PNNL-27526

# Electroplating Zr onto U-Mo

# **Final Report**

May 2018

Kerry Meinhardt Mark Rhodes Michael Catalan Greg Coffey Anthony Guzman

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Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory Richland, Washington 99352

# Summary

During fiscal years 2018 and 2017, Pacific Northwest National Laboratory supported the U.S. High Performance Research Reactor (USHPRR) Convert program via the Fuel Fabrication Pillar by evaluating the technical challenges and opportunities related to the use of electroplating the Zr vapor barrier on U-Mo fuel. PNNL's support covered the main areas:

- 1. Electroplating mini-plate 1 foils
- 2. Scaling up electroplating system to support full-size plate demonstrations (and conversion of the USHPRR)
- 3. Basic science into reducing the  $O_2$  content of the Zr produced by the electroplating process.

# Acronyms and Abbreviations

ASTM	American Society for Testing and Materials
CF	ConFlat
DC	direct current
DE	destructive examination
FY	fiscal year
HF	hydrogen fluoride
MP	mini plate
OCV	open circuit voltage
PNNL	Pacific Northwest National Laboratory
SEM	scanning electron microscopy
U-Mo	uranium molybdenum
USHPRR	U.S. High Performance Research Reactor

# Contents

Sum	mary	y	iii
Acro	onym	ns and Abbreviations	iv
1.0	Bac	kground	1
2.0	Eleo	ctroplating of MP-1 Foils	2
	2.1	Summary Results	3
	2.2	Zirconium Composition	4
3.0	Sca	le Up	7
4.0	Red	luced Oxygen Testing	8
	4.1	System Description	8
	4.2	Testing	10
	4.3	Discussion	12
5.0	Con	nclusions	15
6.0	Ref	erences	16

### Figures

Figure 1. Electroplating Equipment	2
Figure 2. Q2E012 Showing Plating Tracking U-Mo Surface Conditions	4
Figure 3. Foil Post-Plating Images	4
Figure 4. Bellows Design	9
Figure 5. Low Oxygen Plating SEM	.13

#### Tables

Table 1. Process Qualification Matrix	3
Table 2. Zirconium Composition (in ppm)	5
Table 3. Oxygen/Hardness Q1E029	6
Table 4. Plating Parameters	11

# 1.0 Background

During fiscal years (FYs) 2018 and 2017, Pacific Northwest National Laboratory (PNNL) supported the U.S. High Performance Research Reactor (USHPRR) Convert program via the Fuel Fabrication Pillar by evaluating the technical challenges and opportunities related to the use of electroplating the zirconium (Zr) vapor barrier on uranium-molybdenum (U-Mo) fuel. PNNL's support covered three main areas:

- 1. Electroplating of mini-plate 1 (MP-1) foils
- 2. Scaling up electroplating system to support full-size plate demonstrations (and conversion of the USHPRR)
- 3. Testing to reduce O<sub>2</sub> content in salt bath in an effort to produce low-O<sub>2</sub> Zr in the electroplating process.

During late FY 2017, USHPRR and the Fuel Fabrication Pillar down selected among the three competing technologies for the Zr vapor barrier. Plasma spray and Zr electroplating were eliminated and the baseline technology of co-rolling was selected. This report provides a summary and close out of the electroplating activities.

Section 2.0 of this report summarizes the MP-1 electroplating effort; full details may be found in the process qualification report. Section 3.0 summarizes the scale-up activities performed by Plasma Processes. Full details may be found in the final report from Plasma Processes.

Section 4.0 summarizes the work done to understand if the  $O_2$  content of the plated Zr could be lowered by reducing the  $O_2$  content of the salt in an attempt to produce a low- $O_2$  plating; and Section 5.0 provides a summary of the conclusions.

# 2.0 Electroplating of MP-1 Foils

PNNL performed electroplating of depleted U-Mo foils and low enriched U-Mo foils during FY 2017. The depleted U-Mo foils were used for process qualification. Once the system was qualified the MP-1 low enriched uranium foils were plated.

