DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

June 4, 2012 to August 10, 2012

Single Pass Flow-Through Testing of Metals

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ABSTRACT

Single Pass Flow-Through (SPFT) testing has been employed as a method of evaluating the stability of radioactive waste remediation forms. The objective pursued over the course of the 10 week internship was to apply the technique to corrosion analysis of metal alloys. In conjunction with Dynamic Vapor Phase Testing (DVPT) and various spectroscopic techniques, the results of the SPFT test will be used to develop a method for performance analysis that outperforms those most commonly used in industry today. Because of the long duration of the SPFT test, the data from the analyses is not yet available for evaluation. Before starting the test, the surfaces of the metal samples were examined using Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry. The electron micrographs produced provided a detailed look at the imperfections in the surface. Observations made were used to adjust the testing process to diminish error.

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1. INTRODUCTION

After avoiding the conflict that would come to be known as World War II, the 1941 attack on Pearl Harbor by the Imperial Japanese Navy prompted a declaration of war on the Empire of Japan. In January of 1943, after a year of combat, President F. Roosevelt commissioned the Manhattan Project for the development of the first nuclear weapon. The project began with labs in Oak Ridge (Tennessee), Los Alamos (New Mexico), and Hanford (Washington). The results of these projects, other than the fuel for the world's first nuclear weapons, were massive amounts of liquid and solid waste. On site, over 50 million gallons of waste have been stored in underground tanks which have been leaking into the ground. In 1977, President Jimmy Carter created the U.S. Department of Energy (DOE) which would supplant the Atomic Energy Commission and assume responsibility for the Hanford site. Under the Department of Energy, the focus of labs shifted from plutonium production to decommissioning and cleanup processes.

In conjunction with the DOE Environmental Management, Pacific Northwest National Lab's (PNNL) Environmental Systems group focuses on the subsurface sciences. Their scientists conduct research relating to alleviation of contamination inflicted upon the environment by chemicals involved and produced in the production, disposal, and storage of plutonium. Research includes remediation of contaminated soil and groundwater and development of stable waste forms for long term nuclear disposal.

Scientists at PNNL have tested the stability of solid waste forms of the radioactive material, including glass, ceramics, and minerals, using single pass flow-through (SPFT) testing. The SPFT test is a characterization method used to investigate the corrosion properties of glass under a range of tightly controlled parameters. The data produced from the tests are used to model and predict the long term behavior of glass under different conditions. Studies have been performed on titanate ceramics to evaluate it for use as a plutonium waste form, glass waste forms prepared by the vitrification, and the autunite and apatite minerals to assess the leaching and dissolution kinetics.

One of the projects undertaken at PNNL included using SPFT testing as part of a greater corrosion analysis technique. This integrated approach to testing relied primarily on SPFT and Dynamic Vapor Phase Testing (DVPT), paired with spectroscopic analyses, to provide a more complete understanding of the corrosion processes and overall stability of the sample. The advantages of these tightly managed dynamic systems come from the ability to test, over sweeping ranges, the effects of independent environmental variables, such as flow rate, temperature, and pH, on corrosion. Independent analysis allows for quantification of the independent variables, which can be incorporated into a model from which assessments and predictions about the performance of a sample can be shaped.

This integrated testing protocol to corrosion analysis has been proposed as a more comprehensive alternative to the test methods currently employed by military and industry for evaluation of metals used in equipment. It provides a more complete view of the independent contributions of the different variables, allowing for formulation of a comprehensive model for performance assessment which could reduce corrosion triggered maintenance and equipment failures.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Program, an initiative designed by the US Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC) to create a "pipeline" of minority engineers and scientists specially trained and mentored to enter DOE-EM's workforce. During the summer of 2012, DOE Fellow intern, Robert Lapierre, spent 10 weeks doing a summer internship at Pacific Northwest National Laboratory under the supervision and guidance of Dr. Dawn Wellman. Mr. Lapierre's project was initiated in June 4, 2012, and continued through August 10, 2012 with the objective of starting the process of performing Single Pass Flow-Through (SPFT) tests on metal monoliths.

3. RESEARCH DESCRIPTION

The primary objectives of my research were to set up and perform SPFT tests on three (3) types of metal monoliths. The results of the tests would then be incorporated into the integrated testing protocol for evaluating and predicting corrosion. From the beginning of the project it was understood that the experiment was a months long process that would not be completed during my relatively short 10 week stay. Over my stay I would learn to set up the SPFT test, prepare and adjust buffer solutions, and become proficient in the use of Scanning Electron Microscope and Energy Dispersive X-ray Spectrometer (SEM/EDS). The SEM/EDS training was necessary in order to perform pre and post-study surface analysis of the metal samples.

