

# Surface Contaminants of Niobium

by Dan Kapner

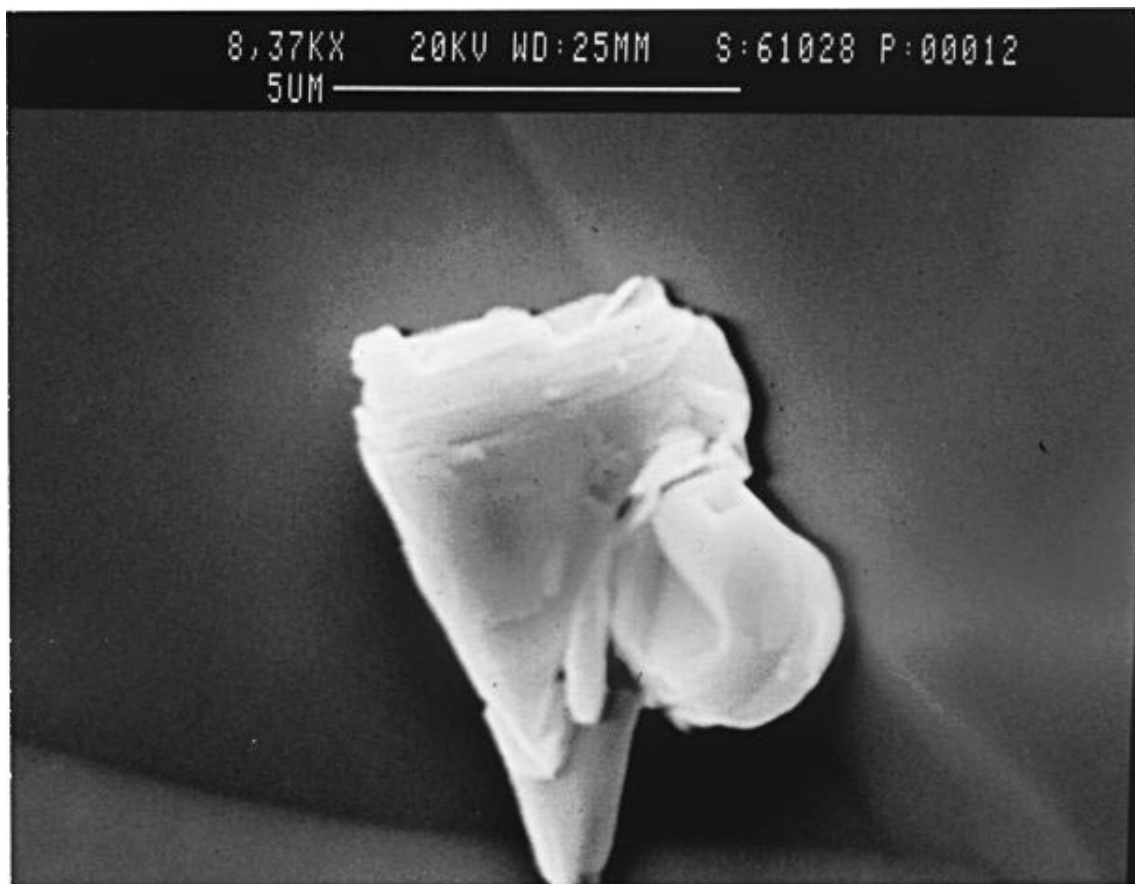


Figure 1 : A particle made of Tellurium and Copper found on coupon B2-68, probably collected during extended drying.

The purpose of this research was to recognize surface contaminants, such as shown in figure 1, and their origins on niobium

sample coupons after putting them through various stages of the processes that are applied to niobium RF cavities. The coupons are one inch diameter circles punched out of one sixteenth inch niobium sheets. These sheets come covered in a protective pink plastic coating. The coupons are punched out of the sheet with a pneumatic punch. The plastic coating is then removed and a hole of approximately one eighth inch diameter, from which the coupon is hung with Teflon coated wire, is made near the edge with a manual punch. The number of the coupon is then engraved in the back. To check the coupons for contamination, a certain area of them is scanned using a Scanning Electron Microscope. The elemental compositions of particles are determined using X-ray spectroscopy(EDX).

Coupons R1 and R2 are made of Russian niobium RRR 500, all other samples in this study were taken from Teledyne Wah Chang RRR 250 #167v.

The main cleaning agent used is BCP, i.e. 1:1:2 nitric, fluoric, and phosphoric acids. When etching, we supply an excess of BCP and stir the coupons around approximately every fifteen seconds to dislodge any buildup of dissolved materials around it. Initially, coupons were etched in 1:1:2 BCP by dropping them into the acid and then removing them with Teflon tongs. These samples had an average of about 150 particles per square millimeter. Most particles were between .5 and 2 micrometers. There were far too many particles to analyze any significant portion, so we changed the procedure so that we used a stainless steel ladle to lift the sample from the back, not touching the surface we intended to analyze. The coupons removed with the ladle were Coupons 1 & 2.

Coupons 1 and 2 were etched in BCP, scooped out of the acid with a stainless steel ladle under the coupon, rinsed briefly and transferred to the ultra-clean room where they dried face up on a clean wipe. Once dry, the coupons were moved into an aluminum sample holder, still in the ultra-clean room, covered with a Teflon plate and loaded into the microscope. The Teflon plate was removed once the microscope was under vacuum. Particles labeled as “not checked” did not provide a good spectrum for analysis, usually because of their extremely small size. The samples were recessed one eighth of an inch below the surface of the sample holder so that the Teflon would not touch them.

