LAB 04

EDS IN THE SEM

REPORT BY: SHILPIKA CHOWDHURY

TEAM MEMBER NAME: Henry Geerlings, Ashley Tsai, Chris Chuang, Sam McAlpine
LAB SECTION No. 105 GROUP 2

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ABSTRACT

The goal of this experiment was to observe Energy Dispersive Spectroscopy (EDS) spectrums of four different Copper-Nickel samples with various Cu-Ni concentrations. These samples were 50Cu-50Ni, 20Cu-80Ni, 10Cu-90Ni, and 100Cu. From the lab, we found that the coating on the surface was less oxidization and more organic (carbon content). We also found that the precision of measurements in EDS is enhanced by first polishing the sample. This reduces the surface oxygen and carbon content and decreases error.

INTRODUCTION

The Scanning Electron Microscope (SEM) is a powerful tool not only for imaging the surface of various samples but also for Energy Dispersive Spectroscopy (EDS).

Scanning electron microscopes take advantage of the dispersive properties of electrons, which do not penetrate deeply into the sample. Compared to other electron microscopes, like transmission electron microscopes, SEMs can image bulk samples because the machine takes advantage of backscattered beam.

The basic parts of a scanning electron microscope are an electron source, a high voltage across the electron source and the sample to accelerate electrons toward the sample, electromagnetic lenses to focus electrons, temperature control aspects, and a data collection system or detector. Standard SEMs collect backscattered electrons as they diffract off the sample at high angles of incidence. This is the most common detector found. Unlike diffractometers, the SEM does not rely on a 2θ angle in the user interface, but rather acts more like a light microscope.

Some SEMs are also equipped with the ability to detect, count, and analyze x-rays that have been scattered off a sample. With this type of detector, it is possible to determine the elemental composition of samples. The detector used in this lab is similar to Si(Li) type detectors but does not use Lithium and therefore does not need extremely low temperatures to prevent lithium from diffusing out. These detectors often need some sort of cooling (liquid nitrogen for Si(Li) or simply peltier for this ultra-pure Si with novel geometry).

The SEM can display information as either an image or as spectrum as described above. The resolution of the image is dependent on probe size and volume of the tested sample. The range of EDS that can be achieved is also dependent on the voltage across the electrodes, which in this case is 15kV.

The types of information determined by EDS are described more fully in the *Methods* section, however the main types are point analysis, line profile analysis, and digital x-ray maps.

EXPERIMENTAL PROCEDURES

For this experiment, our materials were a Hitachi TM-3000 SEM with EDS software and Bruker Nano X-Flash 430-H detectors, four copper-nickel samples (50Cu-50Ni, 20Cu-80Ni, 10Cu-90Ni, and 100Cu), and diamond polishing paste.

Before beginning both sections of the lab, we initialized the Hitachi TM-3000 SEM and the Bruker Nano X-Flash 430-H detector. The voltage for this SEM was preset to 15kV.

SEM IMAGE COLLECTION

Each of the Cu-Ni samples was first loaded into the SEM, and an exploratory image to determine surface quality and any interesting surface features was taken at 10,000x after focusing the sample. After focusing, we returned the viewer to 100x for EDS analysis.

EDS DATA COLLECTION

After taking the initial SEM image from the viewer, *Quantax 70* software was used to calibrate and modify spectral output in the form of point, line, and elemental distribution maps. These types of data were each specifically collected for different analytical reasons.
The point map compared integrated elemental contents in a particular area which was determined by the user. Numerical data was collected specifically comparing Nickel to Copper only and once comparing Nickel, Copper, Oxygen and Carbon. The purpose of this second data quantification was to determine what was formed on the surface of unpolished samples. In addition to numerical data, a spectrum was also collected from each sample.

The line scan profile was used to determine compositions of defects or particulates on the surface of the sample. A line over which analysis would be done was drawn over pure sample and partially over a defect. The relative elemental compositions of each region on the line were displayed and saved, which would elucidate the elemental composition in terms of the indicated elements, Cu, Ni, C, and O. The analysis profile and the location within the image along which the line scan was taken were both recorded for each sample.

Finally, the elemental distribution map showed the topographic distribution of elements. First images were collected which only quantified Copper and Nickel, where both the area on the surface was collected as well as peak distributions, and then the same was repeated including carbon and oxygen.

Each of these steps was executed on an unpolished sample first, then the sample was polished using 1μm diamond particle paste and all steps were repeated.

EXPERIMENTAL RESULTS

In all x–ray experiments, the background radiation was found to be 0.02 mR/hr using a Geiger counter during and before data collection. The data for each sample is assembled onto separate pages for readability.

SAMPLE 1: 50CU-50NI

UNPOLISHED

Figure 1: Unpolished 50Cu-50Ni sample at magnification 10,000X. This magnification was used in order to observe any nicks or scratches in the surface of the sample. In this sample, there appear to be small darker spots on the surface with unknown composition. This sample is unpolished, but there are still many scratches along this region of the sample surface.

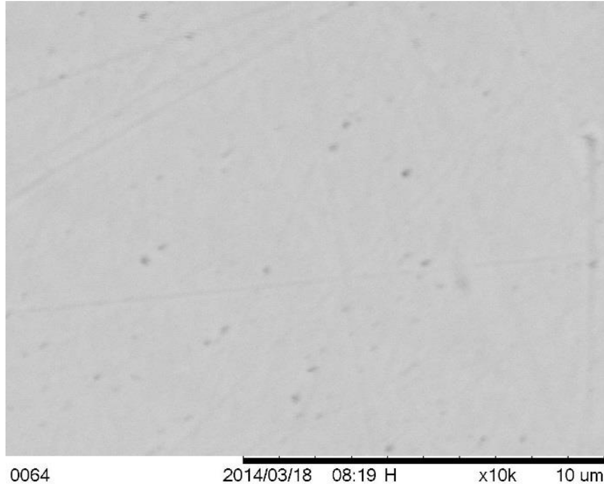


Table 1: Tabulated data from point analysis of the unpolished 50Cu-50Ni sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 52.6:47.4, meaning the sample is not exactly 50-50 as expected. **B** Analysis of sample including both carbon and oxygen. This analysis resulted in a much higher incidence of carbon on the surface of the sample compared to the amount of oxygen found (4.3% vs 0.26%)

A

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	54739	55.726	52.60025046	50.616	1.773
Nickel	28	K-series	69316	50.216	47.39974954	49.383	1.551
			Sum:	105.94	100	100	

B

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	54727	53.732	50.25990504	40.835	1.711
Nickel	28	K-series	69291	48.268	45.14881506	39.715	1.492
Carbon	6	K-series	3563	4.6225	4.323756272	18.585	0.642
Oxygen	8	K-series	715	0.2860	0.267523624	0.8632	0.074
			Sum:	106.91	100	100	

Figure 2: Line analysis data for unpolished 50Cu-50Ni. **A** Line spectrum indicating relative concentrations of various elements (Ni, Cu, C, and O). Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. The sample lacked large characteristic particles on the surface and as a result there are not particularly notable variations in relative element concentrations.

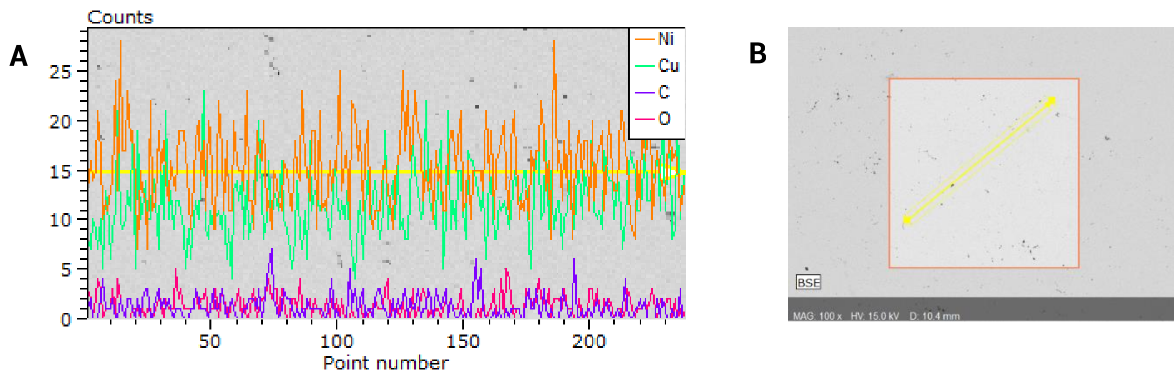
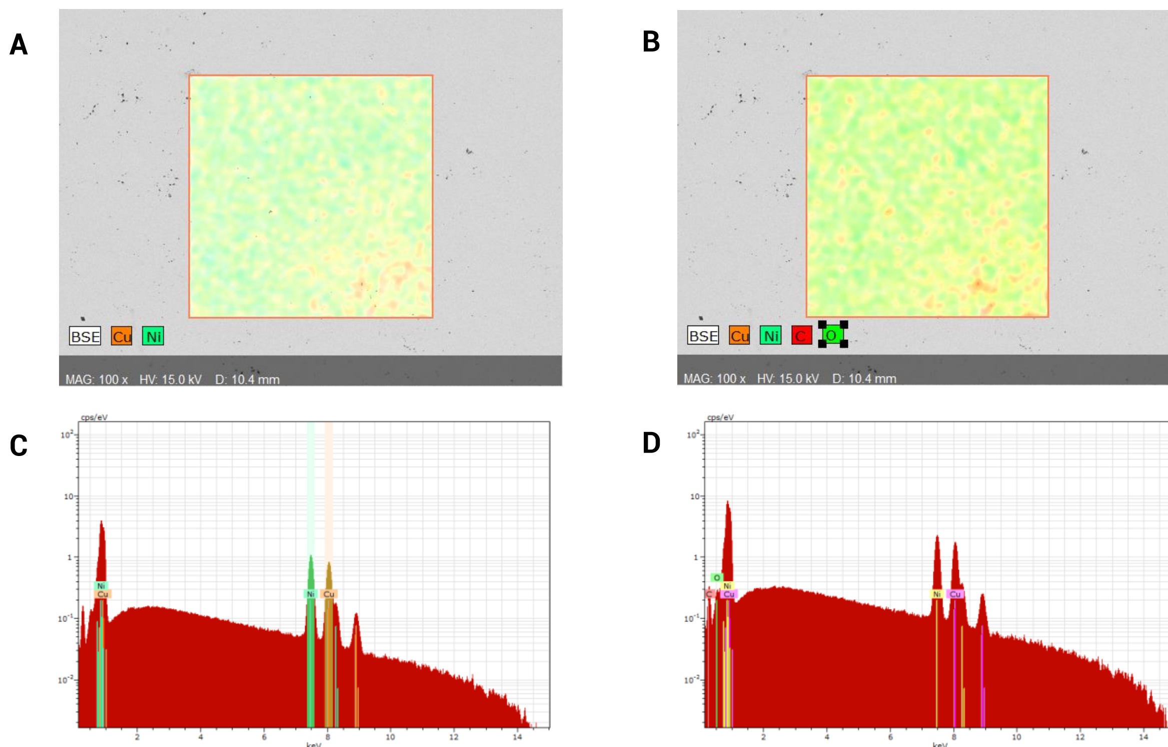


