Degradation of Structural Alloys in Molten LiCl-Li$_2$O-Li

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Abstract

The necessity to curtail carbon emissions to limit anthropogenic climate change is at odds with the continued increase in energy demand caused by economic and population growth in the developing world. In order to simultaneously increase the standard of living for billions of people while limiting greenhouse gas emissions, it is necessary to develop and implement carbon free sources of energy on a large scale. Such energy sources should cover increases in capacity and replace legacy coal and nuclear power plants. Nuclear fission provides a powerful, compact, and reliable source of electricity and process heat. However, the long-term storage of nuclear waste poses a number of environmental and nuclear weapons proliferation concerns. Reprocessing of used nuclear fuel (UNF) offers the promise of reducing both the longevity and volume of waste, while simultaneously reducing nuclear security concerns and increasing the energy generated by a given quantity of mined uranium.

Pyroprocessing technology has been developed to separate the fission products from the remaining actinide elements using electrochemical separations in a molten salt electrolyte. The incorporation of oxide based nuclear fuels from light water reactors requires the reduction of this material to a metallic form. Currently, the state-of-the-art process for this reaction is electroreduction in a molten LiCl-Li$_2$O electrolyte maintained at 650°C. In order to achieve a high reduction efficiency, the applied potential necessarily surpasses the reduction potential of Li$_2$O, causing the formation of metallic Li at the cathode. As metallic
Li is soluble in molten LiCl, the electrolyte becomes a ternary mixture of LiCl, Li$_2$O, and Li. While the increasing concentration of Li during the electrolytic reduction of UNF has been widely observed, little work has been performed thus far to investigate the effect of metallic Li on the corrosion of the structural materials used to contain the electrolyte. This is the first study to explore the long-term effect of metallic Li dissolved in LiCl-Li$_2$O on alloys.

Knowledge of the corrosion rate of a material in a given environment is necessary in order to accurately predict the expected lifetime of a component, thus preventing expensive and potentially hazardous failures. As such, the work presented in this dissertation was performed to elucidate the corrosion mechanisms and the rate of material degradation of structural materials during extended exposure to molten LiCl containing varying concentrations of Li$_2$O and Li. Stainless Steel 316L (SS316L) was studied since the current containers for engineering scale oxide reduction processing are constructed of this material. Inconel 625 (I625) was also studied as an alternative to SS316L due to its high temperature corrosion performance in other systems, and previous short-term studies that have shown good performance in the LiCl-Li$_2$O-Li system. Duplicate samples of each material were exposed to molten LiCl containing 1 or 2wt% Li$_2$O and 0, 0.3, 0.6, or 1wt% Li for periods of 500 and 1000 hours, at a temperature of 650°C inside an Ar glovebox. Post exposure analysis of the sample surfaces was conducted via scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDS) and focused ion beam (FIB) milling, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. SEM-
EDS analysis was also performed on the sample cross section after both FIB milling and mechanical cross sectioning.

Both SS316L and I625 formed a protective oxide layer composed primarily of LiCrO$_2$ in the absence of metallic Li, which limited the degradation of both alloys. However, the presence of metallic Li in the molten salt solution prevented the formation of this protective oxide layer, resulting in extensive attack of the base materials. In both cases, selective dissolution of minor alloying elements was observed. In SS316L, intergranular attack of the base alloy resulted from the selective dissolution of Cr, Mo, and Mn, while I625 showed the selective dissolution of Cr, Mo and Nb, and a porous, Ni foam like microstructure was observed. Corrosion rates were approximately an order of magnitude greater in the tertiary LiCl-Li$_2$O-Li electrolyte than observed in LiCl-Li$_2$O in the absence of Li. Thus, these results should be taken into consideration when designing systems for the oxide reduction of UNF.
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Scholarly Work

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3) A. Merwin, W. Phillips, and D. Chidambaram, ‘On the Formation of Clusters of Li8 in Molten Solutions of LiCl-Li’ in Session L02: Molten Salts and Ionic Liquids 20 – Solute and Solvent Properties II of the 230th Meeting of the Electrochemical Society, Honolulu, HI, October 2-7 (2016).

2) W. Phillips, A. Merwin, and D. Chidambaram, Electrochemical Performance of the Li-Bi Reference Couple in Molten LiCl-Li2O-Li, Abstract number 969 in High Temperature Corrosion in Complex Environments, Session of the 229th Meeting of the Electrochemical Society, San Diego, May 29th-June 2nd (2016).

1) W. Phillips, A. Merwin, and D. Chidambaram Corrosion behavior of Monel 400 in Molten LiCl-Li2O-Li, Abstract number 970 in High Temperature Corrosion in Complex Environments, Session of the 229th Meeting of the Electrochemical Society, San Diego, May 29th-June 2nd (2016).
Chapter 1: Introduction

1.1: Global Energy Needs

Throughout human history, increased standards of living have directly correlated to increased energy usage. The industrial revolution exploited the vast quantities of energy contained in the hydrocarbons of fossil fuels, which has allowed for the improvements in quality of life, standard of living, and life expectancy that have occurred in the past two centuries. As the benefits of high energy consumption make their way to the developing regions of the world, total energy consumption continues to rise, along with economic prosperity. Combined with continued population growth, particularly in sub-Saharan Africa and Asia, global energy demand is projected by the International Energy Agency to increase by at least 50% between 2019 and 2040 [1].

As the scientific understanding of the earth’s climate has grown, so too has our knowledge that the carbon emissions associated with the burning of fossil fuels have multiple deleterious effects on the environment [2]. Anthropogenic climate change is a direct result of the large quantities of fossil fuels that have been burned for energy production and their associated carbon emissions over the past two centuries. In order to limit the rise in global average temperatures, a concerted global effort to limit greenhouse gas emissions is necessary. Technologies such as wind, solar, geothermal, hydro, and nuclear power are capable of providing vast quantities of carbon free energy, and growth in generation capacity for all of these resources must occur over the next few
decades if we are to successfully curtail the worst predictions of climate scientists.

1.2: Nuclear Energy

While renewable energy sources such as wind, solar, geothermal, and hydro power should all be implemented to the full extent possible, they all have limitations: wind and solar are intermittent and unreliable, while geothermal and hydroelectric are highly localized. Full decarbonization of the world energy supply necessitates the inclusion of nuclear in the mix, due to its high reliability, energy density, safety, and baseload power capability [3, 4]. In addition to growth in production capacity to account for increased energy demand, it is also necessary to replace generating capacity that is being phased out, such as legacy nuclear plants that are reaching their design lifetimes, and coal fired power plants. Nuclear power is uniquely suited to supplying the baseload demand due to its high average capacity factor and the economy of operation once installed [4].

1.3: Used Nuclear Fuel

Along with concerns over the possible proliferation of nuclear weapons, long term storage of used nuclear fuel (UNF) is an issue that must be dealt with in an environmentally responsible way. The back end of the fuel cycle is an essential component of a sustainable and environmentally responsible nuclear industry, but is often hampered by concerns of nuclear weapons proliferation and unfavorable economics. Currently, the preferred solution to deal with UNF is to
deposit the fuel in a geologic repository, where it should be maintained undisturbed and intact until the residual radioactivity decays to background levels. Due to the high levels of transuranic (TRU) isotopes present in UNF such as Pu\textsuperscript{239} and Am\textsuperscript{241} and their long half-lives, this means a once through fuel cycle will necessitate the assurance of safe storage for tens of thousands of years [4]. Concerns with our abilities to design for these time frames has meant that the licensing of a permanent geological storage facility has been beset with controversies since the beginning of the nuclear industry in the U.S. [5]

1.4: Reprocessing

While a once through fuel cycle results in extremely long-lived waste, it is possible to separate the TRU elements and unburned uranium from UNF through chemical and metallurgical means and recycle them into freshly fabricated fuel for use in a suitably designed reactor. The so-called closed fuel cycle with complete recycle of transuranic elements theoretically results in a decrease in the longevity of the final waste form from tens of thousands of years to approximately 300 years, while simultaneously reducing the volume stored by a factor of 20 and increasing the energy extracted from a given amount of mined material, although this has yet to be implemented commercially [5, 6].

Two general methods for reprocessing have been developed. The first process developed was the plutonium-uranium redox extraction (PUREX) process, which is based on aqueous chemical separations. PUREX was developed as part of the Manhattan project for the production of high purity
plutonium for weapons cores [4]. Consequently, this process poses a significant proliferation risk due to the stream of pure fissile material. Despite this, both France and Japan have developed commercial reprocessing capabilities based on the PUREX process, and have successfully demonstrated the ability to recycle a significant amount of the fissile inventory of UNF through the use of mixed oxide (MOX) fuel. Unfortunately, the neutronic limitations of thermal spectrum light water reactors (LWR) limit the ability to continually reprocess MOX fuel due to the buildup of the heavier TRU isotopes, meaning that complete recycle of all TRU is not possible without the implementation of other reactor types [4].

1.5: The Integral Fast Reactor and Pyroprocessing

The integral fast reactor (IFR) concept was conceived by Argonne National Laboratory (ANL) in the 1970’s as a way to close the nuclear fuel cycle at a single site via the use of a sodium cooled fast reactor (SFR) using metallic fuel and an on-site fuel processing plant to reprocess used fuel and manufacture new fuel for reuse in the reactor [5, 6]. The reprocessing technology was based on molten salt electrochemical methods, and the central operation was termed the electro refiner (ER). Fast spectrum reactors operate without the use of a moderator, and fission occurs primarily via high energy neutron capture. This allows for the efficient burning of fertile as well as fissile heavy isotopes.

The experimental breeder reactor 2 (EBR-II) was built at the desert site of ANL West, which is now the current location of Idaho National Laboratory (INL).
EBR-II served as the reactor for the IFR concept, with a hot cell built adjacent to the reactor that included the operations necessary to take fuel from the reactor core, de-clad the sodium bonded fuel, reprocess the fuel and cast new fuel rods. By all accounts, the IFR project was successful in demonstrating the technical viability of a closed fuel cycle based on a SFR and molten salt based reprocessing technologies [5, 6].

1.6: Electroreduction of Used Nuclear Fuel in LiCl-Li$_2$O-Li$_2$O

Molten salt based pyrochemical reprocessing methods necessitate a metallic feedstock in order to facilitate the separation of U and TRU from the fission products. Consequently, the reduction of UO$_2$ is an important head-end process for the incorporation of oxide used nuclear fuel (UNF) into a pyrometallurgical-based fuel cycle. The most widely researched UNF reduction method is a high temperature, molten salt based electrochemical reduction process that was originally developed by ANL [7, 8]. In addition to ongoing work at ANL, this technology is currently being investigated by researchers at INL, the Korean Atomic Energy Research Institute (KAERI) in South Korea, the Central Research Institute of Electric Power Industry (CRIEPI) in Japan, the Indira Gandhi Center for Atomic Research (ICGAR) in India, and at a small number of research universities in the United States.

The electroreduction of UO$_2$, as well as various fission products and actinide oxides, is accomplished by loading de-clad UNF pellets into a stainless steel 316L (SS316L) basket, which is then immersed in a molten LiCl-Li$_2$O
electrolyte maintained at 650°C. The fuel basket is then cathodically polarized against an anode made of suitable material, typically Pt. A reference electrode is employed for accurate monitoring of the applied potentials and process control. A schematic diagram of this process is shown in Figure 1.1 [9].

Figure 1.1: Schematic diagram of the electroreduction process for UNF [9].

The applied potential must be beyond the reduction potential of UO$_2$, which is -2.40V vs. Pt. During the first stage of the reduction process, the
reduction of UO$_2$ proceeds directly via an electrochemical reduction pathway represented by the half-cell reactions given in Equations 1 and 2:

\[
\text{Cathode: } U^{4+} + 4e^- \rightarrow U \quad (1)
\]

\[
\text{Anode: } 2O^{2-} \rightarrow O_2 + 4e^- \quad (2)
\]

The reduction of UO$_2$ begins at the edge of the basket, and progresses radially inward [10, 11]. As the reduction proceeds, the process becomes diffusion limited and the over-potential required to maintain a desired current increases during galvanostatic operation [10, 11]. This increasing over-potential eventually reaches the reduction potential of Li$_2$O, which is at -2.47V vs. Pt. Attempts to completely reduce UO$_2$ to metallic form potentiostatically below the reduction potential of Li$_2$O have been unsuccessful at producing acceptable yields [8, 12]. Consequently, metallic Li is generated at the cathode as the reduction proceeds. This metallic Li acts as an additional chemical reduction pathway for UO$_2$, represented by Equation 3 [8]:

\[
UO_2 + 4Li \rightarrow U + 2Li_2O \quad (3)
\]

It has been suggested that in theory, if the applied electrolytic current is interrupted upon completion of the reduction of UO$_2$, minimal excess Li will be produced, as Li will be consumed quickly in the presence of UO$_2$ via Reaction 3. However, a reliable method to determine the correct cutoff point has not yet been devised, and the typical practice is to terminate the process when approximately 150-200% of the theoretical charge required for the complete reduction of UO$_2$ has been passed [13]. This has been shown by leading researchers in the U.S.
and Korea to be effective at producing a high reduction yield [8, 14]. Additionally, the underpotential deposition (UPD) of Li at the surface of U₃O₈ at potentials more noble than required to reduce bulk Li has been reported to occur, indicating that the generation of some quantity of Li may be unavoidable [15].

Unfortunately, the presence of metallic Li in the system introduces complications in materials compatibility and solution chemistry that must be taken into account during the design and operation of an electroreduction cell. Due to the non-zero solubility of Li in LiCl, some of the Li generated at the cathode dissolves into the electrolyte, forming a ternary LiCl-Li₂O-Li system, the properties of which differ greatly from LiCl-Li₂O [13, 16, 17]. As stated above, significant quantities of Li are generated in-situ, and as such, it can be assumed that the electrolyte is saturated with Li after extended periods of operation. The nature of the dissolution mechanism of Li in LiCl has been debated in the literature. In addition to physical dissolution via Bredig’s F⁻ centered model [18], some researchers have hypothesized a colloidal suspension or metal fog [19, 20], while others have suggested the presence of excessively reduced sub-halide compounds such as Li₂Cl [21]. Sub-halide compounds have been shown to be present in other molten metal-halide salt systems where the salt cation is identical to the dissolved metal, as is the case with Bi-BiI₃ [18]. Previous work by our group detected the presence of Li₈ nanoclusters in LiCl-Li₂O-Li solutions at 650° via in-situ Raman spectroscopy, and hypothesized that the dipole of the Li₈ nanocluster structure is responsible for the colloidal dissolution of Li into LiCl-Li₂O [22]. The possible presence of multiple dispersion mechanisms in addition
to physical dissolution may partially explain the difficulty other researchers have experienced while attempting to quantify the solubility limit of Li in LiCl, which has been shown to vary depending on differences in experimental parameters employed, such as agitation and sampling technique [17]. Although the absolute limit of Li dispersion in LiCl is not known and may not be possible to quantify, 0.3wt% Li is a useful approximation for the apparent solubility limit [17, 20, 23, 24]. While the dissolution mechanism of Li in LiCl is not the focus of this work, it is useful to understand the nature of the solution chemistry to inform the experimental design and interpret the results of the present investigation.

The generation of Li concurrently with the reduction of UO$_2$ also leads to current inefficiencies and consumption of Li$_2$O as the process proceeds [17]. Upon dissolution into the electrolyte, Li can spontaneously recombine with the O$_2$ generated at the anode, resulting in a reduction in efficiency. Dissolved Li can also be consumed through reaction with most other oxides present in the system, such as MgO anode shrouds and reference electrode sheaths, or the oxide layers on alloy surfaces [17, 25]. Additionally, the presence of Li in LiCl increases its electrical conductivity, allowing electrons to pass from the anode to the cathode directly through the salt. Any electron that passes through the electrolyte directly will not contribute to the reduction of UO$_2$ and thus reduces current efficiency. The combination of all of these effects are responsible for the necessity for passing large excess charge beyond that predicted theoretically.
The presence of dissolved Li also leads to challenges with the degradation of materials that must come into contact with the electrolyte. Common engineering ceramics such as Al₂O₃ and MgO [17, 26, 27] have been shown to undergo severe degradation when exposed to LiCl-Li₂O-Li solutions, while ZrO₂ has been shown to be reduced to a combination of Zr and Li₂ZrO₃ in LiCl-1wt%Li₂O melts [28]. The corrosion of structural alloys is also greatly affected by the presence of Li metal, and is the primary focus of this dissertation. The following discussion is intended to offer background on the processes responsible for the corrosion of metals in molten salts and liquid metals.

1.7: Corrosion in Molten Salts

Understanding of the effect the solution chemistry has on materials exposed to the molten LiCl-Li₂O-Li system is important for the safe and economical design of vessels and other components for use during the electrolytic reduction of used nuclear fuel. Fortunately, much work has been conducted on corrosion of materials used for the construction of molten salt reactors (MSR), particularly during the molten salt reactor experiment (MSRE) of the 1960’s and 1970’s, and this work can serve to inform the present study.

The high temperature molten salt environment of MSRs and other molten salt systems imposes severe demands on the corrosion performance of the materials used to construct the vessels and components exposed to the salt. Fluoride salts are typically considered as the fuel and/or coolant salts due to their favorable neutronic properties [29, 30], however, some newer designs for fast
spectrum MSRs are focused on isotopically enriched chloride salts [31]. Consequently, much of the discussion below uses fluoride salts as examples, but these concepts are generally applicable to corrosion in chloride salts. Typically, the molten salt in a salt fueled MSR is composed of fluorides of Li, Be, Zr, or Na, with additions of UF$_3$/UF$_4$, ThF, as well as the fluorides of the fission products that form stable compounds with fluorine [29, 30]. Temperatures in typical MSR designs routinely exceed 550°C, with some designs, such as the very high temperature reactor (VHTR), exceeding 850°C during routine operation to achieve higher thermodynamic efficiency and provide high temperature process heat for chemical facilities [32]. Consequently, it is critical that the corrosion mechanisms affecting structural materials be well understood and the corrosion rate of these alloys be minimized prior to the construction of a reactor. The following sections highlight the different mechanisms by which corrosion occurs and the ways in which a material can be designed to withstand these conditions. Emphasis is placed on the corrosion of Hastelloy-N in molten LiF-BeF$_2$, as this system has been the subject of the majority of corrosion studies in molten salts. LiF-NaK-KF and LiCl-NaCl molten salts have also been proposed and tested for MSR primary and secondary loop service. There are many similarities between the corrosion behavior of alloys in these salts and LiF-BeF$_2$ salts, which have been studied extensively, but there are important departures for each class of molten salt that bear on the selection of container materials, the development of cleaning procedures and on the development of chemistry controls.
1.7.1: Corrosion - Thermodynamic Considerations

The high temperatures in these molten salt systems accelerate the kinetics of reaction between the salt and the reactor materials. Additionally, molten fluoride and chloride salts both act as a flux to remove most oxide layers present on the surface of a material, largely negating the usefulness of the protective surface oxides of active elements such as Cr, Al, or Si typically relied on for corrosion protection for stainless steels and many nickel alloys [33]. Consequently, corrosion typically occurs rapidly at the beginning of exposure to molten salts as the oxide layers dissolve into the solution and impurities are consumed. Table 1.1 gives the Gibbs free energy of formation for various fluoride compounds of interest for MSR designs, with salt fluoride compounds given in the left two columns, and fluoride compounds of common alloying elements given in the right two columns [33].
Table 1.1 Gibbs free energies of formation per mole of fluorine for various fluoride compounds at 727°C (* indicates value is at 754°C). Compounds with more negative Gibbs free energies of formation are more thermodynamically stable and are likely to form at the expense of compounds with less negative Gibbs free energies of formation (6).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G_f$ (Kcal/mol·F)</th>
<th>Compound</th>
<th>$\Delta G_f$ (Kcal/mol·F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>-125</td>
<td>AlF$_3$</td>
<td>-90</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>-113</td>
<td>CrF$_2$</td>
<td>-75.2</td>
</tr>
<tr>
<td>NaF</td>
<td>-112</td>
<td>CrF$_3$</td>
<td>-72.3</td>
</tr>
<tr>
<td>RbF</td>
<td>-112</td>
<td>FeF$_2$</td>
<td>-66.5</td>
</tr>
<tr>
<td>KF</td>
<td>-109</td>
<td>FeF$_3$</td>
<td>-60.6*</td>
</tr>
<tr>
<td>BeF$_2$</td>
<td>-104</td>
<td>WF$_6$</td>
<td>-56.8</td>
</tr>
<tr>
<td>ZrF$_4$</td>
<td>-94</td>
<td>NiF$_2$</td>
<td>-55.3</td>
</tr>
<tr>
<td>HF</td>
<td>-66.2</td>
<td>MoF$_3$</td>
<td>-52.5*</td>
</tr>
</tbody>
</table>

Thermodynamically, compounds with more negative free energies will form more readily than compounds with less negative free energies.

Consequently, once the initial surface oxide layer is removed from the alloy, corrosion proceeds by attack of the most active element in the material. This was observed during the material exposure tests performed concurrently with the Aircraft Reactor Experiment (ARE), where the corrosion rate of the alloys studied was directly proportional to the chromium content in the alloy [29, 30, 34]. This led to the reduction of chromium contents in the composition of Hastelloy-N, which was developed following the ARE, to levels just sufficient to provide
adequate resistance to corrosion in the high temperature air environment experienced outside of the reactor vessel [29, 30].

1.7.2: Corrosion – Impurity Effects

Although pure fluoride and chloride salts are thermodynamically stable with respect to container materials, and corrosion is minimal in these conditions, small amounts of impurities present during the preparation or introduced during the processing of the salt can greatly impact the corrosion rates observed. Impurities such as water, oxygen, or hydroxides can be present in the salt if proper purification techniques are not followed. These impurities can produce HF or HCl through the reactions given below, which is a highly corrosive acid and will rapidly etch structural materials [33]. Here, Me is used to represent any metallic element.

\[
MeF(l) + H_2O(g) = MeOH(l) + HF(g) \quad (4)
\]

\[
2MeF(l) + H_2O(g) = MeO(l) + 2HF(g) \quad (5)
\]

Impurities of Ni and Fe fluorides present in the salt due to the manufacturing process can react with Cr present in the alloy due to the thermodynamic considerations listed above and lead to accelerated corrosion at the beginning of exposure [33]. Fortunately, the effects of impurities are limited to the initial exposure to the molten salt environment, and after the initial period of rapid corrosion during which time the impurities are consumed, the corrosion rate settles to a slow and stable rate that is limited by the diffusion of Cr to the surface [30, 33, 35].
1.7.3: Corrosion – Thermal Gradients

The large temperature gradients inherent to a MSR can also lead to corrosion problems. Since the solubility limits of the corrosion products in a molten fluoride are highly temperature dependent, it has been observed that there can be mass transport loops that develop in the MSR from areas of high temperature to areas of low temperature [30, 33]. The cold areas, such as heat exchangers, act as sinks where precipitation and accumulation of corrosion products occur. Thus, the concentration of the corrosion products in the system is limited by the solubility limit in the cold side of the loop. Consequently, the solubility limit in the hot side is never reached, leading to a continuous flux of material from the hot side of the reactor to the cold side. In addition to the constant level of corrosion experienced on the hot surfaces in the reactor, the buildup of precipitated corrosion products in the heat exchanger can impede the flow of coolant, causing blockages and possibly localized salt freezing [30, 33]. While this is less of a concern in the batch processes employed during pyroprocessing, large vessels containing many kilograms of molten salt will inherently have some temperature gradient that may play a minor role in the corrosion of the vessel.

1.7.4: Corrosion – Dissimilar Materials

The use of dissimilar materials within a MSR is unavoidable in practice, as the moderator will be constructed of graphite, and there will be at least one metallic alloy used to construct the reactor vessel, piping, and other ancillary
equipment. The use of multiple alloy compositions and/or other materials, such as SiC composites for heat exchangers, is likely [36]. In the oxide reduction operation, the majority of components can be constructed from a single alloy, with the primary exception being the anode which is typically a noble metal such as Pt. The effects that the use of dissimilar materials have on the corrosion mechanisms at play in a reactor have been studied, however, the full extent to which these material choices affect the long term performance of reactor materials is not certain [30, 33].

Activity gradients caused by the presence of dissimilar materials can lead to the depletion of an element from an alloy with high concentration and deposition of that element on another alloy with low concentration of the element of interest. This mechanism can accelerate corrosion of the alloy with high activity, and lead to preferential leaching of specific elements. Another possibility is the formation of compounds that are thermodynamically more stable than the constituent species, as has been observed with the formation of chromium carbides on the surface of graphite when both graphite and Cr containing alloys are exposed to the same melt [33]. This mechanism acts as a sink for Cr, leading to the depletion of Cr from the base alloy at accelerated rates.

1.7.5: Corrosion – Redox control

By controlling the oxidation state of species in the salt with multiple soluble valence states, for example U which can form UF₃ and UF₄ corresponding to U³⁺ and U⁴⁺, respectively, it is possible to control the aggressiveness of the corrosive
attack by the salt on the container materials [33]. The control of the oxidation state of the salt changes the electrochemical potential of the salt, and is termed the redox control. The Nernst equation relates the ratio of oxidation states to electrochemical potential, as shown below in equations 6 and 7.

\[
M^{n+} + ne^- \leftrightarrow M \tag{6}
\]

\[
E = E^0 + 2.3 \times \frac{RT}{nF} \log\left(\frac{[M^{n+}]}{[M]}\right) \tag{7}
\]

By controlling the ratio of U$^{3+}$/U$^{4+}$ it is possible to favor reducing conditions, whereby the corrosive attack of the salt on container materials is reduced [36]. However, it is important that the conditions do not become so reducing that the precipitation of dissolved species becomes problematic, such as is the case with the formation of uranium carbide compounds under highly reducing conditions [33]. The ideal ratio whereby corrosion and precipitation were both minimized was found to be a U$^{3+}$/U$^{4+}$ ratio of 0.005 to 0.06 [30]. This corresponds to a U$^{4+}$/U$^{3+}$ ratio of 200-16:1. Figure 1.2 shows clearly how the redox potential of the salt affects the intensity of intergranular cracking observed on Hastelloy-N [36].
1.7.6: Corrosion – Tellurium based intergranular corrosion and embrittlement

An important and unforeseen corrosion problem encountered during the MSRE was the reaction of the base alloy with fission products contained in the fuel salt, most notably Te [30]. As a chalcogen, Te exhibits similar properties to Se, S, and O, and readily forms compounds with negative valence states, however, it is somewhat unique in that it can also form compounds where it has a positive charge. In fluoride salts, Te forms compounds with Ni and Cr through the reactions given in equations 8 and 9 below due to the instability of tellurium fluoride [33].

\[
xTe + yNi \rightarrow Ni_y Te_x
\]  
(8)

\[
xTe + yCr \rightarrow Cr_y Te_x
\]  
(9)

These reactions occur preferentially at the grain boundaries, leading to intergranular corrosion and stress corrosion cracking that significantly weakens the alloy.

The deleterious effects of Te on the long term performance of Hastelloy-N and other Ni base alloys lead to development efforts at ORNL to minimize the effects of Te [36]. Two methods were found to be effective at limiting the crack
intensity: redox control to keep the salt under reducing conditions, and the addition of Nb as an alloying element at concentrations between 1-2wt%, as shown in Figure 1.3 [36]. The redox control method limits the formation of Te compounds by limiting the potential for oxidation in the system, while the mechanism by which Nb acts to limit the effects of Te induced cracking is not entirely known, but one possible explanation is the formation of NbTe surface layers on the alloy preferentially to the diffusion of Te into the grain boundaries [30]. These investigations indicated that the use of Nb modified Hastelloy-N in conjunction with redox control would sufficiently limit corrosion over the design lifetime of a MSR [30].

1.7.7: Corrosion in Chloride Molten Salts

Chloride molten salts have also been proposed for MSR service as they have high stability and low vapor pressures, and can provide a harder neutron spectrum than fluoride salts for fast reactor designs. Oak Ridge National Lab prepared a very comprehensive review of these salts properties for use in assessing their use for the NGNP heat transfer loop and their results are summarized here [37]. The corrosion databases for these classes of salts are insufficiently developed and contain data based upon salts with large and unquantified impurity inventories. There has not been extensive characterization of the effect of moisture and impurities on the corrosion of alloys in these salts and cleaning procedures have not been developed to the same standard as for fluoride salts, which had the advantage of being extensively developed through Oak Ridge National Laboratory’s (ORNL) molten salt reactor experiment. In
addition to the unreliability of the data on corrosion in these salts due to impurity content, there is little high temperature data for corrosion with these salts above 800°C.

Chloride molten salts behave similarly to more common fluoride salts in that they flux passive layers from container walls and have a similar electrochemical sequence to fluoride salts. Despite this, passive oxide layers are in general more stable in chloride salts than in fluoride melts. There are many important differences in corrosion chemistry however, and chloride molten salts for MSR applications still require extensive exploration. The thermodynamic driving force for corrosion in Cl salts seems to be slightly greater that for fluoride salts based on a comparison of the free energy of formation of halide compounds, but it is noted that this analysis is highly simplistic and ignores deviations from ideal solution behavior; this is an area requiring further study. Additionally, there will be important differences in coordination chemistry as the most stable form of uranium is UCl$_3$ in chlorides and UF$_4$ in fluorides.

Extensive research is required to further characterize chloride molten salt corrosion behavior and interactions with candidate container materials. The author of the ORNL assessment of chloride salts for use in MSR systems recommends that an improved method for purification of chloride salts be developed and implemented as a standard method for corrosion tests [37]. Once impurity factors can be controlled, the thermodynamic driving force and propensity for corrosion must be examined more extensively and compared with
fluoride salts. In conjunction with this effort, corrosion controls, especially redox buffers for chloride salt systems, can be explored and more conclusive decisions about the suitability of chloride salts and appropriate materials can be made if there are advantages for chloride salts when compared with fluoride salts.

1.8: Lithium induced corrosion

Some research has been performed on the corrosion of structural materials to be used for the containment of metallic lithium. Lithium is considered as both a coolant and tritium source for fusion reactors due to the n, α reaction with Li$^6$ that yields both tritium and helium; however, most work for fusion reactors has focused on refractory metals such as Ta and W due to the high temperatures involved in fusion confinement.

The primary consideration when selecting a metal or alloy for the containment of metallic Li is the solubility of certain metallic elements in molten Li. Consequently, examination of the binary phase diagrams of Li with Al, Cd, Cu, Pb, Mg, Ag, Sn, and Zn reveals that these elements are not suitable for inclusion in the alloys used to contain metallic Li due to their mutual solubility [38]. Similar examination reveals that the elements Ti, V, Cr, Ni, Fe, Zr, Nb, Mo, Ta, and W do not have appreciable solubility in molten Li and can thus be considered for use in structural alloys. Our previous work on the corrosion of Monel 400, which is a Ni-Cu based alloy, in molten LiCl-Li$_2$O-Li showed increased degradation of the base material as the Li concentration was increased, implying the solubility of alloying elements in metallic Li is of great importance when selecting an alloy for
containment in this system [39]. A review written by Chopra et al. on the corrosion by liquid metals for fusion applications showed that the primary effects of molten Li on the corrosion of austenitic stainless steels, such as SS316, was the selective dissolution of Ni and Cr from the base alloy, accompanied by the formation of a ferrite layer on the surface of the material over the course of 5000 hr, with corrosion rates being highly influenced by the impurity level of the molten metal [40]. This indicates that even elements without appreciable solubility in pure metallic Li may be corroded by the presence of impurities, similar to the case with corrosion in molten salts.

A second, and perhaps more relevant consideration for the present work, is the lack of data on the thermodynamic stability of oxide films in the presence of metallic Li. The primary corrosion prevention mechanism of stainless steels and Ni-based super alloys is through the formation of a Cr oxide-based surface film. The highly reducing nature of metallic Li means that most oxide films will react with Li, thus negating their usefulness at preventing corrosion. In the case of containment of pure metallic Li, if the underlying base material is compatible with metallic Li, this is not of major concern; however, in the present study, the elimination of the oxide film by metallic Li solvated in LiCl-Li₂O exposes the base material to the molten salt. As will be shown in Chapters 2, 3, and 4, this results in much higher corrosion rates than would be otherwise observed during exposure to pure metallic Li or pure molten salt conditions.
Intergranular corrosion was the primary method of attack observed by DeVries in low carbon and alloy steels, which was assisted by the formation of Li carbides and sulfides at the grain boundaries [38]. Dissolution of Fe and Ni at the grain boundaries was also observed, while stress corrosion cracking was observed in all Ni-based alloys, rendering them incompatible with molten Li. This leads to consideration of the phenomena of liquid metal embrittlement (LME) whereby the exposure of a metal or alloy to a liquid metal leads to the severe degradation of the structural properties of that alloy [41]. The factors influencing the appearance of LME include, but aren’t limited to, the metallurgical structure of the base material, grain boundary structure, and point defects, along with the thermodynamics of new surface formation, applied stress, impurities present in the base material, and the liquid metal to which the alloy is exposed. In depth discussion of the LME of alloys is beyond the scope of this work, but the reader is directed to a recent book published by E. Schukin, et al. on this effect if more information is desired [41].

