Part of the B2 (in Cornell nomenclature) Nb plate is shown in a low-magnification SEM image in Figure 1.

Figure 1. Cornell Nb test plate B2, SLAC SEM. Shown are two of five raised test Pedestals.

Each mesa on B2 is assigned a “Pedestal” name, PD1, PD2, ..., and each starburst crater has the ID number of the previously-surveyed pre-breakdown Ni particle (P1, P2,...) that was responsible for the breakdown, SB1, SB2,....

The B2 plate was seeded with one-micron diameter nickel (Ni) spheres in methanol from a glass pipette. It is these particles (shown in Figure 2) which were generally the causes of breakdowns. Greg points out that the general carbon contamination measured on the plate is due to a combination of methanol and poor vacuum. After seeding, but before breakdown testing, particle locations were mapped in the Cornell SEM. A cluster of spheres was imaged in our SEM and is shown in Figure 2. Ni spheres almost always were clumped together, according to Greg, but it is unknown whether a breakdown was initiated by one sphere in the clump.

Figure 2. Cluster of one-micron diameter Ni seed particles, SLAC SEM. Left image shows Nb grain structure with cluster at center. Right-hand image is increased magnification of the cluster. EDX spectrum from small square window in right-hand image is shown at bottom.

AES, EDX, SEM and X-ray Photoelectron Spectroscopy (XPS) are briefly described in the Appendix. SLAC’s AES spectrometer is optimized for low-current primary-electron fluence, for the purpose of reducing surface modification effects (electron-induced gas adsorption/desorption and surface chemistry). Most commercial labs use high fluence for cost-effective, but potentially damaging, speedy analysis. Each technique has its place. Similarly, our EDX x-ray detector is optimized for the detection of low energy x-rays generated from low-Z (down to boron) materials. This importantly enhances carbon sensitivity, the most common surface contaminant. Most commercial labs detect higher energy x-rays, to enhance bulk sensitivity for the general purpose of providing the elemental composition of bulk, and not surface, material. Again there is a tradeoff in the choice of techniques.

The B2 plate was examined at SLAC by the least contaminating techniques first, AES and XPS, and then put into the SEM for imaging and EDX analysis. The documentation provided by Greg shows pictures of the SBs taken by Cornell SEM. We have scanned these photos and include them below for comparison with our results. Using the SEM, we were able to clearly image almost most of these SBs at SLAC. SBs are easily obscured by carbon contamination, as pointed out by Hasan and Greg. We were, however, able to locate the SB centers using Greg’s excellent SB grain boundary “map”, so the visual loss of the occasional SB did not preclude our analyses of its crater

Three SBs were examined with AES, to confirm that the SLAC low electron beam-exposure version of AES gives elemental detectability confirmation of the Cornell AES result. Most of our attention was focussed on examining the plate with EDX, to determine if we are capable of locating residues in the SB craters with this technique. This is goal is quite apropos for SLAC because of our routine use of EDX, which is much more rapid than AES, to characterize breakdowns on Cu.

3. Results

This kind of study involves pictures, lots of pictures. The format we use is to show images from Cornell's and SLAC's work, for direct comparison. Most commentary will be included in the Figure captions which are in bold type to facilitate reading. Then the results are summarized in the Discussion section.

Figures 3 and 4 have been borrowed from Hasan's talk, as a summary of the breakdown process on Nb (and, presumably, Cu). Of particular interest is the formation of the SB by the pre-breakdown plasma. Cornell AES maps show fluorine (F) present on the surface but missing from the SB and crater arc location, where it is burned off by the plasma activity.

Figure 3. The schematic progression, from top to bottom, of the breakdown process on Nb cavity surfaces. The charged gas-ion cloud ("plasma") is believed responsible for the starburst patterns.

Figure 4. Frequency of impurity occurrences in SB craters in Cornell Nb cavity material.

Starting with Pedestal 2, Figure 5 is the Cornell SEM image of SB 37. It's possible that this feature is actually two SBs because both P31 and P32 residues are within. This is a classic Cornell SB: thread-like filaments, dark appearance (low secondary electron yield) and particle crater near the center.

Figure 5a. Starburst 37, Pedestal 2, Cornell SEM. Included within SB 37 are former Ni particles P31 and P32. Rectangular bright particle is carbonaceous debris.

Figure 5b. Starburst 37, Pedestal 2, SLAC SEM. The faint rectangular boxes on the image right are the result of changes to the surface fluorine layer by the SEM electron beam, causing a change to the secondary electron contrast.