Figure 3: Area sample data for unpolished 50Cu-50Ni sample. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is roughly uniform. **B** The addition of carbon and oxygen considerations had a difficult to observe effect on the spectrum. The overall color of the image become slightly greener, indicating a possible oxide layer on the sample. However, this change is hue is much more directly a result of carbon on surface of the sample. **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



SAMPLE 1: 50CU-50NI

POLISHED

Figure 4: Polished 50Cu-50Ni sample at magnification 10,000X. This magnification was used in order to observe any nicks or scratches in the surface of the sample. In this sample, there appear to be small darker spots on the surface with unknown composition. This sample is polished, but there are still many scratches along this region of the sample surface. The scratches on the surface appear to be about 1 μm wide.

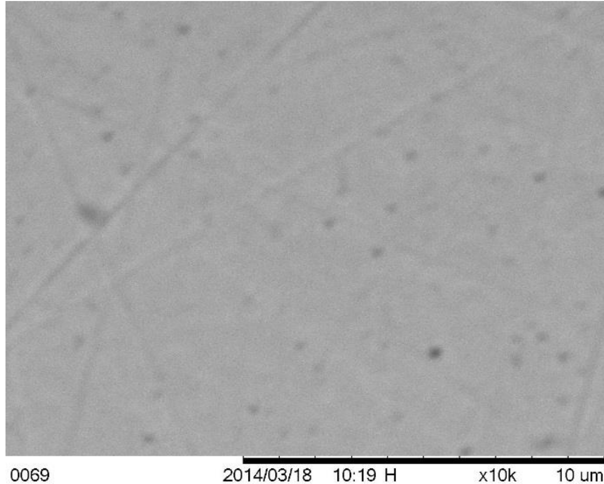


Table 2: Tabulated data from point analysis of the polished 50Cu-50Ni sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 53.2:46.8, meaning the sample is not exactly 50-50 as expected. **B** Analysis of sample including both carbon and oxygen. This analysis resulted in a much higher incidence of carbon on the surface of the sample compared to the amount of oxygen found as before, but the ratio of each is smaller than before polishing (4.3% vs 0.26% to 3.2% vs. 0.009%). Nearly all the oxygen has been removed.

A

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	48269	53.496	53.16434937	51.1824	1.703
Nickel	28	K-series	60281	47.127	46.83565063	48.8175	1.457
			Sum:	100.62	100	100	

B

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	48270	52.313	51.50180788	43.9014	1.6667
Nickel	28	K-series	60280	46.048	45.33407982	41.8389	1.4250
Carbon	6	K-series	2219	3.2047	3.155033388	14.2288	0.4815
Oxygen	8	K-series	21	0.0092	0.009078918	0.03073	0.0049
			Sum:	101.57	100	100	

Figure 5: Line analysis data for polished 50Cu-50Ni. **A** Line spectrum indicating relative concentrations of various elements (Ni, Cu, C, and O). Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. The sample lacked large characteristic particles on the surface and as a result there are not particularly notable variations in relative element concentrations.

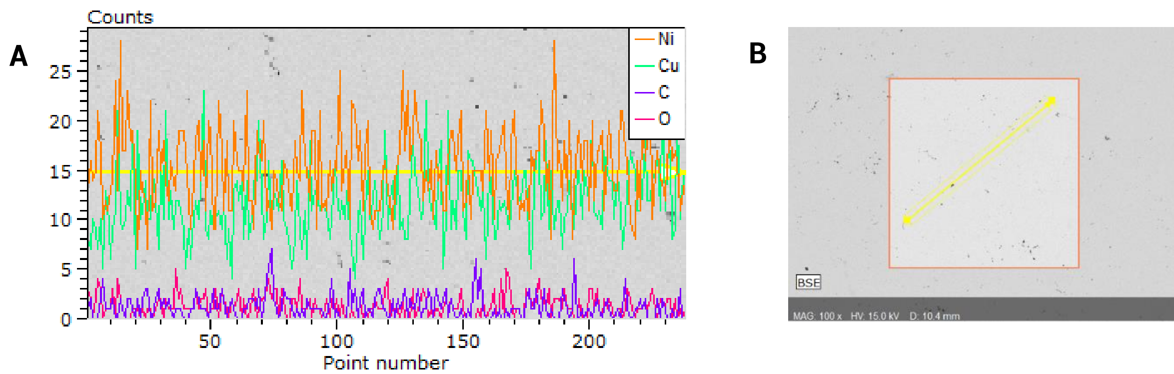
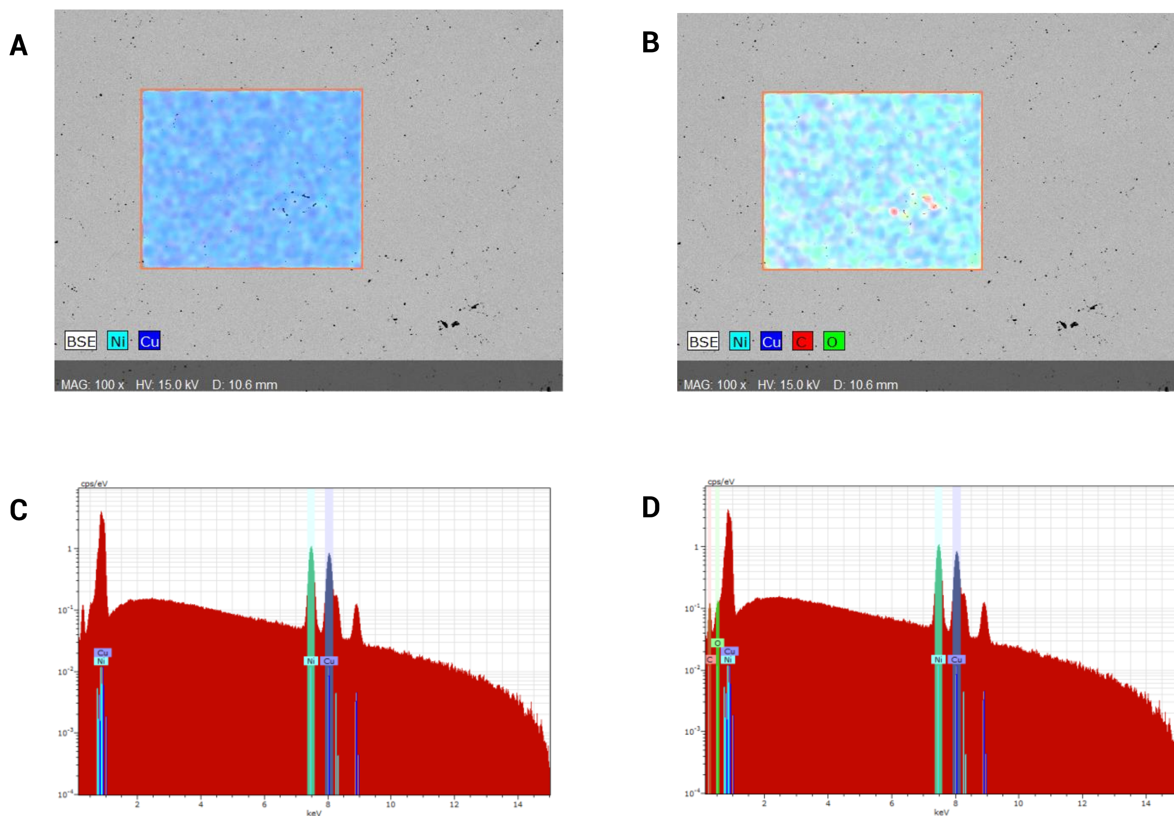


Figure 6: Area sample data for polished 50Cu-50Ni sample. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is roughly uniform. **B** The addition of carbon and oxygen considerations had a difficult to observe effect on the spectrum. The change in color is less distinct than when the sample was unpolished. **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



SAMPLE 2: 20CU-80NI

UNPOLISHED

Figure 7: Unpolished 20Cu-80Ni sample at magnification 10,000X. This magnification was used in order to observe any nicks or scratches in the surface of the sample. In this sample, there appear to be small darker spots on the surface with unknown composition. This sample is unpolished, but the surface scratches were harder to see. Also, the black particulates were of very small size.