1.9: Corrosion in Molten LiCl-Li\textsubscript{2}O-Li

While the literature concerning corrosion in molten halide salts is rich in diversity and discussion of corrosion mechanisms, very few studies have investigated the effect of solvated lithium metal in lithium chloride [25, 39, 42-47]. The studies that have been reported have been mainly of short term duration and have been conducted under widely varying experimental parameters. Consequently, these studies conflict in their analysis on the effect of Li\textsuperscript{0} on the
corrosion of various materials in the molten LiCl-Li$_2$O-Li system. Initial studies by Indacochea at ANL under inert atmosphere conditions showed minimal corrosion, however, due to the evaporation of both Li and Li$_2$O over the course of these experiments the solution chemistry was likely not maintained as that which was intended to be studied [42]. A following study, also by Indacochea et al., was performed under an Ar atmosphere containing 10% O$_2$ and showed much higher corrosion rates, and the formation of multiple metallic oxides on the sample surfaces, which may serve to inform the corrosion expected during a possible atmospheric contamination[43]. Recent work by Choi, et al. showed drastic degradation of pure metallic Ni in molten LiCl-Li$_2$O in the presence of either metallic Li or O$_2$ gas, but minimal degradation if neither impurity was present [47]

Previous work in our laboratory has attempted to elucidate the effect of Li$^0$ and Li$_2$O on the corrosion of Stainless Steel 316L (SS316L), Inconel 625, and Monel 400 by parametrically varying the concentrations of Li$_2$O, Li, and impurity H$_2$O independently [25, 39, 46]. These studies showed that material degradation depends on the concentration of Li$_2$O and Li, and the presence of impurity H$_2$O. These studies also showed that the mechanism of material degradation changes depending upon the concentration of Li in the system. At low concentrations of Li, the attack is based primarily on the O$^{2-}$ activity in the melt, while corrosion more similar to liquid metal attack occurs at high Li$^0$ concentrations. In the absence of Li metal, Merwin noted the formation of bulk LiCrO$_2$ on the sample surface in the absence of Li, and detected small amounts of this compound via XPS up to Li concentrations of approximately 0.6wt% [25, 46]. While these studies are
extremely valuable for identification of the corrosion products and informing the mechanisms responsible for material degradation in the LiCl-Li₂O-Li system, the short-term nature of these exposure tests necessitated the continuation of this work to verify these findings.

1.10: Overview

This dissertation is thus primarily focused on the long-term effect of solvated metallic Li on the corrosion behavior of structural materials in the LiCl-Li₂O-Li system. Both Stainless Steel 316L (SS316L) and Inconel 625 (I625) were studied via exposure testing for periods of 500 and 1000 hours. Further experimental details are noted in each chapter. Chapter 2 presents the findings from the work performed on SS316L while Chapters 3 and 4 present the findings on the corrosion behavior of I625 in LiCl-Li₂O-Li. Chapter 5 summarizes the conclusions of these studies with a discussion of the general mechanisms observed and gives possible paths forward with suggestions for future work. Additionally, the appendices present additional work performed over the course of this doctoral dissertation that have not been yet been submitted for publication, and the supplemental information file for the publication of chapter 4. Specifically, Appendix 1 contains the supplemental information file for Chapter 4. Appendix 2 discusses the necessity and theoretical background of reference electrode development for the LiCl-Li₂O-Li system and presents several theoretical options for further investigation, along with preliminary results. Appendix 3 briefly discusses the degradation of ceramic materials in the LiCl-Li₂O-Li system and
presents the theoretical considerations necessary for development of ceramics in this system. Appendices 4 and 5 contain supplemental information and data collected from the long-term corrosion studies of SS316L and IN625, respectively. Finally, Appendix 6 shows the results of the Li evaporation study used to determine the salt replacement interval for the long-term corrosion studies of SS316L and IN625.
Chapter 2 : High Temperature Corrosion of Stainless Steel 316L in LiCl-Li2O-Li


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Abstract:

Exposure testing of Stainless Steel 316L was performed in LiCl-Li2O-Li solutions at 650°C for periods of 500 and 1000 hours to investigate the effect of metallic Li on corrosion of materials used to contain the LiCl-Li2O electrolyte for the electrolytic reduction of used nuclear fuel. Melt compositions studied consisted of LiCl containing 1 or 2 wt% Li2O and 0, 0.3, 0.6, or 1wt% Li. Post exposure surface analysis was performed using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. Cross sections of the samples and gravimetric analyses were performed to determine the time-averaged corrosion rate for each sample. Lithium metal induced attack rates were found to be as high as 2.91 mm/y. In the absence of solvated Li in the LiCl-Li2O system, LiCrO2, Li2CrO4, and NiFexCr2-xO4 were observed to be the primary corrosion products. When Li was present in the melt, the oxidized alloying elements were only detectable via X-ray photoelectron spectroscopy, and the surface was primarily comprised of bare metal.
2.1: Introduction

Reduction of used oxide-based nuclear fuel is a necessary step for the incorporation of the large stockpile of used fuel from light water reactors into a pyrometallurgical-based fuel cycle [7, 8, 48]. The electrolytic oxide reduction operation developed by ANL is the preferred method for the reduction of used nuclear fuel (UNF) and has been the subject of continued development [7, 11, 12, 49-55]. In this process, declad, crushed, and pelletized UNF is placed in a stainless steel basket and cathodically polarized versus a suitable anode at a potential sufficient to reduce the oxides present at the cathode [55]. Li$_2$O is added in concentrations of 1-2wt% to provide an initial source of O$^{2-}$ ions, which are then oxidized at the anode to form oxygen gas. The concentration of Li$_2$O must be carefully controlled, as the reduction of the lanthanides and minor actinides becomes thermodynamically unfavorable at high O$^{2-}$ activities, and the anodic dissolution of Pt becomes problematic at low O$^{2-}$ activities [11, 56-58]. As the reduction proceeds, the actinide and lanthanide oxides are reduced to metallic form, while the salt soluble fission products (i.e. Cs, Sr, I, Br, etc.) form salts and dissolve into the electrolyte. Due to the close reduction potentials of Li$_2$O and UO$_2$ of -2.40V and -2.47V vs. O$^{2-}$|O$_2$), respectively, and the necessity of applying a high overpotential to achieve a high reduction yield, metallic Li is generated at the cathode [8, 13, 17, 55].

The Li generated at the cathode acts as an additional reduction pathway for UO$_2$ through direct chemical means; however, due to the solubility of Li in
LiCl, some of the metallic Li dissolves into the electrolyte [17, 20, 21, 58-62]. Dissolution of Li into LiCl has been noted by a number of researchers, and causes a number of changes in physical, electrical, and chemical properties of the electrolyte, as well as causing current inefficiency [17]. The exact solubility limit of Li in LiCl has proven to be experimentally difficult to determine [16, 59, 60]. A number of different dissolution mechanisms have been proposed by other researchers, but a consensus has yet to be reached within the community. The f-center model proposed by Bredig, et Al. treats the excess electron from solvated Li$^0$ as an anion vacancy, with the electron delocalized from any individual Li$^+$ ion core [18, 59]. In this model, the solution behaves somewhat similarly to a liquid metal, with free electrons contributing to increased electrical conductivity. This model has successfully predicted the increase in solution conductivity for other alkali halide – alkali metal systems, however, the solution conductivity of the LiCl-Li system is anomalous in that it does not increase at the rate predicted by the f-center model [17, 59]. Previous work in our laboratory using in-situ Raman spectroscopy has provided evidence of the presence of Li$_8$ nanoclusters in solution as a colloidal suspension [22]. If Li$_8$ clusters are present in the LiCl-Li system, they would act to keep the valence electrons of the Li$_8$ cluster localized, thus reducing the rate of electrical conductivity increase associated with the progressive addition of Li$^0$ to LiCl. As the clusters would be present as a colloid, the solubility of Li$^0$ in LiCl would be dependent on the specific experimental parameters, leading to the variation in the measured values for solubility reported by other researchers [22].
Regardless of the molecular interactions at place within the LiCl-Li system, understanding of the effect the solution chemistry has on materials exposed to the molten LiCl-Li$_2$O-Li system is important for the safe and economical design of vessels and other components for use during the electrolytic reduction of used nuclear fuel. Corrosion in LiCl-Li$_2$O under oxidizing conditions has been widely investigated [63-70]. The most successful model of corrosion in this system is based on the Lux-Flood model of salt basicity where the rate of material degradation is dependent upon the activity of the O$^{2-}$ anion [33, 63, 71]. In addition to O$^{2-}$ activity, corrosion in molten salts is also governed by the inclusion of impurities in the melt, such as moisture or metal chlorides [33]. While the literature concerning corrosion in chloride salts is rich in diversity and discussion of corrosion mechanisms, very few studies have investigated the effect of solvated lithium metal in lithium chloride [25, 39, 42-47]. The studies that have been reported have been mainly of short term duration and have been conducted under widely varying experimental parameters. Consequently, these studies conflict in their analysis on the effect of Li$^0$ on the corrosion of various materials in the molten LiCl-Li$_2$O-Li system.

Previous work in our laboratory has attempted to elucidate the effect of Li$^0$ and Li$_2$O on the corrosion of Stainless Steel 316L (SS316L), Inconel 625, and Monel 400 by parametrically varying the concentrations of Li$_2$O, Li, and impurity H$_2$O independently [25, 39, 46]. These studies showed that material degradation depends on the concentration of H$_2$O, Li$_2$O and Li, and that a transition from corrosion based primarily on the O$^{2-}$ activity in the melt at low Li$^0$ concentrations
to corrosion more similar to liquid metal attack occurs at high Li\(^0\) concentrations. However, the short-term nature of these exposure tests necessitated the continuation of this work to verify our previous findings. In this light, the current study focuses on the corrosion of SS316L over extended time periods when exposed to LiCl containing Li\(_2\)O and Li at various concentrations. This paper presents the information gathered from SEM-EDS of the sample surfaces and cross sections, as well as XRD, XPS, and Raman spectroscopy of the surfaces to elucidate the mechanisms responsible for material degradation.

2.2: Materials and Methods

All experiments were performed in a Vacuum Atmospheres OMNI-LAB glovebox under an Ar atmosphere containing less than 2ppm O\(_2\) and less than 1ppm H\(_2\)O. Anhydrous LiCl and Li\(_2\)O were obtained from Alfa-Aesar and were of 99% and 99.5% purity, respectively. Li metal of 99% purity was purchased from Strem Chemicals. 99% purity Ni crucibles were obtained from Alfa-Aesar. SS316L coupons were cut from a 3.048mm plate obtained from McMaster-Carr, with the certified composition given in Table 2.1.

Table 2.1: Certified composition of the SS316L plate used in this study.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>70.1</td>
<td>16.5</td>
<td>10</td>
<td>2</td>
<td>1.3</td>
<td>0.014</td>
</tr>
</tbody>
</table>

The salt compositions studied consisted of LiCl containing 1 and 2wt% Li\(_2\)O and 0, 0.3, 0.6, and 1wt% Li, with exposure periods of 500 and 1000 hours.
Total salt mass contained in each crucible was 50g. Duplicate samples were exposed for each data point, and 500 hour and 1000 hour exposures were conducted in parallel, with the 500 hour samples removed from the experiment upon completion of the allotted exposure period. The furnace configuration used for this study is shown in Figure 2.1. A 6.5 inch inner diameter, 6 inch tall cylindrical heater from Watlow (1500 watts) was used to maintain a temperature of 650±5°C for the duration of the exposure period. A 6 inch diameter graphite block was machined to accommodate 5 Ni crucibles, with slots machined to accommodate the sample hanging rods. This configuration allowed for repeatable placement of the samples within the melt during the salt replacement procedure outlined below. Two identical furnaces were constructed to maximize the number of experiments that could be ran in parallel. In operation, four experiments were ran simultaneously in each furnace, which allowed for an additional crucible location to be used for salt replacement purposes.
Prior to exposure, the metal samples were cut into 1.27cm by 1.27cm squares using a CO\textsubscript{2} laser. The samples were then polished to a 1 μm surface finish on both sides using a diamond abrasive and spot welded to loops of SS316L wire for suspension from the sample hanging rods, as was performed in our previous studies [25, 39, 46]. Sample hanging rods were made of like material to the samples, as alumina rods proved to be incapable of withstanding the highly reducing atmosphere directly over the molten solutions containing metallic Li for the duration of these experiments. The mass of each sample was recorded immediately prior to exposure using a high precision balance.
2.3: Experimental

Due to the evaporation of Li and Li$_2$O over time and the extended exposure periods of this study, the salt charge for each test was replaced once every 96 hours to maintain the solution chemistry. To minimize the effects of impurity H$_2$O, LiCl was dried in a vacuum oven in air at 200°C for 24 hours before being transferred into the glovebox for storage [19, 25]. Immediately prior to insertion in the primary furnace, a cleaned Ni crucible (99% purity, Alfa Aesar) containing the weighed amount of LiCl was dried under Ar for 2hr in a dedicated furnace maintained at 550°C. After insertion into the primary furnace, the LiCl was allowed 1 hour to reach thermal equilibrium, after which time the required mass of Li$_2$O and Li were added to the molten salt. The melt was allowed to equilibrate for another hour prior to the transfer of the corrosion specimens from the old salt charge to the new salt charge. Sample transfer was accomplished through the use of specially fabricated tongs. Following transfer of the samples to the new salt charge, the old salt charge was removed from the furnace and allowed to cool to room temperature.

Following completion of the exposure period, the samples were removed from the furnace and allowed to cool to room temperature in the glovebox atmosphere. All samples were stored in the Ar glovebox between analytical procedures. As it was unknown if the surface films formed on the corrosion specimens would be stable in atmosphere, surface analysis was performed both prior to and following removal of the residual salt layer. Following the initial
surface analytical procedures, residual LiCl was removed by placing each
sample in 25ml of HPLC grade methanol for 15 minutes with constant agitation.
Prior to the methanol rinsing procedure, all surface analysis was performed
under inert atmosphere or vacuum conditions, depending on technique. The data
presented here was collected following the methanol rinsing procedure, as the
residual salt layer significantly interfered with surface analysis. No chemical or
morphological changes were observed as a result of the methanol rinsing
procedure. Gravimetric weight change measurements were performed following
the methanol rinsing procedure.

Post exposure surface analysis was performed using scanning electron
microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS),
Raman Spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron
spectroscopy (XPS). Following the completion of all surface analytical techniques
performed in this study, the samples were cross sectioned to investigate the
nature and depth of degradation of the samples. Initially, focused ion beam (FIB)
milling was used to mill a trench in the samples to minimize possible
morphological and chemical changes to the internal structure of the samples;
however, it was found that the depth of attack for samples exposed to melts
containing Li was much greater than practical to investigate using this technique
alone. Consequently, all samples exposed to Li containing melts were cross
sectioned using a Buehler cubic-BN wafering blade on a slow speed saw and
polished according to Buehler’s recommended polishing techniques to a 0.05μm
surface finish prior to analysis. Samples exposed to LiCl-Li$_2$O in the absence of
Li were investigated using only FIB milling for cross sectional analysis due to the relatively shallow depth of attack.

SEM of the sample surfaces was performed using a Hitachi S-4700, while EDS data was collected via the attached Oxford Instruments energy dispersive X-ray spectrometer. The W cold field emission source was operated at an accelerating voltage of 5kV for surface morphology images, while 20kV was used for collection of EDS spectra. Emission current was maintained at 10mA. FIB milling and subsequent SEM-EDS analysis for cross sectional images was performed using a FEI Scios dual-beam FIB/SEM equipped with a TEAM Pegasus Integrated EDS-EBSD. The same dual-beam FIB/SEM was used to perform the SEM-EDS analysis of all of the cross sectioned samples, including those mechanically cross sectioned and polished. The electron beam was operated at 20kV for both imaging and EDS analysis.

Following the methanol rinsing procedure, the final mass of each sample was recorded, and the exposed surface area was calculated based on the measured submersion depth of each sample. The average corrosion rate in mm/year and the mass loss rate in mg cm\(^{-1}\) hr\(^{-1}\) was then calculated based on the mass change, density of the alloy, exposed surface area, and length of exposure.

X-ray diffraction was performed using a Rigaku Smartlab X-ray diffractometer with a Cu k\(\alpha\) source operating at 44kV and 40mA. Parallel beam optics in a grazing incidence angle configuration were used for detection of the
thin surface films formed on the samples in this study. The incidence angle was set at 1°, and the diffraction pattern was recorded over a 2θ range of 10° to 90° for all diffraction patterns. For each diffraction pattern, the scan speed was optimized to yield an intensity of 5000 counts for the highest peak, while the step size was varied to give 5 steps at the full width at half-maximum intensity of the narrowest peak.

Raman spectroscopy was performed using a Thermo-Scientific DXR Raman microscope utilizing a 10mW 532nm continuous wave laser. Spectra were collected through the 50x objective lens of the microscope using a 50μm incident beam slit. The collection time was 4 seconds per spectra, and 16 individual spectra were averaged to give the spectra reported here.

X-ray photoelectron spectroscopy was performed using a PHI 5600 spectrometer equipped with an Al-Kα source with a photon energy of 1486.6eV. The source was operated at an accelerating voltage of 14kV and an anode power of 300W. The spectrometer dispersion and work function were calibrated to the Au 4f7/2 peak at 84.00eV and the Cu 2p3/2 peak at 932.67eV to an accuracy of ±0.05eV. Survey spectra were recorded with a step size of 0.5eV, while narrow scans were collected at a step size of 0.025eV for the elements detected on the sample surfaces. Peak fitting was performed with SDP version 4.6 Gaussian fitting software. Charge correction was performed to the adventitious C 1s peak at 284.8eV.
2.4: Results

2.4.1: Scanning Electron Microscopy

The morphologies observed via SEM were highly dependent on the Li concentration in the molten salt solution. The SEM micrographs obtained from SS316L samples exposed to LiCl-2wt% Li$_2$O containing 0, 0.3, 0.6, and 1wt% Li at 650°C for 1000hr and washed with methanol are shown in Figure 2.2, while the area averaged EDS composition of the primary constituents of the sample surface for these regions are given in Figure 2.3. The differences in the surface morphology caused by the varying concentrations of Li in LiCl-2wt% Li$_2$O correlates to the changes in surface chemistry observed via Raman, XPS, and XRD presented below. The unique surface morphology observed at 0.3wt% Li may be indicative of the simultaneous action of electrochemical corrosion and liquid metal attack, while the similarity between the morphologies observed at 0.6 and 1wt% Li indicate that corrosion at these concentrations is firmly within the liquid metal attack regime. Morphologies similar to those observed here were reported in a recent publication by researchers at KAERI who investigated the corrosion behavior of Ni in molten LiCl-Li$_2$O-Li [47]. A number of void spaces were also observed on the surface of all samples exposed to melts containing metallic Li, indicating possible locations where the intergranular corrosion observed on the sample cross sections was initiated. These voids were typically located at high angle grain boundaries, further supporting this hypothesis.
Figure 2.2: SEM micrographs of SS316L exposed to LiCl-1wt% Li2O at 650°C containing A) no Li, B) 0.3wt% Li, C) 0.6wt% Li, and D) 1wt% Li for 1000hr, following the methanol rinsing procedure.
Figure 2.3: Average composition of the SS316L samples exposed to LiCl-1wt% Li$_2$O-Li solutions for 1000hr for the regions shown in Figure 2.2.

From Figure 2.3, it can be observed that the surface of the SS316L sample exposed to LiCl-1wt% Li$_2$O-0wt% Li at 650°C for 1000hr is primarily composed of Cr-based oxide films, with minor contributions of Ni and Fe. This is in good agreement with the Raman, XRD, and XPS data presented in their respective sections, which all indicate that these surfaces are composed primarily of LiCrO$_2$, while small quantities of Li$_2$CrO$_4$ and NiFe$_x$Cr$_{2-x}$O$_4$ are predicted by Raman and XPS. When the Li concentration in the molten salt solution is 0.3wt%, the Cr content of the surface is depleted compared to the
base alloy while the Fe content is increased. Beyond the solubility limit of Li, at 0.6 and 1wt% Li, Cr is depleted slightly further and O is not detectable, while both Fe and Ni are present at levels nominal for SS316L, indicating a bare metallic surface. A slight enrichment of Ni on the SS316L sample exposed to LiCl-2wt% Li-1wt% Li for 1000hr is in agreement with our previous work, and is indicative of liquid metal like attack by Li [25]. Similar trends were observed for samples exposed to LiCl-Li$_2$O-Li containing 1 and 2wt% Li$_2$O and 0, 0.3, 0.6, and 1wt% Li for 500 and 1000hr.

Also of interest is the observation of sensitization on a small area on the SS316L sample exposed to LiCl-2wt% Li$_2$O-0.6wt% Li at 650°C for 1000hr. Sensitization of austenitic stainless steels is a well-known issue at high temperatures, where the formation of chromium carbides and their subsequent concentration at the grain boundaries leads to intergranular corrosion and loss of strength [72]. The characteristic enrichment of Cr at the grain boundaries typical of sensitization can clearly be observed in the Cr Kα EDS map in Figure 2.4, while the specific compositions for spots 1 and 2 marked on the SEM micrograph and EDS map are given in Table 2.2.
Figure 2.4: SEM micrograph (left) and EDS map of Cr of the same location (right) for the SS316L sample exposed to LiCl-2wt% Li2O-0.6wt% Li at 650°C for 1000hr. The elemental compositions obtained via EDS analysis for spots 1 and 2 are given in Table 2.2.

Table 2.2: EDS composition spot analysis for the locations marked on the SEM micrograph in Figure 2.4, above.

<table>
<thead>
<tr>
<th>Element</th>
<th>Spot 1 Atomic%</th>
<th>Spot 2 Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>26.69</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>1.21</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>27.05</td>
<td>4.28</td>
</tr>
<tr>
<td>Mn</td>
<td>1.09</td>
<td>1.46</td>
</tr>
<tr>
<td>Fe</td>
<td>28.52</td>
<td>50.05</td>
</tr>
<tr>
<td>Ni</td>
<td>15.44</td>
<td>44.21</td>
</tr>
</tbody>
</table>

The detection of S along with chromium carbide formation at Spot 1 is in good agreement with literature, as S is known to accelerate the sensitization of austenitic stainless steels [72]. As expected, the vicinity of spot 1 area (spot 2) has much lower concentration of chromium, which is below the concentration in base alloy. The low carbon content of the SS316L used for this study is intended to minimize this issue by preventing the formation of carbides. Of great importance to the present work, the operating temperature of the electrolytic reduction of UNF at 650°C is also ideal to cause sensitization of austenitic
stainless steels, as chromium carbides are insoluble at this temperature and the diffusion of C through the microstructure allows for their formation and migration to the grain boundaries.

2.4.2: Cross Section SEM-EDS

The SEM image obtained for the FIB milled trench from the SS316L samples exposed to LiCl-1wt% Li\textsubscript{2}O-0% Li for 500hr and 1000hr are shown in Figure 2.5. It can be observed that the attack first proceeds inward from the sample surface in an intergranular fashion prior to consuming the grains themselves, likely assisted by the sensitization of the material seen in Figure 2.4. The depth of attack into the sample is approximately linear with length of exposure, with the total depth of attack being 13μm and 27μm for 500hr and 1000hr, respectively, while the thickness of the outer oxide layer is approximately 3μm for the 500hr sample and 7.5μm for the 1000hr sample.

Figure 2.5: FIB milled and SEM imaged cross sections of SS316L samples exposed to LiCl-1wt% Li\textsubscript{2}O for 500hr (left) and 1000hr (right).
EDS mapping results for the corroded region of the SS316L sample exposed to LiCl-1wt% Li₂O for 1000hr are shown in Figure 2.6. Here, it can be observed that the corrosion products (dark regions) are enriched in Cr, Mo and O, while the bulk material is relatively depleted in Cr and Mo. This agrees with the findings of previous studies that corrosion in LiCl-Li₂O occurs primarily through preferential attack of the most active alloying elements, namely Cr and Mo [25, 33].

Figure 2.6: EDS mapping results for the SS316L sample exposed to LiCl-1wt% Li₂O for 1000hr.

In the presence of Li, intergranular corrosion was again observed to be the primary method of material degradation, as can be observed in Figure 2.7. However, the lack of a protective oxide layer severely accelerated the attack of the base material.
Figure 2.7: Cross section SEM images and EDS maps of SS316L samples exposed to LiCl-1wt% Li₂O containing 0.3, 0.6, and 1wt% Li for 500 and 1000hr. Areas selected for EDS mapping are delimited in SEM image. Brightness has been adjusted for clarity.

From Figure 2.7, it can be observed that the depth of attack on the base material is approximately linear with time and does not depend on the concentration of Li; however, the severity of the degradation is proportional to the Li concentration in the melt. In all cases, the rate of attack was approximately 2.2 to 2.9mm/year in the presence of Li. The outer layers of the SS316L samples exposed to melts containing Li were depleted in Cr, while small, localized areas of high Cr concentration were observed in intergranular regions, further corroborating the observations of sensitization made in Figure 2.4. A high magnification EDS map of one of these regions on the SS316L sample exposed to LiCl-1wt%Li₂O-0.6wt%Li for 500hr is shown in Figure 2.8, while the spot EDS analysis for the area highlighted in red in the SEM image is given in Table 2.3.
Figure 2.8: Hi-magnification SEM-EDS maps of Fe, Ni, Cr, Mn, and Cl for a Cr rich region of the SS316L sample exposed to LiCl-1wt%Li$_2$O-0.6wt%Li for 500hr. The red spot on the SEM image indicates the location of the spot EDS analysis summarized in Table 2.3.

Table 2.3: Spot EDS analysis for the location on the SS316L sample exposed to LiCl-1wt%Li$_2$O-0.6%Li for 500hr shown in Figure 2.8.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>9.72</td>
<td>26.31</td>
<td>8.88</td>
</tr>
<tr>
<td>N</td>
<td>10.88</td>
<td>25.23</td>
<td>8.87</td>
</tr>
<tr>
<td>Cr</td>
<td>53.57</td>
<td>33.48</td>
<td>1.64</td>
</tr>
<tr>
<td>Mn</td>
<td>1.36</td>
<td>0.81</td>
<td>7.84</td>
</tr>
<tr>
<td>Fe</td>
<td>21.91</td>
<td>12.75</td>
<td>2.74</td>
</tr>
<tr>
<td>Ni</td>
<td>2.56</td>
<td>1.42</td>
<td>5.82</td>
</tr>
</tbody>
</table>

From the SEM-EDS images in Figure 2.8 and spot analysis in Table 2.3, it is apparent that corrosion of the base material is facilitated by the precipitation of Cr and Mn at the grain boundaries in the form of metal carbides and nitrides. These carbides and nitrides are then preferentially attacked by the molten salt, leaving a channel for further intrusion of the salt along the grain boundary. N was
likely incorporated as an impurity from the glovebox atmosphere which reacted with Li$^0$ to form Li$_3$N, which is known to accelerate corrosion in the LiCl-Li$_2$O-Li system [73]. Also, titanium nitride surface films were observed in previous studies, as well as during XPS analysis of these samples [26]. Some of these samples were observed to spontaneously form droplets of water from the cross sectioned surface when exposed to atmosphere, implying LiCl was entrapped within the sample. LiCl is extremely hygroscopic, and will absorb enough water to form a solution, even in relatively dry air, so the formation of water droplets on the cross sectioned surface is indicative of the entrapment of LiCl within the bulk sample. As most other metal chlorides are not hygroscopic to the same extent as Li, this indicates that the Cl observed in Figures 2.7 and 2.8 is primarily in the form of LiCl.

2.4.3: Depth of Attack Analysis

Based on the depth of attack observed in Figure 2.7, the depth of lithium attack was calculated for each sample and are tabulated in Table 2.4. For comparison, the corrosion rates based on gravimetric analysis are presented in Table 2.5.
Table 2.4: Depth of attack observed for SS316L samples exposed to LiCl-1wt% Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt% Li for 500 and 1000hr, and the corrosion rate based on this depth of attack.

<table>
<thead>
<tr>
<th>Li Concentration in Salt (wt%)</th>
<th>Exposure Duration (hr)</th>
<th>Depth of Attack (µm)</th>
<th>Depth of Attack Rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>500</td>
<td>13</td>
<td>0.23</td>
</tr>
<tr>
<td>0</td>
<td>1000</td>
<td>27</td>
<td>0.24</td>
</tr>
<tr>
<td>0.3</td>
<td>500</td>
<td>140</td>
<td>2.45</td>
</tr>
<tr>
<td>0.3</td>
<td>1000</td>
<td>275</td>
<td>2.41</td>
</tr>
<tr>
<td>0.6</td>
<td>500</td>
<td>166</td>
<td>2.91</td>
</tr>
<tr>
<td>0.6</td>
<td>1000</td>
<td>250</td>
<td>2.19</td>
</tr>
<tr>
<td>1</td>
<td>500</td>
<td>120</td>
<td>2.10</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>225</td>
<td>1.97</td>
</tr>
</tbody>
</table>

The lack of spallation of the material based on the gravimetric analysis presented below, along with the morphological changes to the base material shown above indicates that simple mass loss or thickness measurements are not sufficient for assessing corrosion damage in this system. The maximum corrosion rate observed gravimetrically was for the SS316L sample exposed to LiCl-1wt% Li$_2$O-1wt% Li for 500hr, where the corrosion rate was 0.665mm/year, which is well below the attack rate calculated for this sample based on the ingress of attack observed in cross sectional imaging. The high variance observed is thought to be a result of the relatively low absolute weight change per sample, which was on the order of 10s of mg for most samples, as well as ingress of salt into the material. No overall trend in gravimetric weight loss as a function of material, Li$_2$O concentration, Li concentration, or exposure period was observed.

Table 2.5: Calculated corrosion rates for SS316L samples exposed to LiCl-Li$_2$O-Li solutions at 650°C for 500hr and 1000hr. Positive corrosion rates indicate weight loss, while negative corrosion rates indicate weight gain.
<table>
<thead>
<tr>
<th>Wt% Li2O</th>
<th>Wt% Li</th>
<th>Exposure (hr)</th>
<th>Mass Loss Rate (mg cm(^{-1}) hr(^{-1}))</th>
<th>Corrosion Rate (mm year(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>500</td>
<td>0.000</td>
<td>-0.005</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>500</td>
<td>-0.019</td>
<td>0.211</td>
</tr>
<tr>
<td>1</td>
<td>0.6</td>
<td>500</td>
<td>-0.012</td>
<td>0.126</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>500</td>
<td>-0.061</td>
<td>0.665</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>500</td>
<td>-0.010</td>
<td>0.115</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>500</td>
<td>-0.005</td>
<td>0.055</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>500</td>
<td>-0.001</td>
<td>0.016</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>500</td>
<td>0.012</td>
<td>-0.134</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1000</td>
<td>-0.005</td>
<td>0.050</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>1000</td>
<td>-0.006</td>
<td>0.062</td>
</tr>
<tr>
<td>1</td>
<td>0.6</td>
<td>1000</td>
<td>-0.016</td>
<td>0.179</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1000</td>
<td>-0.010</td>
<td>0.112</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1000</td>
<td>-0.008</td>
<td>0.082</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>1000</td>
<td>-0.012</td>
<td>0.130</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>1000</td>
<td>-0.009</td>
<td>0.101</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1000</td>
<td>-0.007</td>
<td>0.073</td>
</tr>
</tbody>
</table>

2.4.4: X-ray Diffraction

Figure 2.9 shows the diffraction pattern obtained for SS316L exposed to LiCl-2wt%Li₂O-0wt%Li at 650°C for 500hr. Peaks characteristic of LiCrO₂, based on PDF card number 01-072-7839, and the base material were observed [74]. No other phases were detected on the sample surface, indicating that the NiFe\(_x\)Cr\(_{2-x}\)O\(_4\) and Li\(_2\)CrO\(_4\) phases predicted by Raman spectroscopy, SEM-EDS, and XPS observations presented below are minor components of the oxide layer present on samples exposed to LiCl-Li₂O solutions in the absence of Li. Similar patterns were obtained for all samples exposed to LiCl-Li₂O solutions in the absence of Li\(^0\).
Figure 2.9: GI-XRD pattern of SS316L exposed to LiCl-2%Li₂O-0%Li for 500hr after methanol rinsing. Peaks corresponding to LiCrO₂ and the base material were observed.

The XRD patterns for SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0, 0.3, 0.6, or 1wt%Li at 650°C for 500hr are shown in Figure 2.10, while Figure 2.11 shows the diffraction patterns for SS316L samples exposed to identical conditions for 1000hr.
Figure 2.10: High resolution grazing incidence XRD patterns for SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0, 0.3, 0.6, or 1wt%Li at 650°C for 500hr. The diffraction pattern for the SS316L sample exposed to LiCl-1wt%Li₂O-0wt%Li shows the peaks identified as LiCrO₂ in Figure 2.10, above. The peaks of LiCrO₂ were not observed on any sample exposed to LiCl-Li₂O in the presence of Li. De-austenization of samples exposed to LiCl-1wt%Li₂O containing 0, 0.6, and 1wt%Li for 500hr was observed.

From these figures, it can be observed that the LiCrO₂ surface films that form in the absence of Li are not detectable via XRD in the presence of Li, corroborating SEM-EDS as well as the Raman spectroscopy and XPS analysis presented in this work [25]. These techniques all show that the presence of Li prevents the formation of appreciable oxide surface films, resulting in severe degradation to the base material. Additionally, de-austenization of the base material was observed on the SS316L samples exposed to LiCl-1wt%Li₂O containing 0, 0.6, and 1wt%Li for 500hr, and LiCl-1wt%Li₂O containing 0 and
0.3wt%Li for 1000hr. This effect was also observed in short term testing of SS316L in molten LiCl-Li2O-Li [25]. The inconsistency with which this phenomena was observed indicates that the solution chemistry does not affect the probability that a particular sample will undergo de-austenization. This is particularly highlighted by the SS316L samples exposed to LiCl-1wt%Li2O containing 0.3, 0.6, and 1wt%Li for 500 or 1000hr, as the samples exposed to identical solution chemistries for different exposure periods did not display similar de-austenization behavior.

Figure 2.11: High resolution grazing incidence XRD patterns for SS316L samples exposed to LiCl-1wt%Li2O solutions containing 0, 0.3, 0.6, or 1wt%Li at 650°C for 1000hr. The diffraction pattern for the SS316L sample exposed to LiCl-1wt%Li2O-0wt%Li shows the peaks identified as LiCrO2 in Figure 2.9, above. The extent of de-austenization of the base material varied among
samples exposed to identical conditions, but otherwise the trends observed in Figure 2.10 remain consistent at longer exposure periods.