Figure 1. Coupons cut from metal samples

The three metals selected for the study were Monel Alloy 400, Inconel 617, and Cathodic Protection Materials (CPM). In the case of the CPM sample, a ribbon was cut into equal sized coupons. Because only the exterior was intended for contact with the environment, the top and bottom cut surfaces of the coupon would be coated in epoxy to limit exposure. The irregular shape of the CPM required that the other two metals, which came in sheet form, be cut to match the surface area of the CPM coupons which was to be exposed in solution.

Before testing, the surfaces of the metal monoliths need to be analyzed by SEM/EDS. For that reason, a large amount of time was spent studying and training on the SEM. The purpose of this analysis is to characterize the surfaces of the different metal monoliths. It is important to find any imperfections in the reactive surfaces because any scratches, nicks, pitting, or cracks could potentially change the dissolution rate. The EDS analysis is useful for estimating the element concentration at points of interest on the sample. While the constantly flowing solution should limit the time for reactions, alteration products could be formed in the test process. A before and after EDS analysis allows us to monitor such change as well as any surface contaminations before starting the SPFT test.

The SPFT setup is designed as a constantly flowing, saturated, corrosion simulation under tightly controlled conditions which, when adjusted, impact the rate of sample dissolution. The system consists of:

- A temperature controlled oven
- pH adjusted buffer reservoir
- Influent pumps, with 6-way valve
- Teflon reactors
- Effluent collection containers

The assembly is set up in and around the oven, which is set at a constant temperature selected for the particular test. The temperature is established using a thermocouple and a Teflon reactor filled with deionized water. The temperature for this experiment was 80°C for all samples.

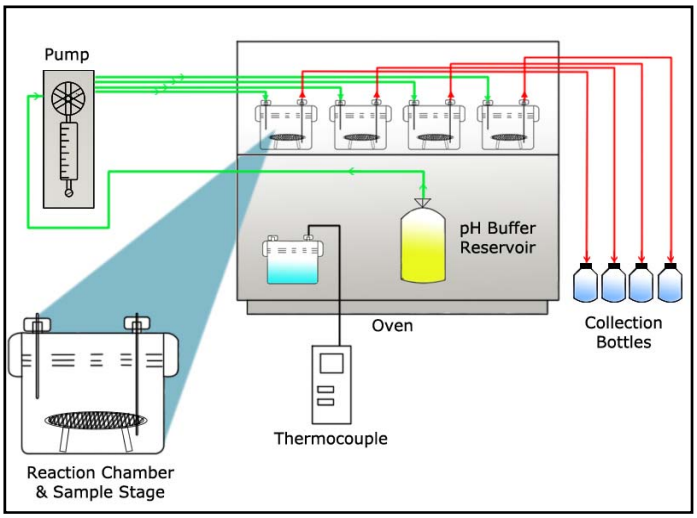

Figure 2. SPFT experimental setup

The range of interest required 6 buffer solutions that spanned from pH 3 to pH 8. The buffer prepared for the solutions with pH ≥ 6 was a 0.05M TRIS (tris(hydroxymethyl) aminomethane) organic buffer while a TRIS HCL buffer was used for solutions with pH ≤ 5. The buffers were prepared in 1 L volumetric flasks. Their pHs were adjusted up or down using LiOH and H_2SO_4, respectively. The bottles of the pH-adjusted buffers were housed inside the oven in order to maintain the desired temperature when extracted by the pump.

The pump aspirates a programmed volume of solution from the reservoir before dispensing it to the Teflon reaction chambers, wherein the sample is held up by a Teflon stage. The pump programming enlisted basic concepts of loops and cycles to design a program for how much the KLOEHN Versa pumps would direct the flow of solution. This step is vital to the accuracy of the study and required constant adjustments because the program dictated the flow rates of the SPFT tests. The experiment required that SPFT tests be run with each of the 6 pHs at 17 different flow rates, ranging from 2 to 250 mL per day. The establishment of the flow rate would prove to be the most difficult and time consuming part of the experiment. The extremely slow flow rates proved to be especially problematic.

Table 1. Rate Based Flow-Through

Flow Rate	1.0L Flowthrough Times	
mL/day	days	hrs
2	500.00	12000.00
5	200.00	4800.00
10	100.00	2400.00
15	66.67	1600.00
20	50.00	1200.00
25	40.00	960.00
30	33.33	800.00
35	28.57	685.71
40	25.00	600.00
45	22.22	533.33
50	20.00	480.00
75	13.33	320.00
100	10.00	240.00
125	8.00	192.00
150	6.67	160.00
175	5.71	137.14
250	4.00	96.00

The effluent solution exits the Teflon reaction chamber into labeled collection bottles. The bottles were periodically changed and labeled based on the time elapsed from the start of the experiment. The amount of effluent collected is determined by weight difference and used to re-evaluate the flow rate. After the test, the effluent solution is sent for analysis by ICP-OES.