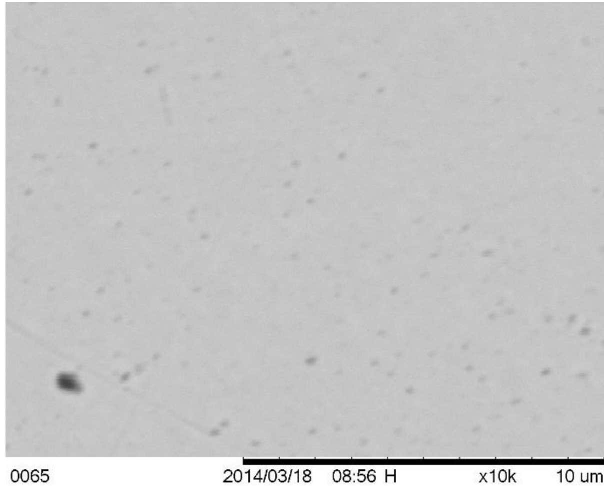


Table 3: Tabulated data from point analysis of the unpolished 20Cu-80Ni sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 22.5: 77.5, meaning the sample is not exactly 20-80 as expected. **B** Analysis of sample including both carbon and oxygen. This analysis resulted in a much higher incidence of carbon on the surface of the sample compared to the amount of oxygen found (2.95% vs 0%). The lack of any oxygen in the sample at all is notable.

A

Element	AN	Series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	121164	79.553	77.50172932	78.8565226	2.443
Copper	29	K-series	25151	23.093	22.49827068	21.1434774	0.749
			Sum:	102.64	100	100	

B

Element	AN	Series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	121157	77.761	75.19688441	68.484	2.389
Copper	29	K-series	25149	22.597	21.85179136	18.381	0.734
Carbon	6	K-series	2550	3.0519	2.951324232	13.134	0.451
Oxygen	8	K-series	0	0	0	0	0
			Sum:	103.41	100	100	

Figure 8: Line analysis data for unpolished 20Cu-80Ni. **A** Line spectrum indicating relative concentrations of various elements (Ni, Cu, C, and O). Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. The sample lacked large characteristic particles on the surface and as a result there are not particularly notable variations in relative element concentrations.

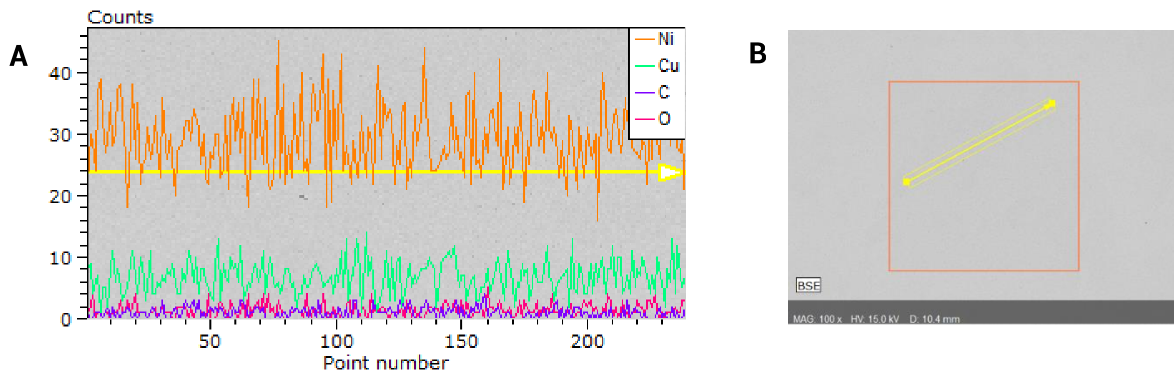
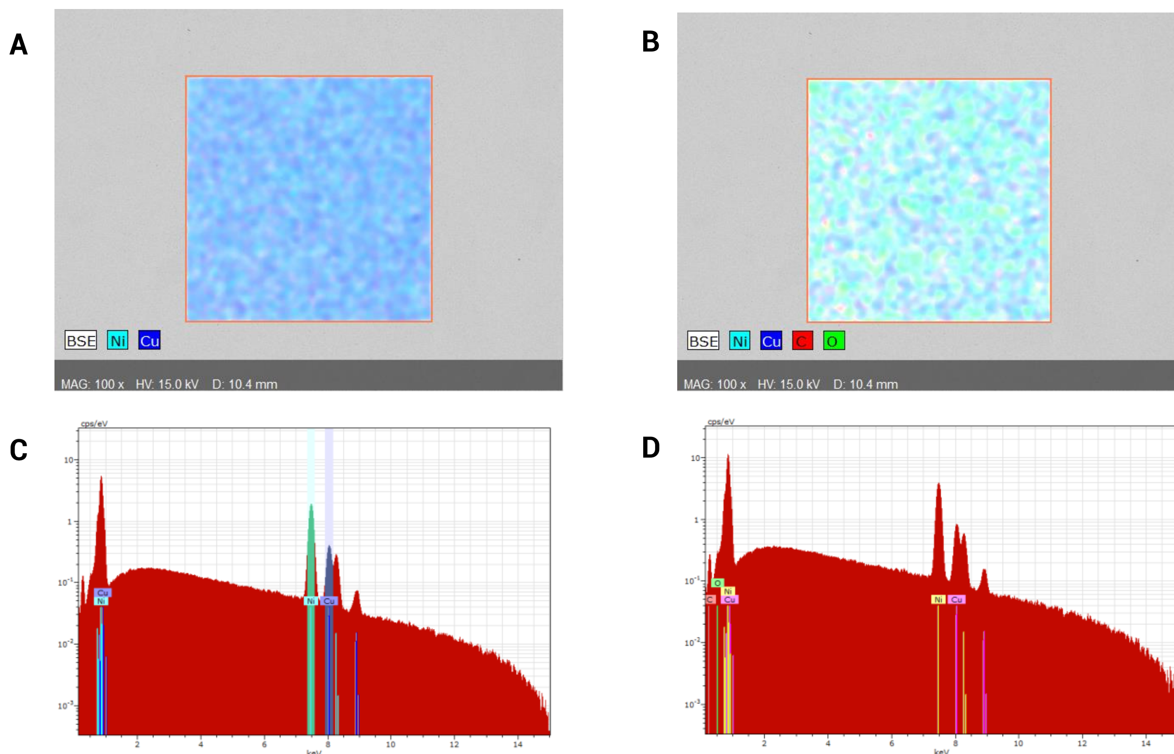


Figure 9: Area sample data for unpolished 20Cu-80Ni sample. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is roughly uniform. **B** The addition of carbon and oxygen considerations had a difficult to observe effect on the spectrum. The overall color of the image became significantly more saturated, which must be a result of carbon on surface of the sample because of how little oxygen was present. **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



SAMPLE 2: 20CU-80NI

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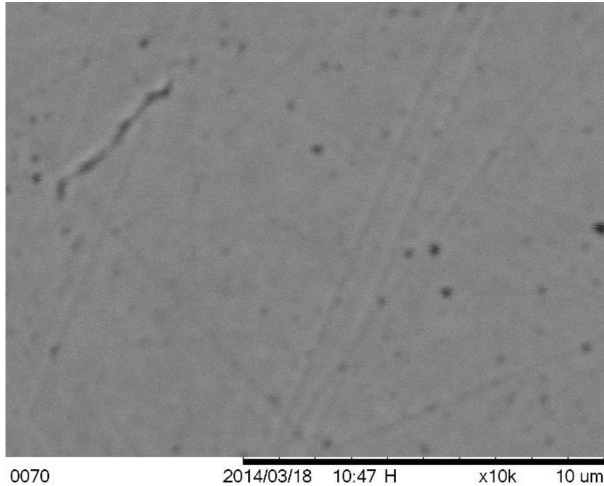


Figure 10: Polished 20Cu-80Ni sample at magnification 10,000X. This magnification was used in order to observe any nicks or scratches in the surface of the sample. In this sample, there appear to be small darker spots on the surface with unknown composition. This sample is polished, and the 1 micron width scratches (likely from the diamond paste) can be seen on the surface. This sample was autocontrasted with the software, but still appeared dark for data collection.

Table 4: Tabulated data from point analysis of the polished 20Cu-80Ni sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 22.5:77.5, which is not much closer than the unpolished version. **B** Analysis of sample including both carbon and oxygen. This is an uncharacteristic increase in incidence of contaminant content. It was possible that there may have been an error during data collection that resulted in this. Both carbon and oxygen increased in relative content.