The samples exposed to LiCl-2wt%Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt% Li displayed similar diffraction patterns as those presented above.

2.4.5: Raman Spectroscopy

The Raman spectrum of SS316L sample exposed to LiCl-1wt%Li$_2$O-0wt%Li at 650°C for 500hr is shown in Figure 2.12. This spectrum displays peaks that were observed in various ratios on all samples exposed to LiCl-Li$_2$O solutions in the absence of Li and is therefore used here as representative of the samples exposed to similar conditions. Both the A$_{1g}$ mode at 572cm$^{-1}$ and the E$_g$ mode at 445cm$^{-1}$ of LiCrO$_2$ are clearly defined [75]. Broad peaks centered at 250cm$^{-1}$, 690cm$^{-1}$, and 845cm$^{-1}$ were also observed. Based on EDS and XPS analysis shown in their respective sections, the peak at 690cm$^{-1}$ can be attributed to the A$_{1g}$ mode of a mixed Ni, Fe, Cr spinel of the form NiFe$_x$Cr$_{2-x}$O$_4$, although the exact composition of this oxide is not easily identified [76]. The position of this peak was also observed to shift slightly on other samples, which can likely be attributed to variations in the stoichiometry of the spinel due to differing exposure periods, melt compositions, and base materials. The peak at 845cm$^{-1}$ is hypothesized to originate from Li$_2$CrO$_4$, based on the presence of Cr$^{6+}$ in the XPS spectra collected from SS316L samples exposed to LiCl-Li$_2$O solutions in the absence of Li. The broad feature centered around 250cm$^{-1}$ could not be positively attributed to any single compound, but may be caused by the
combination of the minor modes of Li₂CrO₄ and minor components of the NiFeₓCr₂₋ₓO₄ spectrum.

Figure 2.12: Raman spectra of the SS316L sample exposed to LiCl-1wt%Li₂O in the absence of Li for 1000hr.

When exposed to LiCl-Li₂O solutions containing Li, these oxide-based surface films are destabilized due to the highly reducing nature of metallic Li. To illustrate the changes to the surface layer present on samples exposed to LiCl-Li₂O solutions as a function of Li concentration, Figure 2.13 shows the Raman spectra obtained from SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr. The spectra collected from samples exposed to LiCl-Li₂O in the presence of Li do not display any discernible
features indicative of the well-developed oxide layer observed in Figure 2.12. Rather, the features observed are broad and are close to the baseline of the instrument, indicating that the oxide layer is tenuously present on these samples.

Figure 2.13: Raman spectra of SS316L samples exposed to molten LiCl-1wt% Li₂O containing 0, 0.3, 0.6, and 1wt% Li for 500 hours. The distinctive peaks characteristic of LiCrO₂, Li₂CrO₄ and NiFeₓCr₂-xO₄ observed on samples exposed to LiCl-Li₂O in the absence of Li are seen to be eliminated by the presence of Li in the melt.

As no investigations into the Raman spectra of Li₂CrO₄ could be found in literature, the spectra of a commercially purchased Li₂CrO₄ standard was collected to confirm that the peak seen at 845cm⁻¹ in Figures 2.12 and 2.13 could be attributed to this compound. The Raman spectrum collected from pure Li₂CrO₄ is shown in Figure 2.14. The assignment of specific vibrational and rotational modes to each of the peaks observed in Figure 2.14 is beyond the
scope of this study. However, it can be seen that the primary features of pure
Li$_2$CrO$_4$ occur between 1000cm$^{-1}$ and 800cm$^{-1}$, with the dominant peak occurring
at approximately 850cm$^{-1}$. Additional minor features are present between 450cm$^{-1}$
and 275cm$^{-1}$. As the oxide layer of the samples is non-homogenous and
consists primarily of LiCrO$_2$ with small amounts of NiFe$_x$Cr$_{2-x}$O$_4$ and Li$_2$CrO$_4$, the
smearing of the features of the Li$_2$CrO$_4$ spectrum to form the single, broad peak
centered around 850cm$^{-1}$ observed on the samples exposed to LiCl-Li$_2$O is
plausible [76].

Figure 2.14: Raman spectrum obtained from Li$_2$CrO$_4$. Collection parameters were identical to
those used for methanol rinsed samples. The primary features of the Li$_2$CrO$_4$ spectrum occur
around 850cm$^{-1}$, with minor features in the range of 450cm$^{-1}$ to 300cm$^{-1}$. 
2.4.6: X-ray Photoelectron spectroscopy

XPS survey scans of the SS316L samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt% Li at 650°C for 1000hr are shown in Figure 2.15. For the SS316L sample exposed to LiCl-1wt%Li$_2$O at 650°C for 1000hr in the absence of Li, the surface is primarily composed of Cr and O, with Ni and Fe detectable in small quantities. For the SS316L samples exposed to LiCl-1wt%Li$_2$O containing 0.6 and 1wt% Li at 650°C for 1000hr, the surface shows a relatively thick Ti-based surface deposit, with high quantities of N and O present. In the case of the SS316L sample exposed to LiCl-1wt%Li$_2$O-0.6wt%Li for 1000hr, this Ti surface film was sufficiently thick to prevent the analysis of the underlying base material. TiO$_2$ is a common impurity in Li$_2$O, and the deposition of Ti based compounds on samples exposed to LiCl-Li$_2$O in the presence of Li was extensively studied during our previous short term studies [26].
Analysis of the alloying elements, especially the Cr 2p spectra, is necessary to determine the corrosion mechanisms of SS316L in LiCl-Li$_2$O-Li, as Cr is the primary element responsible for the formation of oxide films in the absence of Li. Identification of the oxidation state of Cr present on the surface of the SS316L sample exposed to LiCl-1wt%Li$_2$O-Li at 650°C for 500hr was performed by peak fitting the Cr 2p$_{3/2}$ spectra using previously published peak fitting parameters [77]. The peak fit data for all Cr spectra collected on the samples in this study are shown in Figure 2.16, while the peak fitting parameters are given in Table 2.6 [77].
Figure 2.16: Cr 2p XPS spectra collected from SS316L samples exposed to all LiCl-Li$_2$O-Li compositions and exposure periods studied in this work. Charge correction was performed to the adventitious C 1s peak at 284.8eV, and peak fitting parameters for Cr$^0$, Cr$^{3+}$, and Cr$^{6+}$ listed in Table 2.6 were used for all spectra. Cr$^{3+}$ and Cr$^{6+}$ are the only species present in the absence of Li. Cr spectra of SS316L samples exposed to molten LiCl-Li$_2$O in the presence of Li indicate both metallic and oxidized components; however, no discernible trend in oxidation state based on Li concentration, Li$_2$O concentration or exposure period could be determined. Cr was not detectable on the SS316L sample exposed to LiCl-1wt% Li$_2$O-0.6wt%Li for 1000hr due to the thickness of the overlying Ti surface deposit.

Table 2.6: Peak fitting parameters used for Cr 2p$_{3/2}$ spectra reported in Figure 2.16 [77].

<table>
<thead>
<tr>
<th>Peak</th>
<th>BE</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^0$</td>
<td>574.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>576.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Cr$^{6+}$</td>
<td>578.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
As can be observed in Figure 2.16, both Cr\(^{3+}\) and Cr\(^{6+}\) are simultaneously present on all SS316L samples exposed to LiCl-Li\(_2\)O solutions in the absence of Li\(^0\). The presence of Cr\(^{3+}\) and Cr\(^{6+}\) on the samples further supports the presence of both LiCrO\(_2\) (Cr\(^{3+}\)) and Li\(_2\)CrO\(_4\) (Cr\(^{6+}\)) on the surfaces of samples exposed to LiCl-Li\(_2\)O solutions in the absence of Li. In the presence of Li, the highly reducing nature of metallic Li destabilizes the oxide films that are present on the sample surfaces in the absence of Li. However, the transition between electrochemical oxidation of the samples in the absence of Li and liquid metal attack in the presence of high Li concentrations is not abrupt. Our previous short term studies have shown that at concentrations at or below the apparent solubility limit of Li in the system (around 0.3wt%Li) \[16\], there exists a transition region where both modes of attack occur simultaneously\[25, 46\]. The Cr 2p\(_{3/2}\) spectra shown in Figure 2.16 give further evidence for this hypothesis, although there was no discernible trend in the relative ratios of Cr\(^0\), Cr\(^{3+}\), and Cr\(^{6+}\) based on the concentration of Li, Li\(_2\)O, or exposure period.

The presence of Cr\(^{3+}\) is also required for the formation of NiFe\(_x\)Cr\(_{2-x}\)O\(_4\), as both Fe and Cr are in the 3+ oxidation state in this compound, while Ni is present in the 2+ oxidation state. Further confirmation of the presence of NiFe\(_x\)Cr\(_{2-x}\)O\(_4\) is given by the narrow scans of the Ni 2p and Fe 2p spectra for SS316L exposed to LiCl-1wt%Li\(_2\)O-0wt%Li for 500hr, which are shown in Figure 2.17, along with the Ni 2p and Fe 2p narrow scans for the SS316L sample exposed to LiCl-1wt%Li\(_2\)O-0.3wt%Li for 500hr. In the absence of Li, the Ni 2p\(_{3/2}\) peak is located at 853.5eV, while the Fe 2p\(_{3/2}\) peak is located at 710.1eV. These binding energies
and peak shapes correspond to Ni$^{2+}$ and Fe$^{3+}$, respectively [78]. Neither element was detected in the metallic state, confirming the presence of Ni and Fe based oxides on the sample surface. In conjunction with Raman spectroscopy and EDS analysis, this is further evidence supporting the presence of a NiFe$_x$Cr$_{2-x}$O$_4$ based spinel present on the surface of the samples exposed to LiCl-Li$_2$O in the absence of Li. However, when Li was present in the molten salt, only metallically bonded Ni and Fe are present on the sample surface. No charge correction was necessary for the Ni and Fe 2p spectra, indicating that these elements were in direct electrical contact with the base material. Similar spectra were recorded for all other SS316L samples exposed to LiCl-Li$_2$O-Li, indicating that any quantity of Li$^0$ in the melt is sufficient to reduce NiFe$_x$Cr$_{2-x}$O$_4$. 
Figure 2.17: XPS narrow scans for Ni 2p (left) and Fe 2p (right) collected from SS316L exposed to LiCl-1%Li2O-0%Li (Top) and LiCl-1wt%Li2O-0.3wt%Li (Bottom) at 650°C for 500hr. In the absence of Li, Ni is present in the 2+ oxidation state and Fe is present in the 3+ oxidation state based on their binding energies of 853.5eV and 710.1eV, respectively. However, in the presence of Li, all Ni and Fe spectra indicate the presence only of metallic Ni and Fe.

In our previous work, Mo was observed to behave similarly to Cr in some respects, becoming enriched on the surface in the absence of Li, and depleted at higher Li concentrations. As Mo is a minor alloying element of SS316L at around 2wt%, Mo was not observed on all samples. Additionally, in the absence of Li, Mo was not detectable via XPS on any sample due to the thick LiCrO2 surface layer. However, the samples exposed to molten LiCl-2wt%Li2O solutions containing 0.3, 0.6, and 1wt%Li for 500hr all had detectable levels of Mo, the narrow scans of which are presented in Figure 2.18. From the spectra in Figure
2.18, it can be observed that when 0.3wt% Li is present in solution, Mo\(^{6+}\) is the only Mo species observable on the sample surface [79]. However, as Li concentration increases the stability of oxidized Mo is decreased, resulting in a mixed Mo\(^{6+}\)/Mo\(^0\) spectra at 0.6wt% Li and a fully metallic Mo\(^0\) spectra at 1wt% Li [79, 80]. The observation of Mo\(^{6+}\) on samples exposed to high concentrations of Li indicates that Mo is highly active in the LiCl-Li\(_2\)O-Li system, which could explain the depletion of Mo from the surface of SS316L observed via SEM-EDS analysis of the cross section of these samples in section 4.2.

Figure 2.18: Mo 3d XPS spectra of SS316L samples exposed to molten LiCl-2wt%Li\(_2\)O solutions containing 0.3, 0.6, and 1wt% Li for 500hr. As Li concentration in the melt is increased, the Mo oxidation state shifts towards more reduced species. The peak shape for the SS316L sample exposed to LiCl-2wt%Li\(_2\)O-1wt% Li for 500hr is likely the result of differential charging and the charge correction performed to the adventitious C 1S peak at 284.8eV.

Co was also observed on some samples exposed to LiCl-Li\(_2\)O in the presence of Li. Co is not an alloying element of SS316L, but is present as the primary impurity in the Ni crucibles used for these studies at concentrations of less than 1wt%. Consequently, the presence of Co on the surface of the samples exposed to LiCl-Li\(_2\)O solutions in the presence of Li indicates that there is mass transport from the crucible to the samples. Mass transport of Co from the crucible to the samples had not been observed in our previous short term experiments.
[25, 39, 46]. The Co 2p spectra of the SS316L sample exposed to LiCl-1wt%Li2O-0.3wt%Li for 500hr is presented in Figure 2.19, and is typical of Co$^{3+}$, due to its binding energy and peak shape [78]. The cause of the transport of Co from the crucible to the samples and its implications to the degradation of materials in the LiCl-Li$_2$O-Li system as a whole requires further investigation.

Figure 2.19: XPS narrow scan of the Co 2p peak observed on SS316L exposed to LiCl-1wt%Li$_2$O-0.3wt%Li at 650°C for 500hr and rinsed with methanol. The binding energy and shape of the 2p$_{3/2}$ peak of 789.8eV is consistent with the presence of Co$^{3+}$. [81]

2.5: Conclusions

Exposure testing of SS316L samples was performed for 500 and 1000hr intervals in molten LiCl-Li$_2$O-Li solutions containing 1 and 2wt% Li$_2$O and 0, 0.3,
0.6, and 1wt% Li. Morphological and elemental changes to the sample surfaces and cross sections were investigated via SEM and EDS, respectively, while XRD, Raman spectroscopy, and XPS were used to provide further insight into the effect of Li$^0$ on the degradation mechanisms of materials in LiCl-Li$_2$O-Li. Upon exposure to LiCl-Li$_2$O solutions in the absence of Li, SS316L was observed to form a LiCrO$_2$ based surface film, with minor contributions of Li$_2$CrO$_4$ and NiFe$_x$Cr$_{2-x}$O$_4$. The oxide layer limited corrosion to a rate of approximately 0.24mm/year during exposure to molten LiCl-Li$_2$O solutions. The presence of Li in the melt resulted in the destabilization of the protective oxide film formed in LiCl-Li$_2$O solutions, causing substantial damage to the samples in the form of intergranular corrosion. XPS analysis observed that metallically bonded Ni and Fe were present on the surface of all SS316L samples exposed to LiCl-Li$_2$O in the presence of Li, however both Cr and Mo displayed varying degrees of oxidation in the presence of Li. Mass loss rates were low, but cross sectioned samples displayed significant ingress of LiCl and damage to the sample surface, indicating that mass loss measurements alone are not sufficient to characterize corrosion in this system. Intergranular corrosion was facilitated by the precipitation of metal carbides and nitrides along the grain boundaries, resulting in the selective depletion of alloying elements, such as Cr, Mo, and Mn. The rate of material damage was on the order of 2-3mm/year, indicating that the presence of high concentrations of Li during the electrolytic reduction of UNF will dramatically reduce the lifetime of any SS316L components exposed to the electrolyte. The ingress of intergranular corrosion into the material will likely have
a marked effect on the strength of the material due to the effective loss of structural thickness, however, further investigation would be necessary to validate this hypothesis. From the combination of analytical techniques presented in this work, it is hypothesized that cyclical oxidation by $O^{2-}$ ions and reduction by $Li^{0}$ is responsible for the high levels of material degradation in the LiCl-Li$_2$O-Li system.
Chapter 3 : Effect of metallic Li on the corrosion behavior of Inconel 625 in molten LiCl-Li2O-Li

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Abstract:

The corrosion behavior of Inconel 625 in molten LiCl solutions maintained at 650°C and containing various quantities of Li2O and metallic Li was studied for possible application in the electroreduction of used oxide-based nuclear fuel.

This study focusses on the morphological and elemental changes on the surface of the samples with an emphasis on cross-sectional analyses conducted using focused ion beam microscopy. In the absence of metallic Li, a stable oxide film is formed that limits the corrosion of the base material to 0.07mm/year. However, in the presence of metallic Li, the formation of this film is impeded, resulting in dealloying of the base material and the formation of a highly porous microstructure composed primarily of Ni.

Keywords: Hot corrosion, Pyroprocessing, FIB.
3.1: Introduction

In order to reprocess used nuclear fuel (UNF) from light water reactors using pyrometallurgical techniques, a reduction operation is necessary to convert UO$_2$-based UNF into a metallic product that can then be processed in subsequent unit operations [7, 8, 48, 50, 82]. The prototypical process by which the reduction of UO$_2$ is conducted is via the electrolytic reduction operation developed at Argonne National Laboratory (ANL) [7, 49]. In this process, LiCl containing 1 to 2wt% Li$_2$O and maintained at 650°C serves as the electrolyte [56, 83]. The reduction is performed with UNF loaded in a stainless steel cathode basket which is polarized vs. a suitable anode, typically made of Pt, either galvanostatically or potentiostatically [8, 17]. To achieve high reduction yields, it has been shown by a number of researchers that it is necessary to polarize UO$_2$ at potentials beyond the electrochemical window of Li$_2$O, which results in the formation of metallic Li at the cathode [8, 13, 17]. Some of the metallic Li thus generated then metalothermically reduces the UNF in the cathode; however, LiCl is capable of solvating Li to a limited degree, which leads to the formation of a tertiary LiCl-Li$_2$O-Li electrolyte [8, 13, 17]. As the process goes to completion, the electrolyte eventually reaches Li saturated conditions, and may even form and be present as clusters [22]

The dissolution of alkali metals in their respective alkali halides has been well studied over the last century, notably by M.A. Bredig at Oak Ridge National Laboratory, among others [59, 84, 85]. The two primary models of alkali metal –
alkali halide systems are the f- center model and the sub-halide model [84]. In the f- center model typical for alkali metal – alkali halide systems, the excess electron is delocalized from any particular cation core, leaving a free electron that imparts a metallic character to the molten solution [84]. This leads to several orders of magnitude increase in electrical conductivity of solution as the concentration of the alkali metal increases towards saturation, as well as causing a number of other changes in physical and chemical properties. The sub-halide model is typically representative of transition metals and post-transition metals in their respective halides and gives rise to the formation of abnormally reduced species due to the formation of complex molecules that keep electrons localized to the molecular scale, as is typical for the Bi-BiCl$_3$ system [84]. Sub-halide forming systems are not associated with an increase in electrical conductivity in the same manner as the f- center model predicts. Other dissolution mechanisms have also been reported, such as the formation of colloidal suspensions of nanoclusters of Na$_2$ or Li$_8$ in the Na-NaCl and Li-LiCl systems, respectively [22, 84]. It is important to note that none of these effects are mutually exclusive, and it is possible that the simultaneous action of multiple dissolution mechanisms may occur simultaneously in the same system. Of the alkali metal – alkali halide systems, the Li-LiCl system has proven to be particularly challenging in the determination of the solubility limit of the metal in the metal salt, with the apparent solubility limit seeming to vary depending on the experimental methods; however, approximately 0.3wt% has been shown to be a useful estimate at the temperatures of the electrolytic reduction operation [16, 20, 24, 59, 60, 84, 86].
Importantly, the concentration of Li$_2$O has been shown to have minimal effect on the measured solubility limit of Li in LiCl-Li$_2$O [86]. The discrepancy between the various reported values of the solubility limit of Li in LiCl may be due to the simultaneous action of the various dissolution mechanisms theorized for this system [22].

For the electrolytic reduction of UNF to be implemented on a large scale, knowledge of the degradation of materials in contact with the electrolyte is necessary, particularly for the container material. Corrosion in molten LiCl-Li$_2$O under inert or oxidizing atmospheres has been fairly well studied, and the corrosion of various materials has been found to follow similar mechanisms to those observed in other molten salt systems [63-66, 68, 69, 87]. Primarily, the dissolution of alloying elements, and consequently the corrosion rate, is governed primarily by the activity of the O$^{2-}$ ion in the solution according to the Lux-Flood model of salt basicity, as well as by the presence of impurities such as moisture or transition metal halides [33, 63, 71]. For the electroreduction process, such models are insufficient to completely describe corrosion due to the presence of dissolved Li. To date, very few investigations into the effects of Li on the corrosion of materials exposed to this system have been performed [25, 39, 42, 44, 46, 47]. The initial studies conducted by Indocochea, et al. conflicted with studies conducted by Mishra and Olson due to widely varying experimental parameters, leading to confusion about the effect Li had on the degradation observed [42, 44]. Recent studies have been performed to address these issues, but were of short term in nature and did not investigate the degradation of the
materials studied in cross section [25, 39, 46]. These studies showed that a transition from molten salt based corrosion to a liquid metal attack induced degradation occurred at approximately 0.6wt%Li, and that the concentration of both Li and Li$_2$O affected the corrosion processes that were observed. Recent work by researchers at the Korean Atomic Energy Research Institute showed that Ni displayed minimal corrosion in the absence of Li, but underwent significant degradation in the presence of metallic Li [47]. In this light, the current study investigates the corrosion behavior of Inconel 625 (I625) in the LiCl-Li$_2$O-Li$_2$ system at 650°C. To understand the effect of oxide concentration, metal concentration and the period of exposure, the solution chemistries studied consisted of LiCl containing 1 or 2wt% Li$_2$O and 0, 0.3, 0.6, or 1wt% Li, with samples exposure periods of 500 and 1000hr. This study focusses on the observed degradation of I625 under these conditions by determining the changes to the microstructure and elemental composition using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) of the sample surfaces as well as their cross sections.

3.2: Experimental

Experiments were conducted in a Vacuum Atmospheres OMNI-LAB glovebox under Ar containing less than 2ppm O$_2$ and less than 1ppm H$_2$O. Anhydrous LiCl, Li$_2$O, and Ni crucibles were obtained from Alfa-Aesar and were of 99%, 99.5%, and 99% purity, respectively. Li metal of 99% purity was purchased from Strem Chemicals. I625 coupons were cut from a 3.175mm thick
plate obtained from High Performance Alloys. The composition of this alloy as measured via the EDS used for cross sectional investigation was 62.3wt% Ni, 23.5wt% Cr, 6.5wt% Mo, 5.1% Fe, and 2.6wt% Nb.

Studies were conducted using duplicate samples, and 500 hour and 1000 hour exposures were conducted in parallel, with the 500 hour samples removed from the experiment upon completion of the allotted exposure period. A 6.5 inch inner diameter, 6 inch tall cylindrical heater from Watlow (1500 watts) was used to maintain a temperature of 650±5°C for the duration of the exposure period. A 6 inch diameter graphite block was machined to accommodate 5 Ni crucibles, with slots machined to accommodate the sample hanging rods. This configuration allowed for repeatable placement of the samples within the melt during the salt replacement procedure outlined below. Two identical furnaces were constructed to maximize the number of experiments that could be ran in parallel. In operation, four experiments were ran simultaneously in each furnace, which allowed for the extra 5th crucible location to be used for salt replacement purposes.

Prior to exposure, the metal samples were cut into 1.27cm by 1.27cm squares using a CO₂ laser. The samples were then polished to a 1 μm surface finish on both sides using a diamond abrasive and spot welded to loops of SS316L wire for suspension from the sample hanging rods, as was performed in our previous studies [25, 39, 46]. Sample hanging rods were made of like material to the samples, as alumina rods proved to be incapable of withstanding the highly reducing atmosphere directly over the molten solutions containing
metallic Li for the duration of these experiments. The mass of each sample was recorded immediately prior to exposure.

Considering the evaporation of Li and Li$_2$O over time that was observed in other short-term studies and the extended exposure periods of this study, the salt charge for each test was replaced at a period of once every 96 hours to maintain the solution chemistry [25, 26, 39, 46, 88]. To minimize the effects of impurity H$_2$O, LiCl was dried in a vacuum oven in air at 200°C for 24 hours before being transferred into the glovebox for storage [19, 25]. Immediately prior to insertion in the primary furnace, a cleaned Ni crucible containing the weighed amount of LiCl was dried under Ar for 2hr in a dedicated furnace maintained at 550°C. After insertion into the primary furnace, the LiCl was allowed 1 hour to reach thermal equilibrium, after which time the required mass of Li$_2$O and Li were added to the molten salt by placing the Li$_2$O powder and Li pellets on top of the solution. Total salt mass contained in each crucible was 50g. The melt was allowed to equilibrate for another hour prior to the transfer of the corrosion specimens from the old salt charge to the new salt charge. As the concentration of Li was above the solubility limit for the 0.6 and 1wt% tests, a significant fraction was likely present as a colloidal suspension. Sample transfer was accomplished via specially fabricated tongs, which allowed for the transfer time to be less than 5 seconds on average. Following transfer of the samples to the new salt charge, the old salt charge was removed from the furnace and allowed to cool to room temperature. The cooled salt ingot was then dissolved in deionized (DI) water. The Ni crucible was then sanded with 600 grit SiC paper, rinsed with DI water,
cleaned with isopropyl alcohol, and dried under vacuum prior to re-use for the next salt charge for the same solution chemistry conditions. Two Ni crucibles were alternated between for each solution chemistry.

Following completion of the exposure period, the samples were removed from the furnace and allowed to cool to room temperature in the glovebox atmosphere. All samples were stored in the Ar glovebox between analytical procedures. As it was unknown if the surface films formed on the corrosion specimens would be stable in atmosphere, surface analysis was performed both prior to and following removal of the residual salt layer. Following the initial surface analytical procedures, residual LiCl was removed by placing each sample in 25ml of HPLC grade methanol for 15 minutes with constant agitation. Prior to the methanol rinsing procedure, all surface analysis was performed under inert atmosphere or vacuum conditions, depending on technique. The data presented here were collected following the methanol rinsing procedure, as the residual salt layer significantly interfered with surface analysis as has been described earlier [25]. No chemical or morphological changes were observed as a result of the methanol rinsing procedure. Gravimetric weight change measurements were performed following the methanol rinsing procedure.

All samples exposed to Li containing melts were cross sectioned using a Buehler cubic-BN wafering blade on a slow speed saw and polished according to Buehler’s recommended polishing techniques to a 0.05μm surface finish prior to analysis. Samples exposed to LiCl-Li₂O in the absence of Li were investigated
using only FIB milling for cross sectional analysis due to the relatively shallow depth of attack.

SEM of the sample surfaces was performed using a Hitachi S-4700 and EDS data was collected via the attached Oxford Instruments energy dispersive X-ray spectrometer. The electron beam was operated at an accelerating voltage of 5kV for surface morphology images, while 20kV was used for collection of EDS spectra. Emission current was maintained at 10mA. FIB milling and subsequent SEM-EDS analysis for cross sectional images was performed using a FEI Scios dual-beam FIB/SEM equipped with a TEAM Pegasus Integrated EDS-EBSD. The same dual-beam FIB/SEM was used to perform the SEM-EDS analysis of all of the cross sectioned samples, including those mechanically cross sectioned and polished. The electron beam was operated at 20kV for both imaging and EDS analysis.

The exposed surface area was calculated based on the measured submersion depth of each sample. The average corrosion rate in mm/year and the mass loss rate in mg cm⁻² hr⁻¹ was then calculated based on the mass change, density of the alloy, exposed surface area, and length of exposure

3.3: Results

The surface of I625 samples exposed to LiCl-Li₂O solutions in the absence of Li displayed a high degree of crystallinity indicative of a well-formed oxide layer, while the surfaces of samples exposed to LiCl-Li₂O in the presence
of metallic Li showed a very porous, almost sponge-like microstructure. To illustrate these points, the SEM micrographs taken of the I625 samples exposed to LiCl-1wt%Li\textsubscript{2}O containing 0, 0.3, 0.6, or 1wt%Li for 500hr are shown in Figure 3.1.

Figure 3.1: SEM micrographs of I625 exposed to LiCl-1wt%Li\textsubscript{2}O at 650°C containing A) no Li, B) 0.3wt%Li, C) 0.6wt%Li, and D) 1wt%Li for 500hr and rinsed with methanol.

In the absence of Li, the oxide layer is well formed and shows evidence of a multi layered structure that is discussed in greater detail below. EDS analysis of the area shown in Figure 3.1(a) showed that the surface was composed of 22at% Cr, 66at%O, and 13at%Ni, with minor quantities of other elements, indicating a primarily Cr based oxide layer. Li is not detectable via EDS, however,
spectroscopic analysis has definitively shown this compound to be LiCrO$_2$ [89]. The presence of Li in the molten LiCl-Li$_2$O solution destabilizes the oxide layer and forms a very porous microstructure that is similar in appearance to a Ni foam. EDS analysis of these areas consistently showed greater than 80at%Ni, with high depletion of Cr, Mo, and Nb, although the Ni:Fe ratio remained close to that of the base material. There was little difference between the microstructures observed at low and high Li concentrations, with the microstructure of the I625 samples exposed to melts containing 0.3wt%Li displaying microstructures nearly identical to samples exposed to melts containing 1wt%Li. Exposure periods of 500hr and 1000hr both yielded nearly indistinguishable microstructures, as can be observed by comparing the micrographs of I625 samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt%Li for 1000hr shown in Figure 3.2 to the micrographs presented in Figure 3.1.
Variations in Li\textsubscript{2}O concentration and exposure length did not dramatically alter the morphology observed on I625 samples exposed to LiCl-Li\textsubscript{2}O-Li compared to those shown in Figures 3.1 and 3.2. Consistent morphology was observed in the presence of Li, with all samples displaying similar structures. Likewise, in the absence of Li, a well-developed, highly crystalline oxide layer was consistently observed. Additionally, the surface of the I625 sample exposed to LiCl-2wt\%Li\textsubscript{2}O-0wt\%Li for 500hr had a small number of locations where the oxide layer had partially delaminated, which allowed for direct observation of the layered structure of the oxide films formed on I625 during exposure to LiCl-Li\textsubscript{2}O in the absence of Li. SEM micrographs of one of these locations are shown in
Figure 3.3, and the compositions of locations 1 through 4 detected via EDS are given in Table 3.1.

Figure 3.3: SEM micrographs taken at (A) low magnification and (B) high magnification of the highlighted area on the I625 sample exposed to LiCl-2wt%Li$_2$O-0wt%Li at 650°C for 500hr after methanol rinsing. The delamination of the outer surface layer on this sample provided a unique opportunity to examine the layered structure of the oxide films that form on I625 upon exposure to molten LiCl-Li$_2$O in the absence of Li. The compositions of Layers 1 through 4 in image B were obtained via EDS analysis and are given in Table 3.1, below.
Table 3.1: EDS compositional analysis obtained for locations 1 through 4 marked in Figure 3.3B for the I625 sample exposed to LiCl-2wt%Li₂O-0wt%Li at 650°C for 500hr.

<table>
<thead>
<tr>
<th>Element</th>
<th>Layer 1 Atomic%</th>
<th>Layer 2 Atomic%</th>
<th>Layer 3 Atomic%</th>
<th>Layer 4 Atomic%</th>
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<tr>
<td>C</td>
<td>5.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
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<td>11.22</td>
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<td></td>
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<td></td>
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<td>0.47</td>
</tr>
<tr>
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<td>3.33</td>
<td>12.99</td>
<td>20.07</td>
</tr>
<tr>
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<td>3.74</td>
<td>1.21</td>
<td>0.32</td>
</tr>
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<td>80.97</td>
<td>21.44</td>
<td>5.13</td>
</tr>
<tr>
<td>Nb</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
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<td>0.74</td>
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<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td>0.46</td>
<td>0.32</td>
<td></td>
</tr>
</tbody>
</table>

The presence of a multilayered oxide structure is easily discernable in this image. Each layer was analyzed using EDS at the spots marked by the arrows. The layers were numbered 1 through 4 starting with the innermost and proceeding outward. Due to the composition of Layer 2 and the lack of Ti in both Layers 1 and 2, which is present as an impurity in the Li₂O used in this study, it is thought that Layer 1 is the result of the inward diffusion of O into the base material. The O concentration of Layer 2 is much lower than in any of the other layers observed here, and its composition is the most similar to the base alloy, although all areas analyzed were notably depleted in Mo and Nb. The size of the grains in Layer 2 and their relative orientations are also similar to the morphology of the I625 samples exposed to LiCl-Li₂O in the presence of Li, as can be
observed by comparison with Figures 3.1 and 3.2, indicating that this is likely the base material which has been depleted in Cr to facilitate the outward growth of Layers 3 and 4. These outermost layers differ in both morphology and composition, suggesting a difference in the compounds that compose them. Layer 3 is the layer closest to the base material, and has a plate-like morphology. The high Ni content of Layer 3 compared to Layer 4 implies that Layer 3 is composed of primarily NiFe$_x$Cr$_{2-x}$O$_4$ with a relatively low value of $x$, while Layer 4 is primarily LiCrO$_2$ based. Both Layer 3 and Layer 4 have incorporated Ti from the impurities present in the Li$_2$O used in this study. The spheroidal morphology of Layer 4 suggests that its growth begins at specific nucleation sites. Some of these spheroids from Layer 4 appear to be broken or incompletely formed, showing that they are hollow. Figure 3.4 shows the results of EDS mapping of Ni, Fe, Cr, and O for the same location shown in Figure 3.3 which further highlights the differences between the layers observed on this sample.
Cross Section SEM-EDS.— The cross sections of the samples were investigated to determine the depth to which the degradation of the surface penetrated into the bulk of the sample. In the absence of Li, the penetration into the bulk of the sample was minimal, as evidenced by Figures 3.5 and 3.6, which show the FIB milled cross section of the I625 samples exposed to LiCl-1wt%Li2O-0wt%Li at 650°C for 500hr and 1000hr, respectively. Small pores of less than 2μm in diameter were observed immediately below the outer oxide layer for the 500hr sample, corresponding to a layer of Mo enrichment as evidenced in Figure 3.5 (d). As shown in the EDS analysis of this sample previously, the oxide layer does not incorporate a significant amount of Mo, indicating that the surface enrichment of Mo is deleterious to the integrity of the base material. At an exposure period of 500hr, the thickness of the oxide layer is
approximately 1μm, while the thickness of the Mo enriched layer containing the
pores is approximately 2μm. Based on a total thickness of 3μm, the corrosion
rate was calculated to be 0.05mm/year.

