Materials Corrosion in Molten LiF-NaF-KF Eutectic Salt

by

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Static corrosion studies were undertaken to determine the compatibility of several candidate high temperature materials for a heat transfer loop in a molten alkali fluoride eutectic salt, LiF-NaF-KF: 46.5-11.5-42 mol % (commonly referred to as FLiNaK), as well as a molten chloride near eutectic salt, KCl-MgCl$_2$: 68-32 mol %. Several high temperature alloys: Hastelloy-N, Hastelloy-X, Haynes-230, Inconel-617, and Incoloy-800H, Nb-1Zr, a nearly pure Ni alloy Ni-201, and a C/SiSiC ceramic were exposed to molten FLiNaK at 850°C for 500 h in sealed graphite crucibles under an argon cover gas. Corrosion occurred predominantly from dealloying of Cr from the Cr bearing alloys, an effect that was particularly pronounced at the grain boundaries. Corrosion was noted to occur from selective attack of the Si phase in the C/SiSiC ceramic. Alloy weight-loss/area due to molten fluoride salt exposure correlated with the initial Cr-content of the alloys, and was consistent with the Cr-content measured in the salts after corrosion tests. The alloys’ weight-loss/area was also found to correlate to the concentration of carbon present in the nominally 20% Cr containing alloys, due to the formation of chromium carbide phases at the grain boundaries. The corrosion mechanisms for the chloride based salt were found to be similar to those observed in FLiNaK, but the chemical attack was found to be less aggressive.

Sulfamate Ni electroplating and Mo plasma spraying of Fe-Ni-Cr alloy coupons was investigated to mitigate Cr dissolution. A chemical vapor deposited pyrolytic carbon and SiC
coating was also investigated to protect the C/SiSiC composites. Results indicate that Ni-plating has the potential to provide protection against alloy corrosion in molten fluoride salts. Furthermore, the presence of a chromium-oxide interlayer at the interface of the Ni-plating and alloy substrate can further improve the efficacy of the Ni-plating. The pyrolytic carbon and SiC coating on the C/SiSiC composites was effective in eliminating the attack of the Si phase in the composites. Delamination of the Mo coating in FLiNaK prevented further investigation of this promising approach.
Abstract

Use of hydrogen for transportation fuel can potentially supplement gasoline in the mid-term, replace it in the long-term and lead to a lower environmental impact than gasoline if produced through carbon-neutral energy sources. Economical production of hydrogen could be a significant step towards increasing national energy independence. The production of hydrogen utilizing process heat derived from a high temperature nuclear reactor could realize this possibility. For this, the hydrogen production plant should be co-located with a nuclear power plant, but from a safety standpoint it should be separated by a reasonable distance.

Molten salts have the potential to be excellent heat transport fluids for the heat exchange loop because of their high boiling point, low vapor pressure, large specific heat and thermal conductivity, chemical stability, and high density at low pressures. However, materials corrosion has been identified to be a significant problem in these molten salts, particularly at the high temperatures required for thermochemical hydrogen production. With this background, static corrosion studies were undertaken to determine the compatibility of several candidate high temperature materials for the heat transfer loop in a molten alkali fluoride eutectic salt, LiF-NaF-KF: 46.5-11.5-42 mol %, as well as to a molten chloride near eutectic salt, KCl-MgCl₂: 68-32 mol %.

LiF-NaF-KF: 46.5-11.5-42 mol % is commonly referred to as FLiNaK and is emerging as one of the leading candidate salts for the transfer of high temperature process heat from a nuclear reactor to a hydrogen production plant and other chemical industries. KCl-MgCl₂: 68-32 mol %, is another promising salt for this application, and was chosen for limited investigation to compare the corrosion in fluoride-based salts to the chloride-based salts. Heat transfer properties of KCl-MgCl₂ salt approach those of FLiNaK, but it is considerably less expensive. One alloy, Incoloy 800H, was also exposed to molten FLiNaK that was obtained from different sources and therefore purities, primarily to understand the effects of hydrofluorination and salt purity on corrosion.
Several high temperature Fe-Ni-Cr and Ni-Cr alloys: Hastelloy-N, Hastelloy-X, Haynes-230, Inconel-617, and Incoloy-800H, and a C/SiSiC ceramic were exposed to molten FLiNaK with the goal of understanding the corrosion mechanisms and ranking these materials for their suitability for molten fluoride salt heat exchanger and thermal storage applications. The tests were performed at 850°C for 500 h in sealed graphite crucibles under an argon cover gas. Corrosion was noted to occur predominantly from dealloying of Cr from the alloys, an effect that was particularly pronounced at the grain boundaries. In the ceramic, corrosion was noted to occur from selective attack of the Si phase in the C/SiSiC ceramic. Alloy weight-loss per unit area due to molten fluoride salt exposure correlated with the initial Cr-content of the alloys, and was consistent with the Cr-content measured in the salts after corrosion tests. The alloys’ weight-loss/area was also found to correlate to the concentration of carbon present in the nominally 20% Cr containing alloys, due to the formation of chromium carbide phases at the grain boundaries. Two Cr-free alloys, Ni-201 and Nb–1Zr, were also tested. Ni-201, a nearly pure Ni alloy with minor alloying additions, exhibited good resistance to dissolution, whereas Nb–1Zr alloy exhibited extensive embrittlement due to carburization. The differing FLiNaK purification methods were not found to dramatically alter alloy corrosion under the test conditions used in this research. The corrosion mechanisms for the chloride based salt were found to be similar to those observed in FLiNaK, but the chemical attack was found to be less aggressive. Cr and Al dissolution as well as grain boundary attack were markedly lower.

The interaction of several alloys with the graphite container during corrosion testing in the molten salt FLiNaK was investigated. The goal was to determine the role of graphite on the corrosion of alloys during the molten salt exposures. To this end, molten salt exposures of Incoloy-800H in sealed Incoloy-800H crucibles under an argon cover gas were performed to compare with the results obtained from the graphite crucibles. The alloy corrosion mechanisms were similar in both graphite and Incoloy-800H crucibles; however alloy corrosion was
considerably accelerated in the graphite crucibles due to the reduction of Cr from solution by graphite.

Sulfaminate Ni electroplating and Mo plasma spraying of Fe-Ni-Cr alloy coupons was investigated to mitigate Cr dissolution from Fe-Cr-Ni alloys in molten FLiNaK. A chemical vapor deposited pyrolytic carbon and SiC coating was also investigated to protect the C/SiSiC composites from selective chemical attack of the Si phase in molten FLiNaK and KCl-MgCl₂ salts. Results indicate that Ni-plating has the potential to provide protection against alloy corrosion in molten fluoride salts. Furthermore, the presence of a chromium-oxide interlayer at the interface of the Ni-plating and alloy substrate can further improve the efficacy of the Ni-plating in providing this corrosion protection. From an engineering standpoint, Ni electroplating offers a commercially viable, cost effective approach for coating inside surfaces of long tubes and other heat exchange systems. The pyrolytic carbon and SiC coating on the C/SiSiC composites was found to be very effective in eliminating the attack of the Si phase in the composites. Delamination of the Mo coating in FLiNaK prevented further investigation of this promising approach, although prolonged heat treatments under an argon cover gas demonstrated the compatibility of the Mo coating with the base alloy.

Based on the promising results for Ni-plating for corrosion protection in molten FLiNaK salt, a detailed study was undertaken to understand the diffusion of Cr through Ni in this environment. A range of diffusion anneals to investigate the Cr diffusion pathways in Ni-plating were undertaken to determine the kinetics of Cr diffusion through the Ni-plating. Additionally, modification of the Ni-plating by thermomechanical processing to promote secondary recrystallization and large grain growth was also investigated to better understand the kinetics of diffusion of Cr through the Ni-plating and to reduce the effective Cr diffusion rate. Through the diffusion anneal studies a model for the diffusion rate as a function of grain size and temperature was developed that predicted that increasing grain size would dramatically decrease Cr diffusion
to the plating surface. When exposed to FLiNaK both an unmodified plating and a modified Ni
plating, whose grains were increased in size through thermomechanical processing, demonstrated
markedly lower diffusion rates than observed under a helium cover gas without FLiNaK
exposure.