4. RESULTS AND ANALYSIS

Characterization of the metal surface before and after testing is an important part of the SPFT process. For that reason, training on the SEM/EDS was provided by Dr. Brad Johnson, the technical group manager for the Radiological Materials and Technology Development Group at PNNL. After reaching a level of understanding and proficiency that Dr. Johnson was comfortable with, independent access to the SEM/EDS was permitted.

It is worth noting that the EDS used standardless semi-quantitative analysis. Also, references to the metal "surfaces" shall hereafter refer to the area of the metal that will be exposed to test solution while the "cut edge" describes the area not intended for exposure.

Cathodic Protection Materials

The surface of the CPM coupon showed some scratching and grooving that were visible to the naked eye. As the magnification increased to x100 and x200 (Figure 3c & 3d), what seemed like organic contaminants were noticed on the surface. It was anticipated that SEM/EDS analysis would show an increase in carbon and oxygen in the contaminants. The actual EDS spectrograph (Figures 4 & 5) appeared to show similar peaks for carbon and oxygen. Weight % and Atomic % were not checked on a reference point in this sample.

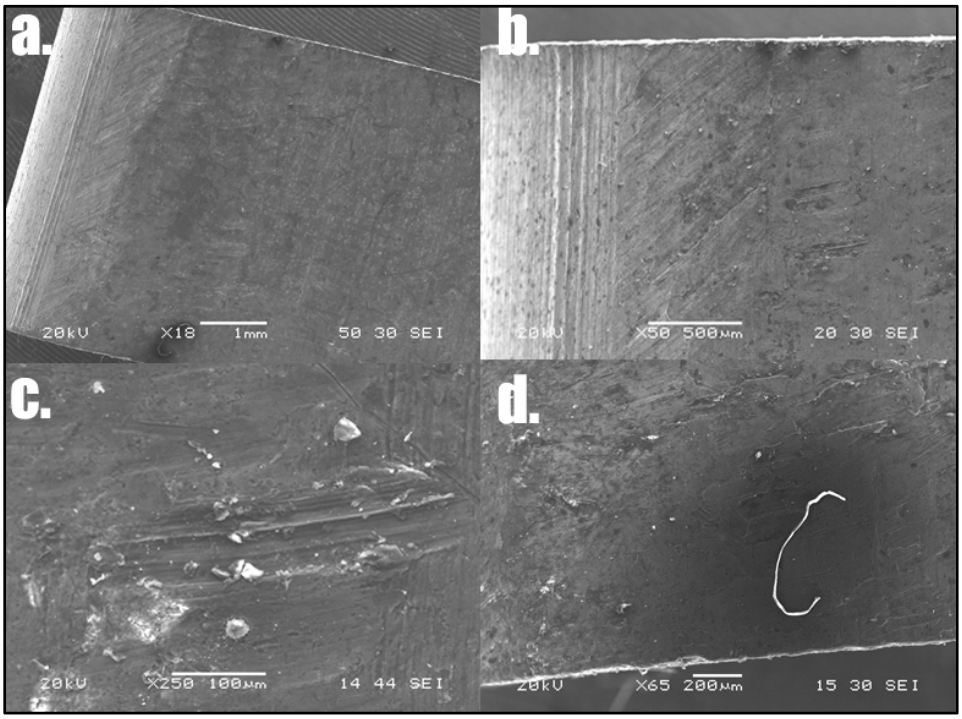

Figure 3. SEM images of the reacting surface of the CPM coupon

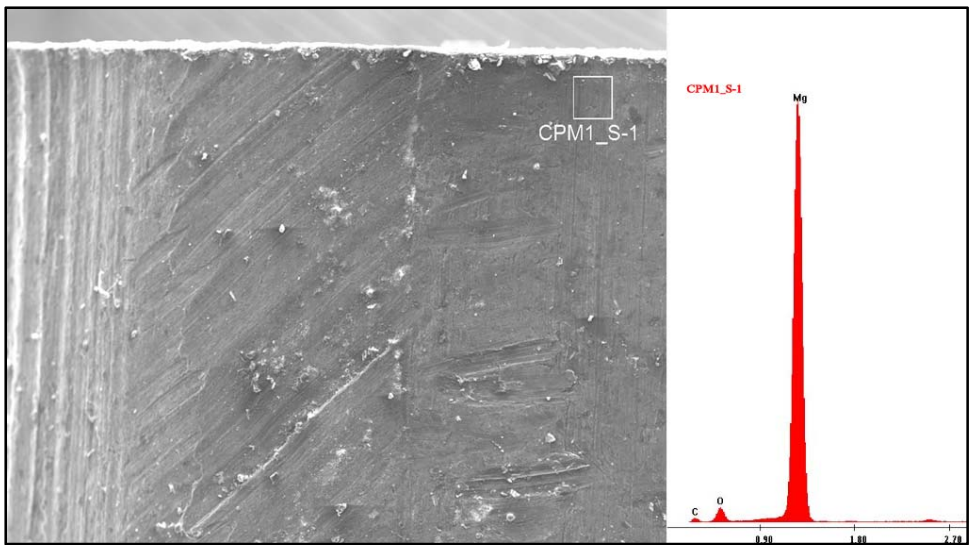

Figure 4. SEM/EDS image and spectrograph of CPM surface

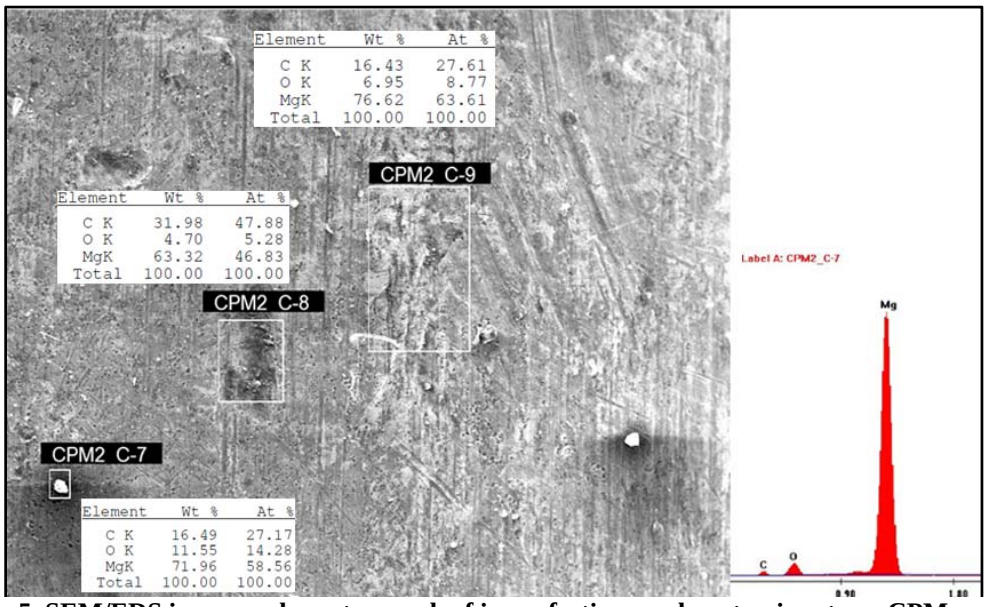

Figure 5. SEM/EDS image and spectrograph of imperfections and contaminants on CPM surface

Inconel 617

The surface of the Inconel 617 coupon showed a rough surface with several dark areas of contamination (Figure 6). The EDS spectrum of the coupon surface (Figure 7) was used as reference to compare to those of contaminants (Figure 8) present. The sharp increases in atomic % of carbon suggest that these are organic contaminants, as expected. A similar increase in oxygen was also predicted but not significantly observed. The SEM image of the cut edge of the Inconel 617 coupon (Figure 9) show a drastically different surface texture compared to the testing surface. The EDS spectra for the edge and surface were very similar, the exception being a peak for zinc which could not be explained.