**Table 1: Contaminants on Coupon 1**

Coupon 1	25 square mm	density(per mm <sup>2</sup> )
total particles:	39	1.56
Titanium	12	0.48

Aluminum	5	0.2
not checked	14	0.56
Fe/Cr/Ni	8	0.32

**Table 2 : Contaminants on Coupon 2**

Coupon 2	25 square mm	density(per mm <sup>2</sup> )
total particles:	46	1.84
Titanium	19	0.76
Aluminum	6	0.24
not checked	14	0.56
Fe/Cr/Ni	7	0.28

After these two coupons were tested, we began to etch samples in sulfuric acid and water overnight - a process that the RF cavities are put through as well to remove iron. When the coupons are etched in sulfuric acid, they are dangled into a bucket where they are covered with de ionized water. Sulfuric acid is then added until the temperature of the solution reaches about 80 degrees centigrade. I usually let the solution cool down a few times and added more acid until it was about a 1:3 ratio of acid to water. After this initial sulfuric etch, the coupons were prepared and treated in the same manner as described. With the intent to minimize the contact of the samples with any other surface or materials, we also began to use a hanging apparatus consisting of Teflon rods, from which Teflon coated wires were hung (figure 11). These wires were threaded through the one eighth inch holes in the coupons. The coupons remained on this hanging apparatus during etching, rinsing and drying. During rinsing, the coupons are removed from the acid and placed into a bucket of de-ionized water. This bucket is moved carefully from the chemical room to the clean room, where de-ionized water is run through the bucket for half an hour to an hour. The bucket is then moved into the class 100 clean room where the coupons are removed to dry.

## The Titanium Problem

Coupon 3 was tested before we began using an overnight sulfuric etch. After we began this procedure, Coupon 3 was etched with sulfuric acid and treated with the same procedure as the other samples.

**Table 3 : Contaminants on Coupon 3. I**

Coupon 3	12 sq mm	density(per mm <sup>2</sup> )
total particles	45	3.75
Titanium	27	2.25
Aluminum	8	0.67

Silicon	1	0.08
Fe/Cr/Ni	1	0.08
not checked	8	0.67

There seemed to be an increasing density of particles each time the microscope was turned on. A second scan of the sample above produced these results

**Table 4 : Contaminants on Coupon 3. II**

Coupon 3	5 sq mm	density(per mm <sup>2</sup> )
total particles	201	40.2
titanium	141	28.2
aluminum	22	4.4
silicon	2	0.4
Fe/Cr/Ni	1	0.2
not checked	35	7

We suspected that something in the microscope's column was the source of these new particles. We took a new sample and scanned a .5 square millimeter area and found 12 particles. After adjusting the aperture on the microscope and then re-scanning the area, we found 23 particles. Repeating the same procedure, we found 32 particles. The sample was left overnight under the electron gun and the next day, the same area was found to contain 41 particles. I concluded that the SEM was the source of these particles. The majority of them were titanium. I called LEO, the company who services the microscope, and they claimed that there was no source of titanium in the microscope unless it contained an ion pump which is used in conjunction with a lanthanum hexaboride filament. This particular microscope does not have such a filament, but apparently, in its past it has, and there was still an old ion trap inside the microscope. Eventually a LEO representative cleaned the SEM and removed the ion trap. The titanium concentration decreased at first, but titanium continued to appear.

To prevent the titanium from contaminating the surfaces, I devised an apparatus that allowed the sample to remain covered while not being scanned. The apparatus consists of a Teflon bracket that slides onto two studs coming out of the SEM door. A Teflon cover that fits on top of the sample holder can be removed by maneuvering the stage underneath the bracket and lowering it until the bracket catches the cover. The samples can then be brought forward and scanned and then recovered while not being examined (figure 10). All Teflon parts were rinsed to remove metallic contaminants in BCP and then cleaned in an ultrasound in methanol.

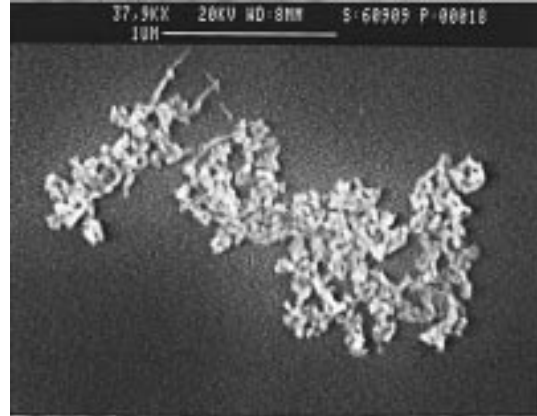
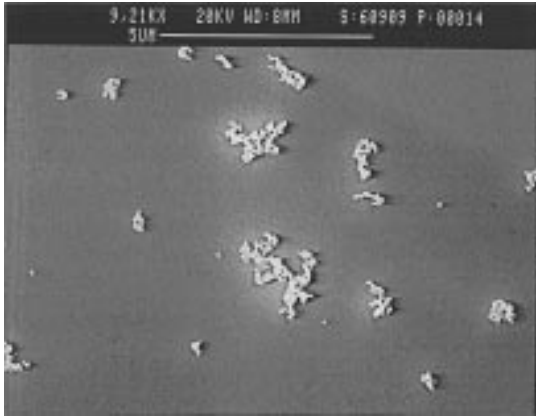


Figure 2 : Hafnium contaminants found on coupon A1-39. Hafnium contaminants were found after short and long etchings of the Teledyne niobium.

