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INTRODUCTION

The pyrochemical conditioning of spent nuclear fuel for the purpose of final disposal is currently being demonstrated at Argonne National Laboratory (ANL). One aspect of this program is to develop a lithium preprocessing stage for the Fuel Conditioning Facility (FCF)[1-3]. Furthermore, a pilot scale of this preprocessing stage is being designed by ANL-W to demonstrate the *in situ* hot cell capability of this process.

In this pilot scale system, fused lithium chloride salt is saturated with molten lithum to form a powerful fluxing compound with a vigorous reducing agent. The result is a fast and efficient reduction of the actinide oxides acording to the generic reaction:

$$MO_{2\,(S)} + 4Li_{(LiCl)} \rightarrow M_{(S)} + 2Li_2O_{(LiCl)} \qquad (1)$$

During this stage of the fuel conditioning, the reduction will take place at a nominal temperature of 650°C in an argon-cell atmosphere contaminated with up to 10,000 ppm nitrogen, 100 ppm oxygen and 100 ppm of moisture [4]. The maximum local temperature was calculated to be 725°C on the inner shell of the reduction vessel during operation.

One of the significant concerns of this project is the system's corrosion response in the presence of irradiated commercial fuel as well as atmospheric impurities. The purpose of this work was to demonstrate the potential corrosivity of the salt matrix in a worse case environment as well as provide a boundary for allowable impurities in the system during operation.

EXPERIMENTAL PROCEDURE

Three magnesia crucibles were each filled with 4 refractory test coupons and a static fluid exposure was performed for 720 hours at 725°C. The salt matrix formation consisted of a fused salt layer saturated with the molten lithium and impurities, a molten lithium layer saturated with the impurities and a vapor region in the crucible. The coupons were partially emersed in the fluid so that they were exposed to the salt, metal and vapor regions. The salt matrix was designed to simulate an initial salt matrix contaminated to 3.3 wt% Li_2O and 0.6 wt% Li_3N. The heated liquid level was measured and the coupons set so that distinct corrosion regions could be examined and evaluated after the exposure to the salt matrix.

Coupon alloy specifications are provided in table 1. These tests emphasized the niobium and tantalum group 5A refractories because of their excellent corrosion resistance to molten lithium below 1200°C [5], especially in the presence of oxygen. The coupons all had a vertical weld strip so that the influence of welding could be examined. In addition to the 5A refractory metals, a proprietary carburization technique developed by Los Alamos National Laboratory was applied to one the Ta-2.5W coupons. A coupon from each item listed in table 1 was suspended in the magnesia crucibles with a stainless steel assembly. Three identical systems were placed in the furnace in order to provide corrosion samples at 720, 1440, and 2160 hours.

RESULTS

At the end of the first time series, the corrosivity of the salt matrix was both severe and extensive. Seven of the 12 samples had completely disintegrated. Of the 5 remaining coupons, the grain boundary attack and thinning of the samples were so thorough that differential mass measurements could not be done quantitatively. Qualitatively, the coupon volume losses ranged from 40% to 70% for the remaining coupons. It was also observed that in terms of a relative comparison of the coupon corrosion rates: Nb-1Zr > Ta > Ta-2.5W > Ta-2.5W (carburized). The Nb-1Zr and Ta coupons lost about 50% to 70%, the Ta-2.5W coupons lost 30% to 40% and the carburized Ta-2.5W coupons lost 15% to 20% of the initial volume. The remaining test series were terminated based on these initial observations.

In addition to the overall corrosivity of the salt matrix, several other physical observations are notable. The 304-SS rod used to suspend the coupons suffered no obvious mass loss; however, the tensile strength was significantly diminished. Also a larger than expected volume of salt was transported from the liquid pool to the cooler pressure boundary at the glove box interface. In an argon atmosphere set at 1.2 atm 30% of the original salt charge crystallized on the seal. One of the most significant problems for the system is the interaction of the crucible material and the salt matrix and work continues to identify the mechanism. The formation of a stable peroxide is not very pronounced in lithium [6], and so no mechanism has been identified for the Li_2O_2 formation.

CONCLUSIONS

In comparing these corrosion results to historic molten lithium and fused salt data one of the most significant results is that the experiment shows the corrosion of the salt matrix to be synergistic as opposed to inhibitive. So for the group 5A refractory metals the combined alkali metal halide salt corrosion will be enhanced for the salt matrix. The impurity levels of the salt will need to be controlled to a finer degree than expected until the corrosion mechanism is discovered. Finally, the Li_2O_2 formation must be examined more closely and quatitatively described.

REFERENCES

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TABLE 1. Test coupon alloy data.

Ingot	Material	Treatment Description	30 Day Exam	60 Day Exam[5]	90 Day Exam[5]
C1440	Pure Ta[1]	No post weld heat treatment	done	N/A	N/A
W5122	Ta-2.5W[2]	Post weld heat treatment; 325 fine graphite carburization - proprietary LANL technique	done	N/A	N/A
W5122	Ta-2.5W[2]	Post weld heat treatment	done	N/A	N/A
None[4]	Nb-1Zr[3]	Post weld heat treatment	done	N/A	N/A

[1] Chemical analysis (ppm): O,N,C,Fe,Ni ≤ 30 ; H,Cr,Ca,Cu,Si,Ti Mo ≤ 10 ; Nb≤ 41 ; W≤ 218.

[2] Chemical analysis (ppm): O,C ≤ 30 ; N,H,Fe,Ni,Cr,Cu,Si,Ti,Mo ≤ 10 ; Nb ≤ 206 ; *W = 2.7 wt%.*

[3] Chemical analysis (ppm): This material meets ASTM-B-394, type 4, R04261 specifications.

[4] No ingot or lot specification data available.

[5] Due to the extensive coupon damage these tests were terminated.