The electrolytes used to deposit Zr are mixtures of  $ZrF_4$  and alkali fluorides. The U-Mo foil was used as the cathode and Zr electrode was inserted into the molten salt to serve as the anode. A current density was applied at a preset temperature and the  $ZrF_4$  was disassociated, resulting in the  $Zr^{4+}$  ions traveling to the foil where they were deposited in a coating layer. The atmosphere (e.g., O<sub>2</sub> and water content) was controlled to ensure the quality of the deposited Zr coating. See Figure 1 for the electroplating system setup.

The concerns related to throughput were never fully addressed. The down-select decision resulted in termination of the electroplating activities in late FY 2017. The full results of the MP-1 activity are documented in the *Electroplating Zr on U-Mo Foils Process Qualification Report* (PNNL 2017).



**Figure 1. Electroplating Equipment** 

#### 2.1 Summary Results

The electroplating of Zr on U-Mo fuel met the requirements identified in the process qualification plan and manufacturing and quality plan. The process provided a Zr coating meeting the thickness and coverage requirements. These results are summarized in Table 1. Thickness was confirmed by optical measurements and weight gain. The optical measurements taken from the destructive examination (DE)-examined foils indicate the plating thickness was as expected (the target mass of about 1 gram corresponded to roughly 0.001-inch thick plating). Targeting slightly over 1 gram for the plating mass ensured the average plating thickness was greater than the minimum required. If the plating mass target was lowered slightly, all elements would be within the 2 sigma min/max calculation.

Requirement Number	Zirconium Plating Qualification Requirement	Pass, Information Only, or Fail	Basis
1	Composition	Information only – several elements are above specification	Chemical analysis
2	Thickness	Pass	DE optical measurements Mass gain measurements Micrometer measurements
3	Coverage	Pass	Visual inspection
4	Surface Condition	Pass	Visual inspection
5	Identifier	Pass	Visual inspection

#### **Table 1. Process Qualification Matrix**

The main concern with releasing PNNL for production of low enriched and highly enriched uranium fuel was the low number of foils that passed inspection (less than 30%). The yield calculation does not include the foils out of specification that were accepted by non-conformance report for DE.

The MP-1 electroplating system was capable of plating to specification and passed all five of the qualification criteria. As can be seen in Figure 2, the Zr plating closely followed the surface conditions of the foil. This is opposite of the baseline process (co-rolled) where the Zr coating tended to fill in the valleys and be thinner on the peaks of the base foil. Figure 3 provides a visual of several plated foils.



Figure 2. Q2E012 Showing Plating Tracking U-Mo Surface Conditions



**Figure 3. Foil Post-Plating Images** 

# 2.2 Zirconium Composition

The results of the as-plated chemical analysis are provided in Table 2 along with a comparison of the American Society for Testing and Materials (ASTM) requirement for Zr stock and the results of the anode chemical analysis. Elements that exceed the ASTM specification maximum impurity limits are

highlighted in grey. The anode value is from the supplier-provided certificate. The columns to the right (2/8/17 through 3/30/17) are the composition resulting from analysis of the as-plated samples. Three separate samples were provided from Q1E029 and a single large sample from Q1E054 that was analyzed twice.

	ASTM-	Meets		Q1E029		Q1E054 <sup>2</sup>		
Element	B352- 11	ASTM B352-11	Anode	2/8/17 (bottom) <sup>3</sup>	3/30/17 (middle)	3/30/17 (top)	3/30/17	3/30/17
Al	75	No	50	83	170	120	84	89
В	0.5	Yes	0.4	<.25	<.25	<.25	<.25	<.25
С	270	Yes	140	<20	70	50	<20	<20
Ca		Yes	0	<10	<10	<10	<10	<10
Cd	0.5	Yes	0.4	<.25	<.25	<.25	<.25	<.25
Co	20	Yes	13	<10	<10	<10	<10	<10
Cr	200	Yes	80	<50	<50	<50	<50	<50
Cu	50	Yes	12	<25	<25	<25	<25	<25
Fe	1,500	Yes	180	<50	<50	<50	<50	<50
Н	25	No	10	63			63	74
Hf	100	Yes	60	<25	<25	<25	<25	<25
Mg	20	Yes	11	<10	<10	<10	<10	<10
Mn	50	Yes	13	<25	<25	<25	<25	<25
Мо	50	Yes	20	<10	83	29	<10	<10
N	80	Yes	30	<20	<20	<20	<20	<20
Nb		Yes		<50	<50	<50	<50	<50
Ni	70	Yes	50	<35	<35	<35	<35	<35
0	1,000	No	170	48,000	36,000	38,000	36,000	34,000
Si	120	Yes	60	<10	<10	<10	<10	<10
Sn	50	Yes	10	<25	<25	<25	<25	<25
Ti	50	Yes	20	<25	<25	<25	<25	<25
U	3.5	No	1	45	580	210	30	36
W	100	Yes	30	<25	<25	<25	<25	<25