## Light Etching

Coupons A1-A6, from the 167v sheet, were prepared, washed and then etched in sulfuric acid overnight. All six were etched for four minutes in BCP. A1 was rinsed for one hour in de-ionized water and then scanned. Unknown particles are those that provided no spectrum upon analysis, indicating that they are either niobium particles or too small to obtain a good spectrum.

**Table 5 : Contaminants on Coupon A1**

Coupon A1	2.5 sq mm	densities(per mm <sup>2</sup> )	
total particles	50	20	
Aluminum	26	10.4	
Silicon	15	6	
Hafnium	4	1.6	
Tungsten	1	0.4	
Fe	1	0.4	
unknown	3	1.2	

Titanium particles were omitted from this table and from all proceeding tables.

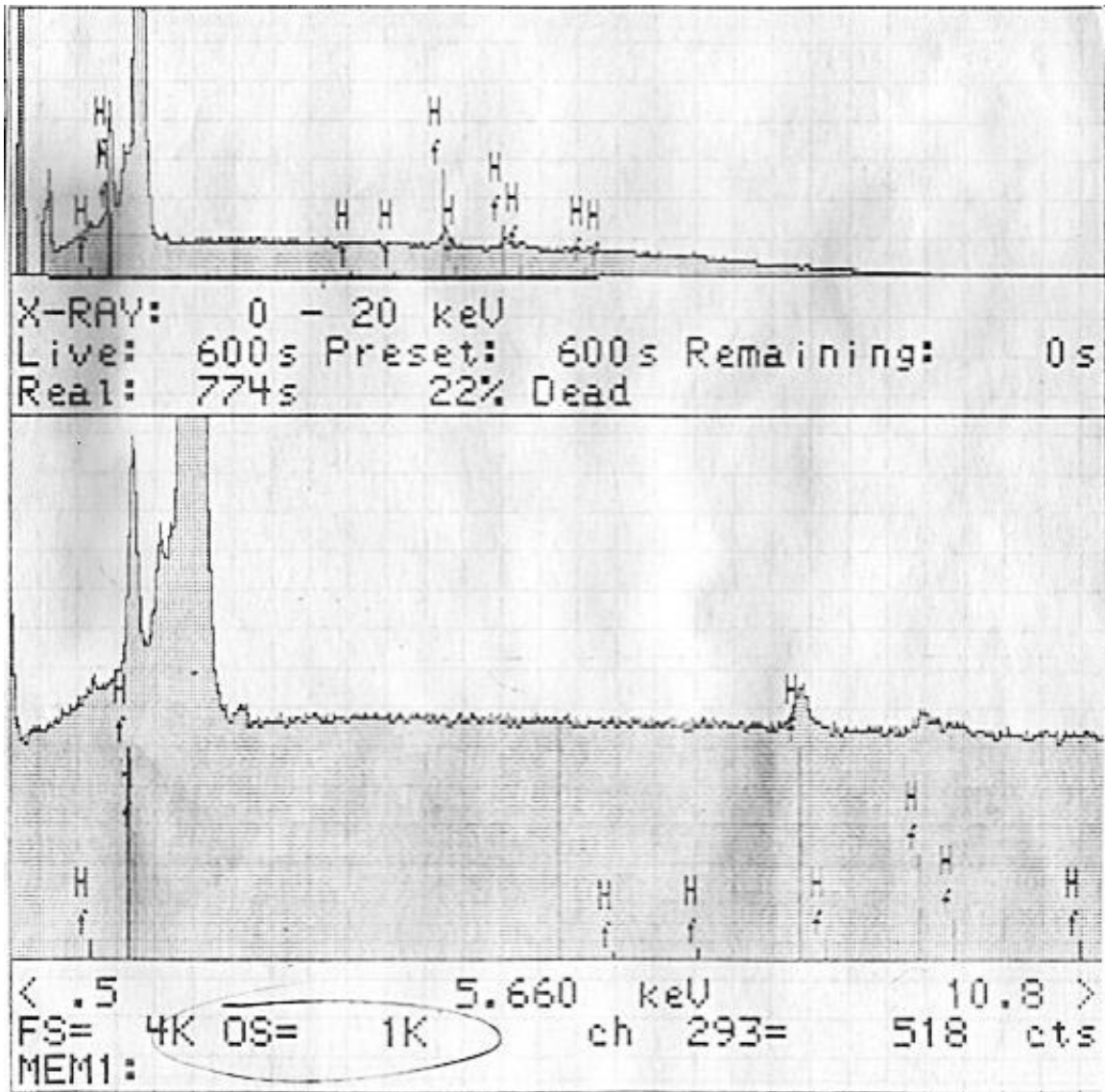


Figure 3 : An EDX spectrum of a particle containing Hf.

Coupon A3 was rinsed at the same time as A1, remained in DI water for four days and was then rinsed again for half an hour and allowed to dry.

**Table 6 : Contaminants on Coupon A3**

Coupon A3	area 3 sq mm	densities
total particles	47	15.67
Aluminum	21	7.00
Silicon	12	4.00
Hafnium	12	4.00
Fe	1	0.33
unknown	1	0.33

Later, a coupon C1, etched in sulfuric acid overnight and then etched in BCP for four minutes, provided similar results. By this point, a niobium sample holder had been substituted for the aluminum one, suspecting that this holder was a source of aluminum particles like the one shown in figure 4.