A

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	87983	79.466	77.51880298	78.8728484	2.441
Copper	29	K-series	18246	23.046	22.48119702	21.1271516	0.748
			Sum:	102.51	100	100	

B

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	87985	77.191	74.30241833	65.2321	2.371
Copper	29	K-series	18249	22.402	21.56451838	17.4863	0.728
Carbon	6	K-series	2378	3.8568	3.712464412	15.926	0.568
Oxygen	8	K-series	887	0.4369	0.420598883	1.3546	0.098
			Sum:	103.887	100	100	

Figure 11: Line analysis data for polished 20Cu-80Ni. **A** Line spectrum indicating relative concentrations of various elements (Ni, Cu, C, and O). Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. The sample lacked large characteristic particles on the surface and as a result there are not particularly notable variations in relative element concentrations. The surface of the sample is noticeably less covered with particulate. This is likely a result of polishing.

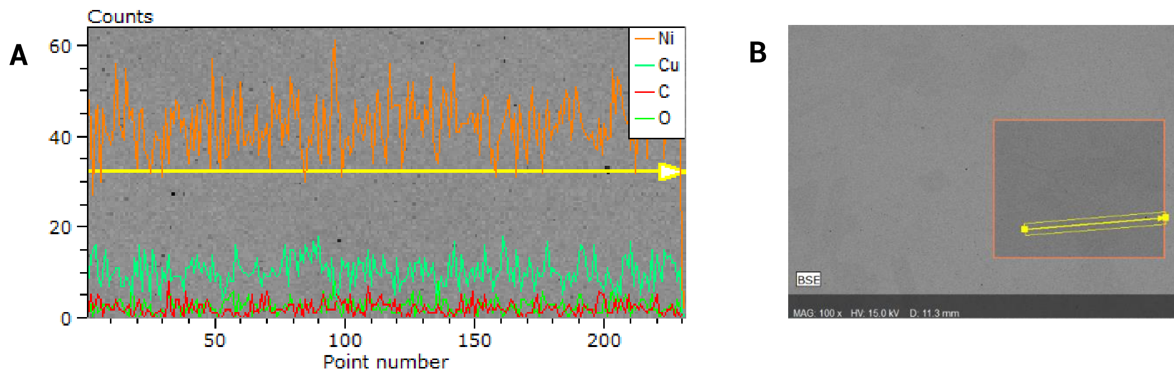
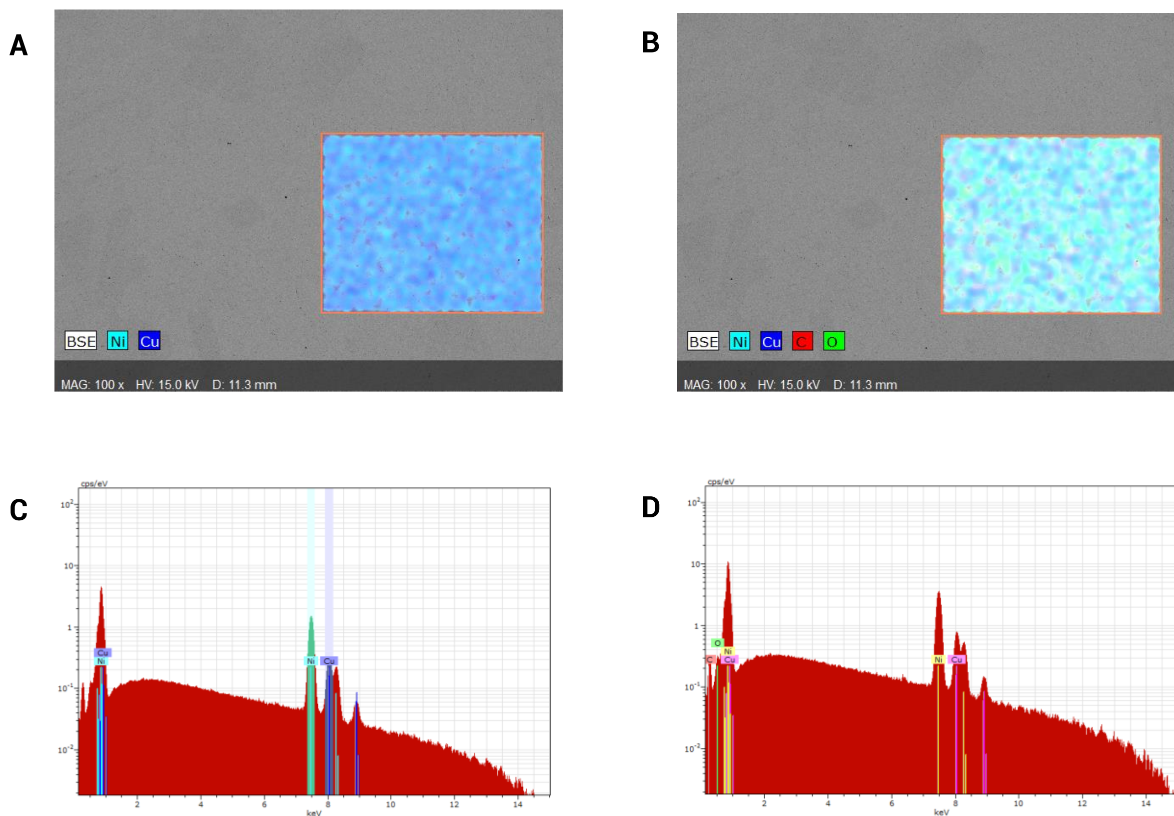


Figure 12: Area sample data for polished 20Cu-80Ni sample. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is roughly uniform. **B** The addition of carbon and oxygen considerations had a difficult to observe effect on the spectrum. **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



SAMPLE 3: 10CU-90NI

UNPOLISHED

Figure 13: Unpolished 10Cu-90Ni sample at magnification 10,000X. This magnification was used in order to observe any nicks or scratches in the surface of the sample. This sample is unpolished, and one of the visible scratches along this region of the sample surface is shown here. The incidence of scratches is in very low density here compared to previous samples.

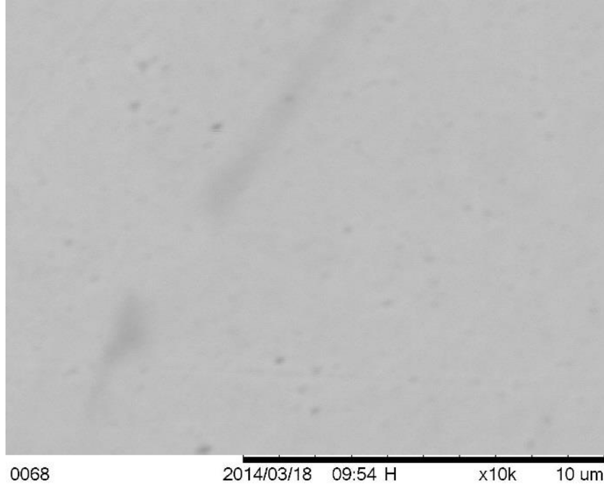


Table 5: Tabulated data from point analysis of the unpolished 10Cu-90Ni sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 11.6:88.4, meaning the sample is not exactly 10-90 as expected. However, this is much closer than other samples. **B** Analysis of sample including both carbon and oxygen. This analysis resulted in a much higher incidence of carbon on the surface of the sample compared to the amount of oxygen found (11% vs 0.4%). This is one of the highest carbon samples that were tested.

A

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	105978	91.992	88.35786629	89.1504	2.821
Copper	29	K-series	10148	12.120	11.64213371	10.8495	0.405387
			Sum:	104.11	100	100	

B

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	105954	87.765	83.39309276	69.3130	2.693
Carbon	6	K-series	3571	5.3786	5.11065638	20.7573	0.742
Copper	29	K-series	10137	11.589	11.01231505	8.45404	0.388
Oxygen	8	K-series	1082	0.5093	0.483935816	1.47556	0.106
			Sum:	105.24	100	100	

Figure 14: Line analysis data for unpolished 10Cu-90Ni. **A** Line spectrum indicating relative concentrations of various elements (Ni, Cu, C, and O). Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. This sample had two large particulates along the investigated line path. The large particle on the left was composed of mainly carbon (red) and the scratch perpendicular to the line had even higher carbon content than the particle.