#### Table 2. Zirconium Composition (in ppm)<sup>1</sup>

As can be seen in Table 2, the electroplated Zr tended to have significantly less trace elements with the noticeable exceptions of aluminum, hydrogen, O2, and uranium. The composition of the anode was provided as a reference to show it was not the source of the higher than expected elements. The source of the uranium is likely from the U-Mo foil.

 <sup>&</sup>lt;sup>1</sup> From ASTM B352-11 (UNS R60001).
<sup>2</sup> Sufficient Zr was available in the sample to repeat the analysis two times.

<sup>&</sup>lt;sup>3</sup> Q1E029 (bottom) was analyzed as QUAL-1 by ATI.

The source of the  $O_2$  was not from a process upset and was most likely coming from two sources. The system was held around 2 PSI above atmosphere with purified Ar to minimize any air leaking in. The Ar was run though a purifier with a titanium metal getter bed at 800°C. This reduced the  $O_2$  in the Ar to around  $1 \times 10^{-12}$  ppm, but it was still not low enough to prevent the Zr from picking up some  $O_2$ . However, this should have been a minor amount of  $O_2$ . The system had around 50 Kg of salt in it. Using a combination of X-ray photoelectron spectroscopy and inductively coupled plasma, the amount of  $O_2$  in the salt due to impurities was estimated to be around 90 grams. To remove that amount of  $O_2$ , around 2 Kg of Zr would need to run through the system if the  $O_2$  was in the Zr at a 5% level. This is far from the ideal way to remove the  $O_2$  from the salt, but the  $O_2$  level in the Zr did fall as the system was operated. In a small-scale system, we tested the use of NF<sub>3</sub> as a means to fluorinate the oxides in the salt. This a technique used in the molten salt reactors to decrease the  $O_2$  content of the salt to reduce the corrosion of the metal piping.

In addition to the chemical analysis, the microhardness of the plated Zr was taken on Foil Q1E029 at three locations (top, middle, and lower). The microhardness test was used as an additional method to approximate the  $O_2$  content in the Zr coating as described below. These are the approximated locations where the Zr was taken for LECO<sup>1</sup>  $O_2$  measurements. Qualitatively, the plating from the top of the foil was more difficult to remove than the bottom. The hardness-to- $O_2$  content relationship was taken from work by Nakatsuka et al. (2012). The  $O_2$  content in the Nakatsuka work was limited to 1,000 ppm  $O_2$ ; however, extrapolating a linear fit of the data to higher  $O_2$  values appears to be in good agreement with the observed Zr  $O_2$  content. The relationship established was y = 36.51x + 451.21 where x is the square root of the wt% of  $O_2$  in ppm and y is the Vickers hardness in MPa. The resulting calculated  $O_2$  based on microhardness matched the  $O_2$  levels measured (this is an order of magnitude estimation) as shown in Table 3.

Location	Vickers Estimate	LECO
Тор	48,936	38,000
Middle	36,523	36,000
Bottom	37,854	48,000

Table 3. Oxygen/Hardness Q1E029

Due to the concern regarding high  $O_2$  content within the zirconium, PNNL evaluated the possibility of a low- $O_2$  plating. The results of this activity are provided in Section 4.0.

<sup>&</sup>lt;sup>1</sup> LECO is trademark of the original name for Laboratory Equipment Corporation and the provider of analytical instrumentation.

