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Linear Collider Collaboration Tech Notes

High-Pressure Water-Rinse Cleaning of Copper

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Copper, niobium and stainless steel surfaces were cleaned by high-pressure water-rinsing spray. Surface chemical and topographic analyses show that the HPWR process is neither a contaminating nor a significantly eroding process.

1 Introduction

Cornell University, CERN, KEK and Jefferson Lab use high pressure water rinsing (HPWR) in preparing superconducting cavities for ring installation. Work in those labs show that HPWR is useful in eliminating particles which can lead to high field breakdown during cavity operation. Although, at this date, particles alone do not appear to be the source of breakdowns in NLCTA test accelerating structures, it is useful to evaluate HPWR as a final cleaning step on the assembled structures, where the overall structure size and complexity prevents the use of other types of cleaning. Something resembling a spray-wand could be "snaked" down the completed structure, followed by filtered nitrogen gas drying.

To test this possibility, copper (Cu) coupons were cleaned by Greg Werner at Cornell's Newman Lab using HPWR after prior extensive surface analysis and characterization at SLAC, consisting of weighing by microgram balance, measuring for contamination with x-ray photoelectron spectroscopy (XPS), measuring surface topography by atomic force microscopy (AFM) and assessing surface particle density by secondary electron microscopy (SEM) and energy-dispersive x-ray spectrometry (EDX). The measurements were repeated after return. The principals of these techniques are briefly described in the Appendix. For comparison, stainless steel (S/S) and niobium (Nb) coupons were also tested. Nb sheet for the coupons was kindly provided by H. Padamsee, Cornell.

The surface finish was deliberately left "as-machined", rather than polished, to follow the surface roughness, through rinsing, in the event that the high pressure water flow caused material erosion. Erosion is of concern because material loss in the accelerating structure iris apertures would lead to a resonant frequency tune shift.

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2 Experimental Details

Test coupons (Figure 1) were produced from class 1 OFE copper, 304 stainless steel and niobium. All coupons were machined with conventional HSS tooling, and engraved on the backside with "134" and "135" for Cu, "S-1" for S/S and "N-1" for Nb. They were subsequently cleaned chemically in the SLAC Plating Shop, and stored in clean polypropylene wafer boxes. Care was taken to preserve the state of the coupon surface from that point on. The SLAC chemical cleaning recipes were C01A for Cu, C02A for S/S and C54A for Nb.

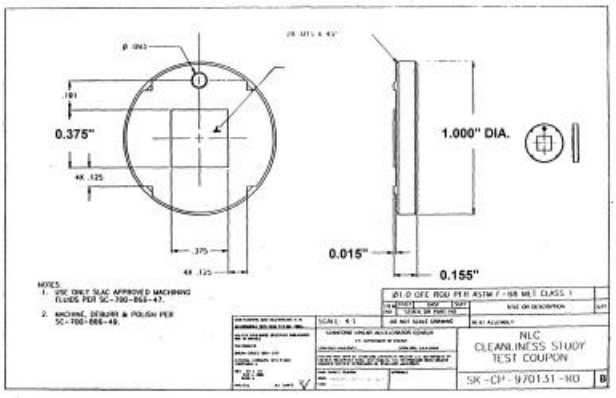


Figure 1. NLC cleanliness study test coupon. The central 0.375" square "mesa" was the area of study.

Analyses were performed in the sequence "least-surface-modifying first" of weighing, XPS, AFM, SEM.

Each sample was HPW-rinsed in a raster-scan pattern. The nozzle, containing four water jets, turned at one rotation/45 seconds as it descended 2 cm in 5 minutes toward each coupon. The coupon was covered with a mask that exposed only the central "mesa" to the water rinse. The coupons were dried in the clean room face-up for 1.5-2.5 hours and were then re-packaged in the wafer carriers, and sealed in a bag filled with filtered argon. Between measurements at SLAC, the coupons were stored in their individual wafer containers in a dry-nitrogen flushed dessicator.

3. Results

Weighing:

The material thickness loss, t, is given by :

$$t = mass / density \times area$$

The densities are roughly the same for Cu, Nb and S/S, with the thickness per μgram, on the mesa, about forty atomic layers or 10 nmeters of material.