**Table 7 : Contaminants on Coupon C1**

Coupon C1	2 sq mm	densities
Total particles	21	10.50
Hafnium	9	4.50
Aluminum	1	0.50
Silicon	6	3.00
Carbon	1	0.50
Iron	1	0.50
unknown	3	1.50

Except for the disappearance of aluminum, the results for a light etch were fairly consistent. But from where were the Hf, Si, C, and Fe particles coming?

## Heavy Etching

Coupon A4 was re-etched for 35 minutes, for a total etching of 39 minutes, rinsed for 40 minutes and then dried hanging for three hours. A5 and A6 underwent the same treatments but, unfortunately, the water system drained while rinsing them and they had to be discarded.

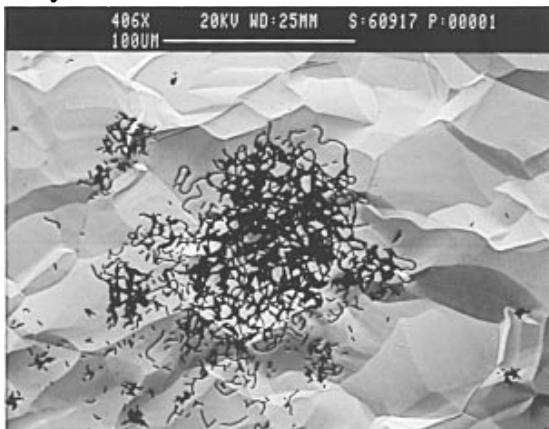


Figure 4 : Residue after a twelve day submersion in de-ionized water on A2-39 (left) and an Aluminum contaminant found on A1-39.

**Table 8 : Contaminants on coupon A4**

Coupon A4	12.5 sq. mm densities(per mm <sup>2</sup> )	
Total particles	56	4.48
Hafnium	33	2.64
Aluminum	16	1.28
Silicon	2	0.16
Iron	1	0.08
unknown	4	0.32

Coupons A1, A2, and A3 were then re-etched for 35 minutes and rinsed for ten minutes in de ionized water. A day later they were re-rinsed for one hour and A1 was then dried for two hours and forty five minutes.

**Table 9 : Contaminants on Coupon A1-39**

Coupon A1-39	11.5 sq mm	densities(per mm <sup>2</sup> )	
total particles	17	1.48	
Hafnium	6	0.52	
Aluminum	8	0.70	
Iron	2	0.17	
Silicon	1	0.09	

Meanwhile, coupon A2-39 had been sitting in de ionized water for twelve days and the surface was now contaminated with dark masses of curved lines (figure 4). Unfortunately, these lines provided no spectrum. We soon realized that the x-ray spectrometer's computer was set so that any peak that had the energy equal to or less than the carbon K line would not be shown. It is possible that these contaminants were carbon, possibly some bacteria that grew on the surface during its twelve day submersion. The coupon was then re-etched for four minutes, rinsed and dried: At this point the niobium sample holder replaced the aluminum sample holder. The sample holder was made, cleaned, and etched in sulfuric acid and water overnight, and then etched for about an hour in BCP.

**Table 10 : Contaminants on Coupon A2-43**

Coupon A2-43	10.5 sq mm	densities(per mm <sup>2</sup> )	
total particles	32	3.05	
Hafnium	14	1.33	
Cerium	1	0.10	
Unknown	17	1.62	

After heavy etching, the density of particles had fallen considerably. But some particles, like the hafnium of figures 2 and 3,



still remained. Were these particles from the environment or from the niobium itself?

## Prolonged Drying

Perhaps some particles were collecting on the surface of the niobium during drying. Although the coupons were dried in the class 100 or better clean room, the size of particles we were observing were less than a micron, a size near the limit of the clean-room filter's capacities. We wanted to know what the difference in particle densities would be if a coupon were dried horizontally and with a drop of water placed on it. Coupons B1-B4 were created and etched overnight in sulfuric acid and water. I placed a depression in the center of coupon B2 by placing another piece of niobium above it and partially punching the two of them. The indentation was one quarter of an inch wide. This was done so that B2 would not come into contact with the stainless steel punch. B2 was etched for 30 minutes in BCP and rinsed in de-ionized water for 40 minutes. This coupon was then set into the niobium sample holder (horizontally) to dry for nineteen hours. I made sure there was water in the depression by dripping water off another coupon that had simultaneously been going through all the same procedures as B2. Areas both inside and outside the depression were scanned.