Careful observation of the EDS maps in figure 3.5(b through f) show that
Cr is depleted in this region. Consequently, our hypothesis is that the pores are a
result of the diffusion of Cr towards the surface to form the outer oxide layer,
causing contraction of the base material at the interface between the base alloy
and the oxide layer. As corrosion proceeds, the diffusion of Cr from the bulk alloy
becomes the limiting factor, and the surface of these voids then offer the path of
least resistance to allow reaction of Cr with the salt to form the Cr-based oxide
layer. The increased volume of the oxide eventually fills in the void space. The
growth and subsequent infill of these voids may give rise to the multi-layered
oxide structure observed on the samples exposed to identical conditions for
1000hr in Figure 3.6. The lack of voids observed in Figure 3.6 may be due to the
path required for diffusion of Cr from the alloy. This is supported by near
complete depletion of Cr in the Ni and Fe rich layers between the Cr-based
oxides.
For the I625 sample exposed to LiCl-1wt%Li$_2$O-0wt%Li for 1000hr, the corrosion rate was approximately 0.07mm per year, indicating that corrosion was approximately linear for these experiments. The oxide film was well developed, and showed a multi-layered structure similar to that shown for the I625 sample.
exposed to LiCl-2wt%Li₂O-0wt%Li for 500hr in Figures 3.3 and 3.4. The Mo enriched layer below the outer corrosion layer was still observed, however, there were no voids located in this area as there were on the 500hr sample. Mo accumulation was also observed at the grain boundaries, along with Cr and Nb, which is likely due to thermal aging of the microstructure, rather than a result of exposure to the molten LiCl-Li₂O solution [90]. Although enrichment of Cr, Mo, and Nb were observed along the grain boundaries, carbon was not observed at these locations, so it cannot be concluded that sensitization was observed. Corrosion did not proceed along the grain boundaries, so it seems that the enrichment of the grain boundaries in Cr, Mo, and Nb did not negatively impact the observed corrosion rate. However, sensitization followed by intergranular corrosion was observed in our previous work on SS316L under similar conditions [88].
Figure 3.6: SEM micrograph (a) and EDS mapping analysis of the FIB milled trench on the I625 sample exposed to LiCl-1wt%Li₂O-0wt%Li for 1000hr showing variations in concentration of (b) Cr, (c) Ni, (d) Mo, (e) Fe, (f) Nb, (g) Ti, and (h) O. The multi-layered structure observed here corresponds to a similar oxide layer structure observed in Figures 3.3 and 3.4. Again, Mo enrichment is seen immediately below the corrosion layer, without significant incorporation of Mo into the oxide layer itself. The precipitate seen at a depth of 17μm consists largely of Ti, Mo, and Nb. Cr, Mo, and Nb were also observed to be enriched along the grain boundaries.
As was observed via SEM imaging of the sample surfaces, the cross sections of the 1625 samples exposed to LiCl-Li₂O in the presence of Li were consistent in morphology and showed an outer layer of a highly porous Ni rich foam-like structure. The formation of this porous layer is believed to be a result of the selective dissolution of Cr, Mo, and Nb from the base material, leaving the Ni-Fe matrix in place, similar to the formation of Rainey Nickel by the selective dissolution of Al from Ni-Al alloys [91]. This mechanism is likely similar to the void formation observed in Figure 3.5(a), as diffusion of elements within the alloy is unlikely to be affected by the solution chemistry. The SEM images of the cross sections of the 1625 samples exposed to LiCl-1wt%Li₂O containing 0.3, 0.6, or 1wt% Li at 650°C for 500 and 1000hr are shown in Figure 3.7. For the sample exposed to LiCl-1wt%Li₂O-0.3wt%Li for 500hr, the porosity penetrated into the surface to a depth of approximately 30μm, corresponding to a corrosion rate of 0.53mm/year. However, all other samples consistently showed a penetration depth of 15μm, regardless of Li concentration or period of exposure, indicating that a direct measure of the corrosion rate is not necessarily applicable for these specimens. The similarity in the morphology and depth of attack regardless of Li concentration or exposure period indicates that there may be a threshold concentration of Li necessary to cause this morphology and that threshold is likely below 0.3wt%, and the reactions responsible for pore formation may not be diffusion controlled. Further studies at Li concentrations below 0.3wt% would be necessary to determine at what concentration this morphology begins to be observed as well as the mechanisms responsible for pore formation. Due to the
presence of metallic Li, liquid metal embrittlement may play a role in the
formation of the microstructures observed here, although verification of this
hypothesis would require further investigation.

Figure 3.7: Cross section SEM images for I625 samples exposed to LiCl-1wt%Li₂O containing
0.3wt% Li for (a) 500hr or (b) 1000hr, 0.6wt% Li for (c) 500hr or (d) 1000hr, or 1wt% Li for (e)
500hr or (f) 1000hr. The porous microstructure observed via SEM of the sample surface was
also observed in cross section, and was consistent amongst sample exposed to LiCl-Li₂O in the
presence of Li.

The variation in composition as a function of depth was investigated via
EDS of the cross sections. As all samples exposed to LiCl-Li₂O in the presence
of Li displayed similar variations in composition, the SEM-EDS results for the I625 sample exposed to LiCl-1wt%Li$_2$O-1wt%Li at 650°C for 1000hr are shown in Figure 3.8, while spot EDS analysis for the locations shown in Figure 3.8(a) are given in Table 3.2. Cr, Mo, and Nb are all significantly depleted from the material remaining in the porous layer, leaving primarily Ni, with Fe remaining at approximately the same ratio as in the base material. The depletion of Cr, Mo, and Nb was also observed to irregularly penetrate into the sample beyond the depth of the porous layer. The loss of the amount of Cr, Mo, and Nb necessary to reach the composition of spot 1 shown in Figure 3.8(a) represents the loss of a significant fraction of the material, which may account for the porous microstructure seen on this sample and other I625 samples exposed to LiCl-Li$_2$O in the presence of Li.
Figure 3.8: SEM micrograph (a) and EDS mapping analysis of the cross section of the I625 sample exposed to LiCl-1wt%Li₂O-1wt%Li for 1000hr showing variations in concentration of (b) Cr, (c) Ni, (d) Mo, (e) Fe, and (f) Nb. Locations marked 1, 2, and 3, were analyzed via point analysis, which is presented in Table 3.2.

Table 3.2: EDS spot analysis of the locations demarked in Figure 3.8(a) for the I625 sample exposed to LiCl-1wt%Li₂O-1wt%Li for 1000hr. The outermost layer was depleted in Cr compared to the base material, while the dark spots seen in some locations on these samples did not show any observable variation in composition compared to the base material.

<table>
<thead>
<tr>
<th>Element</th>
<th>Spot 1 (wt%)</th>
<th>Spot 2 (wt%)</th>
<th>Spot 3 (wt%)</th>
</tr>
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<td>-</td>
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<td>2.97</td>
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<tr>
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<td>Fe</td>
<td>8.35</td>
<td>5.17</td>
<td>5.17</td>
</tr>
<tr>
<td>Ni</td>
<td>81.48</td>
<td>62.45</td>
<td>60.98</td>
</tr>
</tbody>
</table>
3.4: Conclusions

I625 samples were exposed to molten LiCl solutions containing 1 or 2wt% Li\textsubscript{2}O and 0, 0.3, 0.6, or 1wt% Li maintained at 650°C for periods of 500 and 1000hr to investigate the effect of metallic Li on the degradation of the material. In the absence of metallic Li, I625 formed a highly crystalline, stable oxide film with a multi-layered structure that limited corrosion to approximately 0.05 to 0.07mm/year. The presence of metallic Li in solution prevented the formation of any substantial oxide film, resulting in a highly porous, foam-like structure. The depletion of Cr, Mo, and Nb from the surface was also observed on these samples via EDS, indicating that these elements were preferentially leached from the base material by the molten solution. The loss of these elements from the sample surface, which together constitute one-third of the material, is likely responsible for the highly porous microstructure observed.
Abstract:
This study explores the surface chemistry of Inconel 625 samples exposed to molten LiCl-Li$_2$O-Li solutions at 650°C for 500 and 1000hr and aims to understand the effect of solvated Li on corrosion behavior in molten LiCl-Li$_2$O-Li. The surfaces of Inconel 625 samples were analyzed using X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy. The oxide films formed on the surface of the samples in the absence of Li is composed of LiCrO$_2$, with small contributions of Li$_2$CrO$_4$ and NiFe$_x$Cr$_{2-x}$O$_4$. The presence of Li was observed to destabilize these compounds, resulting in a primarily metallic surface with trace amounts of oxidized Cr, Mo, and Nb present depending on the concentration of Li in solution.

Keywords: High temperature corrosion, Lithium chromate, Electrolytic reduction, Pyroprocessing
4.1: Introduction

This study discusses the effect of metallic Li dissolved in molten LiCl-Li$_2$O solutions on the corrosion behavior of Inconel alloy 625 (625), as applies to the electrolytic reduction of oxide based used nuclear fuel (UNF). A thorough introduction including the motivation and background for this work is provided in an earlier study [92]. Briefly, the formation of metallic Li in the molten LiCl-Li$_2$O electrolyte used for the electrolytic reduction of oxide based UNF has been noted by a number of researchers to occur [8, 17]. Formation of metallic lithium is a side reaction that occurs as a result of the high reduction potential in the process that is necessary to reduce uranium oxide to uranium metal. As the reduction proceeds, it can be assumed that the concentration of Li in the electrolyte approaches saturated conditions [17]. While the dissolution mechanism of Li in LiCl and its effects on the physical chemistry of the solution have been well studied, corrosion in this tertiary LiCl-Li$_2$O-Li solution has not been extensively studied [22, 59, 60, 84]. Additionally, the studies that have been conducted have been of short duration and have shown conflicting results due to widely varying experimental conditions employed [25, 39, 42, 44, 46, 47]. Consequently, this study was performed to elucidate the mechanisms responsible for material degradation in conditions applicable to the electrolytic reduction of UNF.

Previous work from our group reported the morphological and elemental changes to the base material surface and cross section via scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) for
both stainless steel 316 (SS316) and l625 [88, 92]. The results presented there showed that a stable Cr-based oxide film forms on the surface of l625 upon exposure to molten LiCl-Li₂O solutions at 650°C in the absence of Li⁰ [92]. This oxide film was found to limit the corrosion of these samples to a rate of approximately 0.05 to 0.07 mm/year [92]. However, in the presence of Li, this oxide film was destabilized, resulting in the preferential dissolution of the active alloying elements, namely Cr, Mo, and Nb, and a porous microstructure at the sample surface (92, Appendix 1 Figs. A1-4 and A1-5). This porous structure extended into the surface to a depth of 15 to 30µm [92]. This study aims to better understand the corrosion mechanisms involved by understanding the surface chemistry of l625 using X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The results of these surface analytical techniques are presented in this work.

4.2: Experimental

I625 coupons were cut from a 3.175mm plate obtained from High Performance Alloys with the following nominal composition: 58wt% Ni, 20-23wt% Cr, 5wt% Fe, 8.0-10.0wt% Mo, 3.15-4.15wt% Nb, 0.5wt% Mn, 0.4wt% Al, 0.4wt% Ti, and 0.5wt% Si. The composition of this alloy as measured via the EDS used for cross sectional investigation was 62.3wt% Ni 23.5wt% Cr, 6.5wt% Mo, 5.1% Fe, and 2.6wt% Nb. Duplicate coupons were exposed molten solutions of LiCl containing either 1 or 2wt% Li₂O, and either 0, 0.3, 0.6, or 1wt% Li over exposure periods of either 500 or 1000 hours. Considering the evaporation of Li and Li₂O
over time that was observed in other short-term studies and the extended exposure periods of this study, the salt charge for each test was replaced at a period of once every 96 hours to maintain the solution chemistry [25, 26, 39, 46, 88]. To minimize the effects of impurity H$_2$O, LiCl was dried in a vacuum oven in air at 200°C for 24 hours before being transferred into the glovebox for storage. Additionally, the LiCl was baked for 2 hours at 550°C immediately prior to melting and subsequent addition of Li$_2$O and Li [19, 25]. The surface analysis presented here was conducted on the samples prepared for our previous work [92]. More details on the experimental procedure and morphology of these samples can be found in that publication [92]. All surface analysis was performed prior to removal of the residual salt layer, as well as following removal of the salt layer, which was accomplished by rinsing the sample in 25mL of ACS grade methanol for 15 minutes with continuous agitation.

Great care was taken to maintain sample integrity at all times during analyses. Prior to methanol rinsing, all surface analyses was conducted under inert or ultra-high vacuum (UHV) conditions, as dictated by each technique. Raman studies were performed inside the Ar glovebox using a fiber optic coupled probe. For XPS analyses, the samples were transferred from the glove box to the UHV chamber in a sealed transfer chamber to prevent atmospheric contamination (PHI Model 04-110). This transfer vessel has been extensively verified to protect reactive samples from atmospheric contamination during transfer under various conditions [93]. A glove bag was installed on the transfer port of the XPS and purged with dry nitrogen for 30 minutes prior to sample
removal to reduce atmospheric contamination of the samples during removal from the instrument. The samples were then re-sealed inside the PHI 04-110 transfer chamber for transfer back to the glovebox. As described in our earlier work, XRD studies were then conducted on samples which were sealed in plastic bags in the argon atmosphere of the glovebox [25, 26, 39, 46, 88]. No hydrated LiCl peaks were detected via XRD, indicating that there was insignificant moisture contamination on the samples to this point, however, peaks indicative of LiCrO$_2$ were observed on the samples exposed to LiCl-Li$_2$O in the absence of Li (see supplemental information, Appendix A1). Finally, sample surfaces were studied using SEM-EDS prior to methanol rinsing [92]. Due to the design of the transfer port of this instrument, it was necessary to momentarily expose the samples to atmosphere prior to pumping down of the SEM entry chamber. Total exposure time to atmosphere was less than 30 seconds. After SEM studies, the samples were then immediately rinsed with methanol as described above to remove the residual salt layer. Moisture content of the methanol was not analyzed, but typical moisture concentration was specified to be lower than 100 ppm. Following removal of the salt layer, the samples were immediately re-analyzed via SEM-EDS. No morphological or compositional changes were detected following methanol rinsing. Samples were stored inside the Ar glovebox at all times other than for analysis. The surface analytical results from post methanol rinse were consistent with the results from pre-methanol rinse; however, the removal of the residual salt allowed for more accurate determination of the surface chemistry, as in many cases, the residual salt layer
partially obscured the surface from analysis, particularly with XPS (see supplemental information, Appendix A1). The lack of substantial surface oxides on the samples exposed to LiCl-Li$_2$O solutions containing Li indicate that the surface analysis procedures outlined above had minimal impact on the surface chemistry of these samples. As has been shown previously, no chemical or morphological changes to the sample surface were observed to result from the methanol rinsing procedure [25, 26, 57]. As such, the spectra reported here were collected from the sample surfaces following removal of the salt layer due to the improved data quality afforded by the increased signal to noise ratio.

X-ray diffraction was performed using a Rigaku Smartlab X-ray diffractometer with a Cu kα source operating at 44kV and 40mA. Parallel beam optics in a grazing incidence angle configuration were used for detection of the thin surface films formed on the samples in this study. The incidence angle was set at 1°, and the diffraction pattern was recorded over a range of 10° to 90° 2θ for all diffraction patterns. For each diffraction pattern, the scan speed was optimized to yield an intensity of 5000 counts for the highest peak, while the step size was varied to give 5 steps at the full width at half-maximum intensity of the narrowest peak.

Raman spectroscopy was performed using a Thermo-Scientific DXR Raman microscope utilizing a 10mW 532nm continuous wave laser. Spectra were collected through the 50x objective lens of the microscope using a 50μm
incident beam slit. The collection time was 4 seconds per spectra, and 16 individual spectra were averaged to give the spectra reported here.

X-ray photoelectron spectroscopy was performed using a PHI 5600 spectrometer equipped with an Al-Kα source with a photon energy of 1486.6eV. The source was operated at an accelerating voltage of 14kV and an anode power of 300W. The spectrometer dispersion and work function were calibrated to the Au 4f7/2 peak at 84.00eV and the Cu 2p3/2 peak at 932.67eV to an accuracy of ±0.05eV. Survey spectra were recorded with a step size of 0.5eV, while narrow scans were collected at a step size of 0.025eV for the elements detected on the sample surfaces. Peak fitting was performed with SDP version 4.6 Gaussian fitting software. Charge correction was performed to the adventitious C 1s peak at 284.8eV.

4.3: Results

4.3.1: XRD

The X-ray diffraction pattern collected for the I625 sample exposed to LiCl-1wt% Li2O-0wt% Li at 650°C for 1000hr is shown in Figure 4.1. The peaks displayed in this pattern are representative of those collected for all samples exposed to molten LiCl-Li2O solutions in the absence of Li0. The only crystalline phases detected on these samples were the base material and peaks consistent with LiCrO2 [74]. When this result is considered along with Raman and XPS analysis of these samples shown below, it can be concluded that the oxide scale
is composed largely of LiCrO$_2$ when I625 is exposed to molten LiCl-Li$_2$O solutions in the absence of Li.

**Figure 4.1:** XRD pattern collected from the I625 sample exposed to LiCl-1wt% Li$_2$O-0wt% Li at 650°C for 1000hr. Peaks indicative of the base material and LiCrO$_2$ were observed.

The presence of Li$^0$ in solution creates a very reducing environment, preventing the formation of the well-developed LiCrO$_2$ films observed on these samples in the absence of Li. Consequently, the diffraction patterns for all samples exposed to LiCl-Li$_2$O solutions containing Li displayed diffraction patterns indicative only of the base material, as can be observed in Figures 4.2 and 4.3. These figures show the diffraction patterns of I625 samples exposed to LiCl-1wt% Li$_2$O solutions containing 0, 0.3, 0.6, or 1wt% Li for 500hr (Figure 4.2) or 1000hr (Figure 4.3). This corresponds with the observation made using SEM.
of the highly porous metallic surfaces on I625 samples exposed to LiCl-Li$_2$O in the presence of Li [92].

Figure 4.2: XRD spectra of I625 samples exposed to LiCl-1wt% Li$_2$O containing 0, 0.3, 0.6, and 1wt% Li at 650°C for 500hr. In the absence of Li, both LiCrO$_2$ and the base material were observed; however, in the presence of Li, on the base material was present.
Figure 4.3: XRD spectra of I625 samples exposed to LiCl-1wt% Li$_2$O containing 0, 0.3, 0.6, and 1wt% Li at 650°C for 1000hr. In the absence of Li, both LiCrO$_2$ and the base material were observed; however, in the presence of Li, only the base material was present.

4.3.2: Raman Spectroscopy

Raman spectra, shown in Figure 4.4, also confirms the presence of LiCrO$_2$ in the absence of Li, with the Raman spectra of the four samples exposed to molten LiCl-Li$_2$O solutions in the absence of Li displaying prominent peaks of both the LiCrO$_2$ A$_{1g}$ and E$_g$ modes at 572cm$^{-1}$ and 445cm$^{-1}$, respectively [75]. An additional hump on the shoulder of the LiCrO$_2$ A$_{1g}$ peak is believed to be indicative of a spinel of the type NiFe$_x$Cr$_{2-x}$O$_4$ based on the work of Hosterman [76]. The exact composition of this compound is unknown, but is likely skewed towards Cr-rich compounds, due to the relatively low concentration of Fe in the I625 alloy. The I625 sample exposed to LiCl-1wt% Li$_2$O at 650°C also displayed
features at 845 cm$^{-1}$ and 340 cm$^{-1}$ that indicate the presence of Li$_2$CrO$_4$ based on the collection of Raman spectra of this compound in our laboratory. It is currently unknown why the other I625 samples exposed to similar conditions did not display the features of Li$_2$CrO$_4$.

Figure 4.4: Raman spectra of I625 samples exposed at 650°C to LiCl containing a) 1 wt% Li$_2$O for 500 hr, b) 1 wt% Li$_2$O for 1000 hr, c) 2 wt% Li$_2$O for 500 hr and d) 2 wt% Li$_2$O for 1000 hr. The A$_{1g}$ and E$_g$ peaks of LiCrO$_2$ and a hump indicative of the A$_{1g}$ peak of NiFe$_x$Cr$_{2-x}$O$_4$ were observed on all samples exposed to LiCl-Li$_2$O solutions in the absence of Li. Additionally, the I625 sample exposed to LiCl-1 wt% Li$_2$O for 1000 hr displayed peaks indicative of Li$_2$CrO$_4$.

The effect of Li on the Raman spectra of I625 exposed to LiCl-Li$_2$O-Li solutions can be observed in Figure 4.5, which shows the Raman spectra of I625 samples exposed to LiCl-1 wt% Li$_2$O solutions containing 0, 0.3, 0.6, and 1 wt% Li at 650°C for 500 hr. The well-defined Raman modes observed in Figure 4.4 are seen to be largely absent in the presence of Li. The broad features that roughly
align with the positions of the compounds observed in the absence of Li may indicate minute quantities of these compounds on the sample surface. XPS analysis presented below confirms the presence of small amounts of oxidized Cr, Mo, and Nb on the surface of the I625 samples exposed to LiCl-Li$_2$O in the presence of Li.

![Raman spectra](image)

**Figure 4.5**: Raman spectra obtained from the surfaces of I625 samples exposed to LiCl-1wt% Li$_2$O containing 0, 0.3, 0.6, or 1wt% Li at 650°C for 500hr. The clearly defined Raman modes present in Raman spectra of samples exposed to LiCl-Li$_2$O in the absence of Li are not observed on the surface of samples exposed to LiCl-Li$_2$O in the presence of Li.

### 4.3.3: XPS

The surface sensitivity and chemical state analysis provided by XPS allowed for the investigation of the corrosion products present on the surface of
the samples, even at the low thicknesses observed on the I625 samples exposed to molten LiCl-Li$_2$O solutions containing Li. Comparison of spectra taken prior to and following methanol rinsing showed no change in surface chemistry caused by the rinsing procedure (see supplemental information, Appendix A1), allowing for the chemical analysis presented below; however, the presence of a Ti-based deposit on some of the samples prevented accurate quantitative analysis of the surface composition. Figure 4.6 shows the XPS survey spectra recorded from the I625 samples exposed to LiCl-1wt% Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt% Li at 650°C for 1000hr. Survey spectra of the I625 samples exposed to varying Li$_2$O concentrations and exposure periods showed similar features and trends. In the case of the samples exposed to LiCl-Li$_2$O solutions in the absence of Li, the surface was primarily composed of Cr, O, and Li, further confirming the presence of LiCrO$_2$ on these samples. For the I625 sample exposed to LiCl-1wt% Li$_2$O for 1000hr, Ni was also detected via XPS; however, Ni was not detected on the surface of the other samples exposed to LiCl-Li$_2$O solutions in the absence of Li, further indicating that this sample had somewhat different surface chemistry when compared to the other samples exposed to similar conditions.

For I625 samples exposed to LiCl-Li$_2$O in the presence of Li, Ni was the primary element present, while the Cr level was depleted and most of the primary alloying elements were detected in trace amounts. Our previous work has shown these compounds were also detected on the surface of numerous samples that do not contain Ti as an alloying element, notably SS316L (14,15) and thus must be the result of electroless deposition of Ti oxide and nitride compounds.
from Ti impurities present in the Li$_2$O used in these studies [26]. This will not be discussed further in the present work.

The chemistry of Cr, being the primary alloying element in I625 as well as being responsible for corrosion inhibition through the formation of stable oxide films, is important to understand thoroughly. XPS narrow scans of the Cr 2p$_{3/2}$ spectra obtained from the surface of the I625 samples exposed to LiCl containing 1 or 2wt% Li$_2$O and 0, 0.3, 0.6, or 1wt% Li for 500hr are shown in Figure 4.7, while the Cr 2p$_{3/2}$ spectra of I625 samples exposed to similar conditions for 1000hr are shown in Figure 4.8. Peak fitting was performed using previously
published fitting parameters, with charge correction performed to the adventitious C 1s peak at 284.8eV [77]. In the absence of Li, the Cr spectra consistently showed the presence of Cr\(^{3+}\), which is necessary for the formation of LiCrO\(_2\), confirming the observations made via XRD and Raman spectroscopy that show this compound is present on the surface of these samples. Additionally, Cr\(^{6+}\) is also present to a minor degree on these samples, which supports the observation via Raman of the presence of Li\(_2\)CrO\(_4\) in small amounts in the oxide film. As both Li\(_2\)O concentration and exposure period increase, the proportion of Cr\(^{6+}\) to Cr\(^{3+}\) increases, indicating that the formation of LiCrO\(_2\) and Li\(_2\)CrO\(_4\) are governed by the activity of the O\(^{2-}\) ion in solution, and that LiCrO\(_2\) may be converted to Li\(_2\)CrO\(_4\) over time. In the presence of Li\(^0\), neither of these compounds are stable in bulk form, as indicated by XRD, Raman, and SEM-EDS observations; however, a nominal amount of Cr\(^{3+}\) and to a lesser extent Cr\(^{6+}\) were observed via XPS alongside metallic Cr\(^0\), indicating that O\(^{2-}\) in solution continues to play a role in the corrosion process at concentrations of Li in solution of at least 1wt%. Cr\(^{6+}\) was not observed on all samples when Li metal was present in solution. While the formation of Cr\(^{6+}\) is unlikely from a thermodynamic perspective in pure LiCl-Li\(_2\)O, it was consistently observed in this study, as shown both via XPS and Raman. The formation of Li\(_2\)CrO\(_4\) was also hypothesized to be the dissolution mechanism of the Cr-based oxide film by researchers at KAERI [63]. The solubility of CrO\(_4^{2-}\) in LiCl-Li\(_2\)O may lower the activation energy necessary to facilitate the formation of the Cr\(^{6+}\) oxidation state. Due to the difficulty associated with completely removing moisture from highly
hygroscopic LiCl, the source of oxygen for the formation of the oxide layers observed in the absence of metallic Li was likely from impurity moisture remaining in the molten salt. In the case of the samples exposed to melts containing metallic Li, the excess Li would react with any moisture present in the salt to form Li$_2$O and H$_2$ gas, effectively eliminating this source of oxygen. The mechanism for the formation of the trace quantities of oxides present on the surface of the samples exposed to LiCl-Li$_2$O melts containing Li is currently unknown, and will require further investigation.
Figure 4.7: Cr 2p$_{3/2}$ XPS spectra of I625 samples exposed for 500hr to LiCl containing a) 1% Li$_2$O 0% Li, b) 1% Li$_2$O 0.3% Li, c) 1% Li$_2$O 0.6% Li, d) 1% Li$_2$O 1% Li, e) 2% Li$_2$O 0% Li, f) 2% Li$_2$O 0.3% Li, g) 2% Li$_2$O 0.6% Li, and h) 2% Li$_2$O 1% Li.

Table 4.1: Peak fitting parameters for Cr 2p$_{3/2}$ spectra shown in Figures 4.7 and 4.8. Charge correction to the adventitious C 1s line at 284.6eV was performed.

<table>
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Figure 4.8: Cr $2p_{3/2}$ XPS spectra of l625 samples exposed for 1000hr to LiCl containing a) 1% Li$_2$O 0% Li, b) 1% Li$_2$O 0.3% Li, c) 1% Li$_2$O 0.6% Li, d) 1% Li$_2$O 1% Li, e) 2% Li$_2$O 0% Li, f) 2% Li$_2$O 0.3% Li, g) 2% Li$_2$O 0.6% Li, and h) 2% Li$_2$O 1% Li.

While Ni was not observed on the surface of most of the samples exposed to LiCl-Li$_2$O in the absence of Li, it was observed on the l625 sample exposed to LiCl-1wt% Li$_2$O for 1000hr, as well as on all samples exposed to LiCl-Li$_2$O-Li
solutions. As shown in Figure 4.9, in the absence of Li, Ni was observed in a mixed valence state, showing both metallic as well as oxidized character. The presence of oxidized Ni on the surface of this sample supports the observations made via Raman of the presence of a spinel of the form NiFe$_x$Cr$_{2-x}$O$_4$ in the oxide film of these samples. Fitting of these spectra was not performed due to the known difficulties associated with peak fitting Ni 2p XPS spectra without precise parameters obtained from standards with identical composition [78]. Peaks shapes and positions consistent with metallic Ni were observed on all samples exposed to LiCl-Li$_2$O in the presence of Li. No charge correction was necessary for the Ni spectra.

Figure 4.9: Ni 2p XPS narrow scans obtained from the I625 samples exposed to LiCl-1wt% Li$_2$O containing a) 0wt% Li, b) 0.3wt% Li, c) 0.6wt% Li, and d) 1wt% Li at 650°C for 1000hr. In the absence of Li, Ni is observed in a mixed metallic and oxidized state, indicating the presence of small amounts of Ni compounds in the oxide layer. In the presence of Li, Ni was only observed in the pure metallic state. No charge correction was performed necessary for Ni, indicating that it was consistently in electrical contact with the base material.
While Mo was not observed in detectable quantities via XPS of the surfaces of I625 samples exposed to LiCl-Li₂O solutions in the absence of Li due to the thick LiCrO₂ surface film and the relatively low concentration of Mo in the base alloy, it was observed on the surface of the majority of the samples exposed to LiCl-Li₂O in the presence of Li. The XPS narrow scans of the Mo 3d region are shown in Figure 4.10. At 0.3wt% Li, Mo behaved similarly to Cr in that it was present in a mixed metallic and oxidized state [79, 80]. Due to the noise, presence of multiple overlapping peaks on these spectra, and the known tendency for photoreduction of Mo, peak fitting was not performed, although the apparent positions of the primary peaks are demarked by vertical lines on the charts in Figure 4.10. The I625 samples exposed to LiCl-Li₂O in the presence of 0.6 and 1wt% Li showed only the characteristic asymmetric peaks of metallic Mo. This transition from mixed metallic and oxidized character at low Li concentrations to a purely metallic state at higher Li concentrations indicates that the activity of Li in solution is not unity until beyond the solubility limit.
Figure 4.10: Mo 3d XPS narrow scans obtained from the surface of I625 samples exposed for 1000hr to molten LiCl containing a) 1wt% Li$_2$O and 0.3wt% Li, b) 1wt% Li$_2$O and 0.6wt% Li, c) 1wt% Li$_2$O and 1wt% Li, d) 2wt% Li$_2$O and 0.3wt% Li, e) 2wt% Li$_2$O and 0.6wt% Li, and f) 2wt% Li$_2$O and 1wt% Li. At concentrations of 0.3wt% Li Mo shows a mixed oxide state.

While both Cr and Mo were observed to be present in a mixed state containing oxidized and reduced species in the presence of Li, Nb was only observed in oxidized states [94]. The narrow scans of the Nb 3d region obtained from the surface of I625 samples exposed to molten LiCl solutions containing 1 or 2wt% Li$_2$O and 0.3, 0.6, or 1wt% Li for 1000hr are shown in Figure 4.11, with the exception of the I625 sample exposed to LiCl-1wt% Li$_2$O-1wt% Li for 1000hr, as Nb was not detected on this sample. The presence of only oxidized Nb even
in the presence of high Li concentrations is counter intuitive, as work by Jeong, et al. showed that the reduction of Nb₂O₅ to metallic Nb was able to be accomplished in LiCl-Li₂O, primarily through the indirect reaction with Li which was electrolytically generated at the cathode, similar to the reduction of UO₂ [95].

Figure 4.11: Nb 3d XPS narrow scans obtained from the surface of I625 samples exposed for 1000hr to molten LiCl containing a) 1wt% Li₂O and 0.3wt% Li, b) 1wt% Li₂O and 0.6wt% Li, c) 2wt% Li₂O and 0.3wt% Li, d) 2wt% Li₂O and 0.6wt% Li, and e) 2wt% Li₂O and 1wt% Li. Nb was not observed on the I625 sample exposed to LiCl-1wt% Li₂O-1wt% Li for 1000hr. Nb was observed to be present as Nb³⁺ and Nb⁵⁺, however, metallic Nb was not observed.

Minor alloying elements, Fe and Al, were not analyzed in this study. The oxide film on the samples exposed to LiCl-Li₂O in the absence of Li did not have detectable quantities of Fe on its surface, however Fe was detected in extremely
small quantities on some of the samples exposed to LiCl-Li$_2$O solutions containing Li. Auger electrons from Ni using the Al Kα source interfered with these peaks, and switching the X-ray source to Mg Kα X-rays did not provide adequate signal intensity to reliably peak fit the Fe 2p spectra. Detection was not consistent from sample to sample. Consequently, interpretation of the Fe 2p spectra was not attempted. Al was not detected on the surface of any sample via XPS, regardless of X-ray source.