The use of the anodic stripping voltammetry and potentiometry electrochemical techniques
was also investigated for evaluation of \textit{in situ} Cr dissolution in molten salts and to provide the
basis for the development of an online corrosion diagnostic in this environment. Both techniques
have presented promising preliminary results and warrant further investigation.
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1 Introduction

Molten fluoride salts have been proposed for use as primary reactor coolants, media for transfer of high temperature process heat from nuclear reactors to H₂ production facilities [1], for solar thermal energy storage [2], and as a means to raise heat-to-electricity conversion efficiencies of solar power towers to about 50% [3]. These salts are characterized by high thermal conductivities, high specific heats, low viscosities, and high boiling points.

Materials corrosion has however been recognized as an issue in high temperature molten salts, and particularly in the molten fluoride salts. In most high temperature industrial environments, materials derive their corrosion resistance from the formation of a tenacious surface film of an oxide of Cr, Al, or Si; elements that are added to the base alloy [4, 5]. In molten fluoride salts these passive oxide films are chemically unstable, and corrosion is driven largely by the thermodynamically driven dissolution of alloying elements into the molten salt environment [6, 7]. An understanding of the propensity of molten fluoride salts to leach out elemental constituents from an alloy can be achieved from phase diagrams, acid–base effects, and the redox potential of the alloy-salt system [8].

In molten fluoride salts, the most active alloying element is selectively attacked by dissolution [8]. A National Aeronautic and Space Administration (NASA) study determined that the tendency for common alloying constituents to corrode in molten fluoride salts increased in the following order: Ni, Co, Fe, Cr, Al, with Al being the most prone to dissolution [2]. In Fe-Ni-Cr based alloys, the primary constituent that is most prone to dissolution is Cr, and in general, Cr content of an alloy correlates with weight-loss [2, 9]. The attack on Cr is all the more significant at carbide forming temperatures (~650°C-1200°C) due to its tendency of Cr-carbides to form at the grain boundaries, that lead to localized attack resulting in mostly unconnected voiding along the grain boundary network [10]. Pure Ni is largely immune to dissolution attack in molten
fluoride salts, but Ni in its elemental form lacks the high temperature strength to be used as a material for structural components.

It is desirable to use conventional superalloys that have relatively high Cr and C contents because of their well established high temperature creep rupture strength and resistance to air oxidation on the outside of a pipe. The alloys investigated in the present study include Ni-based high temperature alloys, Hastelloy-N, Hastelloy-X, Haynes-230, and Inconel-617, an Fe–Ni-based alloy Incoloy-800H, Ni-201 a nearly pure Ni alloy with minor alloying additions, and a refractory alloy Nb–1Zr. The present study was undertaken to evaluate the alloy stability against corrosion attack in FLiNaK salt at 850°C, while developing a fundamental understanding of the mechanisms of corrosion in these alloys in this molten salt environment. This high test temperature was selected because it approaches the maximum temperature expected on the hot side of a reactor-to-H₂-production-plant heat transfer system; the peak helium temperature from the helium cooled high temperature reactor has been estimated to be about 900°C by ORNL [1].

Ni and Mo coatings and a ceramic composite coating were also investigated for molten salt compatibility. A detailed study was undertaken to investigate the viability of a sulfamate Ni electroplated alloy (Incoloy-800H initially, but later a model alloy similar in composition to Incoloy-800H) because of the aforementioned chemical inertness of Ni. A Mo plasma spray coating was investigated because like Ni, Mo is also stable in molten fluorides, but Cr has a much lower interdiffusion rate in Mo than in Ni. A C/SiSiC and PyC and SiC coated C/SiSiC composite were also investigated. These composites were of interest due to their suitability as a material for the H₂ chemical plant process heat exchanger.
2 Background

2.1 Molten Fluoride and Chloride Salt Heat Transfer Media

Interest in the use of molten salts as a heat transfer media in the nuclear field gained traction with the successful use of uranium fuel bearing salts in the aircraft reactor experiment which used NaF-ZrF₄-UF₄ (53-41-6 mol%) salt for the development of a nuclear powered aircraft [11]. This was followed by the molten salt reactor experiments (MSRE) at ORNL which utilized LiF-BeF₂-ZrF₄-UF₄ (65-30-5-0.1 mol%) for fuel salt and FLiBe (2LiF-BeF₂) for the secondary coolant [12]. Fuel bearing molten fluoride salts share several of the same issues as non-fuel bearing salts but the UF₄ component is known to be more aggressive on structural components than non-fuel bearing salts. Non-fuel bearing salts have also been investigated as heat transfer agents in several solar thermal systems (NaNO₃-KNO₃) as well as by ORNL (NaF-NaBF₄) as a secondary coolant for the molten salt reactor [13]. However, the boiling point of NaNO₃-KNO₃ is well below the desired temperatures for H₂ production, and NaF-NaBF₄ exhibits undesirably high vapor pressure at the same temperatures. Additionally, NASA conducted corrosion experiments with a range of alloys in LiF-19.5CaF₂ and NaF-27CaF₂-36MgF₂ for thermal energy storage applications [2]. The salts used by NASA were designed to store energy at near constant temperature using the thermal arrest that occurs during melting and freezing and were optimized to have large heats of fusion, with melting points near 766°C and 930°C that are undesirably high for a heat transfer fluid [2]. Although the NASA and ORNL molten fluoride salts were different chemically from FLiNaK, many of the same chemical attack mechanisms were observed in this study.

From the standpoint of the next generation nuclear plant (NGNP) program H₂ and process heat applications, it is important to select a salt that possesses good heat transfer characteristics, is relatively easy to handle, and not prohibitively expensive. Some considerations included the following: Li may transform into tritium, but lower Z salts are desirable from the standpoint of
heat transfer [14]. The heat transfer salt must not be appreciably reduced by structural metals and alloys, and must be in near thermodynamic equilibrium with the alloying constituents [15]. Beryllium containing salts are generally undesirable because of their toxicity and associated expenses in handling.

Based on the above issues it was decided that most of our experiments be performed using FLiNaK salt, with a couple tests utilizing 68%KCl-32%MgCl₂ (mol%) for comparison purposes. FLiNaK salt is a eutectic mixture of three fluorides, with a composition 46.5%LiF-11.5%NaF-42%KF (mol %) and has a melting point of 454°C [16]. FLINAK is well suited for the temperature range of this study (700°C to 1100°C), due to its low volatility (low vapor pressure), its relative ease of handling, and lack of nuclear activation issues as a medium for an intermediate heat transfer loop. This salt is a good representation of fluoride salts in general such that the principles underlying corrosion of alloys and alloy selection can be readily translated to compositional variants of this salt.

**Salts Considered and Their Physical Properties**

The physical and chemical properties as well as the economics of the molten salt heat transfer agent are all important considerations and a compromise between must be made to arrive at a salt for large scale heat transfer applications. For example, a molten salt with outstanding heat transfer characteristics would be unworkable if it induced rapid corrosion in service or was simply too expensive. Thus a compromise between the physical properties relevant to heat transfer and the chemical performance issues such as volatility and corrosion, as well as costs is required in order to select the most appropriate heat transfer salt.