**Table 11 : Contaminants Inside Depression on Coupon B2**

B2 (inside)	4.23 sq mm	densities (per mm ^2)	
total particles	53	12.53	
Hafnium	20	4.73	
Fe, Cr, Ni	5	1.18	
Silicon	6	1.42	
Carbon	2	0.47	
Unknown	20	4.73	

**Table 12 : Contaminants Outside Depression on Coupon B2**

B2 (outside)	2.5 sq mm	densities(per mm^2)	
Total particles	15	6	
Hafnium	7	2.8	
Unknown	8	3.2	

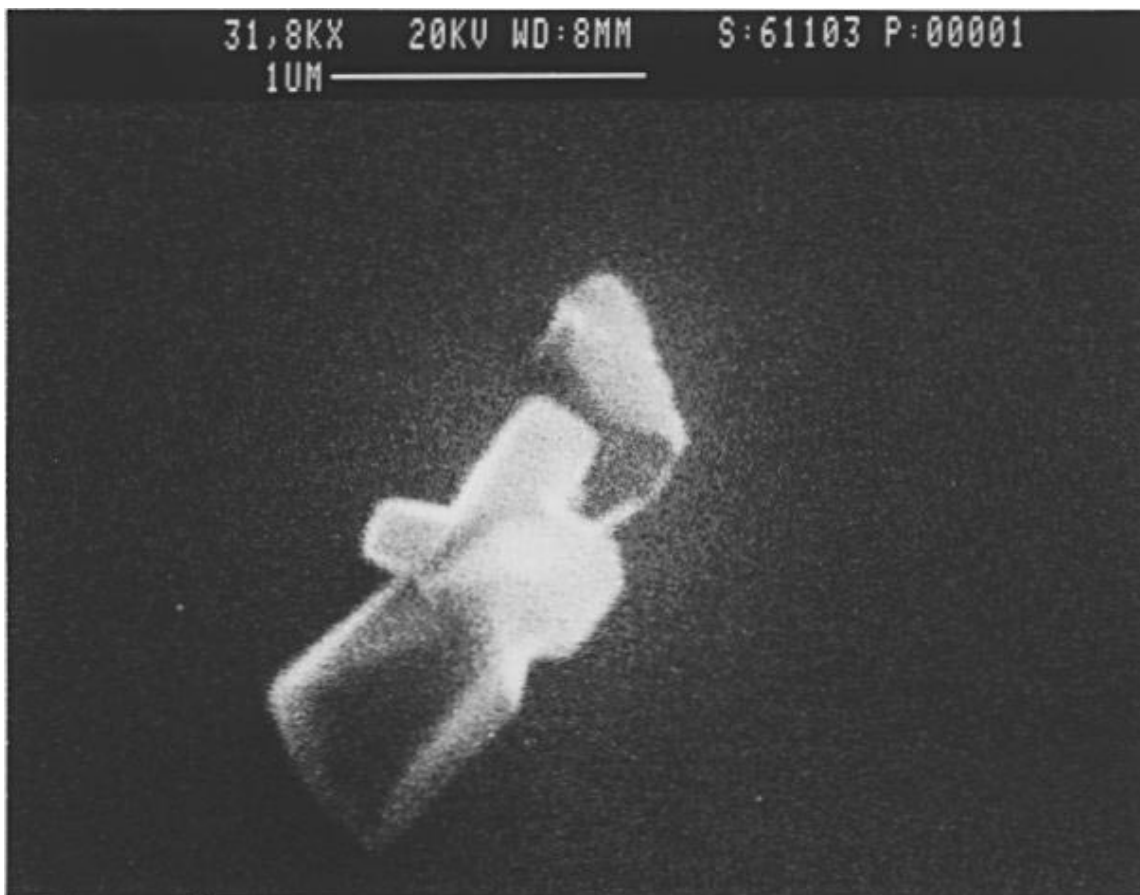


Figure 5 : A carbon contaminant found on B2-68.

We wanted to re-etch B2 and repeat this scan. Several times, B2 was re-etched and scanned and found to be contaminated ( $>100$  particles/sq mm) after the minimal drying time (~3 hours). After a total etching time of 68 minutes, the coupon was laid out to dry, there was no coupon off which to drip water, so I dripped water off the Teflon cover (which is ultrasounded in methanol before every scan). B2 dried for three hours and forty five minutes.

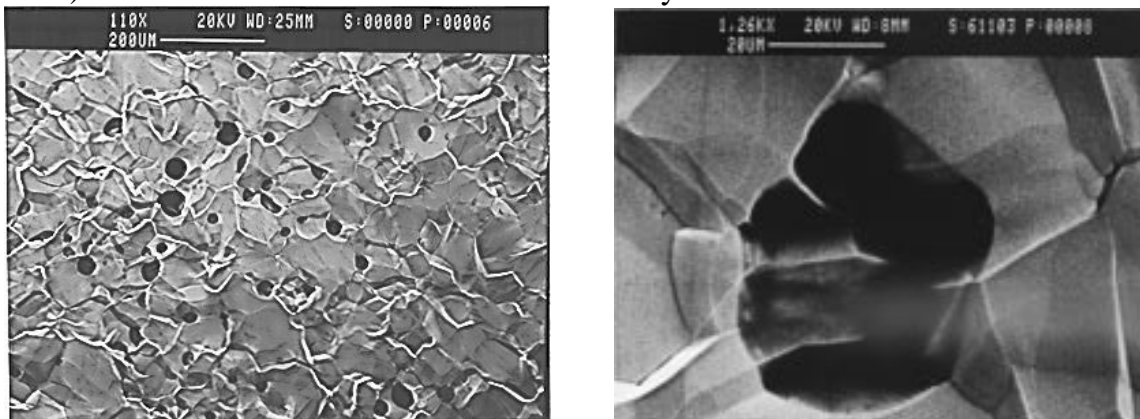


Figure 6 : Carbon splotches found on B2-68, probably a result of water running off the Teflon cover.

Inside the depression there was a high concentration of carbon splotches (figures 6, 7, 8, 9) (by this point the spectrometer's computer had been readjusted to show all peaks). Outside the depression there were some similar splotches, but fewer in density than inside. It is likely that the source of these carbon splotches was the Teflon cover, as no splotches were seen when water was dripped off niobium. There were also some carbon particles found on these coupons (figure 5).