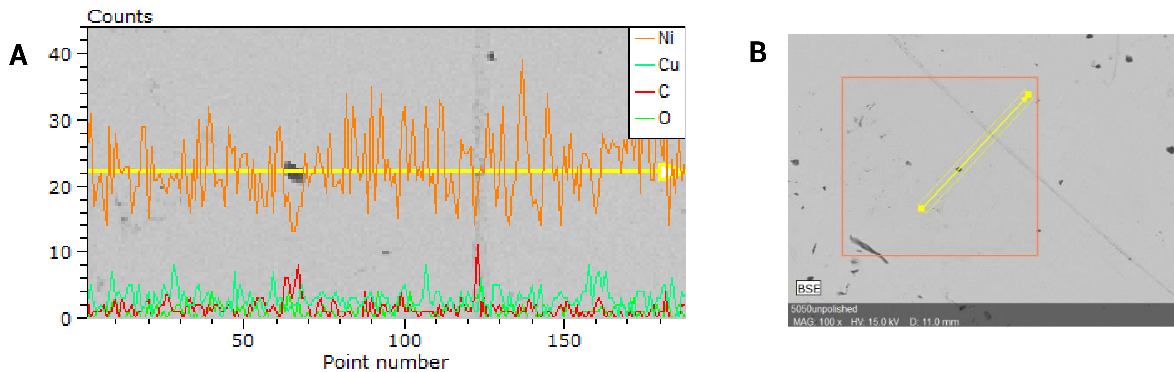
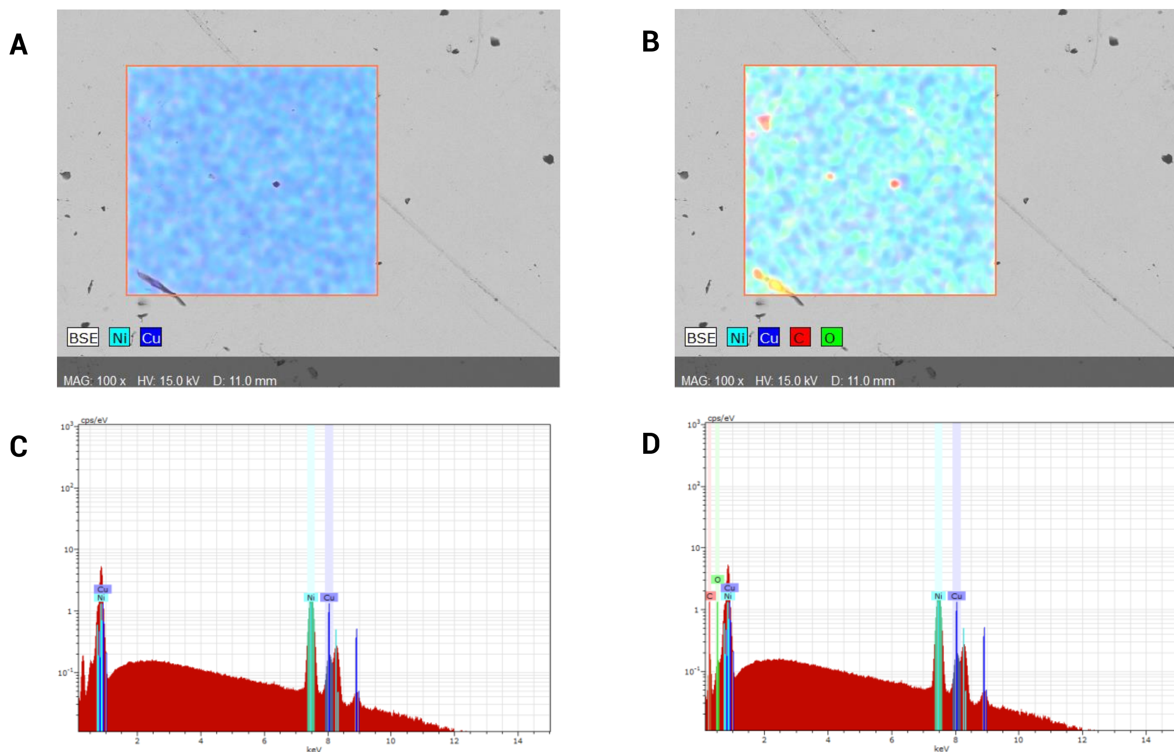


Figure 15: Area sample data for unpolished 10Cu-90Ni sample. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is only uniform before revealing carbon. **B** The addition of carbon and oxygen show obvious regions of concentration on the sample, with higher density in regions where particulate matter exists. **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



SAMPLE 3: 10CU-90NI

POLISHED

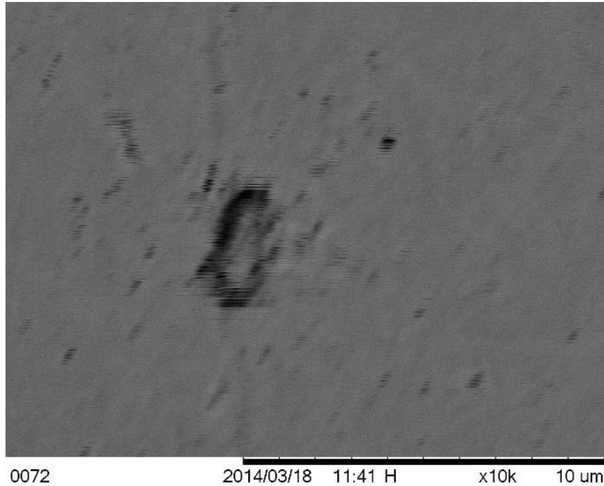


Figure 16: Polished 10Cu-90Ni sample at magnification 10,000X. This magnification was used in order to observe any nicks or scratches in the surface of the sample. Deeper nicks and scratches were focus on in this sample, instead of just lines. This sample is polished, but there is still clearly defects in the surface. This defect is clearly larger than a micron.

Table 6: Tabulated data from point analysis of the polished 10Cu-90Ni sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 11.5:88.5, meaning the sample is not exactly 10-90 as expected. This value is similar to the unpolished data. **B** Analysis of sample including both carbon and oxygen. Once again, the amount of carbon and oxygen in the sample is higher after polishing compared to before.

A

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	97764	90.201	88.46949493	89.2553	2.767
Copper	29	K-series	9279	11.756	11.53050507	10.7446	0.393
			Sum:	101.95	100	100	

B

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Nickel	28	K-series	97754	87.790	85.49919761	76.3086	2.694
Carbon	6	K-series	2014	3.3458	3.258505499	14.2115	0.508
Copper	29	K-series	9274	11.454	11.15564307	9.19617	0.384
Oxygen	8	K-series	178	0.0889	0.086653824	0.28371	0.047
			Sum:	102.67	100	100	

Figure 17: Line analysis data for polished 10Cu-90Ni. **A** Line spectrum indicating relative concentrations of various elements (Ni, Cu, C, and O). Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. After polishing, the number of surface defects significantly decreased. Therefore, it is difficult to see a change in defects. However, the once defect visible on the right side of the image does not appear to result in a carbon concentration change, which may be a result of polishing.

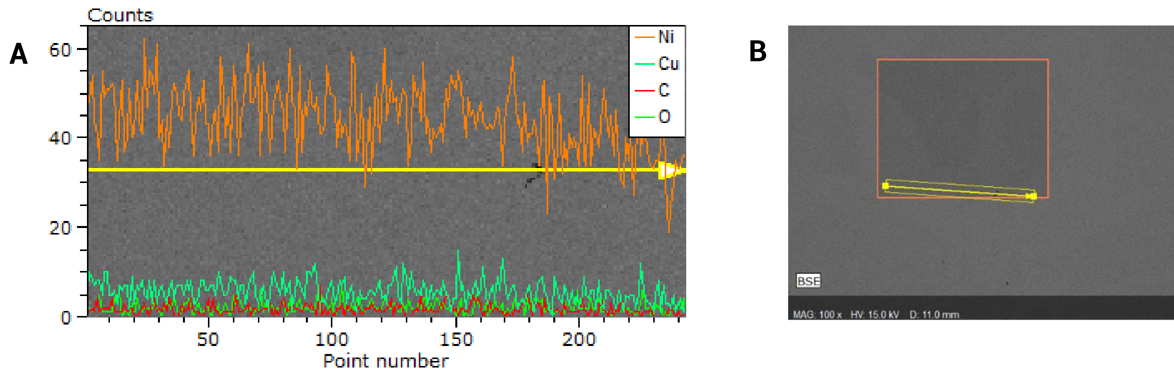
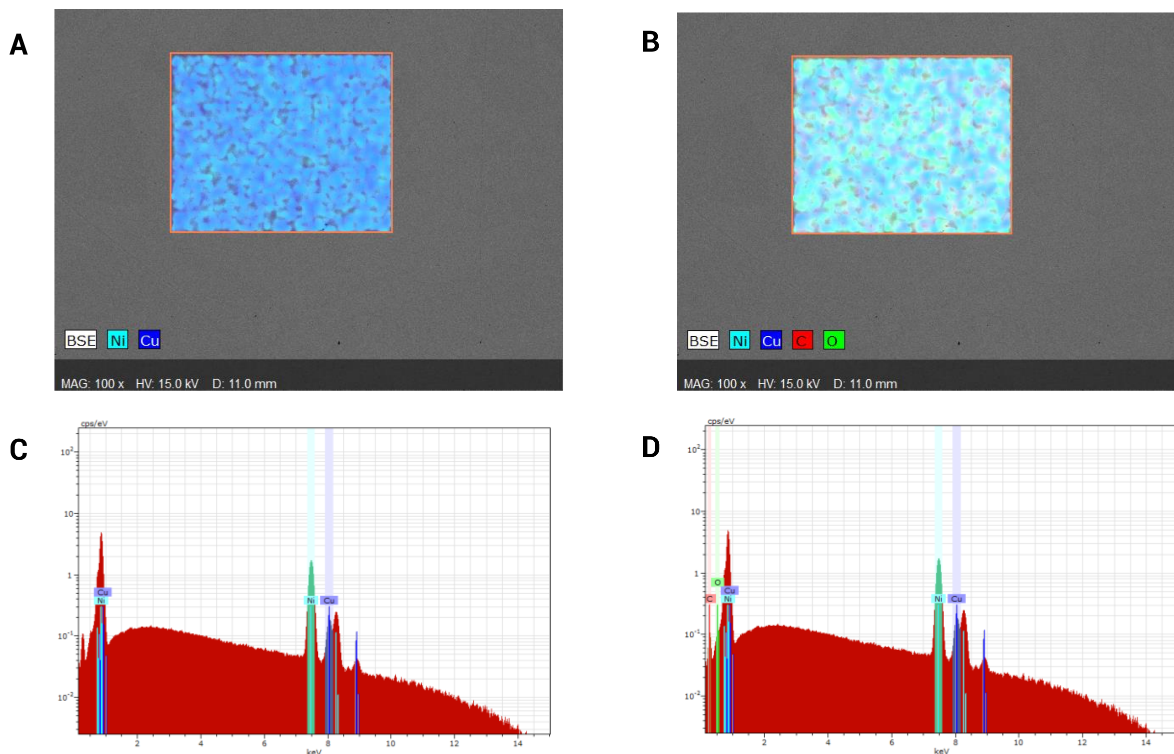