Many salts were considered for study in the alloy/molten salt static exposure tests. Table 2.1-1 shows important properties of some of these salts. After a review of the literature, consultation with researchers at ORNL and the University of California at Berkeley, it was concluded that the majority of the corrosion studies should be performed in FLiNaK salt. FLiNaK, from the
standpoint of turbulent-forced-convection heat-transfer performance, has the best overall characteristics of any salt in Table 2.1-1 [1]. FLiNaK is an ideal salt for initial study because it has very good heat transfer properties (i.e. high volumetric heat capacity, low viscosity, low vapor pressure, and high thermal conductivity) and favorable methods found for corrosion prevention in FLiNaK would likely be readily transferable to other salts [1]. KCl-MgCl₂ is a near eutectic composition chloride salt, that melts at 426°C. This salt was chosen for limited investigation because its heat transfer properties approach those of FLiNaK, but this chloride is considerably less expensive.

Table 2.1-1. Comparison of salt properties for salts of interest in the present work, have been used in the nuclear field and water. “a” : Estimated by extrapolation of lower-temperature data (~1100°C) or assumption of ideal mixture behavior. (Source: [1])

<table>
<thead>
<tr>
<th>Salt (composition in mol %)</th>
<th>Formula weight (g/mol)</th>
<th>Melting point (°C)</th>
<th>Boiling Point (°C)</th>
<th>900°C vapor pressure (mm Hg)</th>
<th>density (g/cm³) 700 °C</th>
<th>ρ°Cp, volumetric heat capacity (cal/cm³·°C) 700 °C</th>
<th>μ, viscosity (cP) 700 °C</th>
<th>k, thermal conductivity (W/m-K) 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF-NaF-KF (46.5-11.5-42)</td>
<td>41.3</td>
<td>454</td>
<td>1570°</td>
<td>~0.7</td>
<td>2.02</td>
<td>0.91</td>
<td>2.9</td>
<td>0.92</td>
</tr>
<tr>
<td>LiCl-KCl (59.5-40.5)</td>
<td>55.5</td>
<td>355</td>
<td>~1400°</td>
<td>5.8</td>
<td>1.52</td>
<td>0.435</td>
<td>1.15</td>
<td>0.42</td>
</tr>
<tr>
<td>KCl-MgCl₂ (68-32)</td>
<td>81.4</td>
<td>426</td>
<td>&gt;1418</td>
<td>&lt;2.0</td>
<td>1.66</td>
<td>0.46</td>
<td>1.40</td>
<td>0.40</td>
</tr>
<tr>
<td>NaF-NaBF₄ (8-92)</td>
<td>104.4</td>
<td>385</td>
<td>694</td>
<td>9500</td>
<td>1.75</td>
<td>0.63</td>
<td>0.90</td>
<td>0.40</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>18</td>
<td>0</td>
<td>100</td>
<td>--</td>
<td>1.0 @ 20°C</td>
<td>0.44 @ 20°C</td>
<td>1.0 @ 20°C</td>
<td>0.6 @ 20°C</td>
</tr>
</tbody>
</table>

Properties of FLiNaK Salt

Several correlations exist for the physical properties of FLiNaK as functions of temperature, and those pertinent to the proposed study are shown in the Appendix of this thesis. The most important properties from the experimental design perspective were the salts’ melting and boiling points, and the temperature dependence of viscosity and density.
2.2 **Corrosion in Molten Fluorides**

In most high temperature environments corrosion can be controlled by one of the following mechanisms, (i) by the formation of a protective film, or (ii) by the establishment of a thermodynamic equilibrium between the material and the environment [4]. Elements such as Cr, Al, and Si are added to alloys to promote the formation of self-healing protective oxide films that act as diffusion barriers and prevent further rapid oxidation in oxidizing environments such as air. Prevention of hot corrosion (sulfidation and oxidation from molten salt deposits left from fuel impurities) in fossil fueled boilers and turbines also relies on passive films of Cr and Al oxides present at the alloy surface [5]. Additionally, chemical additions to the fuel aid in removal corrosive salt slags [5]. Gas turbines and boilers that burn fossil fuels use these corrosion prevention methods extensively.

Molten fluoride salt corrosion of most high temperature alloys however, is fundamentally different from air oxidation and hot corrosion [6]. Unlike conventional air/aqueous oxidation, the protective oxide films are soluble in molten fluoride salts or otherwise unprotective [15]. The corrosion rate therefore depends on the thermodynamic driving force and the kinetics of the various corrosion reactions [15]. In general, there are three driving forces for corrosion in molten fluorides: impurities, temperature gradients, and activity gradients. An understanding of a molten fluorides salts’ propensity to remove alloy constituents from an alloy can be made by observation of the phase diagrams for the mixtures, understanding of the acid-base effects, and the redox potential that will be present in the system [8]. For the various elemental components of an alloy, the free energy of formation of the corresponding fluorides and oxides can be used to determine the most reactive components and these components can be expected to be selectively attacked in the melt; this has been found to be the case for Al and Cr [8]. Hastelloy-N, designed specifically for use with molten fluoride salts, contains a minimum concentration of Cr (~ 6%) to mitigate air-side oxidation, since it is undesirable from the chemical standpoint of molten fluoride salt
corrosion [1, 8]. In corrosion studies with temperature gradients, the temperature dependence of solubility of alloying species must be considered. It has been found that Cr will be dealloyed primarily in high temperature regions where selective attack results in the formation of voids [8], and plates out in the relatively cooler sections of the system. For the molten fluoride salt that is used in this experiment, FLiNaK, preventing corrosion in any other way but the attainment of a thermodynamic equilibrium is virtually ruled out. However, there are several possible ways to attain a thermodynamic equilibrium, such as applying a coating that will reduce the thermodynamic potential or by directly altering the salt chemistry.

2.2.1 Activity Gradient Driven Corrosion

Acid-Base Chemistry

The acid base properties of molten salts can be understood through their Lewis acid-base properties [8]. A Lewis acid is defined as an electron pair acceptor, and a Lewis base as an electron pair donor. The alkali metal fluorides tend to easily give up their fluoride ions and form complexes (a central atom or ion, acting as a Lewis acid, is coordinated by one or more molecules or ions which act as Lewis bases) which interact with the acidic salts, stabilizing the acidic component thereby reducing the thermodynamic/chemical activity as shown in equation 2.2.1-1 for a ZrF$_4$ salt [8].

\[
\text{ZrF}_4 + 2\text{F}^- \rightarrow \text{ZrF}_6^{2-} \quad \text{Equation 2.2.1-1}
\]

The complex ions immobilize and tie up the F$^-$ ions and are thought of as basic [17]. By this definition, FLiNaK is a very basic molten salt [8]. The excess or deficit of F$^-$ ions influences many of the properties of the salt and has been shown to have a strong influence on the activity coefficients of dissolved metallic ion species in molten fluoride mixtures [17]. Understanding
this behavior is important for predicting equilibrium concentrations of reactive components in solution.

**Salt Fluxing Reactions**

Fluxing reactions are those that occur when a reaction product barrier becomes non protective due to the formation of a soluble species [18]. Most metal oxidation products are highly soluble in molten fluorides [15]. There are a number of fluxing mechanisms and the dominant one depends on the experimental conditions [18]. Alloy composition, temperature, deposit characteristics, and salt composition can all affect fluxing processes [18]. In molten salts, the equilibrium of the salt constituents and their ionic complexes can be used to define the acidity [18]. In basic salt fluxing, a metal constituent combines with a negatively charged anion (i.e. F\(^-\)) and forms a species that is soluble in the molten salt. In acidic salt fluxing a metal oxide that would normally form a protective barrier would be stripped of the O and form a metal ion and O\(^+\) cation [18]. Due to the basicity of FLiNaK salt, it is expected that basic fluxing will be the dominant fluxing mechanism.