4.4: Conclusions

Investigation of the surface chemistry of 1625 samples exposed to molten LiCl-Li$_2$O-Li solutions at 650°C for 500 and 1000hr was performed via XRD, Raman spectroscopy, and XPS. In the absence of solvated Li$^0$, the surface of 1625 forms a stable LiCrO$_2$ based surface film with minor inclusions of Li$_2$CrO$_4$ and NiFe$_x$Cr$_{2-x}$O$_4$ which acts to limit corrosion of the base alloy. Corrosion of the base alloy in molten LiCl-Li$_2$O is thus expected to be dictated by the O$^{2-}$ activity and the presence of impurities, similar to the corrosion processes typical in other molten salt systems [33]. When Li is dissolved in the molten LiCl-Li$_2$O system, the formation of a bulk oxide film is not possible due to the highly reducing conditions caused by metallic Li; however, XPS analysis showed that the active alloying elements Cr, Mo, and Nb were all present to varying degrees in oxidized states on the sample surfaces, even up to high concentrations of Li in solution. This indicates that there is a synergistic effect between the oxidation caused by the O$^{2-}$ ions and the reducing nature of solvated Li$^0$ that allows for the effective
dissolution of Cr, Mo, and Nb, although further investigation would be necessary to confirm this hypothesis. Our earlier work showed that the alloy was depleted of these elements at the sample surface and in the regions displaying the highly porous microstructure seen via SEM-EDS. Consequently, it is likely that the diffusion of Cr, Mo, and Nb through the alloy microstructure and their subsequent dissolution into the molten LiCl-Li₂O-Li system is responsible for the porosity observed in that study.
Chapter 5 : Conclusions and Future Work

5.1: Conclusions

Both SS316L and I625 exhibited similar corrosion phenomena, with a protective LiCrO$_2$ based oxide film forming on the surface upon exposure to LiCl-Li$_2$O in the absence of dissolved Li. Minor components of Li$_2$CrO$_4$ and NiFe$_x$Cr$_{2-x}$O$_4$ were also observed on these samples, with I625 forming the most fully developed oxide layer with a well-defined crystalline structure. These oxide films were successful in limiting corrosion to an acceptable level, with SS316L showing a corrosion rate of approximately 0.2mm/year, while the corrosion rate was approximately 0.1mm/year for I625. A multilayered oxide structure was observed on I625, with the outermost layer being composed primarily of LiCrO$_2$ and the inner layers incorporating progressively more Ni and Fe oxides.

While both SS316L and I625 performed acceptably upon exposure to LiCl-Li$_2$O containing no metallic Li, the addition of Li metal to the solution resulted in a very reducing environment, and protective oxide layers were not found to form on the sample surface. The removal of the oxide layer resulted in the exposure of the base material directly to the highly corrosive LiCl-Li$_2$O-Li solution, and severely accelerated corrosion. For both SS316L and I625, this resulted in the selective dissolution of certain alloying elements. Particularly, Cr, Mo, Nb, and Mn were all depleted from the sample surfaces, depending on alloy composition. For SS316L, this resulted in intergranular corrosion that penetrated the sample at a rate of approximately 2-3mm/year. Evidence of salt intrusion into the base
material was also observed on SS316L, as were Cr carbides immediately preceding the intruded salt. This indicates that, similar to corrosion by pure metallic Li, intergranular attack of metallic carbides is the primary corrosion mechanism. In 1625, the selective dissolution of Cr, Mo, and Nb lead to the formation of a highly porous microstructure, similar in nature to a Ni foam. Evidence of oxidized Cr, Mo, Nb, and Mn was observed via XPS analysis, depending on the alloy composition. Both Ni and Fe were always observed in the metallic state on samples exposed to LiCl-Li$_2$O-Li solutions. This indicates that there may be a cyclical oxidation-reduction pathway that leads to the selective dissolution of these alloying elements into the molten salt.

These results indicate that the corrosion mechanisms responsible for material degradation in the LiCl-Li$_2$O-Li system are a combination of the corrosion mechanisms that have been observed by other researchers during corrosion studies of alloys in molten salts and liquid metals. The combined effects of molten salt and liquid metal corrosion result in a more severe attack of the base material than would be observed in the isolated cases of pure molten salt or liquid metal corrosion.

These findings have direct impact on the operation and design of engineering scale and production scale UNF oxide reduction systems utilizing LiCl-Li$_2$O based electrolytes. The obvious solution to the problem of accelerated corrosion is to simply increase the wall thickness of the vessel in order to account for the degradation over time. However, a more elegant approach would be to
limit the activity of Li in the melt. This goal could be accomplished by a number of means, however, the most elegant and reliable solution would likely be the simple addition of another cathode basket of UNF that has yet to be reduced. The presence of UO$_2$ in direct contact with the melt would prevent the activity of Li from becoming high enough to cause severe degradation of the vessel, and would also increase the overall current efficiency of the system.

**5.2: Future Work**

Although these studies represent a significant advancement in the understanding of corrosion in molten LiCl-Li$_2$O-Li, numerous avenues for remain uncharted that could help further understand the effect metallic Li has on materials exposed to the conditions present during oxide reduction of UNF. Of these pathways forward for future work, *in-situ* spectroscopy of the surface of corrosion samples would shed light on the nature of the corrosion products at temperature. Advanced fiber coupled Raman probes, high temperature inert atmosphere XRD, and other x-ray spectroscopies could allow for the analysis of corrosion products as they form, rather than the post exposure studies presented in this work. It is possible that chemical or morphological changes occur during cooling or the removal of the residual salt layer, so these *in-situ* studies would be invaluable for understanding the mechanisms responsible for material degradation in LiCl-Li$_2$O-Li.

The difficulty associated with detecting Li was a major limitation in this investigation. Direct chemical analysis of Li is difficult due to its low atomic
number, which results in extremely low energy x-rays and photoelectrons of 52 eV. Typical X-ray detectors for chemical analysis utilize Be windows to isolate the detector from the sample chamber, resulting in the absorption of the characteristic X-rays of Li. Numerous elements exhibit outer shell X-ray and photoelectron emission in this region, further complicating analysis. Secondary ion mass spectroscopy (SIMS) and electron energy loss spectroscopy (EELS) allow for the detection of Li, as do some advanced EDS and wavelength dispersive spectroscopy (WDS) instruments, and the use of these instruments would provide extremely valuable information on the chemical structure and spatial distribution of Li and its compounds on these samples. Particularly with the extreme level of corrosion observed in the presence of metallic Li, it would be useful to be able to determine the distribution of Li through the sample cross sections.

Computational modelling has led to many recent advancements in other fields of materials science but has been slow to be adopted in the field of corrosion research, primarily due to the inherently large multiphase systems that must be simulated for accurate modeling of corrosion environments. However, the continuous increase in the power of high-performance computers has increased the accuracy and number of atoms able to be simulated in atomistic modeling. Application of multiscale computational modeling methods to the corrosion of alloys in molten salts could help to quickly identify potential materials capable of withstanding the demands of these systems. Models verified by experimental results would lead to a deeper understanding of the reaction
pathways, thermodynamics, and kinetics of the corrosion mechanisms in these complicated systems.

Accelerated corrosion testing via electrochemical means is well established as a viable method of estimating corrosion rates in aqueous systems and has been applied to other molten salt systems. The presence of Li and the associated rise in electrical conductivity of the electrolyte complicates the analysis of electrochemical methods for the LiCl-Li$_2$O-Li system, and the lack of a universally accepted reference electrode for this system introduces further complications. The development of reference electrodes was attempted during these studies and is detailed in the appendices, but this work remains unfinished. Additionally, it would likely be necessary to re-derive the Tafel equations for the LiCl-Li$_2$O-Li system to account for the simultaneous action of ionic and electronic conduction in order to fully deconvolute their independent effects on the current-potential curves.

In operation, the oxide reduction electrolyte chemistry is much more complicated than the ternary LiCl-Li$_2$O-Li system studied in this work. High variations in cover gas atmosphere may occur due to both reduction operations which generate O$_2$ gas at the anode and the difficulty of maintaining the atmosphere of a working hot cell. The result of this is a vessel intermittently exposed to relatively high levels of O$_2$ and H$_2$O while at high temperatures. Additionally, salt soluble fission products such as I, Ba, Cs, Te, etc. will all be dissolved into the electrolyte and accumulate as used fuel is processed [8, 50].
While this is a benefit for the overall pyroprocessing flow sheet and simplifies later processing operations, the addition of these elements to the electrolyte complicates the solution chemistry during oxide reduction. Particularly, Te was shown to be of great concern to the corrosion of materials during the molten salt reactor experiment, where it caused intergranular corrosion of various Ni based alloys even at relatively low concentrations [29]. Effect of fission products on the corrosion of structural materials in an operating OR vessel are of great interest, and should be investigated further.

Experimentally studying each of these parameters independently would help to shed light on the mechanisms involved and could keep many graduate students busy; however, it would also be beneficial to study materials exposed to the conditions present concurrently with engineering scale testing of oxide reduction operations. These studies should be long term in nature, with the goal of predicting the expected service life of components used during oxide reduction operations. An economic analysis of the overall oxide reduction operation, with expected service intervals, cost of disposal and replacement of vessels and other components, and operations should also be conducted.
References


[107] R. N. Singh, "Compatibility of Ceramics with Liquid Na and Li," *Journal of the American Ceramic Society*, vol. 59, no. 3-4, pp. 1
Appendices
Appendix 1: Supplemental Information for Chapter 4

Figure A1-1: GI-XRD patterns obtained from the 625 samples exposed to LiCl-2wt%Li2O containing 0, 0.3, 0.6, and 1wt% Li for 500hr prior to removal of the residual salt layer via methanol rinsing. Phases identified consist of LiCl, the base material and small amounts of LiCrO2. The residual salt layer significantly obscures the sample surface when compared to the methanol rinsed data. No peaks characteristic of hydrated LiCl were observed, indicating the samples were not contaminated with moisture.
Figure A1-2: Raman spectra obtained from the I625 samples exposed to LiCl-2wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt% Li for 500hr prior to removal of the residual salt layer via methanol rinsing. LiCrO$_2$ was identified on the surface of the I625 sample exposed to LiCl-2wt%Li$_2$O in the absence of Li metal. The spectra of the samples exposed to LiCl-Li$_2$O containing Li are indicative of the spectral artifacts caused by the fiber optic probe. These are present in the spectra of the sample exposed to LiCl-Li$_2$O in the absence of Li, but are overpowered by the LiCrO$_2$ peak. Consequently, the spectra of the I625 samples exposed to LiCl-Li$_2$O-Li can be interpreted as being a bare metallic surface covered by the residual layer of salt.
Figure A1-3: XPS Cr 2p spectra obtained from the I625 sample exposed to LiCl-1wt%Li₂O in the absence of Li at 650°C for 500 hr prior to and following methanol rinsing. Identical collection parameters were used, and both spectra were charge corrected to the adventitious C 1s peak at 284.8eV. It can be observed that no significant changes to the Cr 2p spectra occurred as a result of the methanol rinsing procedure, although a significant reduction in noise was realized as a result of the removal of the residual salt layer. The residual salt layer completely obscured the sample surface from XPS analysis on some of the other samples in this study, necessitating the methanol rinsing procedure for their analysis.
Figure A1-4: SEM images taken at low and high magnifications of the I625 sample exposed to LiCl-1wt%Li₂O-0wt%Li at 650°C for 1000hr taken prior to and following the methanol rinsing procedure to remove the residual salt layer. The top left image shows the high coverage of the sample surface by the residual salt layer, which prevented accurate surface analysis by XPS, XRD, and Raman. This sample had several locations where the oxide layer was possible to view through gaps in the residual salt layer, allowing for direct comparison of the pre and post-methanol rinsing surface morphology. Comparison of the two images taken at high magnification shows that the morphology of the oxide layer remained unchanged following the methanol rinsing procedure. Please refer to our previous study for further morphological and cross sectional analysis of these samples [92].
Figure A1-5: SEM images taken at low and high magnifications of the I625 sample exposed to LiCl-1wt%Li2O-1wt%Li at 650°C for 1000hr taken prior to and following the methanol rinsing procedure to remove the residual salt layer. For this sample, the consistent surface morphology prior to and following the methanol rinsing procedure is readily apparent, as the salt was largely occluded within the pores of the sponge-like structure of the sample. No formation of an oxide layer or change in morphology were observed to occur as a result of the methanol rinsing procedure, although the residual salt was successfully removed from within the pores. Please refer to our previous study for further morphological and cross sectional analysis of these samples [92].
Figure A1-6: GI-XRD patterns collected from Inconel 625 samples exposed to LiCl-2wt%Li₂O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr prior to the removal of the residual salt layer by rinsing with methanol.
Figure A1-7: GI-XRD patterns collected from 1625 samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.6, and 1wt%Li at 650°C for 1000hr following the removal of the residual salt layer by rinsing with methanol.

Figure A1-8: GI-XRD patterns collected from 1625 samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr following the removal of the residual salt layer by rinsing with methanol.
Figure A1-9: Raman spectra collected from I625 samples exposed to LiCl-2wt%Li₂O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr prior to the removal of the residual salt layer by rinsing with methanol.
Figure A1-10: Raman spectra collected from I625 samples exposed to LiCl-2\%Li$_2$O containing 0, 0.3, 0.6, and 1\%Li at 650°C for 1000hr prior to the removal of the residual salt layer by rinsing with methanol.

Figure A1-11: Raman spectra collected from I625 samples exposed to LiCl-1\%Li$_2$O containing 0, 0.3, 0.6, and 1\%Li at 650°C for 500hr following the removal of the residual salt layer by rinsing with methanol.
Figure A1-12: Raman spectra collected from I625 samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr following the removal of the residual salt layer by rinsing with methanol.
Figure A1-13: Raman spectra collected from I625 samples exposed to LiCl-2wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr following the removal of the residual salt layer by rinsing with methanol.

Figure A1-14: Raman spectra collected from I625 samples exposed to LiCl-2wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr following the removal of the residual salt layer by rinsing with methanol.
Figure A1-15: XPS spectra collected from I625 samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr following the removal of the residual salt layer by rinsing with methanol.

Figure A1-16: XPS spectra collected from I625 samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr following the removal of the residual salt layer by rinsing with methanol.
Appendix 2  Reference Electrode Development for Molten LiCl-Li₂O-Li

A2.1: Background

Due to the uniquely challenging chemical conditions present during the oxide reduction of UNF, a reference electrode that remains stable and usable over an extended period of time has not yet been developed. The most commonly used electrode is the Ni|NiO reference, encased in an MgO sheath with a porous MgO frit at the bottom. Neither MgO nor NiO are stable under Li saturated conditions that are reached upon completion of the reduction of UO₂, leading to the electrode’s degradation. Consequently, studies were conducted to develop an improved reference electrode design for this system. No conclusive results were obtained, but progress was made on the understanding of the challenges that must be overcome in pursuit of a stable, repeatable reference design.

Theoretically, the design of a reference electrode can be broken down into two main parts: the first being the reference couple, M|Mⁿ⁺, and the second being the ion conducting membrane to separate the reference electrode cell from the bulk electrolyte [96, 97]. The present work was concerned with both of these parts, and multiple options exist for both reference couple and ion conducting membrane or electrode sheath for the system in question. This Appendix is concerned with the choice of the reference couple, while Appendix 2 is concerned with the choice of the electrode sheath.
While common reference electrodes for use in aqueous systems at room temperature or slightly elevated temperatures (less than 100°C) are not suitable for use in a high temperature molten salt electrolyte, the theory of operation of a reference electrode in molten salt electrolytes is largely unchanged from those developed for aqueous systems [97]. The choice of a reference couple is guided by the need for a reversible and stable chemical equilibrium to exist between the oxidized and reduced species present in the system [97]. Any material when placed in a solution capable of ionic dissolution, whether it be aqueous or molten salt based, will attempt to reach thermodynamic equilibrium with that solution and the other materials that are exposed to the system by undergoing redox reactions to equalize the chemical activity of each species across the phases present, the general form of which is given in Equation A1.1 and A1.2, below.

**Oxidation:**  \[ M \leftrightarrow M^{n+} + ne^- \] (A1.1)

**Reduction:**  \[ A + ye^- \leftrightarrow A^{y-} \] (A1.2)

As these reactions require an exchange of electrons, it can be inferred that an electric potential will be generated based on the materials in the system and the design of the cell, whether intentional or not. This manifests in a number of ways, depending on the solution and materials in question, and is the basis for the field of electrochemistry [96]. For the design of a reference electrode, it is necessary that the electrode be in a stable thermodynamic equilibrium with the solution that is not easily perturbed by changes in solution chemistry or is sufficiently isolated from the bulk solution to prevent contamination. At
equilibrium, the Nernst equation, given in Equation A1.3 below, provides a convenient means of calculating the potential of a given electrochemical system [96].

\[ E = E^0 - \frac{RT}{nF} \ln \left( \frac{a_{\text{red}}}{a_{\text{ox}}} \right) \]  \hspace{1cm} (A1.3)

Here, \( E^0 \) is the standard potential for a given redox couple compared to a standard electrode (the standard hydrogen electrode in the case of aqueous systems), \( R \) is the ideal gas constant, \( T \) is the temperature in Kelvin, \( n \) is the number of electrons transferred in the half-cell reaction, \( F \) is Faraday’s constant, while \( a_{\text{red}} \) and \( a_{\text{ox}} \) are the activities of the reduced and oxidized species, respectively. Consequently, if the activity of both the oxidized and reduced species present in the system are thermodynamically constrained through the choice of the proper electrochemical couple, the electrode will provide a stable potential that will only vary linearly as a function of temperature.

Constraining the chemical activity of a given species in a system can be achieved in several different ways. First, the activity of a solid metal is defined as being unity as long as it is in its standard state and not actively corroding [96]. It is important to note here that the processing history of the metal, such as cold work, surface preparation, etc. can affect the thermodynamic properties of the metal surface through dislocations, defects, and other surface phenomena, and hence its chemical activity in solution can depart from unity depending on the surface chemistry. Consequently, it is important to ensure that the metal is in its lowest energy state through annealing and/or various means to deposit a pure
metal on a bulk metal substrate. Therefore, most common reference electrode
designs rely on an inert metal whose surface has been deposited in a defined
and repeatable manner to function as both the reduced species as well as the
electrical contact for the electrode [96]. The activity of the oxidized species can
then be constrained by saturating the electrolyte with the corresponding cation.
For example, in the Ag│Ag\(^{+}\) electrode commonly used in aqueous systems, a Ag
rod coated in AgCl is immersed in an aqueous solution saturated with AgCl. As
AgCl is only sparingly soluble in water, very little AgCl is needed to saturate the
solution with Ag\(^{+}\). However, saturation of the solution with the corresponding
anion is also required, and therefore the solution is typically saturated with KCl to
ensure that the activity of Cl\(^{-}\) in the electrode is also unity, although other KCl
concentrations can be used as long as the change in electrode potential caused
by the change in Cl\(^{-}\) activity and AgCl solubility is taken into account [96, 97]. The
addition of KCl also serves to increase the conductivity of the electrode and
balance the charge transfer between positive and negative ions, minimizing the
junction potential of the electrode [96]. A reference electrode functioning in this
manner is known as a reference electrode of the second kind, and is the basis for
all of the electrode designs that will be studied in this work. It is important to note
that if the electrode is contaminated, or poisoned, by another anion or cation, the
activities of these extraneous species will affect the measured potential of the
electrode, leading to drift from the theoretical potential. For example, the
aqueous Ag│AgCl reference electrode is rapidly degraded by the presence of
minute quantities of Br⁻ ions and is not easily regenerated after poisoning of the electrode has occurred [96].

Alternatively, the equilibrium between a gas and liquid phase can also be used as a reference couple, as is the case with the standard hydrogen electrode [96, 97]. An electrode of this type is known as a reference electrode of the first kind. Detailed description of the theory behind hydrogen electrode operation is beyond the scope of the current discussion, but it is mentioned here for completeness. It is possible to build a reference electrode of the first kind for a molten salt electrolyte, and in the case of a LiCl based electrolyte the gas would necessarily be Cl₂ [97]. Working with using gaseous chlorine at 650°C raises obvious safety concerns, however, a small number of researchers have utilized chlorine electrodes in the past for fundamental electrochemical studies in other systems [97]. Numerous difficulties with repeatability were encountered as a result of the sensitivity of the electrode to surface chemistry and the highly corrosive nature of high temperature Cl₂ gas. As the goal of the present work is to devise a stable, repeatable, and easily fabricated design to allow for its implementation in experimental work and engineering scale facilities, the danger, difficulties, and problems with reproducibility associated with a gaseous Cl₂ electrode eliminate this design from further investigation.

If the reference couple is isolated from the bulk electrolyte, the thermodynamic considerations do not have to take the presence of metallic Li in the system into account, and it is possible to use a reference couple that would
be driven from equilibrium if in direct contact with metallic Li. This is extremely attractive theoretically, as the simultaneous presence of both Li and Li$_2$O leads to a paradoxical thermodynamic situation where no redox couple other than Li$\mid$Li$^+$ can exist in true equilibrium with the melt, as any species with a more negative Gibbs free energy of formation than Li$_2$O would cause its reduction to metallic Li, while a species with a more positive Gibbs free energy of formation than Li$_2$O would itself be reduced by the metallic Li in the system. This is summarized by equations A1.4 and A1.5 below.

If $\Delta G_{M\mid M^+} > \Delta G_{Li\mid Li^+}$ then $M + Li_2O \rightarrow MO + 2Li$

Equation A1.4

If $\Delta G_{M\mid M^+} < \Delta G_{Li\mid Li^+}$ then $MO + 2Li \rightarrow M + Li_2O$

Equation A1.5

Depending on the valence state of the species, $M^{n+}$, the stoichiometry of the reactions would change, but a general case of a divalent cation is given here for simplicity. The direct contact of the reference couple with the bulk electrolyte also causes other issues with potential stability in response to changing electrolyte conditions, and possible contamination of the electrolyte with constituent species of the reference electrode. This is especially important for the present work, as a number of salt soluble fission products accumulate in the electroreduction step and contaminate the electrolyte, including Cs, Ba, Sr, Rb, Te, I, and Eu [50, 98]. The presence of these species in the electrolyte will affect the equilibrium
potential of the reference electrode if they were allowed to contact the reference couple directly.

A commonly used reference electrode design, particularly in Japan and Korea, is a \( \text{Li} \mid \text{Li}^+ \) based electrode consisting of a 35at\%Li-Bi alloy contained in a closed end MgO tube with a small 0.7mm diameter hole drilled in the side slightly above the level of the molten Li-Bi alloy [99]. Similar electrodes utilizing Pb in place of Bi function essentially identically. By examining the Li-Bi phase diagram in Figure A2.1, below [100], it can be observed that the 35at\%Li-Bi alloy is a homogenous liquid at 650°C.

![Figure A2.1: Phase diagram for the Li-Bi system [100].](image)
Consequently, the activity of Li in Bi at this composition is not stable according to the Gibbs phase rule, meaning that the potential of the electrode will fluctuate as the activity of Li in the salt phase varies, as this electrode design is in direct contact with the bulk electrolyte [101]. The authors of the paper in which this reference electrode is described note these concerns but state that the 35at%Li-Bi electrode provided adequate stability over a week of experimentation, although no direct evidence is given to support this claim.

In the work of Foster, et al., the potential variance of a similar 5at%Li-Bi electrode due to transport of Li through a porous BeO crucible was unacceptable for precise thermodynamic measurements in a LiCl-LiF electrolyte, and they devised an improved Li-Bi reference electrode by increasing the Li content to 60at%Li-Bi [101]. Re-examination of the Li-Bi phase diagram shows that at this composition, the alloy exists in an equilibrium between two phases: a solid intermetallic compound, Li$_3$Bi, and a liquid solution of Li$_3$Bi in Bi. Due to the presence of these two phases, the activity of Li is held constant over a fairly broad range of compositions, allowing for a stable potential to be achieved despite transfer of Li into or out of the electrode. Liu and Poignet utilized a similar 68at%Li-Bi reference electrode design in their work, substituting a thin walled BN crucible for containment, and found the characteristics of this electrode to be sufficient for the determination of Li activity in LiCl over a comprehensive range of Li concentrations and temperatures [21]. Despite the attractive characteristics of the Li$_3$Bi-Bi reference electrode, little mention of it has been made since Liu and Poignet’s work in the early 1990’s, and no comprehensive evaluation of its
performance has been published in the open literature. For this reason, one of the reference electrode designs studied for this work is based on the 60at\%Li-Bi reference electrode designed by Foster.

**A2.2: Current progress on the Li-Bi reference electrode**

The lack of use of the intermetallic region of the Li-Bi system as a reference electrode may be in large part due to the difficulty associated with its fabrication. Neither Foster nor Liu mention the method with which they fabricated their reference electrodes. Initial attempts at fabricating a Li$_3$Bi-Bi reference electrode for this study were based on direct reaction of Li and Bi in their molten states. The intermetallic compound Li$_3$Bi has an enthalpy of formation of -251.3 kJ/mol at room temperature, which McDeavitt notes is sufficient to cause a 2000°C temperature rise under adiabatic conditions, and the reaction proceeds rapidly upon melting of Li if the two components are mixed directly [102]. Additionally, Li$_3$Bi has a melting point of ~1145°C and a high vapor pressure at this temperature, which leads to significant difficulties associated with its casting. Work with Li$_3$Bi thus far has confirmed the difficulty of controlling the reaction and forming a heterogeneous product. All attempts to form the compound inside the desired containment tube for the reference electrode have resulted in the tube cracking due to the large temperature gradient upon reaction between Li and Bi, and melting the compound upon formation has not been attempted in our laboratory due to the temperature limits of the furnaces in place in our gloveboxes and the sensitivity of the compound to moisture. The most successful
experiments on this work to date have utilized a two piece graphite mold in which a charge of Li was first melted around a Ta rod used for electrical contact, and then the correct amount of Bi was subsequently added incrementally, after which the assembly was annealed at 850°C for 2 hours and allowed to cool. After removing the as-formed electrode, it was obvious that a reaction with the graphite had occurred, likely the formation of Li$_2$C$_2$ [103], and that the Li-Bi slug was heterogeneous, with a high degree of porosity. Further difficulties arise from the high vapor pressures of both Li and Bi at the elevated temperatures present during the reaction which leads to the evaporation of both components and consequent difficulties with producing parts with exact compositions. This is exasperated by the disparity in the atomic mass of Li and Bi of 6.94 and 208.98, respectively, which makes small errors in weight fraction translate to large errors in atomic fraction.

To overcome these difficulties, future work on this electrode will focus on the electrochemical deposition of Li into molten Bi to form the desired 66at%Li-Bi reference in a controlled manner and in the proper geometry. Precise control of the stoichiometry is possible by stopping deposition upon transfer of the desired amount of charge, and the reaction rate is easily controlled by limiting the current and/or controlling the potential. This design would benefit from the stability of the Li$\mid$Li$^+$ couple in the LiCl-Li$_2$O-Li system, be easily fabricable, and be simple to regenerate in-situ if necessary.
A2.3: The Mg|Mg$^{2+}$ electrode

In addition to the Li-Bi reference electrode described above, reference electrodes based on the Mg|Mg$^{2+}$ couple were also studied. MgO is commonly used to fabricate parts such as crucibles, reference electrode containment vessels, and anode shrouds for use in experiments on the electroreduction of UO$_2$ [9, 99]. MgO has been shown to slowly degrade when in contact with LiCl-Li$_2$O-Li solutions; however, the presence of Mg$^{2+}$ in small quantities in the electrolyte presents an opportunity to utilize the Mg|Mg$^{2+}$ couple as a reference electrode. Dr. Willit of ANL suggested a design of an electrode to take advantage of this. The proposed electrode was to be composed of a MgO tube to isolate the electrode from the bulk solution and filled with a LiCl-1wt%Li$_2$O electrolyte to prevent the formation of a concentration cell, while the electrode itself will consisted of an intermetallic Mg-Ni rod. The purpose of using a Mg-Ni intermetallic rather than pure Mg is to lower its chemical activity, as pure Mg is highly reducing and melts at 650°C and would therefore cause significant problems. The Mg-Ni phase diagram, shown in Figure A2.2 below, indicates that Mg$_2$Ni and MgNi$_2$ are the stable intermetallic phases, both of which have melting points well above the operating temperature of 650°C.
Fabrication of either of these intermetallic compounds in the laboratory poses difficulty beyond that of Li$_3$Bi described above due to the much higher melting points of the constituent elements. Fortunately, high purity Mg$_2$Ni is available from Sigma Aldrich in rod form.

A2.4: Experimental: Mg|MgO Reference electrode

All experiments were conducted in the Vacuum Atmospheres gloveboxes used in the previous chapters. For these experiments, the Ar atmosphere was maintained at less than 0.5ppm H$_2$O and less than 1ppm O$_2$. Two identical Mg|Mg$^{2+}$ reference electrodes based on Mg$_2$Ni were constructed, with a schematic diagram of the design shown in Figure A2.3 (not to scale). Mg$_2$Ni rods of $\frac{3}{4}$" diameter and 2" length of 99.9% purity were purchased from Sigma Aldrich.
1/16" diameter x 2" long rods were machined from the bulk material via electrical discharge machining (EDM). Ni plated high temperature crimp connectors were used to connect the short Mg$_2$Ni rods to 1/16" diameter 99.99% purity Ni rods obtained from ESPI metals for electrical contact to the potentiostat. Custom made ¼” OD MgO tubes with ½” long porous frits at one end were obtained from Tateho Ozark for use as the electrode casing. LiCl of 99% purity was obtained from Alfa Aesar and dried in a vacuum oven for 24 hours at 200°C prior to use. Li$_2$O of 99.5% purity was obtained from Strem chemicals. The EDM machined bulk Mg$_2$Ni rod and the electrodes prior to insertion into the MgO sheaths are shown in Figure A2.4.

Figure A2.3: Design of the Mg|MgO reference electrode used in this study.
The electrodes shown in Figure A2.4 were pre-inserted into the MgO sheath such that the gap between the end of the electrode and the porous frit at the bottom of the sheath was approximately 1/8". The electrode was then wrapped in Teflon tape to guarantee a reliable insertion depth during final assembly. As the design of this electrode calls for the same electrolyte composition in the bulk as well as inside the electrode, a batch of 50g of LiCl-Li$_2$O was premade in the MgO crucible obtained from Alfa Aesar. Masses were weighed to mg precision. Pre-dried LiCl was baked at 550°C for four hours prior to raising the temperature to 650°C for one hour to melt. The weighed amount of Li$_2$O was then added to the molten LiCl and allowed to equilibrate for 1 hour. Samples of the salt were then taken using a cold graphite rod immersed quickly into the melt to collect the desired amount of electrolyte for construction of the Mg|MgO reference electrodes. These samples were then crushed and weighed prior to pouring into the MgO sheaths. Both electrodes contained 0.5g of LiCl-1wt%Li$_2$O.
The electrode sheaths were then suspended in the melt overnight prior to final assembly to allow for diffusion of the salt through the porous frit. Subsequently, the electrodes were inserted into the MgO sheaths and allowed to equilibrate for 4 hours prior to the start of open circuit potential (OCP) measurement. A Gamry Ref600 potentiostat was used for collection of the OCP data. Direct connection of the potentiostat cell cable to the electrodes was facilitated by a custom made feedthrough with a 3 meter cell cable. A Faraday cage was also constructed to isolate the electrochemical cell from electromagnetic interference. OCP measurement was conducted over a period of 24 hours.

A2.5: Results

The OCP of the two electrodes as a function of time is shown in Figure A2.5, with the time corresponding to the absolute time from the insertion of the electrodes into the MgO sheaths. Data collection was started at 4 hours after insertion. The potential between the two electrodes at the beginning of the measurement was 4mV, indicating that the initial conditions in the electrodes was near to identical. However, the potential between the two electrodes drifted in a continual manner over time, indicating that equilibrium was not obtained.
Figure A2.5: Open circuit potential recorded between two identical Mg|MgO reference electrodes immersed in LiCl-1wt%Li$_2$O at 650°C over the course of 24 hours. The x-axis gives the time from the initial insertion of the electrodes into the sheaths while at temperature.

The cause for the potential instability was quickly determined upon removal of the electrodes from the melt. The MgO sheaths showed signs of reaction with Mg metal, and the Ni leads showed signs of heat discoloration, as can be seen in Figure A2.6. Additionally, the Mg$_2$Ni electrodes had completely melted away, with some re-solidified metal on the Ni-plated crimp connectors. An exothermic reaction of the Mg in Mg$_2$Ni with one of the components of the electrode design resulted in a large increase in temperature, which melted the electrode. The cause of this is likely due to the high activity of Mg, which may have not been sufficiently reduced by alloying with Ni. Additionally, it is possible that the composition of the Mg$_2$Ni rods were slightly off the stoichiometric value,
as the Mg$_2$Ni intermetallic compound is in equilibrium with a Mg-Ni liquid at 650°C in the case of a slightly Mg rich composition.

Due to the failure of this experiment, further investigation of this electrode design was not pursued. However, the initial similarity of the potentials (~4mV) indicates that the Mg|MgO couple may be able to serve as a reference couple if the activity of Mg can be controlled sufficiently. If MgNi$_2$ were used rather than
Mg$_2$Ni, it is possible that the electrode would have functioned as desired. Unfortunately, the lack of a commercial supplier of the higher Ni content Mg-Ni intermetallic makes further study of this design impractical.