## 3.0 Scale Up

The PNNL MP-1 electroplating system was, by its design, labor intensive and capable of only plating the smaller mini-plates used for the MP-1 experiment. While the MP-1 foils were being fabricated, PNNL and their subcontractor, Plasma Processes, worked on issues related to the use of the electroplating process for full-scale research reactor needs. The results of the scale-up studies are provided in the *Scaled System Studies Final Report*, (Plasma Processes 2017).

As part of the scaled systems studies, Plasma Processes evaluated improvements to the cleaning process and alternative salt compositions. Both activities identified improvements in the existing process that could be implemented to increase the quality and/or throughput of the Zr electroplating process.

## 4.0 Reduced Oxygen Testing

The focus of the basic research and development into the Zr electroplating process during FY 2017 was to see if the O<sub>2</sub> content in the Zr plate could be lowered by reducing the O<sub>2</sub> content of the salts. Testing the salt used in the MP-1 plating system showed around  $0.8 \text{ mol}\% \text{ O}_2$  in the salt. The form  $\text{O}_2$ took in the salt is unknown; however, X-ray diffraction analysis was performed on the salt to see if the compounds could be determined. Unfortunately, any peaks in the spectrum below 5% were down in with the noise making conclusive identification difficult. Some peaks may have been associated with oxyfluoride compounds, but not enough peaks were present to have high confidence in their existence. One possibility was that the  $O_2$  present was one of the salt oxides and or hydroxides. In order for the  $O_2$  to be picked up by the Zr plating it would need to be either electrochemically reduced during plating or chemically reduced by the plated Zr metal. Another possible source of O<sub>2</sub> was from the Ar cover gas. Even though the Ar gas was run through a titanium getter at 800°C, the O<sub>2</sub> partial pressure would still have been very close to 1x10<sup>-32</sup> Po<sub>2</sub>. To prevent Zr from oxidizing at 600°C, the maximum plating temperature, the partial pressure of  $O_2$  needed to be below  $1 \times 10^{-40}$ . The only oxide in the salt that would be stable below this level was LiO; therefore, Zr metal could be pulling the  $O_2$  from multiple compounds in the salt or even from the Ar cover gas. The system test plan was to reduce the amount of  $O_2$  in the salt and have a more sealed system to prevent O2 leakage and decrease the amount of Ar cover gas.

There were only a couple ways to reduce the amount of  $O_2$  in the salt. Plating of Zr melt would slowly remove  $O_2$  from the salt, but required kilograms of plating, and since the rate of removal was so low, the  $O_2$  content in the salt may have remained the same if there was a small amount of  $O_2$  leakage into the system. The other option was to chemically remove the  $O_2$  by reacting it with a fluorinating agent. Fluoride salts used for molten salt reactors and reactor cooling loops need to have the  $O_2$  removed to minimize corrosion. This has typically be done with hydrogen fluoride (HF) gas, but it is difficult to work with being highly corrosive and toxic.

Scheele and Casella (2010) looked at using NF<sub>3</sub> for purifying fluoride salts. The report was a study of the thermodynamic calculations of fluorinating oxides and other impurities typically found in fluoride salt systems for use in reactors. The calculations compared the ability of NF<sub>3</sub> to HF to fluorinate as a function of temperature. In general the NF<sub>3</sub> reactions have a higher  $-\Delta G$  of formation and become more negative/more favorable with temperature, while HF reactions are less favorable and the  $\Delta G$  tends to decrease with increasing temperature. Additionally, NF<sub>3</sub> has very low reactivity at room temperature making it less corrosive while also having lower toxicity. For the reasons above, NF<sub>3</sub> was chosen as the fluorinating agent to reduce the O<sub>2</sub> content in the electroplating salts.