**Thermodynamic Equilibrium**

The redox potential of a salt mixture is its effective potential to oxidize or reduce metal ions in the salt [17]. The redox potential is directly related to the oxidation states of the metal ions in the molten salt mixture that are capable of having multiple oxidation states [17]. LiF, NaF, and KF do not have higher and lower oxidation states, so they cannot be oxidized and can only be reduced to their respective metals [17]. However, HF, FeF\(_2\), and NiF\(_2\) can behave as strong oxidants [17]. In a static system, the dissolved alloying constituents will set the redox potential such that an equilibrium between the salt and the alloy is established (i.e. the saturation limit will be reached).

The difference in the free energy of the salt constituents and the fluorides of the alloying elements is the key driving force for corrosion [6]. Therefore, alkali metals (i.e. Li, Na, K) are
the preferred cations for the salt constituents, and more noble materials (i.e. Ni) are appropriate for the structural container walls [19]. Thus, alloys whose constituents have less negative free energies of fluoride formation are less prone to corrosion and hence better candidates for heat transfer applications from a corrosion standpoint. As temperatures increase, the calculated Gibbs free energy of formation generally becomes less negative (less stable fluoride), but the kinetics of any corrosion reaction also increase. For a given basic fluxing reaction, such as:

\[ x \cdot \text{Me} \text{ (solid)} + y \cdot \text{F}_2 \text{ (gas)} = \text{Me}_x\text{F}_{2y} \quad \text{Equation 2.2.1.-2} \]

where

Me= solid metal

the Gibbs free energy of formation can be calculated by subtracting the Gibbs free energy of the products from the Gibbs free energy of the reactants. The Gibbs free energy of formation was calculated in this way for a number of pure metals of interest using a program that included a large library of Gibbs free energy values, called HSC Chemistry 5.11. A graphical comparison of the Gibbs free energies of formation per F_2 is shown in Fig. 2.2.1-1.
Fig. 2.2.1-1. Gibbs free energy of fluoride formation per F₂ molecule of various metals present in the salt and materials at 1027°C. The more negative the Gibb’s free energy of formation an alloy constituent is in comparison to the salt constituents, the more likely it is to dissolve in the molten salt.

In fluoride salt experiments performed by NASA (to be discussed later), it was found that the tendency for common alloying constituents to be attacked in molten fluoride salts increased in the following order: Ni, Co, Fe, Cr, Al, with Al being the most dissolution prone [2]. A multi-component alloy will be corroded by the oxidation and removal of the least noble component [20]. Furthermore, the refractory metals Nb, Mo, and W and the Ni-Mo based Hastelloy B could be expected to be relatively free from attack [2]. However, Hastelloy-B is not directly applicable to many high temperature systems because it becomes extremely brittle after service between 650°C and 815°C and possesses poor air oxidation resistance. Refractory metals are known to produce volatile oxides when exposed to air at high temperatures [4, 8].
2.2.2 Pure Salt and Alloy Corrosion

In the absence of an oxidizing atmosphere, corrosion of a pure metal Me (Me=Fe, Ni, Co, Cr, or Al) in an alkali fluoride (MF, M=Li, Na, or K) melt would occur by the reaction [2]:

\[ x \cdot \text{Me}(s) + y \cdot \text{MF}(l) = \text{Me}_x\text{F}_y(l) + y \cdot \text{M}(l) \]

Equation 2.2.2-1

Analysis of alloys corroded by molten fluoride salts demonstrates the selective removal by outward diffusion of Cr due to oxidation by the fluoride salt mixture [21]. The dissolution rate will be controlled by the solid state diffusion from the alloy matrix to the alloy surface [15]. Furthermore, it has been observed that the selective removal of Cr from the surface of several stainless steels and Inconel-600 can make them magnetic due to mostly Fe alloy left behind on the surface [21].

Corrosion of refractory alloys is somewhat different. There are no known condensed Nb, Mo, or W fluorides between 727°C and 1127°C, instead gaseous refractory fluorides are the stable phases [2]. Consequently, the reaction of refractory metals Me (Me=Nb, Mo, or W) with an alkali fluoride may be written as [2]:

\[ x \cdot \text{Me}(s) + y \cdot \text{MF}(l) = \text{Me}_x\text{F}_y(g) + y \cdot \text{M}(l) \]

Equation 2.2.2-2

Knowing the concentration of the main alloying elements in the molten salt is important for understanding and predicting alloy corrosion in molten salts. NASA researchers calculated equilibrium concentrations of key constituents in LiF, NaF, and KF melts assuming ideal solution behavior, the results of which are shown in Fig. 2.2.2-1 [2]. From Fig. 2.2.2-1 it can be seen, for
12

elements for which concentrations were calculated, that Al and Cr can be expected to have the largest concentrations in FLiNaK’s constituents, and Ni the lowest.

Fig. 2.2.2-1. Calculated major alloying constituent fluoride equilibrium concentrations of Me₂F₅ (Me=Fe, Ni, Co, Cr, or Al) after corrosion in one mole of either KF, LiF, or NaF melt at 1100 K in an inert atmosphere assuming ideal solution behavior of the melt. (Source: [2]).

2.2.3 Impurity Driven Corrosion

Impurity driven corrosion reactions in a closed system will usually rapidly proceed to completion at all temperatures. If the system is initially not very clean, a rapid initial corrosion rate can be expected, but sustained attack from these reactions will not occur [15]. The most common impurities are oxides and hydroxides formed in the salt by its main constituents during contact with H₂O and O₂ in air, as well as less prevalent metal impurities.

H₂O and oxide contaminants must be removed from fluoride salts to mitigate corrosion [8]. Once the impurities are removed, these salts should be kept away from the atmosphere and
moisture to maintain their purity [8]. Considerable work has been performed on developing purification procedures for molten fluorides at ORNL. H₂/HF sparging was used to remove the moisture/oxide impurities as well as chlorides and sulfur compounds from FLiNaK and FLiBe [8]. After sparging, the salt can be further purified by placing it in contact with an active metal such as Be or Zr [8]. To achieve extremely high purities, the salts may be subjected to electrolysis as a final step [22]. However, it is likely that a less rigorous purification method may be used for coolant salts than those used for fuel-bearing salts towards which much of the purification research at ORNL was oriented [8]. A secondary goal of the molten salt corrosion experiments reported in the present study was to determine whether H₂/HF sparging was necessary or if less pure salts could be used for heat transfer operations.

H₂O and oxides are among the most deleterious contaminants in a molten fluoride salt from the standpoint of corrosion. The reaction of alkali fluorides with moisture generates gaseous HF by:

\[
\text{MF}_2(l) + \text{H}_2\text{O}(g) = \text{MOH}(l) + \text{HF}(g)
\]

Equation 2.2.3-1

\[
2 \cdot \text{MF}_2(l) + \text{H}_2\text{O}(g) = \text{M}_2\text{O}(l) + 2 \cdot \text{HF}(g)
\]

Equation 2.2.3-2

Part of the HF gas will then dissolve in the melt by the reaction

\[
\text{HF}(g) = \text{HF}(l)
\]

Equation 2.2.3-3

H₂ can then be formed by corrosion with the metal alloys via the following reaction:
For example, taking equations 2.2.3-1 through 2.2.3-4 into account, a salt that started off as LiF-NaF-KF will change chemically to become a new salt mixture that contains many other components, for example LiF-NaF-KF-ΣnMOH-ΣnM₂O-ΣnMe₃F_y. The best approach to remove these contaminants and return the salt back to its pure state would be to re-purify it using a hydrofluorination treatment [1].