Figure 5c. Core of SB 37, original P32 location, SLAC SEM. We analyzed all craters in the left image using EDX. Most show a Ni signal. The EDX spectrum at the Figure bottom is from the superposed detector acceptance window on the right-hand image. In addition to Ni, elements seen are oxygen (O), aluminum (Al), and carbon (C). The C is located on the shoulder of the amplifier noise peak at the extreme left of the EDX spectrum. Peak at far right is due to the energy sum of two Nb x-rays entering the detector

simultaneously. All other unlabeled lines are from Nb. F, if present, is masked by the Ni peak. Nitrogen (N), if present, is masked by the lowest energy Nb peak.

Figure 5d. Crater core of SB 37, at original P32 location. SLAC AES. Heavy C apparently obscures the Ni seen in Figure 5b.

Figure 5e. Just above crater but inside SB 37, SLAC AES. Some F and N left from etchants, and a small trace of Ni.

Figure 5f. Just outside SB 37, SLAC AES. Less C, more F.

Figure 5g. Pedestal 2, SLAC wide area XPS. F is generally present, but N is obscured by Nb peaks.

Figure 6b. SB 13, SLAC SEM. Traces of C, O, Al. EDX area is small white box in right image.

Figure 6a. SB 13, Pedestal 3, Cornell SEM. Residue at center was AES-identified as probable silicon (Si) by Cornell, possibly from the particle-dispensing glass pipette. There was no Ni particle originally at this location.

Figure 7a. SB 14, Pedestal 3, Cornell SEM. The original pre-breakdown particle was AES-identified as Si, with a trace of Al and sodium (Na).

Figure 7b. SB 14, SLAC SEM. EDX shows very strong tantalum (Ta), trace of C, O. All craters and hillocks in left image show a similar EDX spectrum. DC breakdown anode was Ta-rich. Hillocks are likely Ta splashes from the anode. Si EDX peak, if present, is masked by the Ta peak.

Figure 8b. SB 38, SLAC SEM. Original Ni particle (P17) location in right image shows C, O, Al, but no Ni.

Figure 8a. SB 38, Pedestal 3, Cornell SEM, see below for original Ni particle (P17) location.

Figure 8c. Pedestal 3, SLAC SEM. The surface roughness appears larger than the one-micron Ni seed particles.

Figure 9a. SB 8 (lower) and 9 (upper), Pedestal 4, Cornell SEM. Ni (no P# assigned) found before and after breakdown in both, by Cornell AES.

Figure 9c. SB 9, SLAC SEM. EDX shows Ni in all three craters and area between them.

Figure 9b. SB 8, SLAC SEM. C, O, Ni, Al. Hillock at One o'clock is Ta-rich.

Figure 10a. SB 18, Pedestal 4, Cornell SEM. Cornell AES mapping shows Si in crater at SB center. The original particle here was Si.

Figure 10b. SB 18, Pedestal 4, SLAC SEM.

Figure 10c. SB 18, SLAC SEM. EDX shows Si barely above background. Usual C and O present.

Figure 10d. Crater center of SB 18, SLAC AES. No Si (but Ta and Al have nearly the same peak location as Si), but Al, N, F, and Ta detected. N and F shouldn't be here but maybe were exposed by arc? No Ta in Cornell AES map of crater.

Figure 10e. Above center but still within SB 18, SLAC AES. Ta present in Cornell AES map of SB.

Figure 10f. Outside, but next to, SB 18, SLAC AES. F is back, as it should be! Ta is still present but at much lower level.

Figure 10g. XPS survey of Pedestal 4.

Figure 11a. SB 22, Pedestal 4, Cornell SEM. SB obscured by post-breakdown testing but particle was originally Ni (P1).

Figure 11b. SB 22, SLAC SEM. Ni, C, O, possibly Al found.

Figure 11c. To upper right of SB 22 crater, SLAC SEM. Very clear Ta splash from anode.

Figure 12a. SB 41, Pedestal 4, Cornell SEM. Crater to right of center was originally Ni (P8). Obviously not the classic SB shape.

Figure 13a. SB 66, Pedestal 4, Cornell SEM. Was Ni (no P# assigned) before breakdown.

Figure 12b. SB 41, SLAC SEM. Again Ni, C, O.

Figure 13b. SB 66, SLAC SEM. Strongest Ni signal from is black spot on crater rim.

Figure 13c. Crater center of SB 66, SLAC AES.

Figure 13f. Survey of Pedestal 4, SLAC XPS.

Figure 13d. Above crater but inside SB 66, SLAC AES.

Figure 13e. Just outside SB 66, SLAC AES.

4. Discussion

First is the SEM image identification of SB's. Of the ten SB's imaged and identified by Greg, the accompanying Cornell photographs clearly showed 37, 13, 14, 8, 9, 22, 18, and 66. SB 38, and 41 were not clearly imaged in the photos. SLAC successfully imaged 37, 9, 22, 18, 41 and 66.