#### 4.1 System Description

A new small-scale plating system was designed and constructed to test the use of NF<sub>3</sub> to reduce the  $O_2$  content of the salt and determine if that would lead to lower  $O_2$  content in the Zr plate. The system salt volume was significantly lower than the plating system for U-Mo MP-1. The system consisted of a 3.5inch outer diameter Inconel retort 9.5 inches long welded to a 6-inch ConFlat (CF) vacuum flange. A Ni CF metal gasket was used here to minimize reaction with the NF<sub>3</sub>, but all other CF gaskets were copper due to their lower temperature. Attached to the CF flange was a 4-inch high vacuum gate valve. This gate valve was actuated through a bellows, eliminating any sliding seals while the static seals were metal. To prevent the use of sliding seals while raising and lowering the samples into the salt, a large edge-welded bellows constructed of stainless steel was attached to the top of the gate valve. This bellows, as seen in Figure 4, had sufficient travel when completely collapsed the plating electrodes were in the salt and when expanded they were be above the gate valve.



Figure 4. Bellows Design

Inside the Inconel retort, a Ni crucible the full length of the retort was used to contain the molten salt. At the top of the crucible two Ni arcs were machined and wedged into the small gap between the crucible and the retort. This was to minimize any salt getting between the retort and crucible and to hold the crucible centered in the retort. The plating leads were constructed of Ni metal rods threaded into the vacuum power feedthroughs. The other end of the rods were threaded to accept and machined Ni sample holder containing a Ni screw used to clamp the sample in place. A water cooled aluminum block was attached to the outside of the retort just below the CF flange and used to prevent the gate valve from being over heated.

The cooling water was run in a closed loop through a radiator cooled by room-temperature air. The retort was inserted into a tube furnace with about 2 inches sticking out of the top. This left the bottom 3 inches of the retort in the hot zone of the furnace. A gas line was welded to the top of the retort to allow vacuum to be pulled on the salt and to pressurize the retort with Ar. Pressure relief valves set to 2 PSI were installed on both this gasline and the gasline that ran to the bellows to prevent the over pressurization of the system. The vacuum line was also ran to the bellows.

Before a samples was lowered into the salt, the bellows section was evacuated and back filled with Ar three times to minimize any  $O_2$  in the system. The final system was very tight and would hold pressure overnight without additional gas.

#### 4.2 Testing

A salt mixture of 1172.6 grams of LiF, 128 g of CsF, and 32.5 grams of ZrF4 was loaded into the crucible and the system sealed. The mixture was heated to 300°C under vacuum overnight to remove any residual water. The system was then back filled with Ar and heated to 920°C. There was approximately a 200°C delta between the furnace set point and the temperature measured in the melt. There was also a very large temperature delta above the salt. This ended up minimizing the amount of salt vapor that would form near the top of the crucible. However with the temperature 100°C lower at 0.5 inch above the melt, it was difficult to lower the plating temperature much below 580°C without a thin skin of frozen salt forming on the surface. This limited the minimum temperature the system could plate but was not an issue for the test performed.

Once the salt was fully melted a few direct current (DC) plating runs were performed. The anode used was Zr metal foil while the cathode was Mo sheet. The system was able to plate Zr onto the Mo, and one of these samples was mounted, cross-sectioned, and hardness of the plating measured by micro indention. It is well documented in the literature that the hardness of Zr metal is proportion to the  $O_2$  content. During work on the MP-1 plating this was confirmed by running both microhardness and LECO  $O_2$  analysis on the same sample. The hardness was not exact, but was a good approximation for the  $O_2$  while being quick and easy to do. Therefore, for this task hardness was the main measure used to determine  $O_2$  content.

Hardness was measured on one of the cleaning run samples prior to running any NF<sub>3</sub> through the system. It had a hardness 936 Vickers averaged from 10 indentions with a standard deviation of 107. Using the estimation described earlier, this corresponded to an O<sub>2</sub> content of approximately 62,000 ppm. Since the system was plating Zr, an initial trial of the NF<sub>3</sub> was attempted. Gas was bubbled through the salt by way of a 1/8" diameter Ni tube submerged into the salt. With the salt at 620°C, a gas flow rate of 10 sccm of Ar with 4% NF<sub>3</sub> was sparged through the salt. After approximately one hour the flow rate fell to around 1 sccm. The cause for the decrease in flow rate was due to the line plugging up. Initially the cause of plugging was unknown, but in hindsight it was most likely due to the NF<sub>3</sub> reacting with the Ni tube forming NiF<sub>2</sub>. NiF<sub>2</sub> has a melt point of 1474°C and, while it is soluble in the salt system, the volume of salt inside the tube was low. The inside diameter of the tube was only 0.055 inch, which would have greatly limited the volume of salt the NiF<sub>2</sub> could have dissolved into. Once the solubility limit was reached, any additional reaction product would have formed a solid, plugging the tube.