**A2.6: Reference Electrode Design: Conclusions and future work**

Significant progress has been made in the theoretical understanding of the design constraints of a reference electrode for the oxide reduction of used nuclear fuel. The Mg$_2$Ni-based electrode investigated in this study did not perform as intended due to the high activity of Mg in this intermetallic compound and the low melting point of the Mg-rich Mg-Ni liquid phase it is in equilibrium with. However, the small initial potential difference between the two identically constructed electrodes indicates that the Mg|Mg$^{2+}$ couple may be able to function as a stable reference couple if the activity of Mg is sufficiently constrained. The Li$_3$Bi-based Li|Li$^+$ electrode has not yet been successfully fabricated due to the difficulties associated with the direct chemical formation of the Li$_3$Bi intermetallic phase. Future studies will focus on the electrochemical formation of this compound via pulsed galvanostatic deposition of Li into a pool of molten Bi.
Appendix 3: Degradation of Ceramic Materials in LiCl-Li$_2$O-Li

As the oxide reduction of used nuclear fuel is inherently an electrochemical process, there are a number of locations in the design of any such system where an electrically insulating material is required to withstand these harsh conditions. Components such as electrical insulators in electrodes, anode shrouds, and others will be made of some sort of ceramic material, and while this section focuses specifically on the selection of a ceramic material for the reference electrode sheath, many of the same material compatibility issues mentioned here are directly applicable to other components in this system.

Selection of the Reference Electrode casing material

As mentioned in Appendix 1, one of the most challenging aspects of reference electrode design for the LiCl-Li$_2$O-Li system is the selection of the ceramic material used for the reference electrode sheath. The primary function of the reference electrode casing material is to isolate the reference electrode and its electrolyte from the bulk electrolyte so that cross-contamination of both is avoided [96, 97]. In order to do this effectively, the material must be resistant to chemical attack by the electrolyte, be insoluble, allow for the diffusion of ions to allow for ionic conductivity, and prevent direct electrical contact between the electrode and the bulk electrolyte. An additional criterion that affects the design is that the ionic resistivity must be sufficiently low to allow for proper functioning of the potentiostat, with typical maximum acceptable resistivity values being
approximately 20kΩ [105]. This can be accomplished through thinning of a section of the casing or using a porous plug at the end, although techniques are available to lower the impedance of a high resistivity reference electrode using an auxiliary capacitively coupled Pt wire if neither of these techniques provide sufficient conductivity [106]. In aqueous systems, silica glass is typically used due to its inertness and the ease with which it can be fabricated, and a porous Vycor glass frit at the end of the electrode allows for ionic contact with the electrolyte [97]. In the LiCl-Li₂O-Li system, the material chosen has a number of extremely difficult challenges that must be overcome to succeed in providing adequate performance for the electrode, which eliminate silica as an option. Most importantly, the material must be inert to the highly reducing nature of metallic Li, while also being insoluble in LiCl-Li₂O and electrically insulating. While quartz can withstand exposure to molten LiCl-Li₂O at 650°C, the presence of Li rapidly degrades this material. Most other commonly used high temperature insulating materials, such as ceramic oxides or nitrides are also rapidly degraded by metallic Li, and most oxides that are more thermodynamically stable in contact with Li are salt soluble. By examining previous thermodynamic calculations on the compatibility of ceramics with metallic Li, shown in Figure A3.1 below, it can be observed that the oxides most likely to be stable are ThO₂, BeO, and MgO, while the most stable nitrides are BN and AlN [107].
Although the radioactivity of ThO$_2$ is not of primary concern during the reprocessing of used fuel, it has limited the commercial use of Th in other industries. Consequently ThO$_2$ is not readily commercially available, which has eliminated this material from consideration in the current study. By quantifying the stability of BeO, MgO, BN, and AlN in molten LiCl-Li$_2$O-Li, this work will
facilitate the design of ceramic equipment such as reference electrodes, anode shrouds, and crucibles for use in electroreduction experiments.

Examples of Ceramic Degradation in LiCl-Li$_2$O-Li

Figure A3.2: Mullite (3Al$_2$O$_3$2SiO$_2$) reference electrode casing after exposure to LiCl-2wt%Li$_2$O-0.2wt%Li for 8 hours.
Figure A3.3: Degradation of alumina (Al₂O₃) rod used to hang samples for exposure testing in LiCl-2wt%Li₂O-0.6wt%Li for Chapters 2, 3, and 4, demonstrating the incompatibility of Al₂O₃ with the conditions in this system. The attack shown here was from the vapor phase above the salt, and was caused by metallic Li and Na vapors (Na is present as the major impurity in all Li compounds used for this study). This degradation occurred in less than 72 hours, and resulted in the complete failure of 6 out of 8 identical rods, resulting in failure of these experiments.
Investigation of the Performance of BeO during exposure to molten LiCl-Li$_2$O-Li

Figure A3.4: BeO rods obtained from American Beryllia Corporation prior to exposure to LiCl-1wt%Li$_2$O-Li solutions at 650°C for 100hr.

Figure A3.5: Low magnification SEM micrograph of a BeO surface after cleaning and sputter coating with 10nm of carbon, prior to exposure to LiCl-Li$_2$O-Li solutions for 100hr.
Figure A3.6: High magnification SEM micrograph of a BeO surface after cleaning and sputter coating with 10nm of carbon, prior to exposure to LiCl-Li2O-Li solutions for 100hr.

Figure A3.7: Raman spectrum of the as received BeO rods used in this study prior to exposure to molten LiCl-Li2O-Li solutions.
Figure A3.8: XPS survey spectrum of BeO standard. Due to the insulating nature of BeO, the spectrum was obtained at the edge of the sample, which was covered with a Mo plate. This minimized charging of the sample during acquisition, but meant the spectrum included Mo from the sample holder. No Mo was present in the BeO sample, and the photoelectron emission lines do not overlap for Be and Mo.
Figure A3.9: Be 1s XPS spectra obtained from the standard BeO rod prior to exposure to molten LiCl-Li$_2$O-Li. The two peaks are indicative of the high degree of differential charging associated with photoelectron emission from ceramic materials.
Figure A3.10: C 1s XPS spectra obtained from the standard BeO rod prior to exposure to molten LiCl-Li₂O-Li. Multiple peaks were observed, indicative of the high degree of differential charging associated with photoelectron emission from ceramic materials.

Figure A3.11: Mo 3d XPS spectra obtained from the standard Mo sample holder used to affix the BeO rod for analysis prior to exposure to molten LiCl-Li₂O-Li.
Figure A3.12: O 1s XPS spectra obtained from the standard BeO rod prior to exposure to molten LiCl-Li$_2$O-Li. The peak at approximately 533.5 eV is due to the oxide layer on the Mo sample holder, while the highly charged O 1s peak at 543 eV is a result of the high degree of charging on the BeO rod.

Figure A3.13: Optical images of BeO rods exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, and 0.6wt%Li at 650°C for 100 hr. Severe degradation of all samples was observed, with the most pronounced degradation occurring at the melt line. The reaction products were highly crystalline...
in nature for the samples exposed to melts containing metallic Li, which made sample characterization hazardous due to the Be content. As such, only Raman analysis was performed on these samples.

Figure A3.14: Raman spectra of BeO rods prior to and after exposure to LiCl-Li$_2$O-Li solutions at 650°C. Bottom spectrum is of the BeO standard shown in Figure A2.4, while the spectra above were taken from the surface of the samples exposed to LiCl-1wt%Li$_2$O containing 0, 0.3, or 0.6wt%Li, as indicated. The similarity of the spectra independent of the presence or absence of Li indicate that the degradation of the BeO in this system is likely due to the presence of Li$_2$O. The compound may be a ternary mixture of Li, Be, and O. Further characterization of these samples was not performed due to the health hazards associated with handling and working with the dust from the sample surfaces.
Appendix 4: Supplemental Information from SS316L Studies

This Appendix gives additional surface analytical data obtained over the course of the exposure studies on SS316L in molten LiCl-Li₂O-Li solutions at 650°C. This information is supplemental to that presented in Chapter 2. The samples analyzed here are the same samples as those analyzed in Chapter 2, and the methods used are the same as those detailed in the experimental section of that Chapter. Discussion is presented as necessary to explain the findings from this data.

Micro-Vickers Hardness Testing

In an attempt to obtain information on the degradation of mechanical properties as a result of exposure to LiCl-Li₂O-Li solutions, micro-Vickers hardness testing was performed on all samples after methanol rinsing. These measurements were performed on a Wilson Tukon 1202 hardness tester using a micro-Vickers square pyramidal indenter. The load force of 500g was applied for 10s per indentation, and 10 indentations were made per sample. Unfortunately, the results of this testing were directly influenced by the morphologies of the samples, meaning that no conclusions about the bulk mechanical properties of the samples could be obtained. The presence of the oxide layer on the surface artificially increased the measured hardness values for all SS316L and I625 samples exposed to LiCl-Li₂O in the absence of Li due to the higher hardness of covalently bonded compounds compared to metals. Similarly, the highly porous morphologies observed on the SS316L samples exposed to LiCl-Li₂O solutions
containing 0.3wt%Li, as well as all I625 samples exposed to LiCl-Li_2O in the presence of Li, lead to artificially lower hardness values. As the SS316L samples exposed to LiCl-Li_2O solutions containing 0.6 and 1 wt%Li showed less porous morphology, the softening due to the microstructure was reduced when compared to the 0.3wt%Li samples. This can be observed in Figure A4.1, which shows the hardness measurements made for SS316 samples exposed to LiCl-2wt%Li_2O solutions containing 0, 0.3, 0.6, and 1wt%Li for 1000hr.

![Graph showing Vickers hardness measurements](image)

**Figure A4.1:** Micro-Vickers hardness measurements made for as received SS316 and SS316 samples exposed to LiCl-2wt%Li_2O containing 0, 0.3, 0.6, and 1wt%Li for 1000hr. Comparison to the morphologies shown in the SEM images presented above shows a direct correlation between surface morphology and hardness, indicating that the hardness measurements made are not representative of the base material.
SEM-EDS data

Figure A4.2: SEM image (left) and EDS maps of O, Cr, Fe, and Ni for an area above the salt level of the SS316L sample exposed to LiCl-2wt%Li₂O-0wt%Li for 1000hr. This area exhibited partial delamination of the surface layer, showing that the surface was composed of Fe and Ni metal, with a Cr based oxide layer underneath.

Figure A4.3: High magnification SEM images of the area shown in Figure A4.2 above the salt level of the SS316L sample exposed to LiCl-2wt%Li₂O-0wt%Li for 1000hr. This figure shows detailed morphology of the area shown in Figure A4.2.
Figure A4.4: SEM images of area on the SS316L sample exposed to LiCl-2wt%Li₂O-0.3wt%Li for 500hr. This area showed a unique morphology, the composition of which indicates the possibility of a chromium oxynitride surface layer. This compound was removed during the methanol rinsing procedure, indicating poor adhesion to the base metal.

Table A4.1: EDS map average composition for location 1 in Figure A4.4.

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Table A4.2: EDS map average composition for location 2 in Figure A4.4

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XRD Data

Figure A4.5: GI-XRD of SS316L samples exposed to LiCl-2wt%Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr prior to the removal of the residual salt layer with methanol.

Figure A4.6: GI-XRD of SS316L samples exposed to LiCl-2wt%Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr prior to the removal of the residual salt layer with methanol.
Figure A4.7: GI-XRD of SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr after removal of the residual salt layer with methanol.

Figure A4.8: GI-XRD of SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr after removal of the residual salt layer with methanol.
Raman Data

Figure A4.9: Raman spectra of SS316L samples exposed to LiCl-2%Li_2O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr prior to the removal of the residual salt layer with methanol.
Figure A4.10: Raman spectra of SS316L samples exposed to LiCl-2wt%Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr prior to the removal of the residual salt layer with methanol.
Figure A4.11: Raman spectra of SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr following the removal of the residual salt layer with methanol.
Figure A4.12: Raman spectra of SS316L samples exposed to LiCl-1wt%Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr following the removal of the residual salt layer with methanol.

Figure A4.13: Raman spectra of SS316L samples exposed to LiCl-2wt%Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr following the removal of the residual salt layer with methanol.
Figure A4.14: XPS survey spectra of SS316L samples exposed to LiCl-1wt%Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 500hr following the removal of the residual salt layer with methanol.
Figure A4.15: XPS survey spectra of SS316L samples exposed to LiCl-1wt%Li2O solutions containing 0, 0.3, 0.6, and 1wt%Li at 650°C for 1000hr following the removal of the residual salt layer with methanol.

ICP-OES data

Figure A4.16: ICP-OES data of the concentration of alloying elements and impurity Ti in the salt ingots dissolved during the exposure of SS316L samples exposed to LiCl-2wt%Li2O-0wt%Li at 650°C. Samples were taken every 96 hours over the course of the 1000hr exposures.
Figure A4.17: ICP-OES data of the concentration of alloying elements and impurity Ti in the salt ingots dissolved during the exposure of SS316L samples exposed to LiCl-2wt%Li2O-0.3wt%Li at 650°C. Samples were taken every 96 hours over the course of the 1000hr exposures.

Figure A4.18: ICP-OES data of the concentration of alloying elements and impurity Ti in the salt ingots dissolved during the exposure of SS316L samples exposed to LiCl-2wt%Li2O-0.6wt%Li at 650°C. Samples were taken every 96 hours over the course of the 1000hr exposures.
Figure A4.19: ICP-OES data of the concentration of alloying elements and impurity Ti in the salt ingots dissolved during the exposure of SS316L samples exposed to LiCl-2wt%Li2O-1wt%Li at 650°C. Samples were taken every 96 hours over the course of the 1000hr exposures.
Appendix 5 : Supplemental Information from I625 Studies

Crucible Pictures

Figure A5.1: Image of Ni Crucible used to expose I625 samples to LiCl-2wt%Li₂O-1wt%Li for 1000hr. Severe degradation was observed, both above and below the melt line. Below the melt line, precipitation of corrosion products was observed which show a purple color. This may be indicative of lithium molybdenum purple bronze (Li₉.₉Mo₆O₁₇), but further analysis would need to be conducted to determine the composition of this corrosion product. Above the melt line, dendritic structures were observed to be etched into the crucible wall, with apparent growth up and over the side of the crucible. This can be most readily observed in the figure on the right.
Appendix 6 : Li evaporation study

In the short term exposure studies of SS316L, IN625, and M400 conducted prior to the longer duration exposure experiments presented here, the required mass of Li and Li$_2$O necessary to achieve a desired melt composition were added at the beginning of the experiment 1 hour prior to the immersion of the samples [25, 39, 46]. Due to the reactive and volatile nature of metallic Li at the operating temperature of 650°C, the mass of metallic Li present in the initial salt charge is depleted over time if no additional action is taken. Li$_2$O also has a significant vapor pressure at these temperatures, and consequently the solution chemistry will necessarily vary over extended time periods. In our previous work, the length of exposure (20-100 hours) was short enough to allow the depletion of Li and Li$_2$O to be negated. However, as the primary objective of the present study is to investigate the effects of metallic Li on container materials in the LiCl-Li$_2$O-Li system over exposure periods of 500 and 1000 hours, it was deemed necessary to replenish the salt periodically to maintain the desired composition. To ensure the accuracy of the salt composition, it was determined that the entire salt charge would be replaced periodically, and the addition of make-up Li and/or Li$_2$O to the existing melt was to be avoided.

To determine the frequency with which the salt must be replaced for these exposures, the evaporation rate of Li in our system was qualitatively observed by calculating the Li concentration in LiCl based on the volume of H$_2$ gas generated upon reaction of a salt sample with water. This was performed by sampling the
salt using a room temperature graphite dipstick, weighing the resulting salt sample, and measuring the H₂ volume generation upon reaction with water using the apparatus shown in Figure A6.1.

![Gas measurement apparatus used for determination of H₂ volume generated from reaction of Li with H₂O.](image)

**Figure A6.1:** Gas measurement apparatus used for determination of H₂ volume generated from reaction of Li with H₂O. The salt sample is placed in a sealed reaction vessel with 10mL of DI H₂O that is connected via a flexible tube to the top of a 5mL burette, which is filled with water. The pressure inside the closed system is maintained at atmospheric pressure via a movable reservoir connected to the bottom of the burette via a second piece of flexible tubing.

The sample masses were recorded to 1 mg precision, and the burette used for measuring the volume of H₂ produced was accurate to 0.05 ml. The calculation of the mass of Li necessary to evolve the volume of gas produced was performed using the ideal gas law, accounting for the atmospheric pressure and the temperature of the laboratory, and assuming complete reaction according to the equation:

\[ 2Li(s) + 2H₂O(l) \rightarrow 2LiOH(aq.) + H₂(g) \]
The conversion factor was updated daily based on barometric pressure data from the National Weather Service. The value of the conversion factor varied between 0.484 and 0.488 mg Li/mL H₂ over the course of the study. The results of this analysis are shown in Figure A6.2. It is important to note that the solubility limit of Li in LiCl is approximately 0.3wt%, but is not well defined due to the possibility of multiple dissolution mechanisms [16, 22]. This accounts for the upper limit of around 0.35wt%Li observed, and the high variance associated with the measurements at high Li concentrations.

![Figure A6.2: Measured Li concentration vs. time for four initial starting compositions of Li.](image)

Based on the results of this study, the salt replacement interval was set to once every 96 hours. In practice, this was the absolute minimum salt change interval due to the large number of experiments that were ran in parallel during these studies.
Appendix 7 : Published Journal Articles
Corrosion of stainless steel 316L in molten LiCl-Li$_2$O-Li

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HIGHLIGHTS
- SS316L exposed to molten LiCl-Li$_2$O-Li undergoes intergranular attack.
- Attack rates as high as 2.9 mm/year were observed in the presence of Li$_2$O.
- LiO$_2$, Li$_2$CO$_3$, and NiFe$_2$O$_4$O$_2$ were seen on SS316L surfaces in absence of Li$_2$O.
- In the presence of Li$_2$O, no bulk oxide film forms to prevent further corrosion.
- A transition between electrochemical and liquid metal attack occurs based on Il$^2$O.

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ABSTRACT
Exposure testing of Stainless Steel 316L was performed in LiCl-Li$_2$O-Li solutions at 650°C for periods of 500 and 1000 h to investigate the effect of metallic Li on corrosion of materials used to contain the LiCl-Li$_2$O-electrolyte for the electrolytic reduction of used nuclear fuel. Melt compositions studied consisted of LiCl containing 1 or 2 wt% Li$_2$O and 0.1, 0.5, or 1 wt% Li. Post-exposure surface analysis was performed using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. Focused ion beam and mechanical cross sections of the samples and gravimetric analyses were performed to determine the time-averaged corrosion rate for each sample. Lithium metal induced attack rates were found to be as high as 2.9 mm/year. In the absence of solvated Li in the LiCl-Li$_2$O system, Li$_2$O$_2$, Li$_2$CO$_3$, and NiFe$_2$O$_4$O$_2$ were observed to be the primary corrosion products. When Li was present in the melt, the oxidized alloying elements were only detectable via X-ray photoelectron spectroscopy, and the surface was primarily comprised of bare metal.

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1. Introduction

Reduction of used oxide-based nuclear fuel is a necessary step for the incorporation of the large stockpile of used fuel from light water reactors into a pyrometallurgical-based fuel cycle [1–3]. The electrolytic oxide reduction operation developed by Argonne National Laboratory is the preferred method for the reduction of used nuclear fuel (UNF) and has been the subject of continued development [4–12]. In this process, heated, crushed, and pressurized UNF is placed in a stainless steel basket and cathodically polarized versus a suitable anode at a potential sufficient to reduce the oxides present at the cathode [12]. Li$_2$O is added in concentrations of 1–2 wt% to provide an initial source of O$^{2-}$ ions, which are then oxidized at the anode to form oxygen gas. The concentration of Li$_2$O must be carefully controlled, as the reduction of the lanthanides and minor actinides becomes thermodynamically unfavorable at high O$^{2-}$ activities, and the anodic dissolution of Pt becomes problematic at low O$^{2-}$ activities [11,13–15]. As the reduction proceeds, the actinide and lanthanide oxides are reduced to metallic form, while the salt soluble fission products (i.e. Cs, Sr, I, Br, etc.) form salts and dissolve into the electrolyte. Due to the close reduction potentials of Li$_2$O and O$_2$(g) of ~2.40 V and ~2.47 V vs. O$^{2-}$/O$_2$, respectively, and the necessity of applying a high overpotential to achieve a high reduction yield, metallic Li is generated at the cathode [2,12,16,17].

The Li generated at the cathode acts as an additional reduction pathway for UO$_2$ through direct chemical means; however, due to the solubility of Li in LiCl, some of the metallic Li dissolves into the electrolyte [15,16,18–23]. Dissolution of Li into LiCl has been noted
by a number of researchers, and causes a number of changes in physical, electrical, and chemical properties of the electrolyte, as well as causing current inefficiency [16]. The exact solubility limit of Li in LiCl has proven to be experimentally difficult to determine [18,20,24]. A number of different dissolution mechanisms have been proposed by other researchers, but a consensus has yet to be reached within the community. The f-center model proposed by Bredeh, et al. treats the excess electron from solvated Li\textsuperscript{2+} as an anion vacancy, with the electron delocalized from any individual Li\textsuperscript{+} ion core [18,25]. In this model, the dissolution mechanism proceeds similarly to a liquid metal, with free electrons contributing to increased electrical conductivity. This model has successfully predicted the increase in solution conductivity for other alkali halide – alkali metal systems, however, the solution conductivity of the LiCl-Li system is anomalous in that it does not increase at the rate predicted by the f-center model [16,38]. Previous work in our laboratory using in-situ Raman spectroscopy has provided evidence of the presence of Li\textsubscript{2} clusters in solution as a colloidal suspension [26]. If Li\textsubscript{2} clusters are present in the LiCl-Li system, they would act to keep the valence electrons of the Li\textsubscript{2} cluster localized, thus reducing the rate of electrical conductivity increase associated with the progressive addition of Li\textsuperscript{+} to LiCl. As the clusters would be present as a colloid, the solubility of Li\textsuperscript{+} in LiCl would be dependent on the specific experimental parameters, leading to the variation in the measured values for solubility reported by other researchers [26].

Regardless of the molecular interactions at place within the LiCl-Li system, understanding of the effect the solution chemistry has on materials exposed to the molten LiCl-Li\textsubscript{2} system is important for the safe and economical design of vessels and other components for use during the electrolytic reduction of used nuclear fuel. Corrosion in LiCl-Li\textsubscript{2} under oxidizing conditions has been widely investigated [27–34]. The most successful model of corrosion in this system is based on the Lu-Hoff model of salt basicity where the rate of material degradation is dependent upon the activity of the O\textsuperscript{2–} anion [27,35,36]. In addition to O\textsuperscript{2–} activity, corrosion in molten salts is also governed by the inclusion of impurities in the melt, such as moisture or metal chlorides [35]. While the literature concerning corrosion in chloride salts is rich in diversity and discussion of corrosion mechanism, very few studies have investigated the effect of solvated lithium metal in lithium chloride [37–44]. The studies that have been reported have been mainly of short-term duration and have been conducted under widely varying experimental parameters. Consequently, these studies conflict in their analysis on the effect of Li\textsuperscript{2+} on the corrosion of various materials in the molten LiCl-Li\textsubscript{2} system.

Previous work in our laboratory has attempted to elucidate the effect of Li\textsuperscript{2+} and Li\textsubscript{2} on the corrosion of Stainless Steel 316L (SS316L), Inconel 625, and Monel 400 by parametrically varying the concentrations of LiCl, Li, and impurity H\textsubscript{2}O independently [41,42,44]. These studies showed that material degradation depends on the concentration of H\textsubscript{2}O, Li\textsubscript{2} and Li, and that a transition from corrosion based primarily on the O\textsuperscript{2–} activity in the melt at low Li\textsuperscript{2+} concentrations to corrosion more similar to liquid metal attack occurs at high Li\textsuperscript{2+} concentrations. However, the short-term nature of these exposure tests necessitated the continuation of this work to verify our previous findings. In this light, the current study focuses on the corrosion of SS316L over extended time periods when exposed to LiCl containing Li\textsubscript{2} and Li at various concentrations. This paper presents the information gathered from SEM-EDS of the sample surfaces and cross sections, as well as XRD, XPS, and Raman spectroscopy of the surfaces to elucidate the mechanisms responsible for material degradation.

2. Materials and methods

All experiments were performed in a Vacuum Atmospheres OMNI-LAB glovebox under an Ar atmosphere containing less than 2 ppm O\textsubscript{2} and less than 1 ppm H\textsubscript{2}O. Anhydrous LiCl and Li\textsubscript{2}O were obtained from Alfa-Aesar and were of 99% and 99.5% purity, respectively. Li metal of 99% purity was purchased from Strem Chemicals. 99% purity Ni crucibles were obtained from Alfa-Aesar. SS316L coupons were cut from a 3.048 mm plate obtained from McMaster-Carr, with the certified composition given in Table 1.

The salt compositions studied consisted of LiCl containing 1 and 2 wt% Li\textsubscript{2}O and 0, 0.3, 0.6, and 1 wt% Li, with exposure periods of 500 and 1000 h. Total salt mass contained in each crucible was 50 g. Duplicate samples were exposed for each data point, and 500 h and 1000 h exposures were conducted in parallel, with the 500 h samples removed from the experiment upon completion of the allotted exposure period. The furnace configuration used for this study is shown in Fig. 1. A 6.5 inch inner diameter, 6 inch tall cylindrical heater from Watlow (1500 W) was used to maintain a temperature of 650 ± 5°C for the duration of the exposure period. A 6 inch diameter graphite block was machined to accommodate 5 Ni crucibles, with slots machined to accommodate the sample hanging rods. This configuration allowed for repeatable placement of the samples within the melt during the salt replacement procedure outlined below. Two identical furnaces were constructed to maximize the number of experiments that could be run in parallel. In operation, four experiments were run simultaneously in each furnace, which allowed for an additional crucible location to be used for salt replacement purposes.

Prior to exposure, the metal samples were cut into 1.27 cm by 1.27 cm squares using a CO\textsubscript{2} laser. The samples were then polished to a 1 μm surface finish on both sides using a diamond abrasive and spot welded to loops of SS316L wire for suspension from the sample holding rods, as was performed in our previous studies [41,42,44]. Sample hanging rods were made of material to the samples, as alumina rods proved to be incapable of withstanding the highly reducing atmosphere directly over the molten solution, housing metallic Li for the duration of these experiments. The mass of each sample was recorded immediately prior to exposure using a high precision balance.

3. Experimental

Due to the evaporation of Li and Li\textsubscript{2}O over time and the extended exposure periods of this study, the salt charge for each test was replaced once every 96 h to maintain the solution chemistry. To minimize the effects of impurity H\textsubscript{2}O, LiCl was dried in a vacuum oven in air at 200°C for 24 h before being transferred into the glovebox for storage [41,43]. Immediately prior to insertion in the primary furnace, a cleaned Ni crucible (99% purity, Alfa Aesar) containing the weighed amount of LiCl was dried under Ar for 2 h in a dedicated furnace maintained at 550°C. After insertion into the primary furnace, the LiCl was allowed 1 h to reach thermal equilibrium, after which time the required mass of Li\textsubscript{2}O and Li were added to the molten salt. The melt was allowed to equilibrate for another hour prior to the transfer of the corrosion specimens from the old salt charge to the new salt charge. Sample transfer was accomplished through the use of specially fabricated tongs.

Table 1

<table>
<thead>
<tr>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>70.1</td>
<td>16.5</td>
<td>10</td>
<td>2</td>
<td>1.3</td>
<td>0.044</td>
</tr>
</tbody>
</table>
Following transfer of the samples to the new salt charge, the old salt charge was removed from the furnace and allowed to cool to room temperature.

Following completion of the exposure period, the samples were removed from the furnace and allowed to cool to room temperature in the glovebox atmosphere. All samples were stored in the Ar glovebox between analytical procedures. As it was unknown if the surface films formed on the corrosion specimens would be stable in atmosphere, surface analysis was performed both prior to and following removal of the residual salt layer. Following the initial surface analytical procedures, residual LiCl was removed by placing each sample in 25 mL of HPLC grade methanol for 15 min with constant agitation. Prior to the methanol rinsing procedure, all surface analysis was performed under inert atmosphere or vacuum conditions, depending on technique. The data presented here was collected following the methanol rinsing procedure, as the residual salt layer significantly interfered with surface analysis. No chemical or morphological changes were observed as a result of the methanol rinsing procedure. Gravimetric weight change measurements were performed following the methanol rinsing procedure.

Post exposure surface analysis was performed using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS), Raman Spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Following the completion of all surface analytical techniques performed in this study, the samples were cross sectioned to investigate the nature and depth of degradation of the samples. Initially, focused ion beam (FIB) milling was used to mill a trench in the samples to minimize possible morphological and chemical changes to the internal structure of the samples; however, it was found that the depth of attack for samples exposed to melts containing Li was much greater than practical to investigate using this technique alone. Consequently, all samples exposed to Li containing melts were cross sectioned using a Buehler cubic BN wafering blade on a slow speed saw and polished according to Buehler’s recommended polishing techniques to a 0.05 μm surface finish prior to analysis. Samples exposed to LiCl-Li2O in the absence of Li were investigated using only FIB milling for cross sectional analysis due to the relatively shallow depth of attack.

SEM of the sample surfaces was performed using a Hitachi S-4700, while EDS data was collected via the attached Oxford Instruments energy dispersive X-ray spectrometer. The W cold field emission source was operated at an accelerating voltage of 5 kV for surface morphology images, while 20 kV was used for collection of EDS spectra. Emission current was maintained at 10 mA. FIB milling and subsequent SEM-EDS analysis for cross sectional images was performed using a FEI Scios dual-beam FIB/SEM equipped with a TEAM Pegasus Integrated EDS-EBSD. The same dual-beam FIB/SEM was used to perform the SEM-EDS analysis of all of the cross sectioned samples, including those mechanically cross sectioned and polished. The electron beam was operated at 20 kV for both imaging and EDS analysis.

Following the methanol rinsing procedure, the final mass of each sample was recorded, and the exposed surface area was calculated based on the measured submission depth of each sample. The average corrosion rate in mm/year and the mass loss rate in mg cm⁻² h⁻¹ was then calculated based on the mass change, density of the alloy, exposed surface area, and length of exposure.

X-ray diffraction was performed using a Rigaku SmartLab X-ray diffractometer with a Cu Kα source operating at 44 kV and 40 mA. Parallel beam optics in a grazing incidence angle configuration were used for detection of the thin surface films formed on the samples in this study. The incidence angle was set at 1°, and the diffraction pattern was recorded over a 2θ range of 10°–90° for all diffraction patterns. For each diffraction pattern, the scan speed was optimized to yield an intensity of 5000 counts for the highest peak, while the step size was varied to give 5 steps at the full width at half-maximum intensity of the narrowest peak.

Raman spectroscopy was performed using a Thermo-Scientific Dilor Raman microscope utilizing a 10 mW 532 nm continuous wave laser. Spectra were collected through the 50° objective lens of the microscope using a 50 μm incident beam slit. The collection time was 4s per spectra, and 16 individual spectra were averaged to give the spectra reported here.

X-ray photoelectron spectroscopy was performed using a PHI 5600 spectrometer equipped with an Al Kα source with a photon energy of 1486.6 eV. The source was operated at an accelerating voltage of 14 kV and an anode power of 300 W. The spectrometer dispersion and work function were calibrated to the Au 4f7/2 peak at 84.00 eV and the Cu 2p3/2 peak at 932.67 eV to an accuracy of ±0.003 eV. Survey spectra were recorded with a step size of 0.05 eV, while narrow scans were collected at a step size of 0.025 eV for the elements detected on the sample surfaces. Peak fitting was performed with SDP version 4.6 Gaussian fitting software. Charge correction was performed to the adventitious C 1s peak at 284.8 eV unless noted otherwise.

4. Results
4.1. Scanning electron microscopy

The morphologies observed via SEM were highly dependent on the Li concentration in the molten salt solution. The SEM micrographs obtained from SSXH samples exposed to LiCl-2wt% Li2O containing 0, 0.3, 0.6, and 1 wt% Li at 650 °C for 1000 hr and washed with methanol are shown in Fig. 2. While the area averaged EDS composition of the primary constituents of the sample surface for these regions are given in Fig. 3. The differences in the surface morphology caused by the varying concentrations of Li in LiCl-2wt% Li2O correlates to the changes in surface chemistry observed via Raman, XPS, and XRD presented below. The unique surface morphology observed at 0.3 wt% Li may be indicative of the simultaneous action of electrochemical corrosion and liquid metal attack, while the similarity between the morphologies observed at 0.6 and 1 wt% Li indicate that corrosion at these concentrations is firmly within the liquid metal attack regime. Morphologies similar
Fig. 2. SEM micrographs of SS316L exposed to LiCl-1wt% Li2O at 650°C containing: A) no Li, B) 0.3 wt% Li, C) 0.6 wt% Li, and D) 1 wt% Li for 1000hr, following the method of rinsing procedure.

Fig. 3. Average composition of the SS316L samples exposed to LiCl-1wt% Li2O-Li solutions for 1000hr for the regions shown in Fig. 2.

to those observed here were reported in a recent publication by researchers at KAERI who investigated the corrosion behavior of Ni in molten LiCl-Li2O-Li [41]. A number of void spaces were also observed on the surface of all samples exposed to melts containing metallic Li, indicating possible locations where the intergranular corrosion observed on the sample cross sections was initiated. These voids were typically located at high angle grain boundaries, further supporting this hypothesis.

From Fig. 3, it can be observed that the surface of the SS316L sample exposed to LiCl-1wt% Li2O-Li at 650°C for 1000hr is primarily composed of Cr-based oxide films, with minor contributions of Ni and Fe. This is in good agreement with the Raman, XRD, and XPS data presented in their respective sections, which all indicate that these surfaces are composed primarily of Li2CrO3, while small quantities of Li2Cr2O4 and NiFeCr2O7 are predicted by Raman and XPS. When the Li concentration in the molten salt solution is 0.3 wt%, the Cr content of the surface is depleted compared to the base alloy while the Fe content is increased. Beyond the solubility limit of Li, at 0.6 and 1 wt% Li, Cr is depleted slightly further and O is not detectable, while both Fe and Ni are present at levels nominal for SS316L, indicating a bare metallic surface. A slight enrichment of Ni on the SS316L sample exposed to LiCl-2wt% Li2O-Li at 1000hr is in agreement with our previous work, and is indicative of liquid metal attack by Li [41]. Similar trends were observed for samples exposed to LiCl-Li2O-Li containing 1 and 2 wt% Li2O and 0, 0.3, 0.6, and 1 wt% Li for 500 and 1000hr.