Figure 18: Area sample data for polished 10Cu-90Ni sample. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is roughly uniform. **B** The addition of carbon and oxygen considerations had a difficult to observe effect on the spectrum. Because there were so few particles on the surface after polishing, the surface appears uniform. **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



SAMPLE 4: 100CU-0NI

UNPOLISHED

Figure 19: Unpolished 50Cu-50Ni sample at magnification 10,000X. This magnification was used in order to observe any nicks or scratches in the surface of the sample. Deep groves are clearly visible in this sample, some of which are larger than 1 micron. The edges of the scratches are also not smooth but rather jagged. This may be the result of increased macroscopic abuse of the sample.

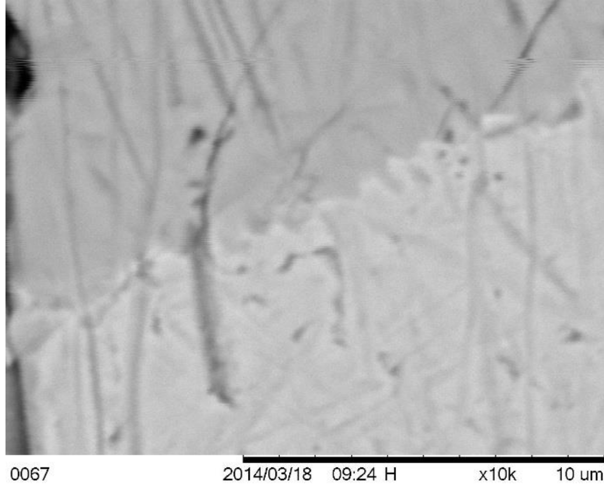


Table 7: Tabulated data from point analysis of the unpolished 100Cu sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 99.7:0.26, which is much closer to accurate than the other samples. **B** Analysis of sample including both carbon and oxygen. The data is in order of wt %, so nickel is at the bottom. Compared to other samples, this sample has much more carbon and oxygen on the surface. This could be due either to increased surface area (from all the scratches) or due to decreased nickel content. Ultimately, there is still nearly 4 times as much carbon in the sample as oxygen, which is a much higher relative oxygen content than in other samples.

A

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	80122	102.592	99.71288111	99.6892	3.244
Nickel	28	K-series	379	0.29541	0.287118894	0.31078	0.033
			Sum:	102.887	100	100	

B

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	80110	94.386	88.87338458	61.8940	2.987
Carbon	6	K-series	6047	9.0165	8.489855103	31.2814	1.158
Oxygen	8	K-series	5082	2.5528	2.403743545	6.64889	0.351
Nickel	28	K-series	347	0.2474	0.233016768	0.17569	0.032
			Sum:	106.20	100	100	

Figure 20: Line analysis data for unpolished 100Cu. **A** Line spectrum indicating relative concentrations of Ni, Cu, C, and O. Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. The sample had a very large eggplant shaped defect which was characterized. The eggplant-shape had a much higher oxygen content than the surroundings, indicating it may be an oxide. This is different from the other samples, which have had primarily carbon defects.

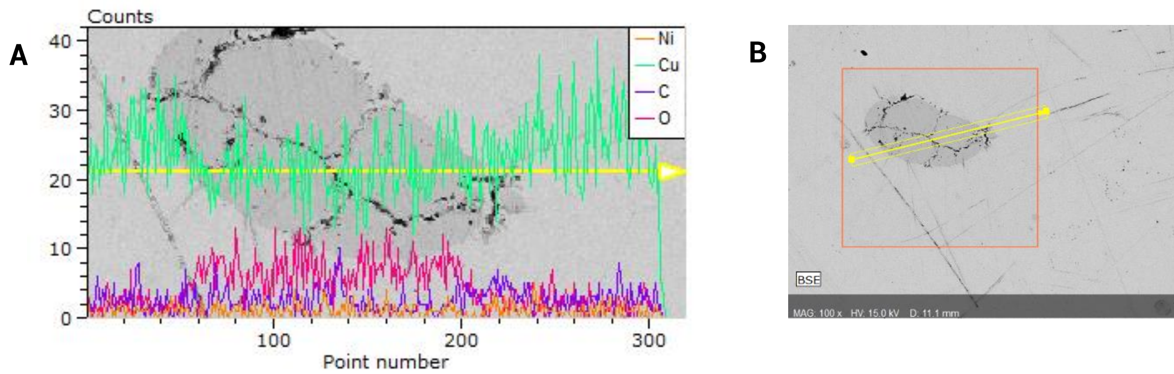
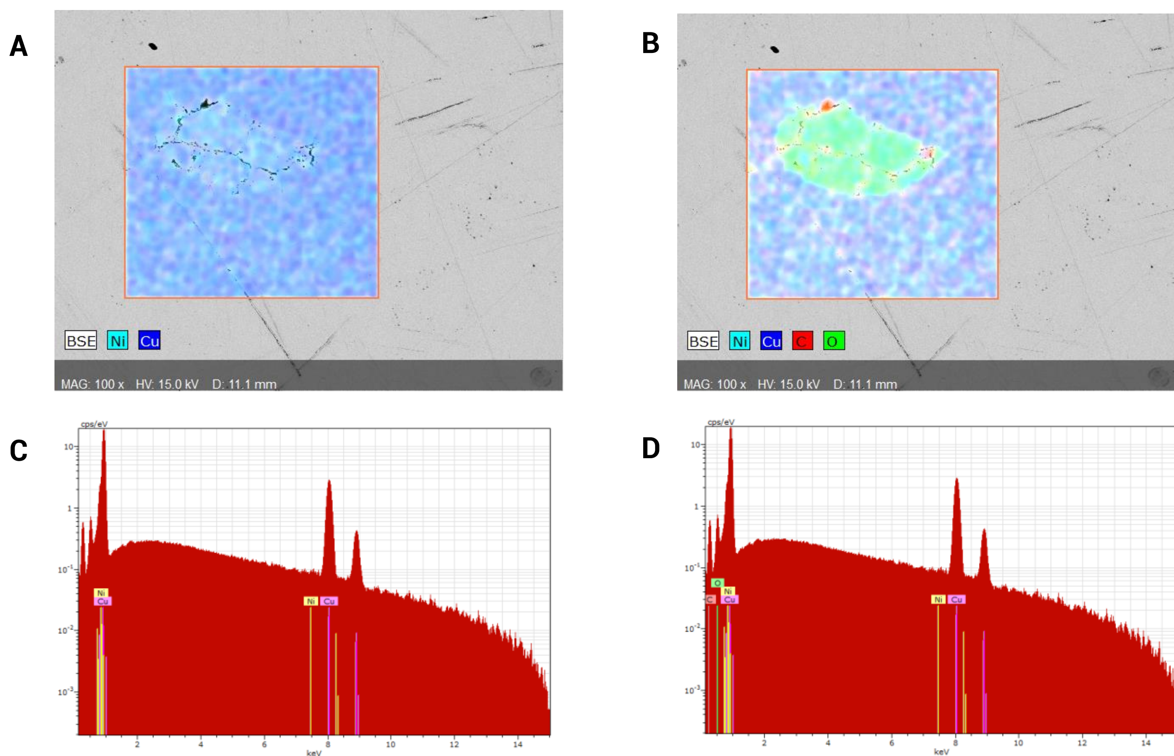


Figure 21: Area sample data for unpolished 100Cu sample. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is roughly uniform. **B** The addition of carbon and oxygen considerations had a difficult to observe effect on the spectrum. The eggplant shape mentioned in the previous figure had an obviously high oxygen content, and the cracks in the defect appear to be mainly carbon **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



SAMPLE 4: 100CU-0NI

POLISHED

Figure 22: Polished 100Cu sample at magnification 10,000X. The sample surface was more uniformly scratched after polishing, with the same grooves of 1 micron in width as found in other polished samples. There were still defects of larger diameter, but those were rarer after polishing.