A couple more plating runs were completed and hardness measurement performed on one of them. The sample had a harness of 832, again averaged of 10 indentions, with a standard deviation of 30. This corresponded to an  $O_2$  content of around 49,000 ppm, which appears to show the  $O_2$  content fell. But the hardness on the second sample fell within one standard deviation of the first sample so it may not have been a statistically significant change.

A second test with NF<sub>3</sub> bubbled through the salt was done, but with a significantly higher flow rate. With a melt temperature of  $620^{\circ}$ C, the 4% NF<sub>3</sub> was bubbled through the salt at a rate of 1 liter/min. In order to prevent plugging, the line used to sparge the salt was increased in diameter from 0.125 to 0.5

inch. However, after about 1 hour the pressure started to rise in the system. The flow was stopped and it was determined the outlet line, also 0.125 inch in diameter, had become partially plugged. This line was changed to 0.5 inch as well. The flow was resumed and  $NF_3$  was sparged through the salt for a total of 6 hours.

Plating done after sparging the  $NF_3$  became problematic. After a couple DC plaiting runs the plating was switched to pulse plating since it appeared there was some high melting point salt or reaction layer forming on the anodes. It was though that, by using pulse plating, this reaction layer could be minimized. The pulse plating parameters are presented in Table 4. The average forward current was 0.283 amps and the plating time was 4 hours.

	Pulse Time On (sec)	Pulse Time Off (sec)	Duration (sec)	Current (amps)
Forward Pulse	0.1	0	1.8	0.37
Reverse Pulse	0.1	0	0.2	0.49

Table 4.	Plating	<b>Parameters</b>
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The pulse plating reduced this reaction layer on the anode; however, the initial plating runs showed mass loss on the Zr anode, but little to no weight gain on the Mo cathode. After a couple runs, the mass of the cathode started to equal the loss on the anode. One sample was measured and showed a hardness of 708 with a standard deviation of 32. This put the  $O_2$  content of the Zr in the 35,000 ppm range.

At this point it looked like the NF<sub>3</sub> was reducing the  $O_2$  content, but the unusual plating behavior after running the NF<sub>3</sub> was not understood. The plan was to sparge NF<sub>3</sub> through the salt another time. The system exhaust line was routed through a mineral oil bubbler to prevent  $O_2$  from back streaming into the system during the NF<sub>3</sub> runs. During the setup for the next run, the wrong valve got opened while the system was under vacuum and the mineral oil in the bubbler got pulled into the bellows section of the system. The bellows was removed and cleaned, but the gate valve could not be removed and cleaned without exposing the salt to air. The top of the valve was cleaned, but without removing it from the system it was not possible to clean the internal sections. The thought was any oil left would get into the system and carburize and then be removed by the NF<sub>3</sub>. The NF<sub>3</sub> would react with the carbon to form CF<sub>4</sub>, which has a high negative  $\Delta G$  of formation. The thought was as the O<sub>2</sub> was being removed, the carbon would be removed as well. After the system was put back together, the NF<sub>3</sub> was sparged through the salt at 580°C at 1 liter per minute for 5 hours.

Unfortunately, the NF<sub>3</sub> did not remove the carbon and this residual carbon in the melted salt caused shorting between the electrodes and made plating difficult. Also not all the oil pyrolized and the oil that was left turned the top half of the chamber into a heat pipe causing the bellows section to get much hotter than normal and required higher furnace set points to get correct melt temperatures. Lastly, the melt temperature of the salt appeared to go up. In hindsight this may have been the result of more NiF<sub>2</sub> being formed causing the melt temperature to rise. This was most likely the cause of no plating being observed on the Mo while still seeing a mass loss on the Zr anode. Most likely the Zr was coming off the anode and reacting with the NiF<sub>2</sub> to form  $ZrF_4$  and Ni metal powder. The Ni would then fall to the bottom of the salt resulting in no plating on the Mo, but the cause was not understood.