The weight gain/loss as a result of the water rinse is:

134 – 4 mgram loss
135 – 4 mgram gain
S-1 - 37 mgram gain
N-1 - 2 mgram gain

The accuracy is about ± 30 μgram, so there appears to be no measureable weight loss/gain as a result of HPWR.

X-Ray Photoelectron Spectroscopy:

After weighing, the coupons were loaded into the UHV XPS unit. XPS is non-destructive and the least-contaminating technique for measuring surface composition, particularly contamination layers. Figure 2 is a spectrum of Cu coupon 135, prior to HPWR processing.

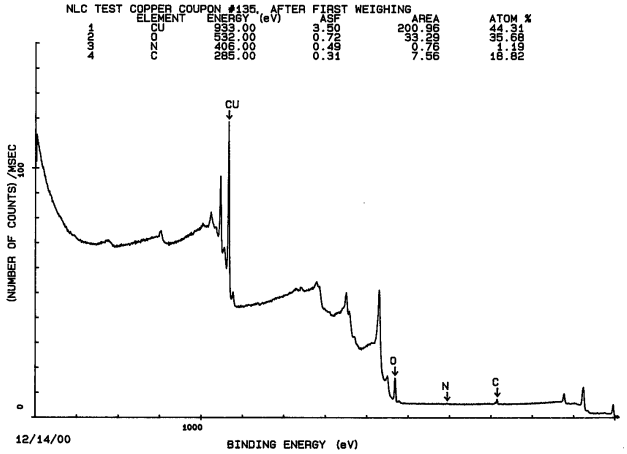


Figure 2. XPS spectrum of Cu coupon #135, prior to HPWR. Atom% values refer to concentration of each element present in the information layer (~5nm), normalized to 100%.

Basically, these pre-HPWR spectra show that the coupon surfaces are UHV-quality clean from the SLAC Plating Shop. The coupon results for each element are summarized in Table 1, both for pre- and post-HPWR. The changes observed are rather small. The Cu coupons have gained a bit of C and lost some O. The C gain is consistent with the reactivity of Cu, compared to S/S.

Oxygen-free water strips small amounts of oxide from some surfaces. But, in general terms, not much has happened to the coupons as a result of the rinsing.

	Cu	Nb	Fe	Cr	Mn	Ni	O	C
134	46						36	18
135	44						36	20
N-1		24					55	21
S-1			15	16	3	3	43	20

Table 1. XPS atomic percentages of elements on Cu, Nb and stainless steel coupons, prior to HPWR.

	Cu	Nb	Fe	Cr	Mn	Ni	O	C
134	46						31	23
135	48						31	21
N-1		22					58	20
S-1			15	14	2	2	45	22

Table 2. XPS atomic percentages of elements on Cu, Nb and stainless steel coupons, after HPWR.

Atomic Force Microscopy:

It was anticipated that the HPWR process might remove native material from the coupons, particularly on the rather soft Cu, so the surface finish was measured with an atomic force microscope. The scan area is rather small, about 70 μ x 55 μ, but a representative area was chosen for scanning using an optical microscope for the setup. The scanning tip is silicon, as shown in Figure 3. The tip was imaged separately in the electron microscope to ensure the it did not wear and bias the results. The same tip was used for all the coupons in this study.

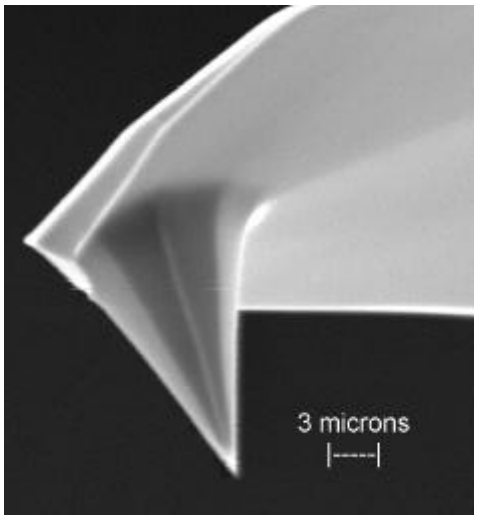


Figure 3. New silicon AFM tip, used for coupons.