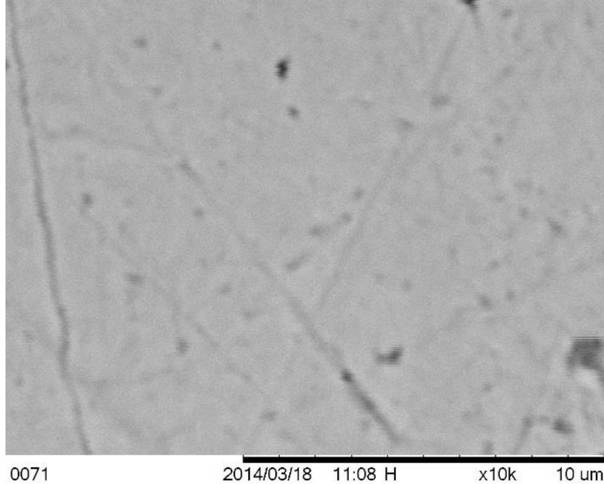


Table 8: Tabulated data from point analysis of the polished 100Cu sample. **A** Analysis of the sample purely with regard to Ni and Cu. These relative values indicate that the ratio of copper to nickel in the sample is roughly 99.8:0.20. **B** Analysis of sample including both carbon and oxygen. The data is in order of wt %, so nickel is at the bottom. After polishing, this sample underwent a significant change in carbon and oxygen content. Carbon was reduced to 2.8% from 8.4% and oxygen was reduced to nearly 0% from 2.4%.

A

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	103155	105.048	99.811049	99.7954	3.3217
Nickel	28	K-series	322	0.19886	0.188950999	0.20454	0.0310
			Sum:	105.247	100	100	

B

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Copper	29	K-series	103150	102.708	96.85303766	86.0546	3.248
Carbon	6	K-series	2213	2.97991	2.810025224	13.2093	0.449
Oxygen	8	K-series	423	0.17014	0.160446004	0.56620	0.058
Nickel	28	K-series	310	0.18716	0.176491117	0.16977	0.030
			Sum:	106.045	100	100	

Figure 23: Line analysis data for polished 100Cu. **A** Line spectrum indicating relative concentrations of various elements (Ni, Cu, C, and O). Behind the spectrum is the image which is being analyzed. **B** Region over which line spectrum data was captured relative to the SEM image which was analyzed. The sample lacked large characteristic particles on the surface and as a result there are not particularly notable variations in relative element concentrations.

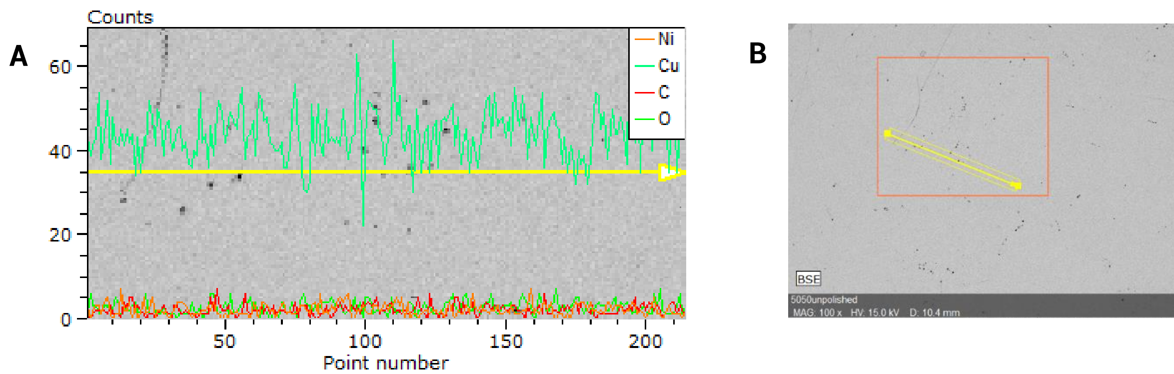
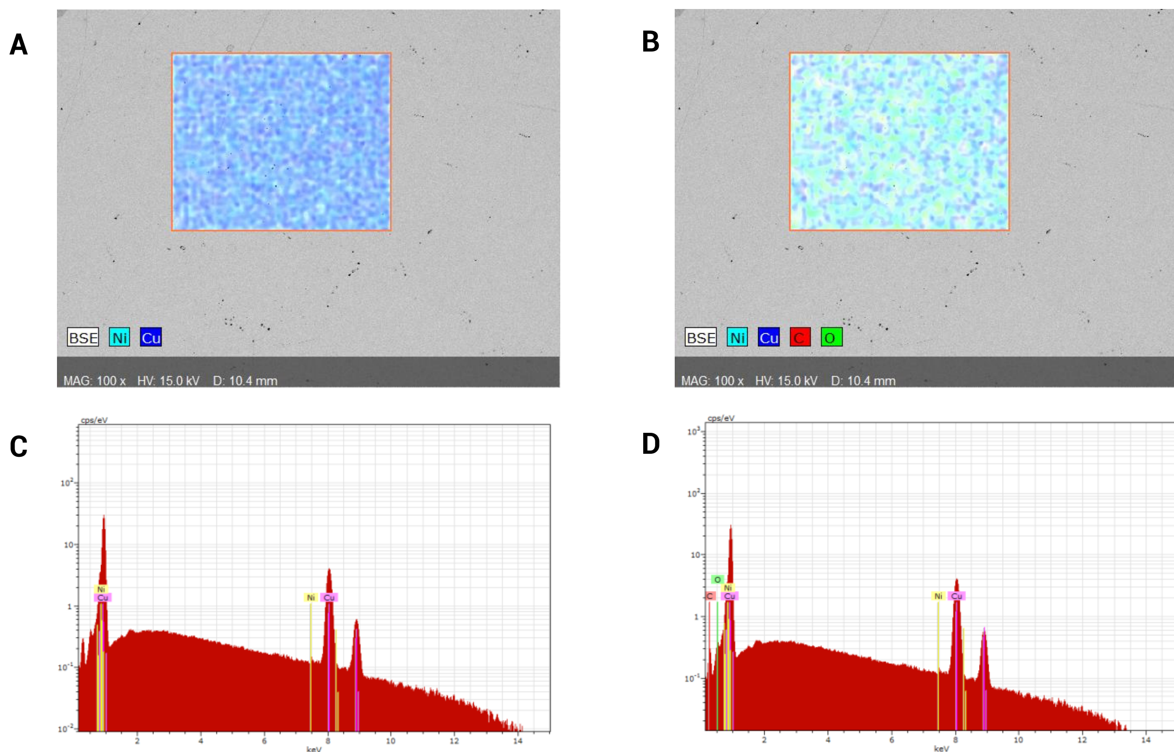


Figure 24: Area sample data for polished 100Cu. **A** Elemental distribution over the sample surface with only Cu and Ni taken into account. From the image, it appears the distribution of copper to nickel in the sample is roughly uniform. **B** The addition of carbon and oxygen considerations had a difficult to observe effect on the spectrum. The overall color of the image become slightly lighter, indicating a possible oxide layer on the sample in addition to higher carbon concentration. The oxygen increase appears to be negligible. **C** Elemental absorption spectrum corresponding to A. **D** Elemental absorption spectrum corresponding to B.



DISCUSSION

The data results for each sample showed definite differences in surface adulterants with and without cleaning. Before cleaning, most samples had higher amounts of both carbon and oxygen compared to after polishing with diamond paste. The removal of the carbon and oxide layer increased the ability for EDM to give an accurate relative concentration of copper to nickel in the sample as well, assuming the expected concentrations are accurate.

DATA ANALYSIS

SAMPLE 1: 50CU-50NI

Figure 1 and Figure 4 both show scratches on the sample surface, however Figure 4, which is the polished version of the sample, shows deeper scratches of about 1μm in width. These deeper are likely due to the polishing process. The shallower grooves are likely due to some oxidation or organic material infill.

Table 1 and Table 2 confirm the expected composition of the sample, with a slight error of 4% off the 50% expected for copper and nickel. The error for the composition as determined by the software was reduced after the sample was polished. This data is tabulated in Table 9 under "Data Reduction, *Changes in Accuracy*" below.

Figure 2 and Figure 5 show the homogeneity of the sample. This sample seemed to be relatively small particulate free, so the line analysis data shows the same average along the selected line. (B) in both figures shows the region analyzed by the line.

Figure 3 and Figure 6 show the uniformity of the distribution of copper and nickel. There does appear to be a slight gradient along the diagonal of the inspected area, however this change seems to be very slight. Depending on how the sample was formed, the sample homogeneity may be effected. As we can see, in Figure 6 there are carbon contaminants visible in red.

SAMPLE 2: 20CU-80NI

Figure 7 and Figure 10 show few scratches on the sample surface. Once again, the polished sample in Figure 7 shows deeper scratches, likely due to the polishing process.

Table 3 and Table 4 confirm the expected composition of the sample, with a slight error of3.1% off the expected percentages for copper and nickel. Show similar trends to the previous sample.

Figure 8 and Figure 11 show the homogeneity of the sample. This samples once again seemed to be relatively small particulate free, so the line analysis data shows the same average along the selected line.

Figure 9 and Figure 12 show the uniformity of the distribution of copper and nickel. There is no visible gradient in these samples, but the effect of carbon on the sample is obvious by the lightening in color between the no carbon oxygen analysis (A) and carbon/oxygen analysis samples (B).

SAMPLE 3: 10CU-90NI

Figure 13 and Figure 16 are sample surface explorations again. Figure 16, the polished sample, has a deeper defect in the surface. This was likely not due to the polishing process because the size of the hole is much larger than the diamonds in the polish. Another note is that this image is much darker than figure 13, which is likely due to different autobrightness/contrast configurations.

Table 5 and Table 6 show a deviation from the expected composition of only 1.7%. It appears that increasing discrepancy in composition between copper and nickel results in more accurate sample composition.

Figure 14 and Figure 17 show the homogeneity of the sample. This sample seemed to be relatively small particulate free in figure 17, but figure 14 shows a definite carbon composition of the particulate.