At this point it would have been better to have pulled the salt and started over, but it was thought that it may be possible to clean the salt up with a combination of NF<sub>3</sub>, filtering, and electrochemical cleaning. The system was cooled and the gate valve pulled. Both the gate valve and bellows were cleaned. Since the salt was exposed any carbon on the top of the salt was removed. Then a blank flange was bolted to the retort and vacuum pulled on the salt while the system was disassembled. After cleaning, the system was reassembled and NF<sub>3</sub> run though it again at  $675^{\circ}$ C at low rate of 2 liters/min for 2 hours.

A couple plating runs were done, but these showed only anode mass loss and no plating on the Mo cathode. Also when the electrodes were pulled they appeared to have a lot of carbon attached. Since the  $NF_3$  did not appear to be reducing the carbon content, a filter basket made of 100 mesh Ni screen was lowered repeatedly into the melt by hand. This was done with the salt melted and the gate valve open to air but with Ar cover gas flowing. The salt was filtered until carbon was no longer observed in the basket.

Four more plating runs were done after filtering with some being DC plating and others pulse plating. After every run the mass gain on, the cathode got closer to the mass loss on the anode. By the fourth run the mass loss and mass gained were within .025 grams of each other. Additionally, the final open circuit voltage (OCV) should have been very near zero if the cathode was completely covered in Zr. The final OCV on this run was 0.012 volts. Hardness was measured on the sample and showed a value of 1091, which was much harder than the previous ones and corresponded to 85,000 ppm. Also after these runs the gate valve got left open to air overnight. Since the  $O_2$  content was much higher NF<sub>3</sub> was ran through the system one more time. This time the temperature of the salt was increased to 720°C, 1 liter/min for 6 hours.

The salt after this run was very yellow, resulting in the suspicion of NiF<sub>2</sub> formation in the salt. Also when a Mo sample holder was dipped into the salt and removed with no current applied it appeared to have a thin layer of Ni on it. The voltage between the sample and the Ni crucible was zero confirming the metal plated out was Ni. This was when all the voltages during the plating and other test started to make sense. It took 12 more plating runs before the anode and cathode changes in weight were equivalent. Scanning electron microscopy (SEM) of one of the earlier plating runs showed the majority of the material plating on the Mo cathode was Ni. In total, 17 more plating runs were done after the last NF<sub>3</sub> run. The final sample was measured for hardness and showed a hardness of 989 with a standard deviation of 91 that corresponded to 70,000 ppm. This was almost the same O<sub>2</sub> content as the system started with and with this result testing was stopped.

#### 4.3 Discussion

Even though a number a mistakes were made during testing that caused the results to be somewhat in doubt it is possible to pull together some general trends. The Ni crucible and thermocouple sheath were used as a pseudo reference to help figure out what was going on with the plating after the NF<sub>3</sub> sparging. After each sparging, NiF<sub>2</sub> was formed by the reaction of the NF<sub>3</sub> with the Ni dip tube. The NiF<sub>2</sub> changed the bath electrochemistry significantly. When the NiF<sub>2</sub> concentration was high, the Mo cathode reduced the NiF<sub>2</sub> without current and formed a thin Ni layer on the Mo. Once this happened there was little to no voltage between the Ni crucible and the Mo cathode. When the NiF<sub>2</sub> was removed, the potential between the Mo and Ni was around -0.020 to -0.080. Additionally there appeared to be some reaction going on with the Zr anode that is currently unknown. With clean salt, the Zr to Ni potential was around -0.7 to -0.9 volts; however, after sparging the voltage was more negative and around -1.6 to -1.2.

When the NiF<sub>2</sub> concentration was high, the anode would lose weight with little to no plating on the Mo cathode. With more plating runs the amount of material on the Mo cathode would increase, but SEM analysis of this plated material showed it was mostly Ni. This was also confirmed by the potentials. At the end of the plating run the potential between the cathode and the Ni would be near zero indicating both were composed of the same material. As more plating runs were done this value would increase. Eventually the voltage between the cathode and Ni would be the same magnitude as the Zr anode to Ni, just opposite sign. This corresponded to final OCV between the anode and cathode of nearly zero, indicating the Zr had been deposited on the Mo cathode.