Post-breakdown residues identified by Cornell AES, and SLAC AES and EDX are summarized in Table I. Si identification is difficult with AES because of interference with Ta and Al peaks at low energy and Ta and Nb peaks at high energy. SLAC EDX agreed with Cornell AES on 3 out of 4 post-breakdown identifications.

SB #	Pre-Test EDX	Post-Test EDX	Post-Test AES	SLAC EDX	SLAC AES
8	Ni	NF	Ni,Ta	Al	
9	Ni	NF	Ni,Ta	Ni,Ta	
13	Si	NF	Na,Si?,Ta?	Si	
14	Si	NF		Ta	
18	Si,Al	NF	Si,Na,Ta	Si	Ta,Al
22	Ni	?		Ni	
37	Ni	Ni		Ni	NF
38	Ni	Ta?		NF	
41	Ni	NF		Ni	
65	Ni,Ta	Ni		Ni	
66	Ni	Ni		Ni	Ni

Table I. Identification of residues on Cornell Nb Plate B2. "Pre-" refers to pre-breakdown analyses by Cornell. "Post-" is after breakdown testing. NF – None Found. Blank box – not tested.

Comparing pre-breakdown identifications, Cornell EDX found 8 Ni and 3 Si particles. SLAC EDX found residues of Ni in 6 and the residue of Si in 2.

Also we found a frequent occurrence of Ta splashes on the cathode. A Cornell AES map of SB 18 showed a rather non-localized distribution of Ta around the crater but our SEM and EDX found hillocks of Ta to be rather common on the cathode plate.

A general observation is the occurrence of peak overlap interferences: Si/Ta and F/Ni in EDX, Si/Al/Ta in AES, and Ta/Nb in XPS. Multiple techniques are sometimes essential for unambiguous identification.

5. Conclusion

- 1) There is identifiable material in the Cornell SBs, whether deliberately seeded (Ni) or adventitious (Si and Ta).
- 2) EDX is routinely effective at locating residues on this particular plate. As Greg points out, EDX might not detect the residues from smaller particles than one-micron Ni.
- 3) AES has good sensitivity for light elements such as C, O, F. EDX is best at metals and higher Z.
- 4) C contamination is a major impediment to efficient AES identification but only a minor annoyance in EDX.

Finally, where are the SB's on SLAC Cu breakdown components? The Cornell picture of SB formation, which identifies F removal as the source of SEM image contrast, also explains why we have not observed them on SLAC Cu surfaces: post-etch thermal processing (such as brazing in hydrogen or vacuum-firing) at SLAC removes trace chemical residues. Our Cu surfaces generally have only very thin native oxide and small amounts of carbon on them and, so, there is little surface contamination for a plasma to strip off and provide secondary electron imaging contrast.

Perhaps the most spectacular is saved for last: a Ni particle, molten., and about to arc.

Figure 14. Pedestal 4, lower right quadrant. Assigned SB 65, Ni particle. This is a site with pre-arc plasma activity, but has not yet arc-ed. Only a few of these have been observed (5% or so of all SBs) by Cornell.

6. Acknowledgement

H. Padamsee and G. Werner of Cornell University have provided the sample plate which is the subject of this document as well as extensive results concerning their study of it. We thank them for their assistance.

7. Appendix

Auger Electron Spectroscopy (AES)

Auger Electron Spectroscopy measures the elemental composition of the top three nanometers of surface. Primary electrons stimulate the ejection of secondary electrons ("Augers") whose kinetic energy is measured by an electrostatic electron energy analyzer. Auger peak heights are related to element concentration but difficult to quantify. This technique has high sensitivity for low atomic number elements as well as 2-dimensional imaging capability.

Energy-Dispersive X-Ray Analysis (EDX)

Energy-Dispersive X-Ray Analysis provides an elemental concentration analysis of the outer several microns of sample surface. High-energy primary electrons generate x-rays in the sample, whose energy is determined by the atomic shell from which they were ejected. The x-ray energy is measured by a silicon-crystal detector and displayed as a series of peaks whose heights are related to elemental concentration.

Scanning Electron Microscopy (SEM)

Breakdown-Damaged Copper Electrode

Scanning Electron Microscopy images surfaces at very high resolution (10 nanometers, depending on atomic number and surface finish). Images are made by scanning a high-energy primary electron beam onto the sample and collecting the low-energy secondary electrons, which are very surface sensitive. Images can be made more sensitive to sub-surface stress by selectively collecting only elastically-scattered ("backscatter mode") primary electrons.

X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (sometimes called "ESCA") measures the chemical composition of the top five nanometers of surface. Soft x-rays stimulate the ejection of photoelectrons whose kinetic energy is measured by an electrostatic electron energy analyzer. Small changes to the energy are caused by chemically-shifted valence states of the atoms from which the electrons are ejected; thus, the measurement provides chemical information about the sample surface.