Corrosion of Cr bearing alloys from impurities often results in rapid initial corrosion, but once the impurities are exhausted, corrosion exhibits a slower linear relationship with time [4]. Several commonly observed corrosion processes from impurities are shown below.

\[
\text{FeF}_2 + \text{Cr} \rightarrow \text{CrF}_2 + \text{Fe}
\]

\text{Equation 2.2.3-5}

\[
\text{FeF}_2 + \text{Ti} \rightarrow \text{TiF}_2 + \text{Fe}
\]

\text{Equation 2.2.3-6}

\[
2\text{FeF}_2 + \text{Zr} \rightarrow \text{ZrF}_4 + 2\text{Fe}
\]

\text{Equation 2.2.3-7}

\[
3\text{NiF}_2 + 2\text{Cr} \rightarrow 2\text{CrF}_3 + 3\text{Ni}
\]

\text{Equation 2.2.3-8}

\[
6\text{HF} + 2\text{Cr} \rightarrow 2\text{CrF}_3 + 3\text{H}_2
\]

\text{Equation 2.2.3-9}

The changes in Gibbs’s free energy for reactions 2.2.3-5 through 2.2.3-9 are strongly negative [23]. In a study of TZM (Ti-Zr-Mo) alloy in the Molten Salt Reactor Experiment fuel salt, LiF-BeF₂-ThF₄-UF₄ (68-20-11.7-0.3 mol %), the Fe contaminant would then plate out on the test coupon and the container wall [23].
2.3 NASA Study

NASA investigated alloy corrosion phenomena in molten fluorides for a variety of alloys. The purpose and design of the NASA tests were somewhat different from those performed by ORNL and those presently being performed at the University of Wisconsin. The NASA tests were crucible tests with an Ar atmosphere maintained at 1 atm. The purpose for the NASA tests was to find an ideal container material and molten fluoride salt combination with the salt possessing a large heat of fusion and high melting point for use as a thermal battery in an orbiting satellite. The molten salt would store heat through phase change while in sunlight, and release it on the dark side of the satellite’s orbit. Therefore, the corrosion tests were performed with salts possessing high heats of fusion, at 100°C above their ~800°C-900°C melting points. Table 2.3-1 and 2.3-2 summarize the alloy compositions and results of the exposures to two molten fluoride salts. NASA found Fe-Ni based alloys exhibited more corrosion than the Ni based alloys (Table 2.3-2), and as seen in Fig. 2.3-1, a correlation exists in which the depth of attack increases with increasing Cr level. Refractory metals and alloys were also investigated and shown to have little corrosion but there are issues in regards to the use of these materials on earth were they would be exposed to the atmosphere. For structural components made of Nb or other refractory based alloys, oxidation protection would have to be provided [24].
Table 2.3-1. Alloys tested in molten fluoride salts by NASA as a part of a thermal energy storage research program. (source: [2])

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition, atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Co-base</td>
<td></td>
</tr>
<tr>
<td>Haynes-188</td>
<td>1.7</td>
</tr>
<tr>
<td>H25</td>
<td>3.4</td>
</tr>
<tr>
<td>Ni-base</td>
<td></td>
</tr>
<tr>
<td>Hastelloy-B</td>
<td>5.9</td>
</tr>
<tr>
<td>False-N</td>
<td>0.5</td>
</tr>
<tr>
<td>Hastelloy-N</td>
<td>5.1</td>
</tr>
<tr>
<td>Hastelloy-S</td>
<td>0.9</td>
</tr>
<tr>
<td>Hastelloy-X</td>
<td>22.1</td>
</tr>
<tr>
<td>Inconel-600</td>
<td>9.7</td>
</tr>
<tr>
<td>Inconel-702</td>
<td>0.5</td>
</tr>
<tr>
<td>Inconel-718</td>
<td>19.5</td>
</tr>
<tr>
<td>Nimonic-75</td>
<td>0.5</td>
</tr>
<tr>
<td>Ni-200</td>
<td>----</td>
</tr>
<tr>
<td>Ni-base</td>
<td></td>
</tr>
<tr>
<td>Fe-base</td>
<td></td>
</tr>
<tr>
<td>19-9DL</td>
<td>64.8</td>
</tr>
<tr>
<td>304</td>
<td>68.5</td>
</tr>
<tr>
<td>310</td>
<td>49.4</td>
</tr>
<tr>
<td>316</td>
<td>62.2</td>
</tr>
<tr>
<td>347</td>
<td>65.3</td>
</tr>
<tr>
<td>A286 (cw 50%)</td>
<td>53</td>
</tr>
<tr>
<td>Armco 18SR*</td>
<td>72</td>
</tr>
<tr>
<td>Incoloy 800</td>
<td>45.1</td>
</tr>
<tr>
<td>Mild steel</td>
<td>98.6</td>
</tr>
<tr>
<td>N-155</td>
<td>31.5</td>
</tr>
<tr>
<td>Nitronic-40</td>
<td>59.3</td>
</tr>
<tr>
<td>PH14-8Mo</td>
<td>70.7</td>
</tr>
<tr>
<td>RA 330</td>
<td>43.8</td>
</tr>
<tr>
<td>Refractory-base</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>----</td>
</tr>
<tr>
<td>Nb-1Zr</td>
<td>----</td>
</tr>
<tr>
<td>Ta</td>
<td>----</td>
</tr>
<tr>
<td>W</td>
<td>----</td>
</tr>
</tbody>
</table>
Table 2.3-2. Summary of results from the NASA experiments on corrosion of various alloys in molten fluoride salts. (source: [2])

<table>
<thead>
<tr>
<th>Composition (atom %)</th>
<th>LiF-19.5CaF$_2$</th>
<th>LiF-19.5CaF$_2$</th>
<th>NaF-27CaF$_2$-36MgF$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (K)</td>
<td>1039</td>
<td>1039</td>
<td>1178</td>
</tr>
<tr>
<td>Exposure Conditions</td>
<td>100hr – 1070 K</td>
<td>500hr – 1070 K</td>
<td>100hr – 1203 K</td>
</tr>
<tr>
<td>Alloy</td>
<td>General Grain Boundary</td>
<td>General Grain Boundary</td>
<td>General Grain Boundary</td>
</tr>
<tr>
<td>Co-base</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-25</td>
<td>--</td>
<td>12</td>
<td>--</td>
</tr>
<tr>
<td>HS-188</td>
<td>--</td>
<td>47</td>
<td>--</td>
</tr>
<tr>
<td>Fe-base</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-9DL</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>304</td>
<td>--</td>
<td>20</td>
<td>--</td>
</tr>
<tr>
<td>310</td>
<td>17</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>316</td>
<td>--</td>
<td>45</td>
<td>--</td>
</tr>
<tr>
<td>347</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>A286</td>
<td>43</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Armco 18SR</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Inconel 800</td>
<td>--</td>
<td>45</td>
<td>--</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PH14-8</td>
<td>14</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>RA-330</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ni-base</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hastelloy-B</td>
<td>8</td>
<td>--</td>
<td>30</td>
</tr>
<tr>
<td>Hastelloy-N</td>
<td>--</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>False-N</td>
<td>--</td>
<td>27</td>
<td>--</td>
</tr>
<tr>
<td>Hastelloy-S</td>
<td>--</td>
<td>--</td>
<td>90</td>
</tr>
<tr>
<td>Hastelloy-X</td>
<td>--</td>
<td>45</td>
<td>--</td>
</tr>
<tr>
<td>Inconel-600</td>
<td>13</td>
<td>34</td>
<td>90</td>
</tr>
<tr>
<td>Inconel-702</td>
<td>15</td>
<td>60</td>
<td>--</td>
</tr>
<tr>
<td>Inconel-718</td>
<td>13</td>
<td>24</td>
<td>45</td>
</tr>
<tr>
<td>Ni-200</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nimonic-75</td>
<td>--</td>
<td>--</td>
<td>30</td>
</tr>
<tr>
<td>Refractory-base</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nb-1Zr</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ta</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>W</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
2.4 **ORNL Development of Hastelloy-N**