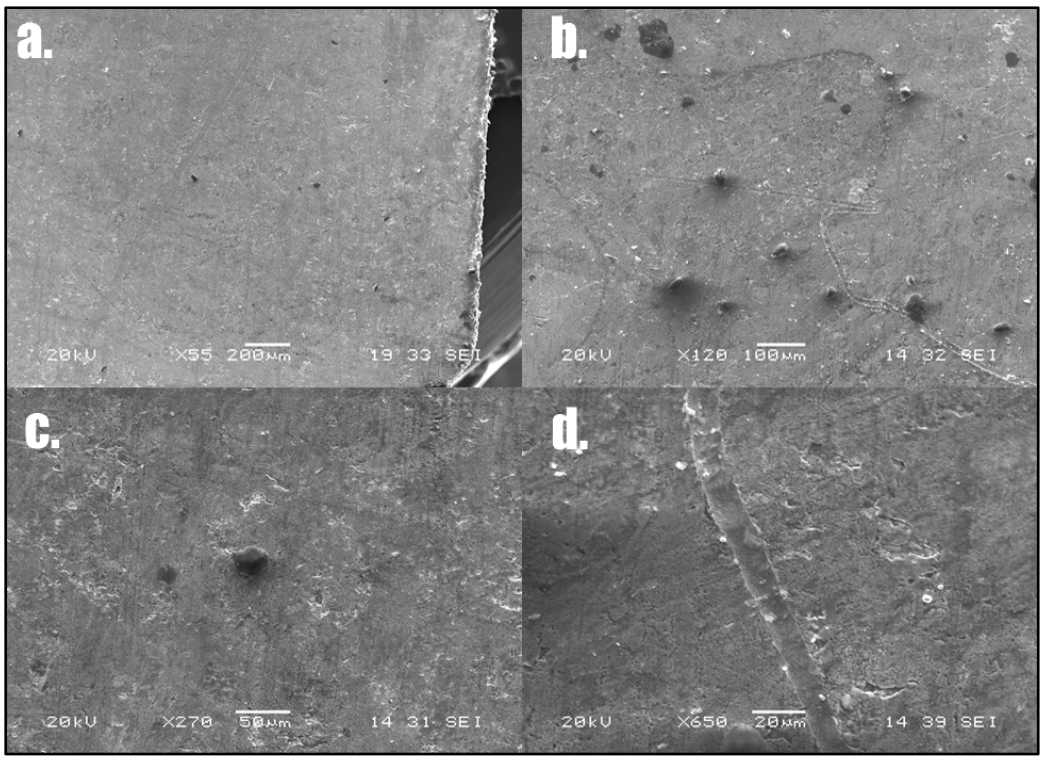

Figure 6. SEM images of the reacting surface of the Inconel 617 alloy

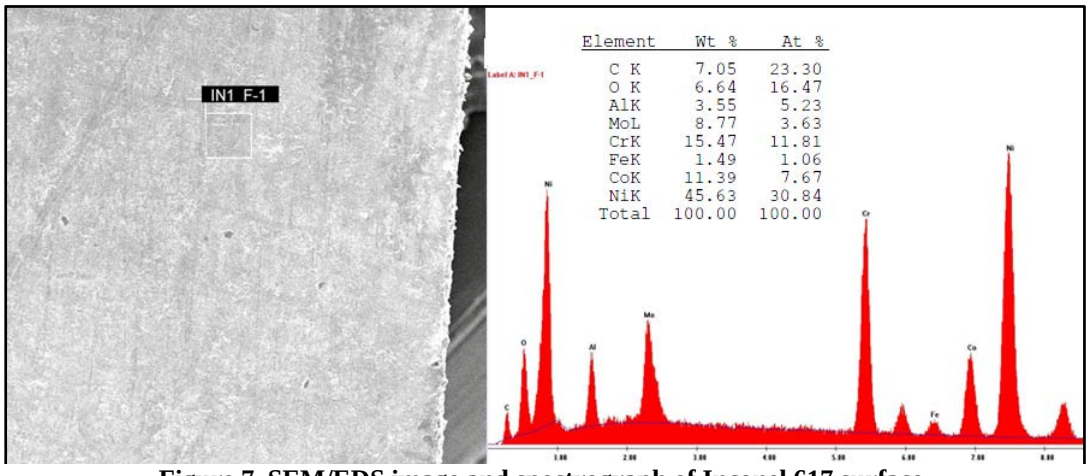

Figure 7. SEM/EDS image and spectrograph of Inconel 617 surface

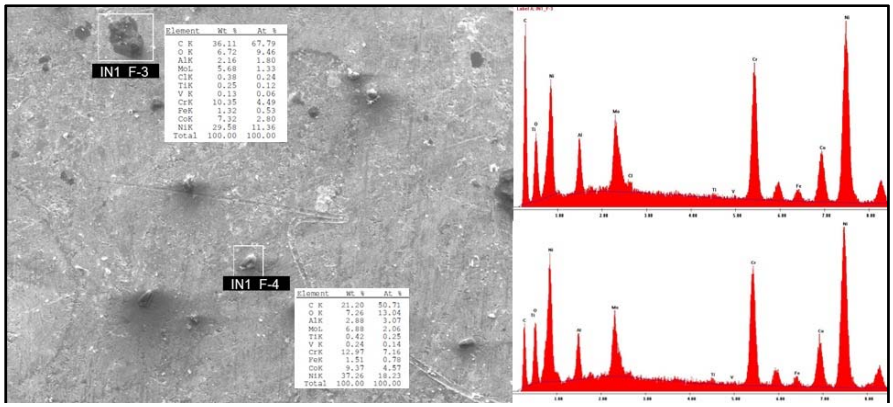

Figure 8. SEM/EDS image and spectrograph of contaminants on Inconel 617 surface

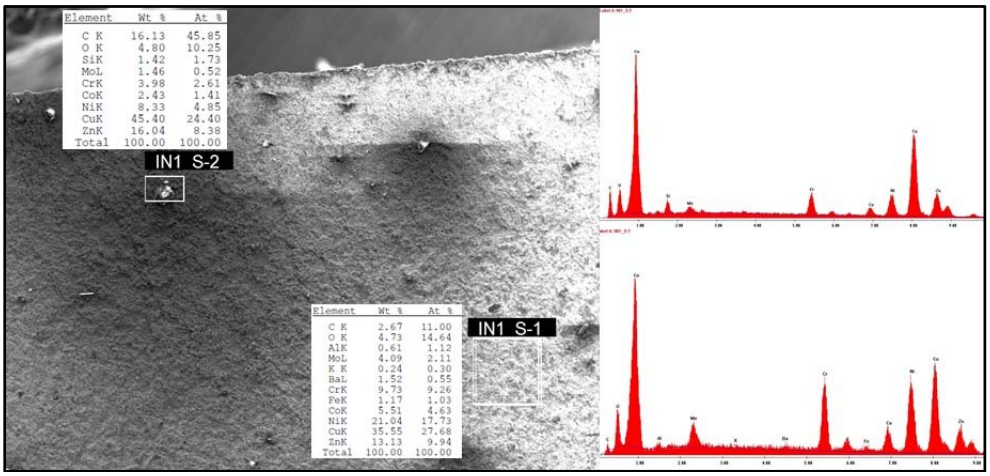

Figure 9. SEM/EDS image and spectrograph of imperfections and contaminants on cut edge of Inconel 617

Monel Alloy 400

The surface of the Monel Alloy 400 appeared to show a uniform pattern of grooves, possibly from the machining process. The imperfections were less numerous on this coupon. The spectra for the pitting and scratching on the Monel Alloy 400 surface (Figure 11) suggested a slightly elevated carbon peak by comparison to the metal reference point analyzed in Figure 13 (labeled MA1-1b). Once again, countering predictions, there was no appreciable increase in oxygen. The large contaminant found on the surface of the Monel Alloy 400 sample shows a large increase in both carbon and oxygen peaks, suggesting the presence of an organic compound (Figure 13). The image and spectrograph lead to the hypothesis that this contaminant is an organic ink or paint used to label the sample that was not noticed before the micrograph was taken.