**Table 13:Contaminants Inside Depression on Coupon B2-68**

B2-68(inside) 5 sq mm		densities(per mm <sup>2</sup> )
total particles	41	8.20
Hafnium	12	2.40
Silicon	3	0.60
Carbon	3	0.60
Copper	1	0.20
Indium	2	0.40
Unknown	20	4.00

**Table 14:Contaminants Outside Depression on Coupon B2-68**

B2-68(outside) 5 sq mm		densities(per mm <sup>2</sup> )
total particles	12	2.40
Hafnium	1	0.20
Carbon	4	0.80
Chromium	1	0.20
Unknown	6	1.20

There was little difference in particle densities between the horizontally dried areas outside the depressions and the previously vertically-dried areas of similar etching time. Yet, within the depressions, where a greater volume of water had remained longer, there was a significant increase in particle densities. Whether this increase was due to particles in the environment collecting on the water, or due to the water itself is a question that might be interesting to pursue.

## Russian Niobium

The source of the hafnium contamination was a mystery,. To determine whether the niobium itself had hafnium in it or if the hafnium's presence was due to our SEM, we created two coupons from Russian niobium. They were prepared as the others were and then etched for four minutes in BCP, rinsed in de-ionized water and then dried vertically.

**Table 15 : Contaminants on Coupons R1&R2 after 4 Minutes Etching**

R1-R2-4	2.5 sq mm	densities	
total particles		2	0.8
Silicon		2	0.8

**Table 16 : Contaminants on Coupons R1&R2 after 44 Minutes Etching**

R1-R2-44	10 sq mm	densities	
total particles		0	0

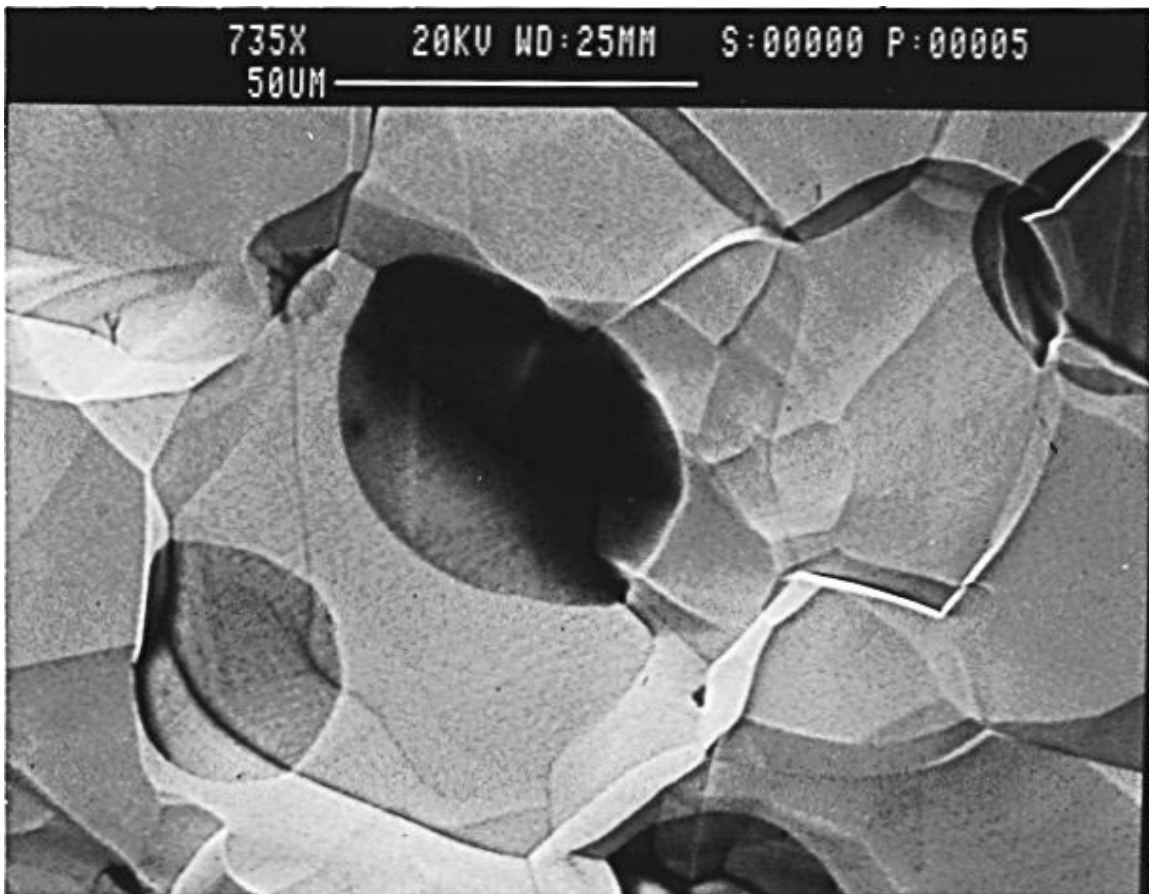


Figure 7 : A carbon splotch on Coupon B2

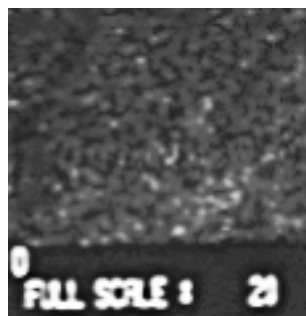
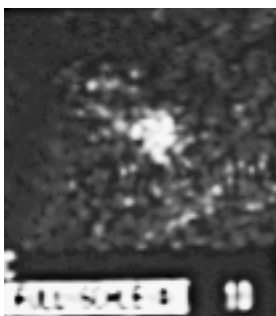


Figure 8 : An x-ray mapping of carbon (left) and oxygen (right) of the splotch shown in Figure 7. White indicates the presence of carbon or oxygen respectively.