High temperature Cr bearing alloys such as Hastelloy have been used despite the selective Cr component dissolution attack because of their acceptable, time-tested, overall high temperature properties [6, 25]. ORNL screened and developed materials in various molten fluorides for use in the aircraft reactor and molten salt reactor experiments and ultimately developed INOR-8, later renamed Hastelloy-N. Hastelloy-N is a Ni-Mo alloy with about 8 % (atomic) Cr [4]. This level of Cr is near the minimum necessary to negate the problem of high temperature air oxidation as seen in Table 2.4-1. Alloys that have higher Cr contents can be expected to undergo more severe corrosion in molten salt as seen in experiments by ORNL and NASA (Fig. 2.3-1).
Table 2.4-1. Weight-gain due to oxidation as a function of Cr content for Ni-17%Mo-Cr alloys at 980°C. (source: [4])

<table>
<thead>
<tr>
<th>% Cr</th>
<th>Weight Gain in 168 hr (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>10.44</td>
</tr>
<tr>
<td>2.83</td>
<td>16.46</td>
</tr>
<tr>
<td>4.61</td>
<td>12.45</td>
</tr>
<tr>
<td>5.43</td>
<td>17.83</td>
</tr>
<tr>
<td>6.19</td>
<td>0.44</td>
</tr>
<tr>
<td>6.83</td>
<td>0.60</td>
</tr>
<tr>
<td>7.97</td>
<td>0.31</td>
</tr>
</tbody>
</table>

2.5 Molten Chloride Heat Treatment Salt Experience

Significant experience with molten chloride salts and their corrosive properties has been obtained by industry owing to their use in molten salt heat treatment and surface treatment baths. Fig. 2.5-1 and Fig. 2.5-2 show compiled corrosion data from two types of molten chloride salt baths. No general trends were found for the data shown. It should be noted that the environment in molten salt heat treatment baths is not as strictly controlled as would be expected for heat transport applications. For example in salt baths used for heat treatments and surface treatments, the movement of parts into the molten salt would continuously add metal impurities, and the salts are usually exposed to air, allowing for O₂ and H₂O impurities as well.
Fig. 2.5-1. Corrosion test results from 30 day field tests performed in neutral salt bath containing BaCl₂, KCl, and NaCl at 845°C. (Source: [26])

Fig. 2.5-2. Corrosion test results from 100 h tests performed in NaCl at 845°C. (Source: [26])

J. Jackson et al. reported on an extensive corrosion study of cast Fe-Ni-Cr alloys in molten heat treatment salts [27]. It was found that grain boundary corrosion along carbide networks was far more severe than metal loss by the bulk grains, and that the grain boundary attack allows for the salt to penetrate into the grain boundaries [27]. Intergranular corrosion rates were found to be
at least ten times greater than normal rates of metal loss [27]. For highly alloyed heat treatment salt containers, failure usually occurred by salt leaking through porous areas generated by the intergranular attack [27]. It was also found that alloy corrosion increased with Cr and C content, and decreased with increasing Ni content [27]. Increasing Nb and Ta in the alloy to form stabilizing carbides (as opposed to laminar grain boundary Cr carbides) was also found to decrease corrosion rates [27].

2.6 Superalloy Microstructure

Considerable research has been performed on the development of superalloys for use in jet engine and gas turbines. This research led to the development of alloys that can be used as structural materials at operating temperatures approaching 2/3 of their melting point on the Kelvin scale [24]. Therefore, while common steels and many Ni alloys can be used in the temperature range 500°C-600°C, superalloys may be used at temperatures in excess of 80% of their melting point [18, 24].

Many superalloys are unsuitable for a molten fluoride salt heat transfer loop. The highest temperature superalloys are directionally solidified single crystal, and many of the others are precipitation strengthened with precipitates that may be unsuitable for piping. Single crystal and directional solidification are unlikely to be used successfully due to: the cost of scaling the heat treatment processes normally used for relatively small turbine blades up for large pipes, the processing necessary for piping would alter the crystal structure, and single crystal and directionally solidified superalloys have anisotropic properties. Most Fe-Ni and Ni base superalloys that are precipitation strengthened have a large Al and Cr component to aid in the prevention of high temperature oxidation and Al and Ti for the precipitation of the strengthening phases, $\gamma'$ and $\gamma''$ [18]. As discussed earlier both Al and Cr are soluble in molten fluoride salts. Therefore, we are left with the solid solution strengthened superalloys as options for molten salt loops. Although solid solution strengthened superalloys can have multiple phases present
(usually carbides), the majority of their strength comes from solid solution strengthening. The role of common alloying elements in Fe-Ni and Ni base superalloys is summarized in Table 2.6-1.

Table 2.6-1 Effects of elemental metal additions to Fe-Ni, Ni, and Co base superalloys. (Source: [28])

<table>
<thead>
<tr>
<th>Effect</th>
<th>Fe-Ni Base</th>
<th>Ni Base</th>
<th>Co Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Solution Strengtheners</td>
<td>Cr, Mo</td>
<td>Co, Cr, Fe, Mo, W, Ta, Re</td>
<td>Nb, Cr, Mo, Ni, W, Ta</td>
</tr>
<tr>
<td>FCC Matrix Stabilizers</td>
<td>C, W, Ni</td>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>MC</td>
<td>Ti</td>
<td>W, Ta, Ti, Mo, Nb, Hf</td>
<td>Ti</td>
</tr>
<tr>
<td>M23C6</td>
<td>--</td>
<td>Cr</td>
<td>Cr</td>
</tr>
<tr>
<td>M23C6</td>
<td>Cr</td>
<td>Cr, Mo, W</td>
<td>Cr</td>
</tr>
<tr>
<td>M6C</td>
<td>Mo</td>
<td>Mo, W, Nb</td>
<td>Mo, W</td>
</tr>
<tr>
<td>Carbonitrides</td>
<td>C, N</td>
<td>C, N</td>
<td>C, N</td>
</tr>
<tr>
<td>Promotes General Precipitation of Carbides</td>
<td>P</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Forms γ’ Ni3(Al, Ti)</td>
<td>Al, Ni, Ti</td>
<td>Al, Ti</td>
<td>--</td>
</tr>
<tr>
<td>Retards Formation of Hexagonal η (Ni3Ti)</td>
<td>Al, Zr</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Raises solvus temperature of γ’</td>
<td>--</td>
<td>Co</td>
<td>--</td>
</tr>
<tr>
<td>Hardening Precipitates and/or Intermetallics</td>
<td>Al, Ti, Nb</td>
<td>Al, Ti, Nb</td>
<td>Al, Mo, Ti, W, Ta</td>
</tr>
<tr>
<td>Oxidation Resistance</td>
<td>Cr</td>
<td>Al, Cr, Y, La, Ce</td>
<td>Al, Cr</td>
</tr>
<tr>
<td>Improves Hot Corrosion Resistance</td>
<td>La, Y</td>
<td>La, Th</td>
<td>La, Y, Th</td>
</tr>
<tr>
<td>Sulfidation Resistance</td>
<td>Cr</td>
<td>Cr, Co, Si</td>
<td>Cr</td>
</tr>
<tr>
<td>Improves Creep Properties</td>
<td>B</td>
<td>B, Ta</td>
<td>--</td>
</tr>
<tr>
<td>Increases Rupture Strength</td>
<td>B</td>
<td>B</td>
<td>B, Zr</td>
</tr>
<tr>
<td>Grain-Boundary Refiners</td>
<td>--</td>
<td>B, C, Zr, Hf</td>
<td>--</td>
</tr>
<tr>
<td>Retards γ’ Coarsening</td>
<td>--</td>
<td>Re</td>
<td>--</td>
</tr>
</tbody>
</table>

2.7 Solid State Diffusion, Grain Growth, and GBE

Since it was seen in the NASA studies (Table 2.3-2) and mentioned in the literature from ORNL that Ni was relatively immune to attack in molten fluorides, it was decided to add a Ni-plated high Cr alloy to the test matrix. However, it was known early on that diffusion of Cr
through the Ni-plating could pose challenges. What follows is a brief introduction to some of the
diffusion issues and methodology commonly used to study solid state diffusion.