Figures 4-6 are 3-dimensional AFM images of the surface topography of three of the coupons. Tables 3 and 4 give the vital statistics of average roughness, R_a, and maximum peak-to-peak height of the coupons' surfaces,

R_{p-p}, before and after rinsing. The exactly same areas on the coupons were probably not scanned before and after HPWR, but were reasonably close.

The AFM images themselves, before and after HPWR, looked similar. The average roughness in the two cases is very close, rising slightly for Cu and dropping slightly for Nb and S/S. For Nb and S/S, the peak-to-peak roughness also drops, suggesting that the improving smoothness came at the cost of exposed machining ridge-tops. The Cu result is a wash – one has higher peak-to-peak, the other lower. The Cu surface is more open and, consequently, more exposed to erosion in valleys as well as peaktops. But the overall change, due to HPWR, is very small for all coupons and on the order of a few tenths of a micron average roughness – consistent with no measurable change in the weights.

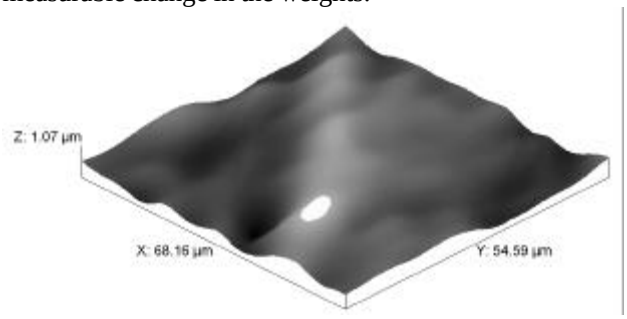


Figure 4. AFM image, Cu coupon 135, before HPWR.

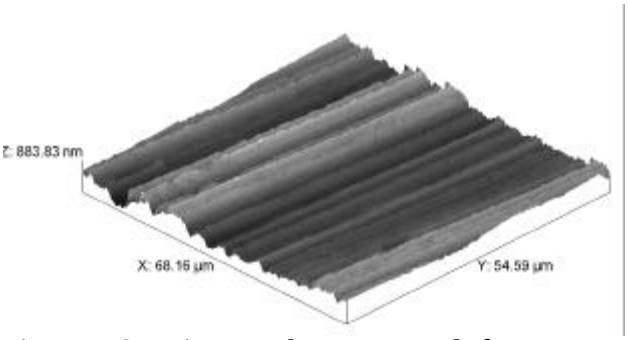


Figure 5. AFM i mage, Nb coupon N-1, before HPWR.

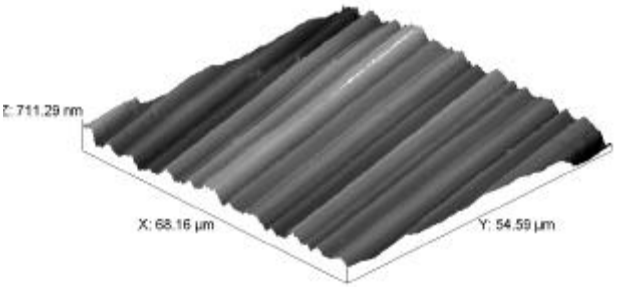


Figure 6. AFM image, S/S coupon S-1, before HPWR.

	Cu134	Cu135	N-1	S-1
R_a	0.07	0.15	0.12	0.09
R_{p-p}	0.54	1.07	0.98	0.95

Table 3. Average roughness factors from AFM, before HPWR. Values are in microns.

	Cu134	Cu135	N-1	S-1
R_a	0.10	0.17	0.11	0.07
R_{p-p}	0.73	0.97	0.81	0.48

Table 4. Average roughness factors from AFM, after HPWR. Values are in microns.