Also of interest is the observation of sensitization on a small area on the SS316L sample exposed to LiCl-2wt% Li2O-0.6 wt% Li at 650°C for 1000hr. Sensitization of austenitic stainless steels is a well-known issue at high temperatures, where the formation of chromium carbides and their subsequent concentration at the grain boundaries leads to intergranular corrosion and loss of strength [46]. The characteristic enrichment of Cr at the grain boundaries typical of sensitization can clearly be observed in the Cr Kα EDS map in Fig. 4, while the specific compositions for spots 1 and 2 marked on the SEM micrograph and EDS map are given in Table 2.

The detection of S along with chromium carbide formation at Spot 1 is in good agreement with literature, as S is known to accelerate the sensitization of austenitic stainless steels [46]. As expected, the area around spot 1 (spot 2) has much lower concentration of chromium, which is below the concentration in base alloy. The low carbon content of the SS316L used for this study is intended to minimize this issue by preventing the formation of
carbides. Of great importance to the present work, the operating temperature of the electrolytic reduction of UNF at 650 °C is also ideal to cause sensitization of austenitic stainless steels, as chromium carbides are insoluble at this temperature and the diffusion of C through the microstructure allows for their formation and migration to the grain boundaries.

4.2. Cross section SEM-EDS

The SEM image obtained for the FB milled trench from the SS316L samples exposed to LiCl-1wt.% Li2O for 300hr and 1000hr are shown in Fig. 5. It can be observed that the attack first proceeds inward from the sample surface in an intergranular fashion prior to consuming the grains themselves, likely assisted by the sensitization of the material seen in Fig. 4. The depth of attack into the sample is approximately linear with length of exposure, with the total depth of attack being 13 μm and 27 μm for 500hr and 1000hr, respectively, while the thickness of the outer oxide layer is approximately 3 μm for the 500hr sample and 7.5 μm for the 1000hr sample.

EDS mapping results for the corroded region of the SS316L sample exposed to LiCl-1wt.% Li2O for 1000hr are shown in Fig. 6. Here, it can be observed that the corrosion products (dark regions) are enriched in Cr, Mo and O, while the bulk material is relatively depleted in Cr and Mo. This agrees with the findings of previous studies that corrosion in LiCl-Li2O occurs primarily through preferential attack of the most active alloying elements, namely Cr and Mo [35,41].

In the presence of Li, intergranular corrosion was again observed to be the primary method of material degradation, as can be observed in Fig. 7. However, the lack of a protective oxide layer severely accelerated the attack of the base material.

From Fig. 7, it can be observed that the depth of attack on the base material is approximately linear with time and does not depend on the concentration of Li; however, the severity of the degradation is proportional to the Li concentration in the melt. In all cases, the rate of attack was approximately 2.2–2.9 mm/year in the presence of Li. The outer layers of the SS316L samples exposed to melts containing Li were depleted in Cr, while small, localized areas of high Cr concentration were observed in intergranular regions, further corroborating the observations of sensitization made in Fig. 4. A high magnification EDS map of one of these regions on the SS316L sample exposed to LiCl-1wt.% Li2O-0.6wt.%Li for 500hr is shown in Fig. 6, while the spot EDS analysis for the area highlighted in red in the SEM image is given in Table 3.

From the SEM-EDS images in Fig. 8 and spot analysis in Table 3, it is apparent that corrosion of the base material is facilitated by the precipitation of Cr and Mn at the grain boundaries in the form of metal carbides and nitrides. These carbides and nitrides are then preferentially attacked by the molten salt, leaving a channel for further intrusion of the salt along the grain boundary. N was likely incorporated as an impurity from the glovebox atmosphere which reacted with LiP to form Li3N, which is known to accelerate corrosion in the LiCl-Li2O-Li system [47]. Also, titanium nitride surface
films were observed in previous studies, as well as during XPS analysis of these samples [48]. Some of these samples were observed to spontaneously form droplets of water from the cross sectioned surface when exposed to atmosphere, implying LiCl was entrapped within the sample. LiCl is extremely hygroscopic, and will absorb enough water to form a solution, even in relatively dry air, so the formation of water droplets on the cross sectioned surface is indicative of the entrapment of LiCl within the bulk sample. As most other metal chlorides are not hygroscopic to the same extent as Li, this indicates that the Cl observed in Figs. 7 and 8 is primarily in the form of LiCl.

4.3. Depth of attack analysis

Based on the depth of attack observed in Fig. 7, the penetration rate was calculated for each sample and are tabulated in Table 4. For comparison, the corrosion rates based on gravimetric analysis are presented in Table 5.

The lack of spallation of the material based on the gravimetric analysis presented below, along with the morphological changes to
Fig. 8. High-magnification SEM-EDS maps of Fe, Ni, Cr, Mn, and Cl for a Cr rich region of the SS316L sample exposed to UCG-1wt%Li2O-0.6wt%Li for 500hr. The red spot on the SEM image indicates the location of the spot EDS analysis summarized in Table 3. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>EDS analysis for the location on the SS316L sample exposed to UCG-1wt%Li2O-0.6wt%Li for 500hr shown in Fig. 8.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Weight %</td>
</tr>
<tr>
<td>C</td>
<td>9.72</td>
</tr>
<tr>
<td>N</td>
<td>10.88</td>
</tr>
<tr>
<td>Cr</td>
<td>53.57</td>
</tr>
<tr>
<td>Mn</td>
<td>1.36</td>
</tr>
<tr>
<td>Fe</td>
<td>21.91</td>
</tr>
<tr>
<td>Ni</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Table 4: Depth of attack observed for SS316L samples exposed to UCG-1wt%Li2O solutions containing 0, 0.3, 0.6, and 1wt% Li for 500 and 1000hrs, and the penetration rate based on this depth of attack.

<table>
<thead>
<tr>
<th>Li Concentration in</th>
<th>Exposure Duration (hr)</th>
<th>Depth of Attack Penetration Rate (nm year^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>500</td>
<td>13</td>
</tr>
<tr>
<td>0</td>
<td>1000</td>
<td>27</td>
</tr>
<tr>
<td>0.3</td>
<td>500</td>
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</tr>
<tr>
<td>0.3</td>
<td>1000</td>
<td>275</td>
</tr>
<tr>
<td>0.6</td>
<td>500</td>
<td>166</td>
</tr>
<tr>
<td>0.6</td>
<td>1000</td>
<td>250</td>
</tr>
<tr>
<td>1</td>
<td>500</td>
<td>120</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>225</td>
</tr>
</tbody>
</table>

Table 5: Calculated corrosion rates for SS316L samples exposed to UCG-Li2O-Li solutions at 650°C for 500hr and 1000hr. Positive corrosion rates indicate weight loss, while negative corrosion rates indicate weight gain.

<table>
<thead>
<tr>
<th>Wt% Li2O</th>
<th>Wt% Li</th>
<th>Exposure Duration (hr)</th>
<th>Mass Loss Rate (mg cm^-2 year^-1)</th>
<th>Corrosion Rate (mm year^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>500</td>
<td>0.000</td>
<td>-0.005</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
<td>500</td>
<td>-0.019</td>
<td>0.211</td>
</tr>
<tr>
<td>0.6</td>
<td>0.012</td>
<td>500</td>
<td>-0.012</td>
<td>0.156</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>500</td>
<td>-0.061</td>
<td>0.665</td>
</tr>
<tr>
<td>0.3</td>
<td>0.012</td>
<td>500</td>
<td>-0.061</td>
<td>0.156</td>
</tr>
<tr>
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<td>-0.061</td>
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<td>0.665</td>
</tr>
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<tr>
<td>1</td>
<td>0</td>
<td>500</td>
<td>-0.061</td>
<td>0.665</td>
</tr>
</tbody>
</table>

No overall trend in gravimetric weight loss as a function of material, Li2O concentration, Li concentration, or exposure period was observed.

4.4 X-ray diffraction

Fig. 9 shows the diffraction patterns obtained for SS316L exposed to UCG-1wt%Li2O-0.6wt%Li at 650°C for 500hr. Peaks characteristic of Li2FeCr2O4, based on PDF card number 01-072-7839, and the base material were observed [49]. No other phases were detected on the sample surface, indicating that the NiFe2Cr2O4 and Li2FeCr2O4 phases predicted by Raman spectroscopy, SEM-EDS, and XPS observations presented below are minor components of the oxide layer present on samples exposed to UCG-Li2O solutions in the absence of Li. Similar patterns were obtained for all samples exposed to UCG-Li2O.
solutions in the absence of Li⁺.

The XRD patterns for SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0.3, 0.6, or 1 wt%Li at 650 °C for 500hr are shown in Fig. 10, while Fig. 11 shows the diffraction patterns for SS316L samples exposed to identical conditions for 1000hr.

From these figures, it can be observed that the Li₂O surface films that form in the absence of Li are not detectable via XRD in the presence of Li, corroborating SEM-EDS as well as the Raman spectroscopy and XPS analysis presented in this work [41]. These techniques all show that the presence of Li prevents the formation of appreciable oxide surface films, resulting in severe degradation to the base material. Additionally, de-austenization of the base material was observed on the SS316L samples exposed to LiCl-1wt%Li₂O containing 0.3, 0.6, and 1 wt%Li for 500hr, and LiCl-1wt%Li₂O containing 0 and 0.3 wt%Li for 1000hr. This effect was also observed in short term testing of SS316L in molten LiCl-Li₂O [41]. The inconsistency with which this phenomena was observed indicates

![Diagram](image1.png)  
**Fig. 10.** High resolution grazing incidence XRD patterns for SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0.3, 0.6, and 1 wt%Li at 650 °C for 500hr. The diffraction pattern for the SS316L sample exposed to LiCl-1wt%Li₂O-0wt%Li shows the peaks identified as LiClO₄ in Fig. 9 above. The peak of LiClO₄ were not observed on any sample exposed to LiCl-Li₂O in the presence of Li. De-austenization of samples exposed to LiCl-1wt%Li₂O containing 0.6, and 1 wt%Li for 500hr was observed.

![Diagram](image2.png)  
**Fig. 11.** High resolution grazing incidence XRD patterns for SS316L samples exposed to LiCl-1wt%Li₂O solutions containing 0, 0.3, 0.6, or 1 wt%Li at 650 °C for 1000hr. The diffraction pattern for the SS316L sample exposed to LiCl-1wt%Li₂O-0wt%Li shows the peaks identified as LiClO₄ in Fig. 9 above. The extent of de-austenization of the base material varied among samples exposed to identical conditions, but otherwise the trends observed in Fig. 10 remain consistent at longer exposure periods.

that the solution chemistry does not affect the probability that a particular sample will undergo de-austenization. This is particularly highlighted by the SS316L samples exposed to LiCl-1wt%Li₂O containing 0.3, 0.6, and 1 wt%Li for 500 or 1000hr, as the samples exposed to identical solution chemistries for different exposure periods did not display similar de-austenization behavior.

The samples exposed to LiCl-2wt%Li₂O solutions containing 0, 0.3, 0.6, and 1 wt%Li displayed similar diffraction patterns as those presented here.

4.5. Raman Spectroscopy

The Raman spectrum of the SS316L sample exposed to LiCl-1wt%Li₂O-0wt%Li at 650 °C for 500hr is shown in Fig. 12. This spectrum displays peaks that were observed in various ratios on all samples exposed to LiCl-Li₂O solutions in the absence of Li and is therefore used here as representative of the samples exposed to similar
conditions. Both the $A_{2g}$ mode at 572 cm$^{-1}$ and the $E_g$ mode at 445 cm$^{-1}$ of LiCoO$_2$ are clearly defined [59]. Broad peaks centered at 250 cm$^{-1}$, 690 cm$^{-1}$, and 845 cm$^{-1}$ were also observed. Based on EDS and XPS analysis shown in their respective sections, the peak at 690 cm$^{-1}$ can be attributed to the $A_{2g}$ mode of a mixed Ni, Fe, Cr spinel of the form Ni$_{Fe}$Cr$_{2}$O$_{4}$, although the exact composition of this oxide is not easily identified [51]. The position of this peak was also observed to shift slightly on other samples, which can likely be attributed to variations in the stoichiometry of the spinel due to differing exposure periods, melt compositions, and base materials. The peak at 845 cm$^{-1}$ is hypothesized to originate from Li$_2$CoO$_4$ based on the presence of Cr$^{3+}$ in the XPS spectra collected from SS316L samples exposed to LiCl-Li$_2$O solutions in the absence of Li. The broad feature centered around 250 cm$^{-1}$ could not be positively attributed to any single compound, but may be caused by the combination of the minor modes of Li$_2$CoO$_4$ and minor components of the Ni$_{Fe}$Cr$_{2}$O$_{4}$ spectrum.

When exposed to LiGa$_2$O$_4$ solutions containing Li, these oxide based surface films are destabilized due to the highly reducing nature of metallic Li. To illustrate the changes to the surface layer present on samples exposed to LiCl-Li$_2$O solutions as a function of Li concentration, Fig. 11 shows the Raman spectra obtained from SS316L samples exposed to LiCl-Li$_2$O solutions containing 0, 0.3, 0.6, and 1 wt% Li at 650°C for 500 hr. The spectra collected from samples exposed to LiCl-Li$_2$O in the presence of Li do not display any discernible features indicative of the well-developed oxide layer observed in Fig. 12. Rather, the features observed are broad and are close to the baseline of the instrument, indicating that the oxide layer is tenaciously present on these samples.

As no investigations into the Raman spectra of Li$_2$CoO$_4$ could be found in literature, the spectra of a commercially purchased Li$_2$CoO$_4$ standard was collected to confirm that the peak seen at 845 cm$^{-1}$ in Figs. 12 and 13 could be attributed to this compound. The Raman spectrum collected from pure Li$_2$CoO$_4$ is shown in Fig. 14. The assignment of specific vibrational and rotational modes to each of the peaks observed in Fig. 14 is beyond the scope of this study. However, it can be seen that the primary features of pure Li$_2$CoO$_4$ occur between 1000 cm$^{-1}$ and 800 cm$^{-1}$, with the dominant peak occurring at approximately 850 cm$^{-1}$. Additional minor features are present between 650 cm$^{-1}$ and 275 cm$^{-1}$. As the oxide layer of the samples is non-homogenous and consists primarily of LiCoO$_2$ with small amounts of Ni$_{Fe}$Cr$_{2}$O$_{4}$ and Li$_2$CoO$_4$, the smearing of the features of the Li$_2$CoO$_4$ spectrum to form the single, broad peak centered around 850 cm$^{-1}$ observed on the samples exposed to LiCl-Li$_2$O is plausible [51].

4.6. X-ray photoelectron spectroscopy

XPS survey scans of the SS316L samples exposed to LiCl-Li$_2$O containing 0, 0.3, 0.6, and 1 wt% Li at 650°C for 1000 hr in the absence of Li, the surface is primarily composed of Cr and O, with Ni and Fe detectable in small quantities. For the SS316L samples exposed to LiCl-Li$_2$O containing 0.6 and 1 wt% LiCl at 650°C for 1000 hr, the surface shows a relatively thick Ti-based surface deposit, with high quantities of N and O present. As the case of the SS316L sample exposed to LiCl-Li$_2$O-0.6 wt% LiCl for 1000 hr, this Ti surface film was sufficiently thick to prevent the analysis of the underlying base material. TiO$_2$ is a common impurity in Li$_2$O, and the deposition of Ti based
compounds on samples exposed to LiCl-Li$_2$O in the presence of Li was extensively studied during our previous short term studies [48].

Analysis of the alloying elements, especially the Cr 2p spectra, is necessary to determine the corrosion mechanisms of SS316L in LiCl-Li$_2$O-Li, as Cr is the primary element responsible for the formation of oxide films in the absence of Li. Identification of the oxidation state of Cr present on the surface of the SS316L sample exposed to LiCl-1wt%Li$_2$O-Li at 650°C for 500hr was performed by peak fitting the Cr 2p$_{3/2}$ spectra using previously published peak fitting parameters [52]. The peak fit data for all Cr spectra collected on the samples in this study are shown in Fig. 16, while the peak fitting parameters are given in Table 6 [52].

As can be observed in Fig. 16, both Cr$^{3+}$ and Cr$^{6+}$ are simultaneously present on all SS316L samples exposed to LiCl-Li$_2$O solutions in the absence of Li. The presence of Cr$^{3+}$ and Cr$^{6+}$ on the samples further supports the presence of both Li$_2$CrO$_4$ (Cr$^{3+}$) and Li$_2$Cr$_2$O$_7$ (Cr$^{6+}$) on the surfaces of samples exposed to LiCl-Li$_2$O solutions in the absence of Li. In the presence of Li, the highly reducing nature of metallic Li destabilizes the oxide films that are present on the sample surfaces in the absence of Li. However, the transition between electrochemical oxidation of the samples in the absence of Li and liquid metal attack in the presence of high Li concentrations is not abrupt. Our previous short term studies have shown that at concentrations at or below the apparent solubility limit of Li in the system (around 0.3 wt%Li) [74], there exists a transition region where both modes of attack occur simultaneously [48,49]. The Cr 2p$_{3/2}$ spectra shown in Fig. 16 give further evidence for this hypothesis, although there was no discernible trend in the relative ratios of Cr$^{3+}$, Cr$^{4+}$, and Cr$^{6+}$ based on the concentration of Li, Li$_2$O, or exposure period.

The presence of Cr$^{3+}$ is also required for the formation of NiFe$_3$Cr$_2$O$_8$, as both Fe and Cr are in the 3+ oxidation state in this compound, while Ni is present in the 2+ oxidation state. Further confirmation of the presence of NiFe$_3$Cr$_2$O$_8$ is given by the narrow scans of the Ni 2p and Fe 2p spectra for SS316L exposed to LiCl-1wt%Li$_2$O-0.0wt%Li for 500hr, which are shown in Fig. 17, along with the Ni 2p and Fe 2p narrow scans for the SS316L sample exposed to LiCl-Li$_2$O-0.3wt%Li for 500hr. In the absence of Li, the Ni 2p$_{3/2}$ peak is located at 853.5eV, while the Fe 2p$_{3/2}$ peak is located at 710.3eV. These binding energies and peak shapes correspond to Ni$^{2+}$ and Fe$^{3+}$, respectively [53]. Neither element was detected in the metallic state, confirming the presence of spinel-based oxides on the sample surface. In conjunction with Raman spectroscopy and EDS analysis, this is further evidence supporting the presence of a NiFe$_3$Cr$_2$O$_8$ based spinel present on the surface of

![Figure 16](image_url)  
**Fig. 16.** Cr 2p XPS spectra collected from SS316L samples exposed to all LiCl-Li$_2$O-Li compositions and exposure periods studied in this work. Charge correction was performed to the adventitious C 1s peak at 284.6eV, and peak fitting parameters for Cr$^{3+}$, Cr$^{4+}$, and Cr$^{6+}$ listed in Table 2 were used for all spectra. Cr$^{3+}$ and Cr$^{6+}$ are the only species present in the absence of Li. Cr spectra of SS316L samples exposed to LiCl-Li$_2$O in the presence of Li indicate both metallic and oxidized components; however, no discernible trend in oxidation state based on Li concentration, Li$_2$O concentration or exposure period could be determined. Cr was not detectable on the SS316L sample exposed to LiCl-1wt%Li$_2$O-0.6wt%Li for 1000hr due to the thickness of the underlying Ti surface deposit.
the samples exposed to LiCl-Li$_2$O in the absence of Li. However, when Li was present in the molten salt, only metallically bonded Ni and Fe are present on the sample surface. No charge correction was necessary for the Ni and Fe 2p spectra, indicating that these elements were in direct electrical contact with the base material. Similar spectra were recorded for all other SS316L samples exposed to LiCl-Li$_2$O-Li, indicating that any quantity of Li$^+$ in the melt is sufficient to reduce NiFe$_2$C$_3$.a$_4$.

In our previous work, Mo was observed to behave similarly to Cr in some respects, becoming enriched on the surface in the absence of Li, and depleted at higher Li concentrations. As Mo is a minor alloying element of SS316L at around 2 wt%, Mo was not observed on all samples. Additionally, in the absence of Li, Mo was not detectable via XPS on any sample due to the thick LiClO$_4$ surface layer. However, the samples exposed to molten LiCl-Li$_2$O-Li$_2$O solutions containing 0.3, 0.6, and 1 wt% Li for 500h all had detectable levels of Mo, the narrow scans of which are presented in Fig. 18. From the spectra in Fig. 18, it can be observed that when 0.3 wt% Li is present in solution, Mo$^{4+}$ is the only Mo species observable on the sample surface [53]. However, as Li concentration increases the stability of oxidized Mo is decreased, resulting in a mixed Mo$^{4+}$/Mo$^5+$ spectra at 0.6 wt% Li and a fully metallic Mo$^5+$ spectra at 1 wt% Li [54,55]. The observation of Mo$^{4+}$ on samples exposed to high concentrations of Li indicates that Mo is highly active in the LiCl-Li$_2$O-Li system, which could explain the depletion of Mo from the surface of SS316L observed via SEM-EDS analysis of the cross section of these samples in section 4.2.

Co was also observed on some samples exposed to LiCl-Li$_2$O in the presence of Li. Co is not an alloying element of SS316L but is present as the primary impurity in the Ni crucibles used for these studies at concentrations of less than 1 wt%. Consequently, the presence of Co on the surface of the samples exposed to LiCl-Li$_2$O solutions in the presence of Li indicates that there is mass transport from the crucible to the samples. Mass transport of Co from the crucible to the samples had not been observed in our previous short term experiments [41,42,44]. The Co 2p spectra of the SS316L sample exposed to LiCl-Li$_2$O-Li$_2$O solutions containing 0.3 wt% Li for 500h is presented in Fig. 19, and is typical of Co$^{2+}$, due to its binding energy and peak shape [33]. The cause of the transport of Co from the crucible to the samples and its implications to the degradation of materials in the LiCl-Li$_2$O-Li system as a whole requires further investigation.

5. Conclusions

Exposure testing of SS316L samples was performed for 500 and 1000h intervals in molten LiCl-Li$_2$O-Li solutions containing 1 and 2 wt% Li$_2$O and 0, 0.3, 0.6, and 1 wt% Li. Morphological and elemental changes to the sample surfaces and cross sections were
investigated via SEM and EDS, respectively, while XRD, Raman spectroscopy, and XPS were used to provide further insight into the effect of LiF on the degradation mechanisms of materials in LiCl-LiF solutions. Upon exposure to LiCl-LiF solutions in the absence of Li, S316L was observed to form a LiClO4 based surface film, with minor contributions of Li2CrO4 and NiFe2O4. The oxide layer limited corrosion to a rate of approximately 0.24 mm/year during exposure to molten LiCl-LiF solutions. The presence of Li in the melt resulted in the destabilization of the protective oxide film formed in LiCl-LiF solutions, causing substantial damage to the samples in the form of intergranular corrosion. XPS analysis observed that metallically bonded Ni and Fe were present on the surface of all S316L samples exposed to LiCl-LiF in the presence of Li, however both Cr and Mo displayed varying degrees of oxidation in the presence of Li. Mass loss rates were low, but cross-sectioned samples displayed significant ingress of LiCl and damage to the sample surface, indicating that mass loss measurements alone are not sufficient to characterize corrosion in this system. Intergranular corrosion was facilitated by the precipitation of metal carbides and nitrides along the grain boundaries, resulting in the selective depletion of alloying elements, such as Cr, Mo, and Mn. The rate of material damage was on the order of 2–3 mm/year, indicating that the presence of high concentrations of Li during the electrolytic reduction of UNF will dramatically reduce the lifetime of any S316L components exposed to the electrolyte. The ingress of intergranular corrosion into the material will likely have a marked effect on the strength of the material due to the effective loss of structural thickness, however, further investigation would be necessary to validate this hypothesis. From the combination of analytical techniques presented in this work, it is hypothesized that cyclical oxidation by LiF ions and reduction by Li2F2 is responsible for the high levels of material degradation in the LiCl-LiF-Li system.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jnucmat.2019.02.007.

References

A7.2: Effect of Metallic Li on the Corrosion of Behavior of Inconel 625 in Molten LiCl-Li$_2$O-Li
Effect of Metallic Li on the Corrosion Behavior of Inconel 625 in Molten LiCl-Li\textsubscript{2}O-Li

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The corrosion behavior of Inconel 625 in molten LiCl solutions maintained at 650°C and containing various quantities of Li\textsubscript{2}O and metallic Li was studied for possible application in the electrodissolution of used oxide-based nuclear fuel. This study focuses on the morphological and elemental changes on the surface of the samples with an emphasis on cross-sectional analyses conducted using focused ion beam microscopy. In the absence of metallic Li, a stable oxide film is formed that limits the corrosion of the base material to 0.035mm/year. However, in the presence of metallic Li, the formation of this film is impeded, resulting in de-lithiation of the base material and the formation of a highly porous microstructure composed primarily of Ni.

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In order to reprocess used nuclear fuel (UNF) from light water reactors using pyrometallurgical techniques, a reduction operation is necessary to convert UO\textsubscript{2}-based UNF into a metallic product that can then be processed in subsequent unit operations.\textsuperscript{1,2} The prototypical process by which the reduction of UO\textsubscript{2} is conducted is via the electrolytic reduction operation developed at Argonne National Laboratory (ANL).\textsuperscript{3,4} In this process, LiCl containing 1 to 2wt% Li\textsubscript{2}O and maintained at 650°C serves as the electrolyte.\textsuperscript{5} The reduction is performed with UNF loaded in a stainless steel cathode basket which is polarized vs. a suitable anode, typically made of Pt, either galvanostatically or potentiostatically.\textsuperscript{5,6} To achieve high reduction yields, it has been shown by a number of researchers that it is necessary to polarize UO\textsubscript{2} at potentials beyond the electrochemical window of Li\textsubscript{2}O, which results in the formation of metallic Li at the cathode.\textsuperscript{3,10} Some of the metallic Li thus generated then thermodynamically reduces the UNF in the cathode; however, LiCl is capable of solvating Li to a limited degree, which leads to the formation of a tertiary LiCl-Li\textsubscript{2}O-Li\textsubscript{2} salt electrolyte.\textsuperscript{7,10} As the process goes to completion, the electrolyte eventually reaches Li saturated conditions, and may even form and be present as clusters.\textsuperscript{11}

The dissolution of alkali metals in their respective alkali halides has been well studied over the last century, notably by M.A. Bredig at Oak Ridge National Laboratory, among others.\textsuperscript{12,13} The two primary models of alkali metal – alkali halide systems are the F-center model and the sub-halide model.\textsuperscript{14} In the F-center model typical for alkali metal – alkali halide systems, the excess electron is delocalized from any particular cation core, leaving a free electron that imparts a metallic character to the molten solution.\textsuperscript{15} This leads to several orders of magnitude increase in electrical conductivity of solution as the concentration of the alkali metal increases toward saturation, as well as a number of other changes in physical and chemical properties. The sub-halide model is typically representative of transition metals and post-transition metals in their respective halides and gives rise to the formation of abnormally reduced species due to the formation of complex molecules that keep electrons localized to the molecular scale, as is typical for the Bi-BeCl\textsubscript{3} system.\textsuperscript{15} Sub-halide forming systems are not associated with an increase in electrical conductivity in the same manner as the F-center model predicts. Other dissolution mechanisms have also been reported, such as the formation of colloidal suspensions of nanoclusters of Na\textsuperscript{+} or Li\textsuperscript{+} in the Na\textsubscript{2}NaCl and Li-Cl solution systems, respectively.\textsuperscript{16,17} It is important to note that none of these effects are mutually exclusive, and it is possible that the simultaneous action of multiple dissolution mechanisms may occur simultaneously in the same system. Of the alkali metal – alkali halide systems, the Li-LiCl system has proven to be particularly challenging in the determination of the solubility limit of the metal in the metal salt, with the apparent solubility limit seeming to vary depending on the experimental methods; however, approximately 0.3wt% has been shown to be a useful estimate at the temperatures of the electrolytic reduction operation.\textsuperscript{12,15-17} Importantly, the concentration of Li\textsubscript{2}O has been shown to have minimal effect on the measured solubility limit of Li in LiCl-Li\textsubscript{2}O.\textsuperscript{18} The discrepancy between the various reported values of the solubility limit of Li in LiCl may be due to the simultaneous action of the various dissolution mechanisms theorized for this system.\textsuperscript{15}

For the electrodissolution of UNF to be implemented on a large scale, knowledge of the degradation of materials in contact with the electrolyte is necessary, particularly for the container material. Corrosion in molten LiCl-Li\textsubscript{2}O under inert or oxidizing atmospheres has been fairly well studied, and the corrosion of various materials has been found to follow similar mechanisms to those observed in other molten salt systems.\textsuperscript{20,21} Primarily, the dissolution of alloying elements, and consequently the corrosion rate, is governed primarily by the activity of the O\textsuperscript{2-} ion in the solution according to the Lux-Flodin model of salt basicity, as well as by the presence of impurities such as moisture or transition metal halides.\textsuperscript{20,21} For the electrodissolution process, such models are insufficient to completely describe corrosion due to the presence of dissolved Li. To date, very few investigations into the effects of Li on the corrosion of materials exposed to this system have been performed.\textsuperscript{22,23} The initial studies conducted by Indocoecha et al. conflicted with studies conducted by Mishra and Olson due to the presence of varying experimental parameters, leading to confusion about the effect of Li on the de-gradation observed.\textsuperscript{23} Since then, recent studies have been performed to address these issues, but were of short term in nature and did not investigate the degradation of the materials studied in cross section.\textsuperscript{24-26} These studies showed that a transition from molten salt based corrosion to a liquid metal attack induced degradation occurred at approximately 0.6wt% Li, and that the concentration of both Li and Li\textsubscript{2}O affected the corrosion processes that were observed. Recent work by researchers at the Korean Atomic Energy Research Institute showed that Li displayed minimal corrosion in the absence of Li, but underwent significant degradation in the presence of metallic Li.\textsuperscript{26} In this light, the current study investigates the corrosion behavior of Inconel 625 (In625) in the LiCl-Li\textsubscript{2}O-Li system at 650°C. To understand the effect of oxide concentration, metal concentration and the period of exposure, the solution chemistries studied consisted of LiCl containing 1 or 2wt% Li\textsubscript{2}O and 0.3, 0.6, or 1wt% Li, with samples exposure periods of 500 and 1000hr. This study focuses on the...
observed degradation of 1625 under these conditions by determining the changes to the microstructure and elemental composition using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) of the sample surfaces as well as their cross sections.

Experimental

Experiments were conducted in a Vacuum Atmospheres OMNILAB glove box under Ar containing less than 2 ppm O2 and less than 1 ppm H2O. Anhydrous LiCl, Li2O, and Ni crucibles were obtained from Alfa-Aesar and were of 99%, 99.5%, and 99% purity, respectively. Li metal of 99% purity was purchased from Strem Chemicals. 1625 coupons were cut from a 3.175 mm thick plate obtained from High Performance Alloys. The composition of this alloy as measured via EDS investigation was 92.55% Ni, 23.54% Cr, 6.54% Mo, 5.1% Fe, and 2.64% Nb.

Studies were conducted using duplicate samples, and 500 hour and 1000 hour exposure age tests were conducted in parallel with the 500 hour samples removed from the experiment upon completion of the allotted exposure period. A 0.5 inch inner diameter, 6 inch tall cylindrical furnace from Watlow (1500 watts) was used to maintain a temperature of 650 ± 5°C for the duration of the exposure period. A 6 inch diameter graphite block was machined to accommodate 5 Ni crucibles, with slots machined to accommodate the sample hanging rods. This configuration allowed for repeatable placement of the samples within the melt during the salt replacement procedure outlined below. Two identical furnaces were constructed to maximize the number of experiments that could be run in parallel. In operation, four experiments were run simultaneously in each furnace, which allowed for the extra crucible crucible location to be used for salt replacement purposes.

Prior to exposure, the metal samples were cut into 1.27 cm by 1.27 cm squares using a CO2 laser. The samples were then polished to a 1 μm surface finish on both sides using a diamond abrasive and spot welded to loops of SS316L wire for suspension from the sample hanging rods, as was performed in our previous studies.8,9,22-30 Sample hanging rods were made of like material to the samples, as aluminum rods proved to be incapable of withstanding the highly reducing atmosphere directly over the molten solutions containing metallic Li for the duration of these experiments. The mass of each sample was recorded immediately prior to exposure.

Considering the evaporation of Li and Li2O over time that was observed in other short-term studies and the extended exposure periods of this study, the salt charge for each test was replaced at a period of once every 96 hours to maintain the solution chemistry.31-34 To minimize the effects of impurity H2O, LiCl was dried in a vacuum oven in air at 200°C for 24 hours before being transferred into the glove box for storage.35 Immediately prior to insertion in the primary furnace, a cleaned Ni crucible containing the weighed amount of LiCl was dried under Ar for 2 hr in a dedicated furnace maintained at 550°C. After insertion into the primary furnace, the LiCl was allowed 1 hour to reach thermal equilibrium, after which the required mass of Li2O and Li were added to the molten salt by placing the Li2O powder and Li pellets on top of the solution. Total salt mass contained in each crucible was 50 g. The melt was allowed to equilibrate for another hour prior to the transfer of the corrosion specimens from the old salt charge to the new salt charge. As the concentration of Li was above the solubility limit for 0.6 and 1wt% tests, a significant fraction was likely present as a colloidal suspension. Sample transfer was accomplished via specially fabricated tongs, which allowed for the transfer time to be less than 5 seconds. Upon completion of the exposure, the old salt charge was removed from the furnace and allowed to cool to room temperature. The cooled salt ingot was then dissolved in deionized (DI) water. The crucible was then washed with DI water, dried with isopropyl alcohol, and dried under vacuum prior to re-use for the next salt charge for the same solution chemistry conditions. Two Ni crucibles were alternated between for each solution chemistry.