### 2.7.1 Nomenclature

A short background on the definitions of several different diffusion terms will now be given.
The tracer diffusion coefficient is named by the method in which it is determined.

\[ D_X^* = \text{tracer diffusion coefficient of component X} \quad \text{Equation 2.7.1-1} \]

For a tracer diffusion measurement, a radioactive element is deposited on an alloy (single grains
if possible to reduce microstructure effects); the alloy and isotope layer is then annealed and
allowed to diffuse. After the diffusion anneal, the alloy is sectioned at specific depths and an
activity is measured, allowing for a determination of activity as a function of depth [29]. If the
element deposited is an isotope of the element that it is deposited on, or an isotope of a
component of a homogeneous alloy, the tracer diffusion coefficient can also be referred to as the
self diffusion coefficient. If the isotope that is plated is not the same element that it is plated on,
the tracer diffusion coefficient is referred to as a chemical diffusion coefficient or impurity
diffusion coefficient. A more succinct way of labeling chemical or impurity coefficients that
conveys more information, is shown below.

\[ D_{XY}^{Z*} = \text{tracer diffusion coefficient of component Z in alloy X Y} \quad \text{Equation 2.7.1-2} \]

Component Z in equation 2.7.1-2 may or may not be component X or Y, and there may be many
alloy components.
Diffusion couples are used to study diffusion in a concentration gradient where the diffusion rate shows concentration dependence. In most cases of substitutional diffusion, the alloying elements diffuse into each other via a vacancy exchange mechanism and hence the diffusion coefficient is termed the interdiffusion coefficient.

\[ D = \text{interdiffusion coefficient} \quad \text{Equation 2.7.1-3} \]

If the system being discussed is a two component system, authors commonly leave off subscripts that describe the system components. The interdiffusion coefficient may be defined as follows for X and Y components.

\[ \tilde{D}_{X,Y} = \text{interdiffusion coefficient of component X in Y} \quad \text{Equation 2.7.1-4} \]

If X and Y are both pure single crystals, then usually \( \tilde{D}_{X,Y} = \tilde{D}_{Y,X} \). For three or more components, the nomenclature becomes more complicated. For a ternary system, two types of interdiffusion coefficients based on Onsager’s reciprocal relations can be defined, as the linear diffusion terms, \( \tilde{D}_{XX} \), and the cross-terms, \( \tilde{D}_{XY} \).

The interdiffusion coefficient for dual component alloys is related to the tracer diffusion coefficients by [30]:
\[ \hat{D} = \left( X_A \cdot D_{AB}^B + X_B \cdot D_{AB}^A \right) \cdot \Phi \]

where

\[ X_A = \text{mass fraction of A} \]
\[ X_B = \text{mass fraction of B} \]
\[ \Phi = \text{Thermodynamic Factor which is unity for ideal solutions} \]

Equation 2.7.1-5

Ternary interdiffusion coefficients can also be related to tracer diffusion coefficients and thermodynamic factors utilizing considerably more complex equations than for binary interdiffusion [31, 32]. Unfortunately, these relations are often of limited practical use because they do not take into consideration microstructural defects that can greatly alter the effective diffusion coefficient.

The intrinsic diffusion coefficients (sometimes called component diffusion coefficients) describe diffusion of components A and B relative to the lattice planes in a concentration gradient, [30, 33].

\[ D_X = \text{intrinsic diffusion coefficient of component X} \]

Equation 2.7.1-6

The intrinsic diffusion coefficients can be deduced from the interdiffusion coefficient if the velocity of the lattice plane is known [30]. Fig. 2.7.1-1 points out many of the just discussed diffusion coefficients and how they are related.
Diffusion can be further defined by the crystal microstructure. For diffusion occurring in the crystal lattice, the **lattice diffusion coefficient** (volume or bulk diffusion coefficient) is used.

\[ D_l = \text{lattice diffusion coefficient} \]  

*Equation 2.7.1-7*
If diffusion in the grain boundary is being discussed then the *grain boundary diffusion coefficient* with the following nomenclature is used:

\[ D_{gb} = \text{grain boundary diffusion coefficient} \quad \text{Equation 2.7.1-8} \]

The last diffusion coefficient to be defined here is the *effective diffusion coefficient* (also called the *apparent* or *measured diffusion coefficient*).

\[ D_{X}^{\text{eff}} = \text{effective diffusion coefficient of component X} \quad \text{Equation 2.7.1-9} \]

The need for this coefficient comes about due to the imperfection in the crystal lattice allowing for multiple diffusion pathways to be operating at once. In polycrystals, both lattice diffusion and grain boundary diffusion occur simultaneously (Fig. 2.7.1-2), and their impact on the overall measured diffusion coefficient depends on multiple factors such as grain size, temperature, and the relative values for \( D_{gb} \) and \( D_l \). The effective diffusion coefficient that will be discussed from hereon will be from substitutional diffusion, following the nomenclature it is:

\[ \tilde{D}_{X}^{\text{eff}} = \text{effective diffusion coefficient of component X} \quad \text{Equation 2.7.1-10} \]
Fig. 2.7.1-2. Figure showing grain boundary diffusion occurring simultaneously with lattice diffusion.

The effective interdiffusion coefficient is often modeled as a combination of the lattice diffusion and the grain boundary diffusion terms, but can also include terms from other contributions such as dislocations or other imperfections [29]. How the contributing terms are weighted depends on the grain boundary width, grain size, grain shape, and whether interdiffusing atoms will tend to segregate at grain boundaries (only lattice and grain boundary diffusion are considered here) [29].

2.7.2 Diffusion Models

Temperature Dependence

Provided that the Ni-plating is even and adherent, the principle pathway for Cr dissolution into the salt will be by diffusing from the base alloy through the Ni-plating to the surface, where it is dissolved. Diffusion coefficients may be described by the empirical Arrhenius relation [30]:

\[ D = D_0 e^{-\frac{Q}{RT}} \]

where 

- \( D \) is the diffusion coefficient
- \( D_0 \) is a pre-exponential factor
- \( Q \) is the activation energy for diffusion
- \( R \) is the gas constant
- \( T \) is the absolute temperature
\[ D = D_0 \cdot e^{\frac{Q}{RT}} \]

where

- \( D \) = diffusion coefficient
- \( D_0 \) = pre-exponential factor
- \( Q \) = activation energy
- \( R \) = noble gas constant
- \( T \) = temperature in Kelvin

Departures from the Arrhenius nature may arise from a variety of causes such as defects associated with impurities or microstructural features such as grain boundaries [30].