The image on the left in Figure 5 is the SEM energy dispersive X-ray analysis from the fourth plating run after the last time the NF<sub>3</sub> was run through the salt. The sample is mostly Ni with some Zr as well as some residual salt. The Zr anode lost 3.16 grams while the Mo cathode only gained 0.91. Final OCV between the anode and cathode was -0.651 indicating it was mostly Ni. The image on the right was the twelfth plating run where the sample was only Zr metal; no Ni was detected. The anode loss 0.6 grams while the cathode gained 0.67 gram. The extra weight was most likely due to residual salt left on the sample. The final OCV between the anode and cathode was -0.032.



Figure 5. Low Oxygen Plating SEM

The formation of NiF<sub>2</sub> was due to NF<sub>3</sub> being a very strong oxidizer. This was because NF<sub>3</sub> decomposes at higher temperatures into the NF<sub>2</sub> and an F radical. The F radicals were very reactive and started reacting with the Ni sparger tube forming NiF<sub>2</sub>. The NiF<sub>2</sub> was soluble in the salt, so any reaction product was dissolved exposing more Ni to react. The gas reacted with most materials and is currently no

known material that will not react with NF<sub>3</sub> above the salt eutectic and be suitable for exposer to the fluoride salts.

In the past when other researchers (Shaffer 1971) tried to lower the  $O_2$  content in fluoride salt systems attempted using just anhydrous HF. This did not work since the HF just fluorinated the metal holding the salt just like the NF<sub>3</sub>, with little to no reduction of the  $O_2$  content. When the HF is reacting with metal it has the following reaction formula where Mo is the metal. The metal reacts with the HF to form a metal fluoride and H<sub>2</sub>.

$$M^0 + xHF \xrightarrow{\sim} MF_x + \frac{x}{2}H_2$$

So to get around this, the concentration of HF was lowered and diluted with  $H_2$  when sparging the molten salt. The  $H_2$  prevents reaction with the metal crucible and plumbing by driving the reaction back to metal and HF. With the addition of  $H_2$  they were able to reduce the  $O_2$  content of the salt. NF<sub>3</sub> is more reactive than HF, causing it to fluorinate the metal at a faster rate. Additionally, the NF<sub>3</sub> gets more reactive with temperature while HF get less. It is highly doubtful adding  $N_2$  to NF<sub>3</sub> would drive the reaction back since  $N_2$  is not reactive and the NF<sub>3</sub> is thermal unstable at higher temperatures. It may be possible to add  $H_2$  to the NF<sub>3</sub> gas to react with the F radical to form HF, but this reaction can be sluggish at lower temperatures and then react explosively when heated. Lastly, NF<sub>3</sub> is expected to have lower solubility in the salt compared to HF lowering the amount of salt it could interact with. In post analysis it would have been better to have dealt with the higher toxicity of the HF and gone with something known to work, which is HF diluted with  $H_2$ ; however, HF will not be able to fluorinate all the salt impurities such as carbon unlike NF<sub>3</sub>. In the end, the testing achieved a Zr hardness around the same value achieved in the SMP-1 plating system. The softest Zr produced was around 715 Vickers or 36,000 ppm, very similar to that achieved in the small system prior to the oil being introduced to the system.

## 5.0 Conclusions

The ability to electroplate Zr onto U and U-Mo metal fuels represents a unique technology available to the nuclear fuel community. While the current technology development level is inadequate to meet the schedule requirements for the USHPRR program, continued investment and research into the basic process may provide significant cost savings in the future.

Prior to investment in the basic process, key technical requirements should be more adequately defined.

- 1. What is an acceptable level of  $O_2$  within the Zr?
- 2. What is an acceptable plating thickness to provide the barrier?
- 3. Can the Cs metal that forms during plating be converted back to CsF with an HF purge? Alternatively, can the Cs metal formation be suppressed?
- 4. Can HF plus H<sub>2</sub> reduce the O<sub>2</sub> content in the salt bath and does that result in a low O<sub>2</sub> content Zr plating.

## 6.0 References

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