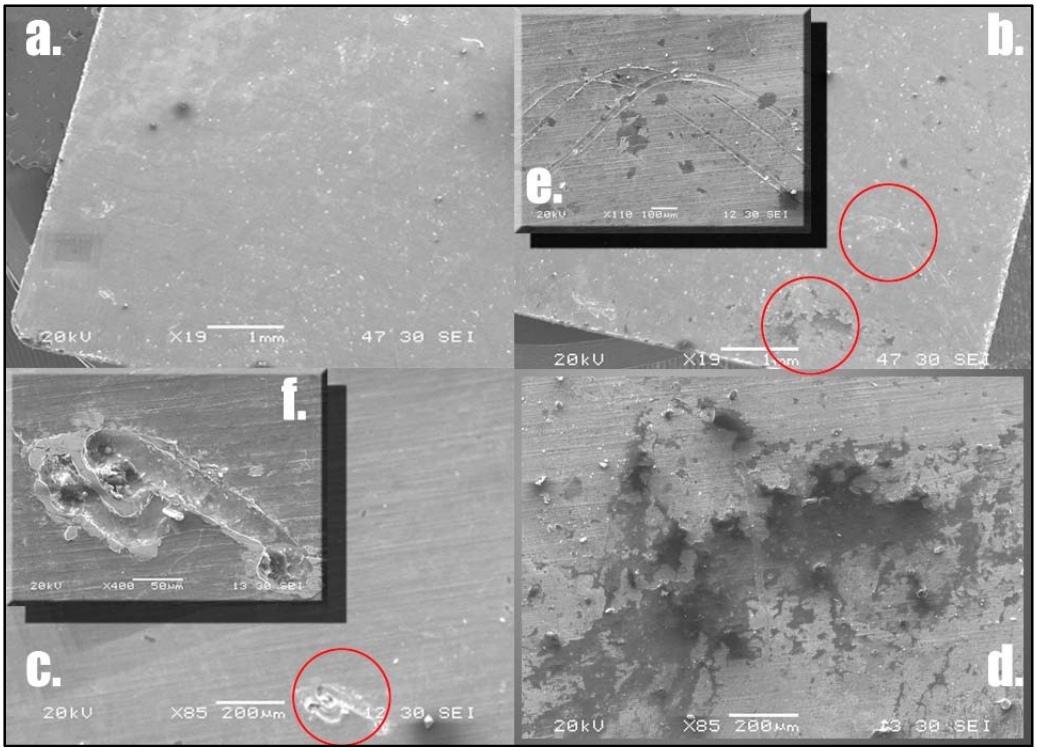

Figure 10. SEM images of the reacting surface of the Monel Alloy 400

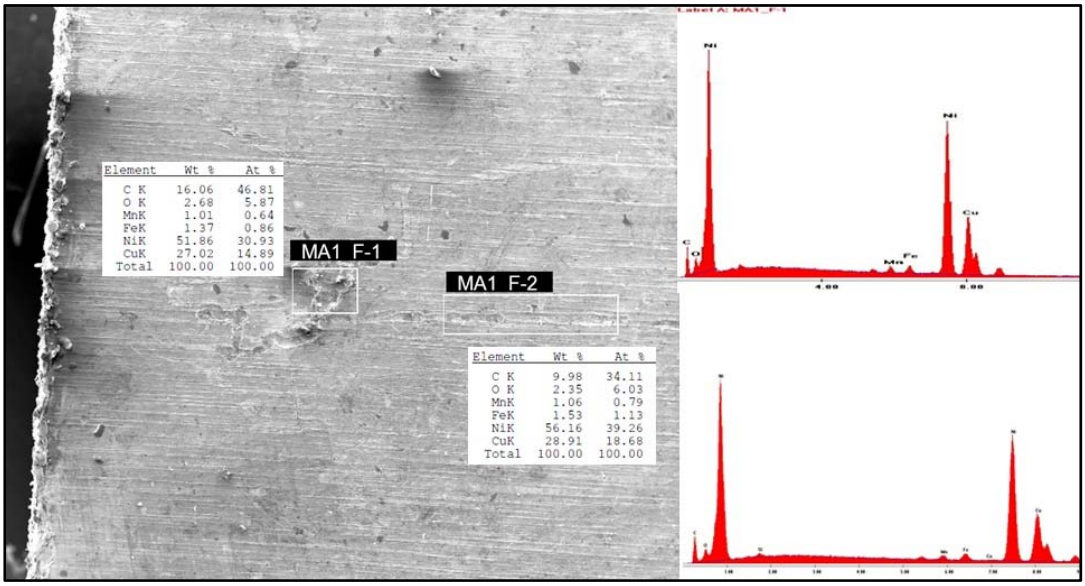

Figure 11. SEM/EDS image and spectrograph of pitting and scratching on the surface of Monel Alloy 400

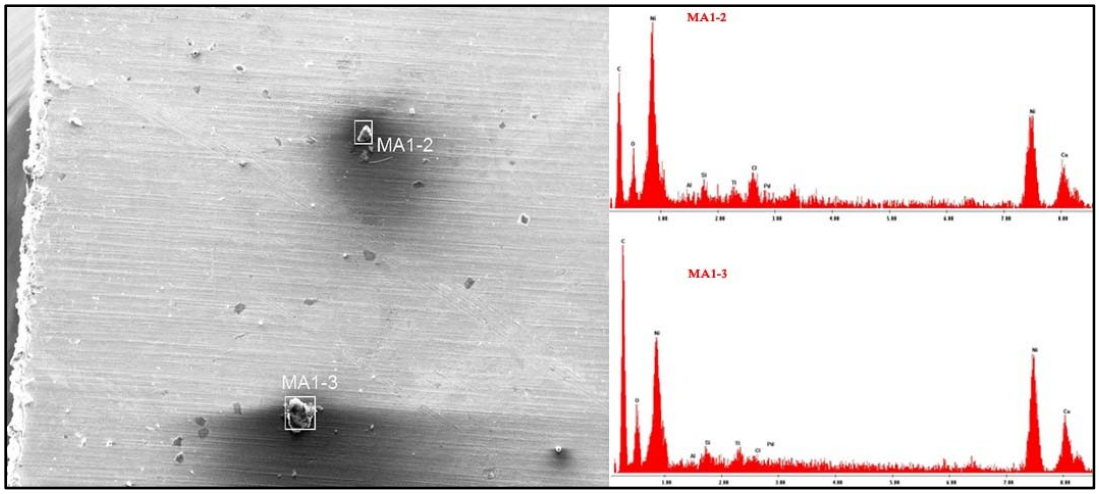

Figure 12. SEM/EDS image and spectrograph of contaminants on Monel Alloy 400 surface