Figure 15 and Figure 18 once again seem to show a uniform distribution of the copper and nickel components. In (B) for both figures we can see the composition of defects on the surface is mostly carbon.

SAMPLE 4: 100CU-0NI

Figure 19 and Figure 22 are the first set of figures in a sample in which the polished version is less scratched than the unpolished version. The can either be a testament to the variability of the SEM because we only sample a small point, or It can be a result of uniformity in scoring caused by polishing. Large defects are removed despite the small defects that are caused.

Table 7 and Table 8 may have some bias, as the sample area has a large defect in it. We selected this area to get a better idea of the effects of particles and defects in a sample. Our error was still incredibly small, at 0.3%. Table 8 avoided the bias by corrosion and had an error of 0.21%. This clearly shows that selecting a region without only large defects increases accuracy of analysis.

Figure 20 and Figure 23 were different in that only Figure 20 had a large defect in the analysis. This defect was clearly composed with large amount of oxygen, and was therefore most likely oxidation of the copper. Figure 23 was much cleaner and it was difficult to determine the composition of the small number of particulates there.

Figure 21 highlights the usefulness of spatial elemental analysis. It is very obvious that the defect has a high concentration of oxygen and is therefore likely corrosion. Figure 24 is once again a uniform region of all copper with a skin of carbon and oxygen on the surface.

DATA REDUCTION

PRE-COLLECTION

During the data collection process, of the images collected there were some that required consideration to optimize results.

The point analysis option allowed the used to select a working area, over which the point integration would be run. Similarly, the area elemental analysis was completed over a user defined area. When selecting these areas, results were made most relevant by choosing the same area for both quantifications and by choosing an area with fewer defects. This allowed for proper quantification of relative copper-nickel values. Alternatively, if a defect was more interesting, then selecting an area with a large defect can elucidate in the "area" viewer what the spatial composition of the sample was.

The line analysis method was intended to investigate particulates that may be contaminating the surface of the sample or for nonuniformity in the sample surface. Therefore, it was best to draw the line through a particle of interest to determine the composition of that particle.

Results of this area choice are particularly visible in the unpolished copper sample, where we were able to determine that the eggplant-shaped defect was oxygen rich and therefore likely a result of oxidation. In addition, line analysis made it clear that the change in oxygen content was a roughly 200% increase. Similarly, it was possible to determine the uniformity of the samples by observing the results of area analysis where there were not large fluctuations in elemental content.

DATA COLLECTION CONSIDERATIONS

When collecting EDS data, there are equipment limitations and concerns which need to be addressed. For example, live vs. dead time and salient features of EDS.

Dead time in any electron microscope is a result of the detector receiving more information than it can handle and results in a lower output count rate than input count to the detector[2]. If the dead time is too high, the detector is being overwhelmed with input beams and the imaging beam should be reduced to not overload the detector. During our sample collection, however, we did not change the beam at all. Therefore, we did not correct for dead time manually. It is possible that during the "auto brightness/contrast" step in the viewer that the beam was changed automatically.

The other salient features of the EDS spectrum in the SEM is that we are limited by a cap at 15eV. If the lines we wish to see are require a higher voltage, we cannot see them. While all peaks appear on the spectrum, some of the peaks are heavily overlapping. This is because SEM is a bulk analysis tool. Small changes in surface composition can be visible, but can also be overshadowed by the bulk material in the background if the characteristic is too small. However, the use of electrons in the microscope allows for much more detailed sensitivity than the x-ray diffractometer because of the strong scattering properties of electrons.

COMPOSITIONAL HOMOGENEITY

Most of the samples tested had copper and nickel uniformly distributed based on observations of area spatial elemental analysis. None of our samples displayed an obvious gradient. The only variation that was seen was based on defects, but these defects were likely local to the surface of the sample and not representative of the entire sample bulk.

The ability to use x-ray mapping in order to determine which regions have different elemental compositions was invaluable to being able to determine composition. In the samples where the imaged region did not have large particles or impurities, the data was much more accurate. But

being able to select for regions without impurities, it is possible to get bulk information rather than dirty information. There were clear indications of solute partitioning on the surface of the samples with impurities, and the partitioning was easily visualized using the line spectrum analysis method.

Another interesting observation is that an unpolished sample does not actually have an oxide layer that interferes strongly and causes error as much as there is a carbon layer on the sample. This is likely because the environment is carbon (and graphite) rich, and the diamond paste may be suspended in a carbon based solution (which explains why it sits in groves on the sample surface).

CHANGES IN ACCURACY

Between polished and unpolished sample data collection there were differences in both copper-nickel ratios and carbon/oxygen content. Table 9 and Table 10 tabulate this data in order to elucidate the changes in accuracy caused by polishing a sample before imaging.

Table 9: Changes in copper and nickel weight percentage errors. The error calculations were done by the EDS software and tabulated here. The change in error is listed as delta. For almost all samples the change was negative, meaning the error was reduced. Only the 100Cu sample had an increase in error for copper. This means that polishing decreased the error when determining weight percentages of a sample

Polish	Sample	wt% Cu	wt% Ni	% Error Cu	Delta Cu	% Error Ni	Delta Ni
No	50-50	52.6002	47.3997	1.773		1.551	
Yes	50-5-	53.1643	46.8356	1.703	-0.03948	1.457	-0.06060
No	20-80	22.4982	77.5017	0.749		2.443	
Yes	20-80	22.4811	77.5188	0.748	-0.00133	2.441	-0.00081
No	10-90	11.6421	88.3578	0.405387		2.821	
Yes	10-90	11.5305	88.4694	0.393	-0.03055	2.767	-0.01914
No	100-0	99.7128	0.28711	3.244		0.033	
Yes	100-0	99.8110	0.18895	3.3217	0.02395	0.031	-0.06060

Table 10: Changes in carbon and oxygen due to polishing in various samples. For all samples but one, polishing reduced the amount of carbon and oxygen in the sample. The 20Cu-80Ni sample that displayed the opposite characteristics may be a result of experimental error.

	50Cu-50Ni			20Cu-80Ni		
Polish	No	Yes	Change	No	Yes	Change
Carbon	4.32375	3.15508	-0.2703	3.0519	3.7124	0.2164
Oxygen	0.26752	0.0090	-0.9660	0	0.4205	0.4205

	10Cu-90Ni			100Cu-0Ni		
Polish	No	Yes	Change	No	Yes	Change
Carbon	5.1106	3.2585	-0.3624	8.4898	2.8100	-5.6798
Oxygen	1.4755	0.2837	-0.8077	2.4037	0.1604	-2.2432

From these two tables it is clear to see that error was mainly reduced by first polishing the sample before executing EDS. While SEM has increased sensitivity and new compositional information, it still enhances our ability to perform accurate measurements by first cleaning the sample for any type of diffraction experiment.

POSSIBLE CONTAMINANTS

There may have been other elements in our sample which caused error. However, because most of our analysis is comparative only with the elements in question, these contaminants did not play a large role in error creation.

ERROR SOURCES

Possible sources of error in this lab were dead time, changes in users, different polishing from different users, and possible changes in humidity. There may also be slight error because a different region of the same samples was examined each time (before and after polishing).

EDS VERSUS PRECISION DIFFRACTOMETRY

When comparing the two methods of analysis, there are advantages to both methods. EDS is much more involved for the user with data collection. A specific area which the user finds most suitable is used to EDS, whereas diffractometry uses a less characterized region for analysis. EDS also occurs in a much more controlled environment, where diffractometry may depend more on sample temperature, strain distributions, and grain size.

The main advantage of EDS over diffractometry, however, is the ability to spatially determine elements. This can be very useful for understanding what is happening in the surface of a sample, and for removing noise by selecting cleaner areas. EDS has a lot more post processing power and simplicity as well despite the increased user involvement. Analyzing additional elements is difficult with diffraction but trivial with EDS.

Both types of compositional analysis improve, however, by cleaning the sample.

CONCLUSIONS

From this lab we concluded that the EDS was useful for spatial compositional analysis, and that the polishing of samples before executing EDS increased the accuracy of weight percentage results.

REFERENCES

[1] R. Gronsky. Lab 04 Manual: EDS in the SEM. *MSE 104.* University of California Berkeley, Berkeley, CA.

[2] B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, 3rd Edition, Prentice-Hall, New York, (2001), p. 319.

APPENDIX

Overflow materials should appear here. Examples include extra data runs, problematic data (such as interrupted data runs), copies of pertinent literature or other documentation, computer source code listings, or derivations of equations.

Additional Information provided when exporting point integral files (only saved for one sample, 100Cu unpolished)

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SerialNumber=103102-03
DataNumber=0067
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TimeCheck=Yes
NumberCheck=Yes
CommentCheck=No
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DPI=193.52
PixelSize=13.13
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AcceleratingVoltage=15000 Volt
DecelerationVoltage=
Magnification=10000
WorkingDistance=12600 um
EmissionCurrent=67400 nA
FilamentCurrent=1750 mA
ObservationCondition=Analy
Brightness=2213
Contrast=3000
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LensMode=
PhotoSize=
Vacuum=High
MicronMarker=10000
SubMagnification=
SubSignalName=
SpecimenBias=
Condencer2=1937
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CalibrationScanSpeed=
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ColorPalette=
ScreenMode=
Comment=[whoa this is awesome]
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