The Russian niobium is remarkably cleaner than the Teledyne. Most remarkable is the complete absence of hafnium. It turns out that in the same plant that processes the Teledyne niobium, hafnium is also processed. This seems a likely source of the hafnium contamination on the Teledyne samples.

### **Conclusions**

Preventing contamination by particles on the order of one micron is very difficult. These particles show varying densities on samples when seemingly small factors are changed such as the orientation of the sample while drying. The environment of the sample must be monitored closely to determine whether contaminants are from the niobium itself. Ion pumps used in conjunction with lanthanum hexaboride filaments in a SEM are a prolific source of titanium particles. On the Teledyne Wah Chang samples, hafnium contamination was present after long and short etches, yet the Russian samples showed no hafnium contamination. This indicates that the hafnium is actually present in the Teledyne niobium itself. Also, the Russian niobium showed much less general contamination than the Teledyne. Finally, the rate of contamination while drying seems to be proportional to the amount of water on the specific part of the sample.

Thanks to Professor Hasan Padamsee and Jens Knobloch for their help, ideas, and guidance.

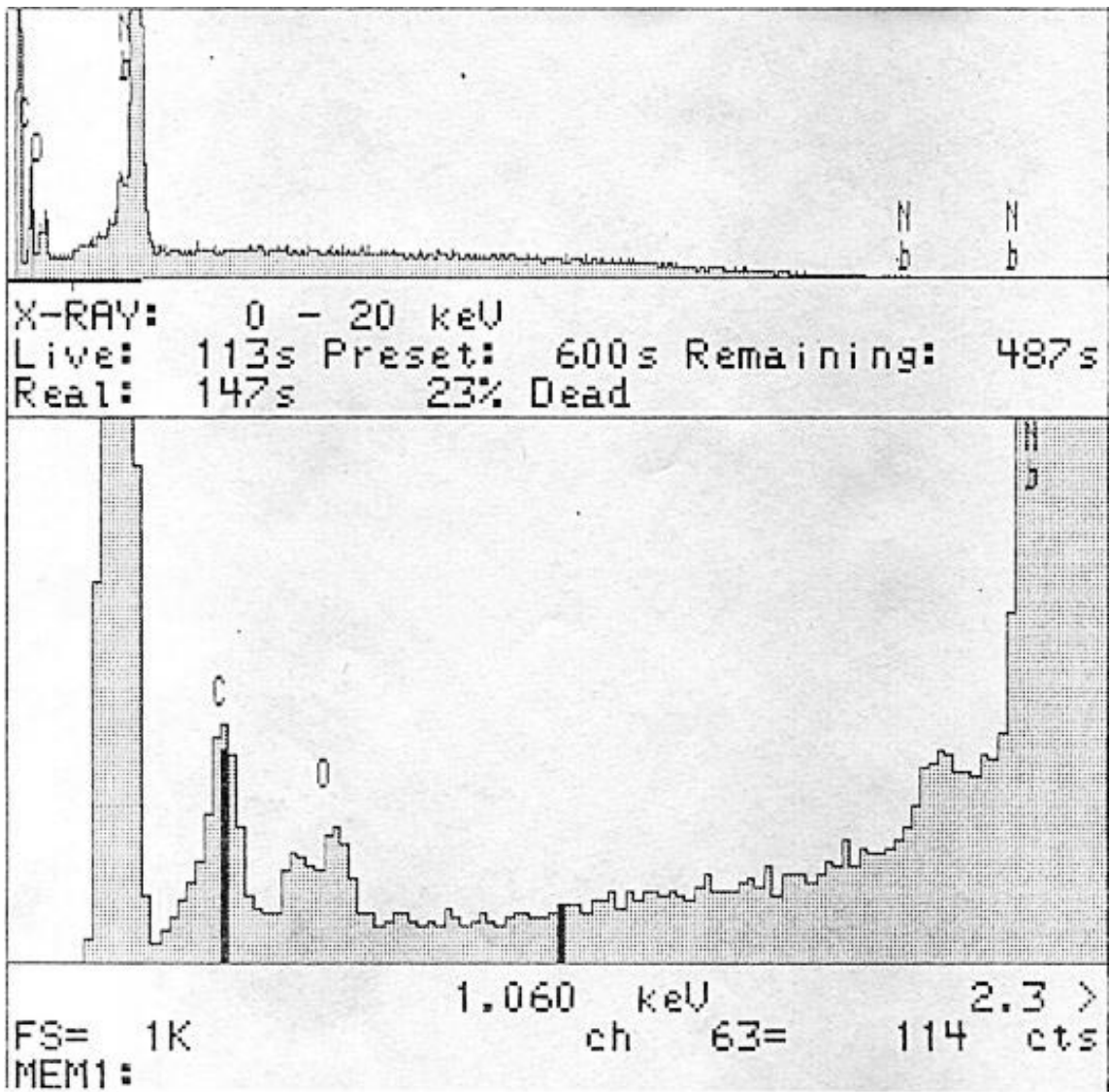
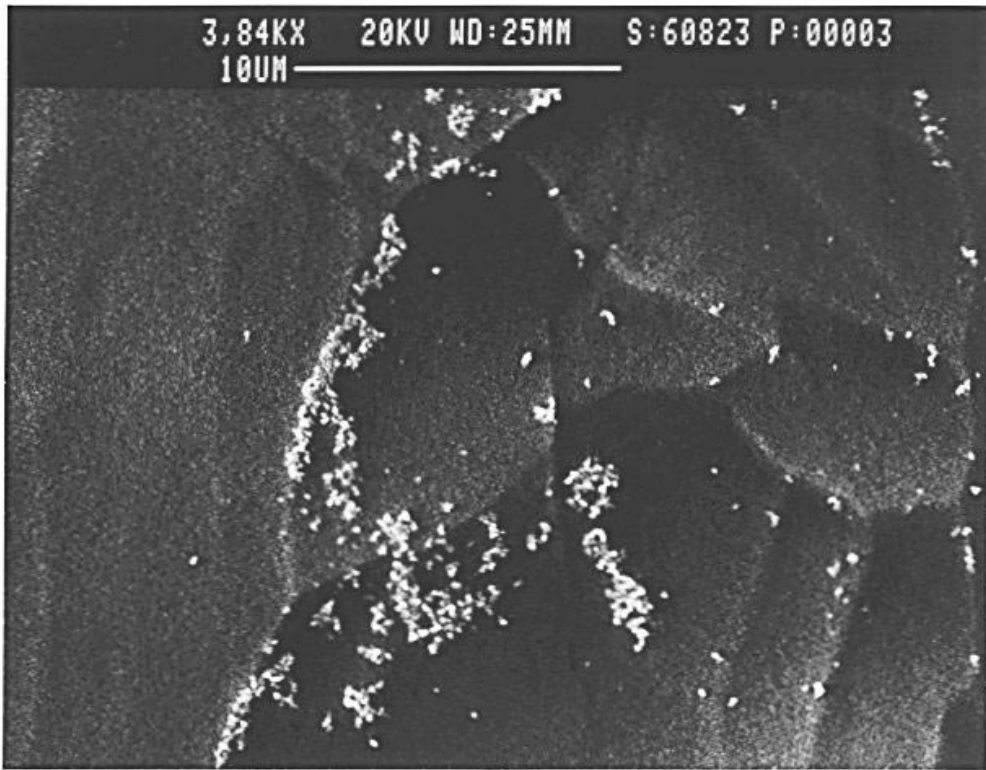
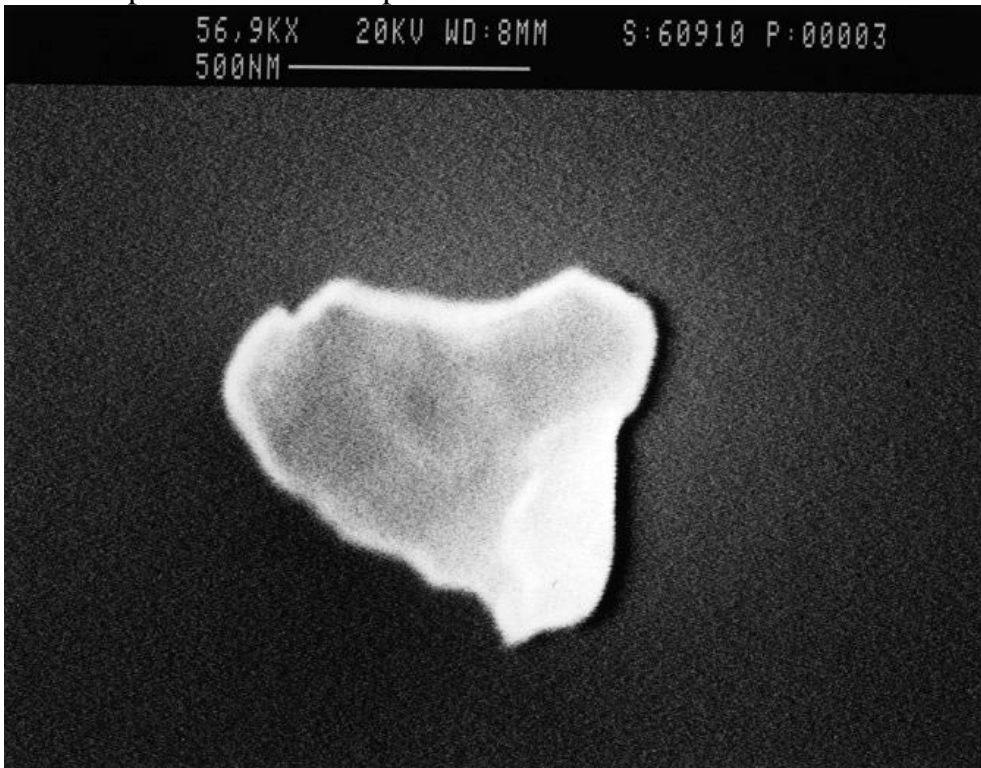


Figure 9 : An EDX spectrum of a particle containing carbon.

Additional Pictures



Silicon particles on coupon A1



An Iron particle on coupon A1-39