Particle Searches:

Finally, the SEM was used to look for residual particles on the coupons. HPWR removal of particles was not the focus of this study. A proper search requires smooth surfaces for the automated particle-seaching software to distinguish particles from background. Such a search is based on backscattered elastic electron signal contrast and brightness levels – virtually impossible on machined surfaces. The focus of this study was to look for signs of surface erosion and it was thought that detecting such erosion would be easiest with a rougher, rather than smoother, surface. The Cu coupons, although not smooth, had a rather featureless surface due to the lack of machining lines. They (134 and 135) were searched with the automated software. The Nb and S/S coupons were highly featured, and their search results could not be unambiguously interpreted. Cu 134 and 135 results are presented below.

Searches for particles >1 µ diameter were done by rejecting found-particles for which the EDX Cu signal was >97%. The assumption is that any non-Cu particle will have >3% of the total EDX signal. The purpose of this construct is to avoid counting, as particles, surface features of native Cu. No attempt was made to find and correlate individual particles found before and after HPRW. The search results were separated for predominant particle content, namely, dust/concrete constituents (Class A) and, everything else.

Class A: Ca or Al or Si or Mg or O
Class B: Other

Cu 134 Statistics

	A	B
Before HPWR	**47**	**33**
After HPWR	**37**	**22**

Cu 135 Statistics

	A	B
Before HPWR	**151**	**38**
After HPWR	**150**	**36**

Result: One reduced, one no change.

5. Conclusion

The primary purpose of this first test with HPWR was to look for signs of water erosion and contamination. Five minutes of rinsing removed a few tenths of a micron of surface at most. Contamination-wise, there is no significant change. Further work in that area requires the use of carefully-contaminated samples of known surface composition to test the ability of HPWR to remove the "dirt".

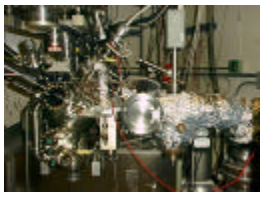
Looking at particle removal on the Cu coupons, it appears that there may be some effect on >1μ diameter particles, but further work on smoother surfaces is necessary to establish firm numbers. Rounding off the total results of the measurements suggests that HPWR is benign and may have particle-removal benefits.

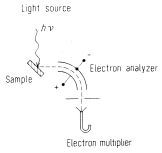
6. Acknowledgement

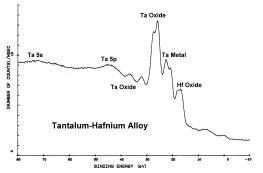
The authors would like to thank Greg Werner and Hasan Padamsee for providing niobium material and HPWR facilities for this study.

7. Appendix

X-Ray Photoelectron Spectroscopy (XPS)

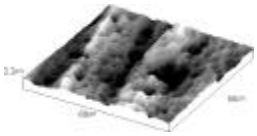




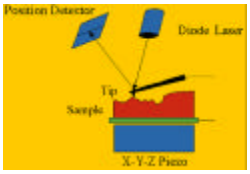


X-Ray Photoelectron Spectroscopy (sometimes called "ESCA") measures the chemical composition of the top five nanometers of surface. Soft x-rays stimulate the ejection of photoelectrons whose kinetic energy is measured by an electrostatic electron energy analyzer. Small changes to the energy are caused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

Atomic Force Microscopy (AFM)

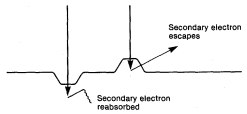


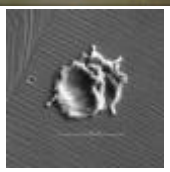
Extruded Aluminum Alloy
Beam Chamber Material



Atomic Force Microscopy is one of a large group of scanning probe microscopies, of which the Scanning Tunneling Microscope was the first and most famous. The AFM is more versatile, however, in that the surface topography of non-electrically conductive samples can be imaged to very high resolution (typically ten nanometers), even in air. Small movements of the sample, during the scanning process, are accomplished by the use of precision piezoelectric manipulators ("inchworms").

Scanning Electron Microscopy (SEM)

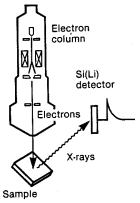


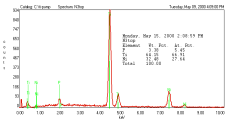


Breakdown-Damaged
Copper Electrode

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.

Energy-Dispersive X-Ray Analysis (EDX)





EDX Spectrum

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.