Following completion of the exposure period, the samples were removed from the furnace and allowed to cool to room temperature in the glove box atmosphere. All samples were stored in the Ar glove box between analytical procedures. As it was unknown if the surface films formed on the corrosion specimens would be stable in atmosphere, surface analysis was performed both prior to and following removal of the residual salt layer. Following the initial surface analytical procedures, residual LiCl was removed by placing each sample in 25 ml of HPLC grade methanol for 15 minutes with constant agitation. Prior to the methanol rinsing procedure, all surface analysis was performed under inert atmosphere or vacuum conditions, depending on technique. The data presented here were collected following the methanol rinsing procedure, as the residual salt layer significantly interfered with surface analysis as has been described earlier.31 No chemical or morphological changes were observed as a result of the methanol rinsing procedure. Gravimetric weight change measurements were performed following the methanol rinsing procedure.

All samples exposed to Li containing melts were cross sectioned using a Buehler cubic-BN wafering blade on a slow speed saw and polished according to Buehler’s published procedures to a 0.05 μm surface finish prior to analysis. Samples exposed to LiCl-Li2O in the absence of Li were investigated using only FIB milling for cross sectional analysis due to the relatively shallow depths of attack. EDS of the sample surfaces was performed using an Hitachi S-4700 and EDS data was collected via the attached Oxford Instruments energy dispersive X-ray spectrometer. The electron beam was operated at an accelerating voltage of 5 kV for surface morphology images, while 20 kV was used for collection of EDS spectra. Emission current was maintained at 10 μA. FIB milling and subsequent SEM-EDS analysis for cross sectional images was performed using a FEI Scios dual-beam FIB/SEM equipped with a TEAM Pegasas Integrated EDS-BSD. The same dual-beam FIB/SEM was used to perform the SEM-EDS analysis of all of the cross sectioned samples, including those mechanically cross sectioned and polished. The electron beam was operated at 20 kV for both imaging and EDS analysis.

The exposed surface area was calculated based on the measured submersion depth of each sample. The average corrosion rate in mm/year and the mass loss rate in ng cm⁻² hr⁻¹ was then calculated based on the mass change, density of the alloy, exposed surface area, and length of exposure.

Results

The surface of 1625 samples exposed to LiCl-Li2O solutions in the absence of Li displayed a high degree of crystallinity indicative of a well-formed oxide layer, while the surfaces of samples exposed to LiCl-Li2O in the presence of metallic Li showed a very porous, almost sponge-like microstructure. To illustrate these points, the SEM micrographs taken of the 1625 samples exposed to LiCl-Li2O containing 0, 0.3, 0.6, or 1wt% Li for 500 hr are shown in Figure 1.

In the absence of Li, the oxide layer is well formed and shows evidence of a multi layered structure that is discussed in greater detail below. EDS analysis of the area shown in Figure 1a showed that the surface was composed of 22% Cr, 66% O, and 13% Ni, with minor quantities of other elements present as a result of pre-existing Ni-based oxide layer. Li is not detectable via EDS, however, spectroscopic analysis has definitively shown this compound to be Li2O3.36 The presence of Li in the molten LiCl-Li2O solution destabilizes the oxide layer and forms a very porous microstructure that is similar in appearance to a Ni foam. EDS analysis of these areas consistently showed greater than 80% Ni, with high depletion of Cr, Mo, and Nb, although the Ni-Fe ratio remained close to that of the base material. There was little difference between the microstructures observed at low and high Li concentrations, with the microstructure of the 1625 samples exposed to melts containing 0.3wt% Li displaying microstructures nearly identical to samples exposed to melts containing 1wt% Li. Exposure periods of 500 hr and 1000 hr both yielded nearly indistinguishable microstructures, as can be observed by comparing the micrographs of 1625 samples exposed to LiCl-Li2O containing 0, 0.3, 0.6, and
Figure 1. SEM micrographs of J625 exposed to LiCl-1wt%Li_2O at 650°C containing A) no Li, B) 0.3wt%Li, C) 0.6wt%Li, and D) 1wt%Li for 500hr and rinsed with methanol.

Figure 2. SEM micrographs of J625 exposed to LiCl-1wt%Li_2O at 650°C containing A) no Li, B) 0.3wt%Li, C) 0.6wt%Li, and D) 1wt%Li for 1000hr and rinsed with methanol.
1wt%Li for 1000hr shown in Figure 2 to the micrographs presented in Figure 1. Variations in Li$_2$O concentration and exposure length did not dramatically alter the morphology observed on the 1625 samples exposed to LiCl-Li$_2$O-Li compared to those shown in Figures 1 and 2. Consistent morphology was observed in the presence of Li, with all samples displaying similar structures. Likewise, in the absence of Li, a well-developed, highly crystalline oxide layer was consistently observed. Additionally, the surface of the 1625 sample exposed to LiCl-2wt%Li$_2$O-0wt%Li for 500hr had a small number of locations where the oxide layer had partially delaminated, which allowed for direct observation of the layered structure of the oxide films formed on 1625 during exposure to LiCl-Li$_2$O in the absence of Li. SEM micrographs of one of these locations are shown in Figure 3, and the compositions of locations 1 through 4 detected via EDS are given in Table I.

The presence of a multilayered oxide structure is easily discernible in this image. Each layer was analyzed using EDS at the spots marked by the arrows. The layers were numbered 1 through 4 starting with the innermost and proceeding outward. Due to the composition of Layer 2 and the lack of Ti in both Layers 1 and 2, which is present as an impurity in the Li$_2$O used in this study, it is thought that Layer 1 is the result of the inward diffusion of O into the base material. The O concentration of Layer 2 is much lower than in any of the other layers observed here, and its composition is the most similar to the base alloy, although all areas analyzed were notably depleted in Mo and Nb. The size of the grains in Layer 2 and their relative orientations are also similar to the morphology of the 1625 samples exposed to LiCl-Li$_2$O in the presence of Li, as can be observed by comparison with Figures 1 and 2, indicating that this is likely the base material which has been depleted in Cr to facilitate the outward growth of Layers 3 and 4. These outermost layers differ in both morphology and composition, suggesting a difference in the compounds that compose them. Layer 3 is the layer closest to the base material, and has a plate-like morphology. The high Ni content of Layer 3 compared to Layer 4 implies that Layer 3 is composed of primarily NiFe$_2$O$_4$, with a relatively low volume of oxide, while Layer 4 is primarily NiO$_2$ based. Both Layer 3 and Layer 4 have incorporated Ti from the impurities present in the LiCl used in this study. The spheroidal morphology of Layer 4 suggests that its growth begins at specific nucleation sites. Some of these spheroids from Layer 4 appear to be broken or incompletely formed, showing that they are hollow. Figure 4 shows the results of EDS mapping of Ni, Fe, Cr, and O for the same location shown in Figure 3 which further highlights the differences between the layers observed on this sample.

### Cross section SEM-EDS

The cross sections of the samples were investigated to determine the depth to which the degradation of the surface penetrated into the bulk of the sample. In the absence of Li, the penetration into the bulk of the sample was minimal, as evidenced by Figures 5 and 6, which show the FIB milled cross-section of the 1625 samples exposed to LiCl-1wt%Li$_2$O-0wt%Li at 650°C for 500hr and 1000hr, respectively. Small pores of less than 2μm in diameter were observed immediately below the outer oxide layer for the 500hr sample, corresponding to a layer of Mo enrichment as evidenced in Figure 5d. As shown in the EDS analysis of this sample previously, the oxide layer does not incorporate a significant amount of Mo, indicating that the surface enrichment of Mo is deleterious to the integrity of the base material. At an exposure period of 500hr, the thickness of the oxide layer is approximately 1μm, while the thickness of the Mo enriched layer containing the pores is approximately 2μm. Based on a total thickness of 3μm, the corrosion rate was calculated to be 0.05mm/year.

Careful observation of the EDS maps in Figures 5b through 5f shows that Cr is depleted in this region. Consequently, our hypothesis is that the pores are a result of the diffusion of Cr toward the surface to form the outer oxide layer, causing contraction of the base material at the interface between the base alloy and the oxide layer. As corrosion proceeds, the diffusion of Cr from the bulk alloy becomes the limiting factor, and the surface of these voids then form the Cr-based oxide layer. The increased volume of the oxide eventually fills in the void space. The growth and subsequent infill of these voids may give rise to the multi-layered oxide structure observed on the samples exposed to identical conditions for 1000hr in Figure 6. The lack of voids observed in Figure 6 may be due to the path required for diffusion of Cr from the alloy. This is supported by near complete depletion of Cr in the Ni and Fe rich layers between the Cr-based oxides.

### Table I. EDS compositional analysis obtained for locations 1 through 4 marked in Figure 3B for the 1625 sample exposed to LiCl-2wt%Li$_2$O-0wt%Li at 650°C for 500hr:

<table>
<thead>
<tr>
<th>Element</th>
<th>Layer 1 Atomic%</th>
<th>Layer 2 Atomic%</th>
<th>Layer 3 Atomic%</th>
<th>Layer 4 Atomic%</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>62.43</td>
<td>11.22</td>
<td>63.07</td>
<td>64.78</td>
</tr>
<tr>
<td>O</td>
<td>1.35</td>
<td>2.56</td>
<td>3.14</td>
<td>3.14</td>
</tr>
<tr>
<td>Mg</td>
<td>0.41</td>
<td>0.27</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>Cr</td>
<td>18.34</td>
<td>3.33</td>
<td>12.99</td>
<td>20.08</td>
</tr>
<tr>
<td>Fe</td>
<td>0.61</td>
<td>3.74</td>
<td>1.21</td>
<td>0.32</td>
</tr>
<tr>
<td>Ni</td>
<td>15.23</td>
<td>80.97</td>
<td>21.44</td>
<td>5.13</td>
</tr>
<tr>
<td>Mo</td>
<td>0.9</td>
<td>0.74</td>
<td>0.46</td>
<td>0.32</td>
</tr>
</tbody>
</table>

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For the 625 sample exposed to LiCl-1wt%Li2O-0wt%Li for 1000hr, the corrosion rate was approximately 0.07mm per year, indicating that corrosion was approximately linear for these experiments. The oxide film was well developed, and showed a multi-layered structure similar to that shown for the 625 sample exposed to LiCl-2wt%Li2O-0wt%Li for 500hr in Figures 3 and 4. The Mo enriched layer below the outer corrosion layer was still observed, however, there were no voids located in the area as there were on the 500hr sample. Mo accumulation was also observed at the grain boundaries, along with Cr and Nb, which is likely due to thermal aging of the microstructure, rather than a result of exposure to the molten LiCl-Li2O solution. Although enrichment of Cr, Mo, and Nb were observed along the grain boundaries, carbon was not observed at these locations, so it cannot be concluded that sensitization was observed. Corrosion did not proceed along the grain boundaries, so it seems that the enrichment of the grain boundaries in Cr, Mo, and Nb did not negatively impact the observed corrosion rate. However, sensitization followed by intergranular corrosion was observed in our previous work on SS316L under similar conditions.

As was observed via SEM imaging of the sample surfaces, the cross sections of the 625 samples exposed to LiCl-Li2O in the presence of Li were consistent in morphology and showed an outer layer of a highly porous Ni rich foil-like structure. The formation of this porous layer is believed to be a result of the selective dissolution of Cr, Mo, and Nb from the base material, leaving the Ni-Fe matrix in place, similar to the formation of Rainey Nickel by the selective dissolution of Al from Ni-Al alloys. This mechanism is likely similar to the void formation observed in Figure 5, as diffusion of elements within the alloy is unlikely to be affected by the solution chemistry. The SEM images of the cross sections of the 625 samples exposed to LiCl-1wt%Li2O containing 0.3, 0.6, or 1wt% Li at 650°C for 500 and 1000hr are shown in Figure 7. For the sample exposed to LiCl-1wt%Li2O-0.3wt%Li for 500hr, the porosity penetrated into the surface to a depth of approximately 30μm, corresponding to a corrosion rate of 0.53mm/year. However, all other samples consistently showed a penetration depth of 15μm, regardless of Li concentration or period of exposure, indicating that a direct measure of the corrosion rate is not necessarily applicable for these specimens. The similarity in the morphology and depth of attack regardless of Li concentration or
Figure 6. SEM micrograph (a) and EDS mapping analysis of the FIB milled trench on the B625 sample exposed to LiCl-1wt%Li$_2$O for 1000hr showing variation in concentration of (b) Cr, (c) Ni, (d) Mo, (e) Fe, (f) Nb, (g) Ti, and (h) O. The multi-layered structure observed here corresponds to a similar oxide layer structure observed in Figures 3 and 4. Again, Mo enrichment is seen immediately below the corrosion layer, without significant incorporation of Mo into the oxide layer itself. The precipitate seen at a depth of 17μm consists largely of Ti, Mo, and Nb. Cr, Mo, and Nb were also observed to be enriched along the grain boundaries.

The variation in composition as a function of depth was investigated via EDS of the cross sections. As all samples exposed to LiCl-Li$_2$O in the presence of Li displayed similar variations in composition, the SEM-EDS results for the B625 sample exposed to LiCl-1wt%Li$_2$O-1wt%Li at 650°C for 1000hr are shown in Figure 8, while spot EDS analysis for the locations shown in Figure 8a are given in Table II. Cr, Mo, and Nb are all significantly depleted from the material remaining in the porous layer, leaving primarily Ni, with Fe remaining at approximately the same ratio as in the base material. The depletion of Cr, Mo, and Nb was also observed to irregularly penetrate into the sample beyond the depth of the porous layer. The loss of the amount

Figure 7. Cross section SEM images for B625 samples exposed to LiCl-1wt%Li$_2$O containing 0.3wt% Li for (a) 500hr or (b) 1000hr, 0.6wt%Li for (c) 500hr or (d) 1000hr, or 1wt%Li for (e) 500hr or (f) 1000hr. The porous microstructure observed via SEM of the sample surface was also observed in cross section, and was consistent amongst samples exposed to LiCl-Li$_2$O in the presence of Li.
of Cr, Mo, and Nb necessary to reach the composition of spot 1 shown in Figure 8a represents the loss of a significant fraction of the material, which may account for the porous microstructure seen on this sample and other I625 samples exposed to LiCl-Li2O in the presence of Li.

Conclusions

I625 samples were exposed to molten LiCl solutions containing 1 or 2wt% Li2O and 0, 0.3, 0.6, or 1wt% Li maintained at 650°C for periods of 500 and 1000hr to investigate the effect of metallic Li on the degradation of the material. In the absence of metallic Li, I625 formed a highly crystalline, stable oxide film with a multi-layered structure that limited corrosion to approximately 0.05 to 0.07mm/year. The presence of metallic Li in solution prevented the formation of any substantial oxide film, resulting in a highly porous, foam-like structure. The depletion of Cr, Mo, and Nb from the surface was also observed on these samples via EDS, indicating that these elements were preferentially leached from the base material by the molten solution. The loss of these elements from the sample surface, which together constitute one-third of the material, is likely responsible for the highly porous microstructure observed.

Acknowledgments

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A7.3: Effect of Metallic Li on the Surface Chemistry of Inconel 625 Exposed to LiCl-Li$_2$O-Li
Effect of Metallic Li on the Surface Chemistry of Inconel 625 Exposed to Molten LiCl-Li2O-Li

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This study explores the surface chemistry of Inconel 625 samples exposed to molten LiCl-Li2O-Li solutions at 650°C for 500 and 1000 h and aims to understand the effect of solubled Li on corrosion behavior in molten LiCl-Li2O-Li. The surfaces of Inconel 625 samples were analyzed using X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy. The oxide films formed on the surface of the samples in the absence of Li is composed of Li2Co3O4 with small contributions of Li2CO3 and Na2Co3O4. However, the presence of Li was observed to destabilize these compounds, resulting in a primarily metallic surface with trace amounts of oxidized Cr, Mo, and Nb present depending on the concentration of Li in solution.

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Experimental

J625 coupons were cut from a 3.175 mm plate obtained from High Performance Alloys with the following nominal composition: 58% Ni, 20-23% Cr, 5% Mn, 5% Mo, 3.15-4.15% Nb, 0.5%-0.6% Al, 0.4%-0.8% Ti, and 0.5%-1% Si. The composition of this alloy as measured via the EDS used for cross sectional investigation was 62.3% Ni, 25.4% Cr, 6.5% Mn, 5% Mo, 0.5% Fe, and 2.6% Nb. Duplicate coupons were exposed molten solutions of LiCl containing either 1 or 2 wt% Li2O, and either 0, 0.3, 0.6, or 1.8% Li over exposure periods of either 500 or 1000 h. Considering the evaporation of Li and Li2O over time that was observed in other short-term studies and the extended exposure periods of this study, the salt charge for each test was replaced at a period of once every 96 hours to maintain the solution chemistry.

To minimize the effects of impurity H2O, LiCl was dried in a vacuum oven in air at 200°C for 24 hours before being transferred into the glove box for storage. Additionally, the LiCl was baked for 2 hours at 550°C immediately prior to melting and subsequent addition of Li2O and Li. The surface analysis presented here was conducted on the samples prepared for our previous work. More details on the experimental procedure and morphology of these samples can be found in that publication. All surface analysis was performed prior to removal of the residual salt layer, as well as following removal of the salt layer, which was accomplished by rinsing the sample in 25 mL of ACS grade methanol for 15 minutes with continuous agitation.

Great care was taken to maintain sample integrity at all times during analyses. Prior to methanol rinsing, all surface analyses was conducted under inert or ultra-high vacuum (UHV) conditions, as dictated by each technique. Raman studies were performed inside the Ar glove box using a fiber optic coupled probe. For XPS analyses, the samples were transferred from the glove box to the UHV chamber in a sealed transfer chamber to prevent atmospheric contamination (PHI Model 04-110). This transfer vessel has been extensively verified to protect reactive samples from atmospheric contamination during transfer under various conditions. A glove box was installed on the transfer port of the XPS and purged with dry nitrogen for 30 minutes prior to sample removal to reduce atmospheric contamination of the samples during removal from the instrument. The samples were then re-sealed inside the PHI 04-110 transfer chamber for transfer back to the glove box. As described in our earlier work, XRD studies were then conducted on samples which were sealed in plastic bags in the argon atmosphere of the glove box. No hydrated LiCl peaks were detected via XRD, indicating that there was insignificant moisture contamination.

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on the samples this point, however, peaks indicative of Li$_2$CrO$_4$ were observed on the samples exposed to LiCl-Li$_2$O in the absence of Li (see supplemental information). Finally, sample surfaces were studied using SEM-EDS prior to methanol rinsing. Due to the design of the transfer port of this instrument, it was necessary to momentarily expose the samples to atmosphere prior to pumping down of the SEM entry chamber. Total exposure time to atmosphere was less than 30 seconds. After SEM studies, the samples were then immediately rinsed with methanol as described above to remove the residual salt layer. Moisture content of the methanol was not analyzed, but typical moisture concentration was specified to be lower than 100 ppm. Following removal of the salt layer, the samples were immediately re-analyzed via SEM-EDS. No morphological or compositional changes were detected following methanol rinsing. Samples were stored inside the Ar glove box at all times other than for analysis. The surface analytical results from post methanol rinse were consistent with the results from pre-methanol rinse; however, the removal of the residual salt allowed for more accurate determination of the surface chemistry, as in many cases, the salt layer partially obstructed the surface from analysis, particularly with XPS (see supplemental information). The lack of substantial surface oxides on the samples exposed to LiCl-Li$_2$O solutions containing Li indicates that the surface analysis procedures outlined above had minimal impact on the surface chemistry of these samples. As has been shown previously, no chemical or morphological changes to the sample surface were observed to result from the methanol rinsing procedure.

As such, the spectra reported here were collected from the sample surfaces following removal of the salt layer due to the improved data quality afforded by the increased signal to noise ratio.

X-ray diffraction was performed using a Rigaku Smartlab X-ray diffractometer with a Cu Kα source operating at 44kV and 40mA. Parallel beam optics in a grazing angle configuration were used for detection of the thin surface films formed on the samples in this study. The incidence angle was set at 1°, and the diffraction pattern was recorded over a range of 10° to 90° 2θ for all diffraction patterns. For each diffraction pattern, the scan speed was optimized to yield an intensity of 5000 counts for the highest peak, while the step size was varied to give 5 steps at the full width at half-maximum intensity of the narrowest peak.

Raman spectroscopy was performed using a Thermo Scientific DSR Raman microscope utilizing a 10mW 532nm continuous wave laser. Spectra were collected through the 50x objective lens of the microscope using a 50μm incident beam slit. The collection time was 4 seconds per spectra, and 16 individual spectra were averaged to give the spectra reported here.

X-ray photoelectron spectroscopy was performed using a PHI 5600 spectrometer equipped with an Al-Kα source with a photon energy of 1486.6eV. The source was operated at an accelerating voltage of 14kV and an anode power of 300W. The spectrometer dispersion and work function were calibrated to the Au 4f7/2 peak at 84.00eV and the Cu 2p$_{3/2}$ peak at 932.67eV to an accuracy of ±0.05eV. Survey spectra were recorded with a step size of 0.5eV, while narrow scans were collected at a step size of 0.025eV for the elements detected on the sample surfaces. Peak fitting was performed with SDP version 4.6 Gaussian fitting software. Charge correction was performed to the adventitious C 1s peak at 284.8eV.

**Results**

**XRD**—The X-ray diffraction pattern collected for the 1625 sample exposed to LiCl-Li$_2$O containing 1% Li$_2$O for 1000hr is shown in Figure 1. The peaks displayed in this pattern are representative of those collected for all samples exposed to LiCl-Li$_2$O solutions in the absence of Li. The only crystalline phases detected on these samples were the base material and peaks consistent with Li$_2$CrO$_4$. When this result is considered along with Raman and XPS analysis of these samples shown below, it can be concluded that the oxide scale is composed largely of Li$_2$CrO$_4$ when 1625 is exposed to melt LiCl-Li$_2$O solutions in the absence of Li.

The presence of Li$_2$O in solution creates a very reducing environment, preventing the formation of the well-developed Li$_2$CrO$_4$ films observed on these samples in the absence of Li. Consequently, the diffraction patterns for all samples exposed to LiCl-Li$_2$O solutions containing Li displayed diffraction patterns indicative only of the base material, as can be observed in Figures 2 and 3. These figures show the diffraction patterns of 1625 samples exposed to LiCl-Li$_2$O solutions containing 0, 0.3, 0.6, or 1wt% Li for 500hr (Figure 2) or 1000hr (Figure 3). This corresponds with the observation made using SEM of the highly porous metallic surfaces on 1625 exposed to LiCl-Li$_2$O in the presence of Li.

**Raman spectroscopy**—Raman spectra, shown in Figure 4, also confirm the presence of Li$_2$CrO$_4$ in the absence of Li. The Raman spectra of the four samples exposed to molten LiCl-Li$_2$O solutions...
in the absence of Li, displaying prominent peaks of both the LiCrO$_2$ $A_{1g}$ and $E_g$ modes at 572cm$^{-1}$ and 445cm$^{-1}$, respectively. An additional hump on the shoulder of the LiCrO$_2$ $A_{1g}$ peak is believed to be indicative of a spinel of the type NiFe$_2$Cr$_2$O$_4$, based on the work of Hosterman. The exact composition of this compound is unknown, but is likely skewed toward Cr-rich compounds, due to the relatively low concentration of Fe in the 1625 alloy. The 1625 sample exposed to LiCl-1wt% Li$_2$O at 650°C also displayed features at 845cm$^{-1}$ and 340cm$^{-1}$ that indicate the presence of Li$_2$CrO$_3$ based on the collection of Raman spectra of this compound in our laboratory. It is currently unknown why the other 1625 samples exposed to similar conditions did not display the features of Li$_2$CrO$_3$.

The effect of Li on the Raman spectra of 1625 exposed to LiCl-Li$_2$O-Li solutions can be observed in Figure 5, which shows the Raman spectra of 1625 samples exposed to LiCl-1wt% Li$_2$O solutions containing 0, 0.3, 0.6, and 1wt% Li at 650°C for 500hr. The well-defined Raman modes observed in Figure 4 are seen to be largely absent in the presence of Li. The broad features that roughly align with the positions of the compounds observed in the absence of Li may indicate minute quantities of these compounds on the sample surface. XPS analysis presented below confirms the presence of small amounts of oxidized Cr, Mo, and Nb on the surface of the 1625 samples exposed to LiCl-Li$_2$O in the presence of Li.

Figure 4. Raman spectra of 1625 samples exposed at 650°C to LiCl containing: a) 1wt% Li$_2$O for 500hr, b) 1wt% Li$_2$O for 1000hr, c) 2wt% Li$_2$O for 1000hr and d) 2wt% Li$_2$O for 1000hr. The $A_{1g}$ and $E_g$ peaks of LiCrO$_2$ and a hump indicative of the $A_{1g}$ peak of NiFe$_2$Cr$_2$O$_4$ were observed on all samples exposed to LiCl-Li$_2$O solutions in the absence of Li. Additionally, the 1625 sample exposed to LiCl-1wt% Li$_2$O for 1000hr displayed peaks indicative of Li$_2$CrO$_3$. 

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Table I. Peak fitting parameters for Cr 2p_{3/2} spectra shown in Figures 7 and 8. Charge correction to the adventitious C 1s line at 284.6 eV was performed.

<table>
<thead>
<tr>
<th>Peak</th>
<th>BE</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr0</td>
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</tr>
<tr>
<td>Cr2+</td>
<td>574.2</td>
<td>2.4</td>
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<td>Cr6+</td>
<td>578.2</td>
<td>1.8</td>
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</tbody>
</table>

the case of the samples exposed to LiCl-Li_{2}O solutions in the absence of Li, the surface was primarily composed of Cr O, and Li, further confirming the presence of LiCoO_{2} on these samples. For the B65 sample exposed to LiCl-LiO solutions for 1000h, Ni was also detected via XPS; however, Ni was not detected on the surface of the other samples exposed to LiCl-Li_{2}O solutions in the absence of Li, further indicating that this sample had somewhat different surface chemistry when compared to the other samples exposed to similar conditions.

For B65 samples exposed to LiCl-Li_{2}O in the presence of Li, Ni was the primary element present, while the Cr level was depleted and most of the primary alloying elements were detected in trace amounts. Our previous work has shown that these compounds were also detected on the surface of numerous samples that do not contain Ti as an alloying element, notably SS316L, and thus must be the result of electrodeposition of Ti oxide and nitride compounds from Ti impurities present in the LiCl used in these studies. This will not be discussed further in the present work.

The chemistry of Cr, being the primary alloying element in B65 as well as being responsible for corrosion inhibition through the formation of stable oxide films, is important to understand thoroughly. XPS narrow scans of the Cr 2p_{3/2} spectra obtained from the surface of the B65 samples exposed to LiCl containing 0.3, 0.6, 1 wt% Li and 0.3, 0.6, and 1 wt% Li at 650°C for 1000h. Survey spectra of the B65 samples exposed to varying LiClO_{2} concentrations and exposure periods showed similar features and trends.
the samples exposed to LiC3-Li2O melts containing Li is currently unknown, and will require further investigation. While Ni was not observed on the surface of most of the samples exposed to LiC3-Li2O in the absence of Li, it was observed on the In2S3 sample exposed to LiC3-1wt% Li2O for 1000h, as well as on all samples exposed to LiC3-Li2O-Li solutions. As shown in Figure 8, in the absence of Li, Ni was observed in a mixed valence state, showing both metallic as well as oxidized character. The presence of oxidized Ni on the surface of this sample supports the observations made via Raman of the presence of a spinel of the form NiFe2O4 in the oxide film of these samples. Fitting of these spectra was not performed due to the known difficulties associated with peak fitting Ni 2p XPS spectra without precise parameters obtained from standards with identical composition. Peaks shapes and positions consistent with metallic Ni were observed on all samples exposed to LiC3-Li2O in the presence of Li. No charge correction was necessary for the Ni spectra.

While Mo was not observed in detectable quantities via XPS of the surfaces of In2S3 samples exposed to LiC3-Li2O solutions in the presence of Li due to the thick Li2O2 surface film and the relatively low concentration of Mo in the base alloy, it was observed on the surface of the majority of the samples exposed to LiC3-Li2O in the presence of Li. The XPS narrow scans of the Mo 3d region are shown in Figure 10. At 0.3wt% Li, Mo behaved similarly to Cr in that it was present in a mixed metallic and oxidized state.26,27 Due to the noise, presence of multiple overlapping peaks on these spectra, and the known tendency for photoreduction of Mo, peak fitting was not performed, although the apparent positions of the primary peaks are demarked by vertical lines on the charts in Figure 10. The In2S3 samples exposed to LiC3-Li2O in the presence of 0.6 and 1wt% Li showed only the characteristic asymmetric peaks of metallic Mo. This transition from mixed metallic and oxidized character at low Li concentrations to a purely metallic state at higher Li concentrations indicates that the activity of Li in solution is not unity until beyond the solubility limit. While both Cr and Mo were observed to be present in a mixed state containing oxidized and reduced species in the presence of Li, Nb was only observed in oxidized states.28 The narrow scans of the Nb 3d region obtained from the surface of In2S3 samples exposed to molten LiC3 solutions containing 1 or 2wt% Li2O and 0.3, 0.6, or 1wt% Li for 1000h are shown in Figure 11, with the exception of the In2S3 sample exposed to LiC3-1wt% Li2O-1wt% Li for 1000hr, as Nb

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Figure 9. Ni 2p XPS narrow scans obtained from the 1625 samples exposed to LiCl-1wt% Li2O containing a) 0wt% Li, b) 0.3wt% Li, c) 0.6wt% Li, and d) 1wt% Li at 650°C for 1000hr. In the absence of Li, Ni is observed in a mixed metallic and oxidized state, indicating the presence of small amounts of Ni compounds in the oxide layer. In the presence of Li, Ni was only observed in the pure metallic state. No charge correction was performed necessary for Ni, indicating that it was consistently in electrical contact with the base material.

Figure 10. Mo 3d XPS narrow scans obtained from the surface of 1625 samples exposed for 1000hr to molten LiCl containing a) 1wt% Li2O and 0.3wt% Li, b) 1wt% Li2O and 0.6wt% Li, c) 1wt% Li2O and 1wt% Li, d) 2wt% Li2O and 0.3wt% Li, e) 2wt% Li2O and 0.6wt% Li, and f) 2wt% Li2O and 1wt% Li. At concentrations of 0.3wt% Li, Mo shows a mixed oxide state.

Figure 11. Nb 3d XPS narrow scans obtained from the surface of 1625 samples exposed for 1000hr to molten LiCl containing a) 1wt% Li2O and 0.3wt% Li, b) 1wt% Li2O and 0.6wt% Li, c) 2wt% Li2O and 0.3wt% Li, d) 2wt% Li2O and 0.6wt% Li, and e) 2wt% Li2O and 1wt% Li. Nb was not observed on the 1625 sample exposed to LiCl-1wt% Li2O-1wt% Li for 1000hr. Nb was not observed to be present as Nb⁷⁺ and Nb⁵⁺, however, metallic Nb was not observed.
was not detected on this sample. The presence of only oxidized Nb even in the presence of high Li concentrations is counter intuitive, as work by Jeong, et al. showed that the reduction of NbO$_2$ to metallic Nb was able to be accomplished in LiCl-Li$_2$O, primarily through the indirect reaction with Li which was electrolytically generated at the cathode, similar to the reduction of UO$_2$. Minor alloying elements, Fe and Al, were not analyzed in this study. The oxide film on the samples exposed to LiCl-Li$_2$O in the absence of Li did not have detectable quantities of Fe on its surface, however Fe was detected in extremely small quantities on some of the samples exposed to LiCl-Li$_2$O solutions containing Li. Auger electrons from Ni using the Al Kα source interfered with these peaks, and switching the X-ray source to Mg Kα X-rays did not provide adequate signal intensity to reliably peak fit the Fe 2p spectra. Detection was not consistent from sample to sample. Consequently, interpretation of the Fe 2p spectra was not attempted. Al was not detected on the surface of any sample via XPS, regardless of X-ray source.

Conclusions

Investigation of the surface chemistry of 1625 samples exposed to molten LiCl-Li$_2$O-Li$_2$O solutions at 650°C for 500 and 1000hr was performed via XRD, Raman spectroscopy, and XPS. In the absence of solvated LiF, the surface of 1625 forms a stable LiCl$_2$O$_3$ based surface film with minor inclusions of Li$_2$Cr$_2$O$_7$ and NiFe$_2$O$_4$ which acts to limit corrosion of the base alloy. Corrosion of the base alloy in molten LiCl-Li$_2$O is thus expected to be dictated by the O$_{2-}$ activity and the presence of impurities, similar to the corrosion processes typical in other molten salt systems. When Li is dissolved in the molten LiCl-Li$_2$O system, the formation of a bulk oxide film on the sample surfaces, even up to high concentrations of Li in solution. This indicates that there is a synergistic effect between the oxidation caused by the O$_{2-}$ ions and the reducing nature of solvated LiF that allows for the effective dissolution of Cr, Mo, and Nb, although further investigation would be necessary to confirm this hypothesis. Our earlier work showed that the alloy was depleted of these elements at the sample surface and in the regions displaying the highly porous microstructure seen via SEM-EDS. Consequently, it is likely that the diffusion of Cr, Mo, and Nb through the alloy microstructure and their subsequent dissolution in to the molten LiCl-Li$_2$O-Li$_2$O system is responsible for the porosity observed in that study.

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