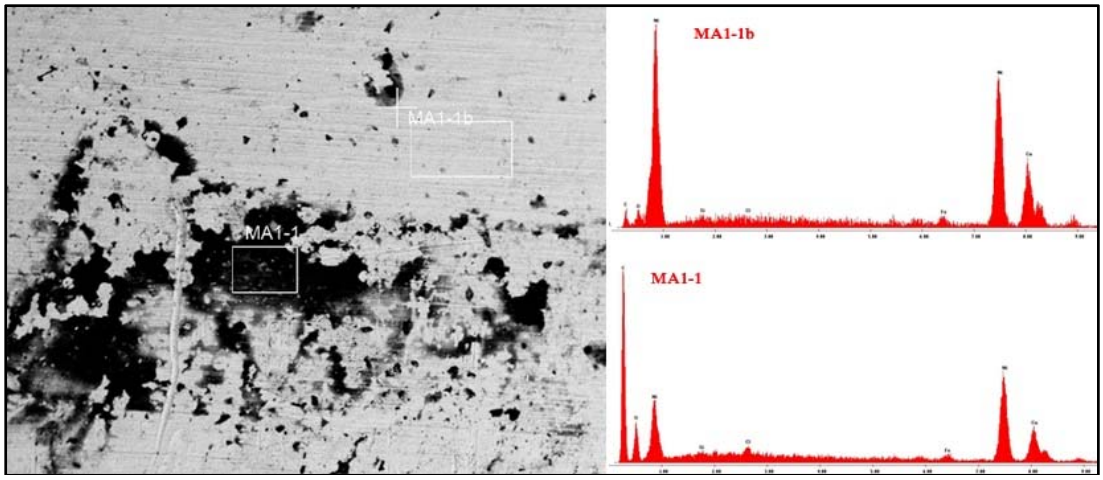

Figure 13. SEM/EDS comparison of contaminant and reference point of Monel Alloy 400 surface

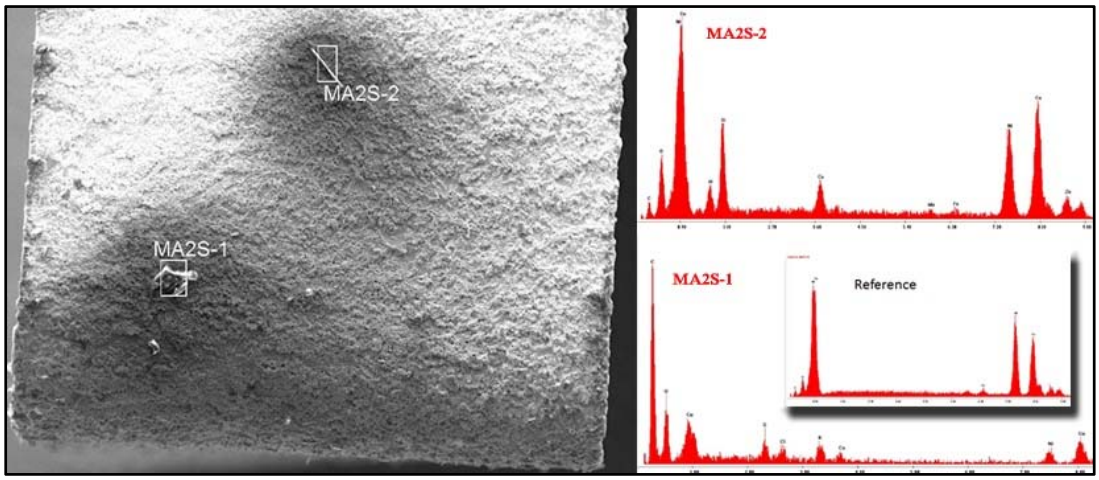

Figure 14. SEM/EDS comparison of contaminants to reference on cut edge of Monel Alloy 400

The images of the cut edges of the Inconel 617 (Figure 9) and the Monel Alloy 400 (Figure 14) show textures drastically rougher than those of the surface. Based on these images, it was predicted that the dissolution rates would be dramatically different than those of the surface. After this observation, the method was adjusted to include the coating of these cut edges with the same epoxy used for the cut face of the CPM samples.

As mentioned previously, SPFT testing is a long process. The experiment is ongoing; therefore, there is no data to present regarding the corrosion testing.

5. CONCLUSION

The SPFT tests that were started over the 10 week internship were far from complete by the end of the summer. The testing protocol is a method that can take several months to produce results. The work that was started over the summer will be continued by PNNL staff and future interns. There is a chance that the SPFT test methods practiced could be applied to ARC or thesis research.

The extensive, 1-on-1 SEM/EDS training received over the duration of the internship is considered prized knowledge gained. The ability to effectively understand and use the instrument will prove to be advantageous in addressing current ARC objectives and any future research. The electron micrographs taken should be useful for characterization of the sample surfaces as well as for comparison when the SPFTs are finally completed.

6. REFERENCES

Wellman, D.M., et al., *Integrated Testing Protocol for Determination and Prediciton of Corrosion Inhibition and Material Longevity*: Pacific Northwest National Laboratory.