**Kinetic Regimes and Hart’s Equation**

Harrison arrived at a convenient diffusion kinetics classification scheme that accounted for grain boundary and lattice diffusion contributions [34]. Harrison’s scheme had three different classifications into which all diffusion data could be allocated (Fig. 2.7.2-1). The data that can be extracted from the concentration profile is dependent on the kinetic regime [30]. In the A regime, the diffusion contours from grain boundaries overlap. In the C regime, lattice diffusion is “frozen out” and only grain boundary diffusion occurs. Whenever the conditions for type A and type C diffusion kinetics are violated, type B kinetics are said to be occurring [34].
The A regime is observed at high temperatures, after long anneals, and/or when the grain size is small [30]. The A kinetic regime is said to be occurring when the lattice diffusion length is larger than the spacing between the grain boundaries [30]:

\[ \sqrt{D_l t} \gg d \]

where

- \( d \) = grain size
- \( D_l \) = lattice diffusion coefficient
- \( t \) = anneal time

**Equation 2.7.2-2**
the onset of the A-regime is often determined by the condition [30]:

\[
\Lambda = \frac{d}{\sqrt{(D_l \cdot t)}} \ll 1
\]

Equation 2.7.2-3

where
\( \Lambda \) = kinetic regime determination parameter

In the B regime, grain boundary and lattice diffusion both occur but the lattice diffusion fields do not overlap so that the condition for this regime is [30]:

\[
\delta \ll \sqrt{D_l t} \ll d
\]

Equation 2.7.2-4

where
\( \delta \) = grain boundary width

The A regime dominates when \( \Lambda \leq 0.4-0.7 \) (the diffusion length is larger than the grain size), and the lower limit for the B regime is commonly mentioned when \( \Lambda \approx 2 \) (diffusion length is about half the grain size) [30]. In type A kinetics diffusion fronts from different grain boundaries overlap and the diffusion length in the bulk exceeds the average grain size; this is often the case with materials with very small grains [35]. On the macroscopic scale, the polycrystal obeys Fick’s law with an effective diffusion coefficient, \( D_{eff} \), and Hart’s equation may be used to find \( D_{gb} \). Hart’s equation is defined as [30, 34, 35, 36, 37]:
\[ \tilde{D}_i^{\text{eff}} = f \cdot D_{gb} + (1-f) \cdot \tilde{D}_i \]

where

- \( D_{gb} \) = grain boundary diffusion coefficient
- \( \tilde{D}_i \) = lattice diffusion coefficient

It has been found that the difference between modeling with square grains compared to parallel grains is small (allowing for ‘leakage’ into the perpendicular grain boundaries) [35]. A segregation coefficient may also be added to the grain boundary diffusion term if the element under study tends to segregate to the grain boundaries [37].

**Experimental Determination of \( D^{\text{eff}} \)**

Fick’s 2\textsuperscript{nd} Law may be used to predict how concentration changes with time:

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \quad \text{Equation 2.7.2-6} \]

Effective interdiffusion coefficients and penetration depths of individual elements may be empirically determined from concentration profiles obtained from diffusion couples [38]. One method of determining \( \tilde{D}_i^{\text{eff}} \) is by fitting a solution of the diffusion equation (Equation 2.7.2-6) to the experimentally obtained concentration profile. If \( \tilde{D}_i^{\text{eff}} \) depends little on concentration, then Equation 2.7.2-6 may be simplified to:
\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

Equation 2.7.2-7

Equation 2.7.2-7 may be solved for an extended source by assuming the boundary conditions:

\[ @t=0, C(x<0) = C_0 \]
\[ @t=0, C(x>0) = 0 \]  

Equation 2.7.2-8

and considering the extended distribution to be made up of an infinite number of line sources and by superimposing the corresponding infinite number of elementary solutions [33], so that:

\[ C(x,t) = \frac{C_0}{2(\pi D t)^{3/2}} \int_{-\infty}^{\xi} e^{-\frac{\xi^2}{4Dt}} d\xi \]  

Equation 2.7.2-9

where the terms may be defined as shown in Fig. 2.7.2-2.

Fig. 2.7.2-2. The extended initial distribution.
The solution to the integral term may be arrived at by use of the error function complement so that [33, 39]:

\[
C(x,t) = \frac{C_0}{2} \cdot \text{erfc} \left( \frac{x}{2 \sqrt{D \cdot t}} \right)
\]

Equation 2.7.2-10

In this solution, for the experiments reported in later sections \(C_0\) is the original Cr concentration in the substrate (base alloy), and the Cr concentration in the Ni-plating is assumed to start out at 0. The origin of the x-axis it deemed to be the Matano interface. The Matano interface defines a plane in the diffusion zone about which there is a balance of mass, i.e. the amount lost by diffusion on one side is equal to the amount gained by diffusion on the other side (shown in Fig. 2.7.2-3) [40]. Under ideal conditions, the Matano interface will occur at the initial interface position [39]. Mathematically, the Matano interface (for Cr diffusion in this case) is defined [33]:

\[
0 = \int_0^{x_{\text{Cr}}} x \, dC
\]

Equation 2.7.2-11

where

\(C_{i\text{Cr}}\) = initial Cr concentration in the substrate
Fig. 2.7.2-3. Figure showing the graphical derivation of the Matano plane. The Matano plane, $X_M$, is where there is a balance of concentration of diffusing species leaving from one side and entering the other side of the plane.

Between 905°C to 1100°C the variation of Cr diffusion coefficients in Ni with Cr concentration in the range of 0-20% Cr has been found to be less than ~50%, so the error from assuming a concentration independent diffusion coefficient for the Ni electroplate/800H system is likely small [41, 42]. For increased accuracy or for when the diffusion coefficient is known to be highly concentration dependent, Boltzmann-Matano analysis may be used to numerically evaluate concentration dependent interdiffusion coefficients from the concentration profile [30].

2.7.3 Grain Growth and Methods to Reduce Effective Diffusion

Grain Growth

Grain boundary migration and grain boundary diffusion are similar processes. The primary difference is that grain boundary diffusion involves transport along the boundary whereas migration requires atomic movement across the grain boundaries [29]. In a single phase metal the rate of grain growth is inversely proportional to the mean grain diameter and increases rapidly with increasing temperature [29]. If grains are initially small, grain growth can be rapid, but the
rate of growth will drop off quickly as the grains increase in size [29]. Grain growth follows the equation [29, 43]:

\[
\frac{1}{d^n} - \frac{1}{d_0^n} = k \cdot t
\]

where
\(d\) = average grain size
\(d_0\) = initial grain size
\(n\) and \(k\) = temperature dependent parameters
\(t\) = time

Due to the very small initial grain size of the Ni-plating used in this study (~90 nm), the initial grain size term is assumed negligible and will be neglected, so the following empirical relationship, based upon the theoretical equation 2.7.3-1, may be used [29]:

\[
\overline{d} = K' \cdot t^n
\]

where
\(\overline{d}\) = average grain size
\(t\) = time
\(K'\) = a proportionality constant that increases with temperature, that itself is Arrhenius so that

\[
K' = K_0 e^{-\frac{Q}{RT}}
\]

\(K_0\) = constant
\(Q\) = boundary mobility activation energy
\(n\) = temperature dependant grain growth parameter
\(R\) = gas constant
\(T\) = temperature
In an ideal system $n=0.5$, however, experimentally derived values only approach 0.5 in very pure metals or at very high temperatures [29]. For short annealing times, the apparent interdiffusivity can appear to be a function of time at a constant temperature due to the grain growth and the resulting decrease in grain boundary area [36]. A significant difference in the effective diffusion coefficient of Cu in Ni has been seen between 10 h and 100 h for temperatures below 600°C, but this was not seen above 600°C [36].

**Grain growth and Grain Size Effect on Measured Diffusion Rates**

The primary differences between measured diffusion rates from diffusion couple data typically found in the literature and the measured diffusion rates of Cr diffusion into sulfamate Ni electroplate relate to the influence of the microstructure. Sulfamate electroplated Ni tends to have some of the smallest grains of all the Ni-plating techniques. M. Seo et al. reported a mean grain size of 123 nm from TEM analysis [44].

Because the grain boundary diffusion contribution to the effective interdiffusion coefficient is dependent on grain size, increasing the Ni-plating grain size can decrease the effective Cr diffusion coefficient in Ni. J. Katz, et al. decreased Cu interdiffusion into sulfamate electroplated Ni by producing a large grained Ni electrodeposit [36, 45]. The tracer diffusion properties of Cu in Ni are similar to Cr in Ni; for lattice diffusion between ~1350 and 1600K, the pre-exponential factors are 0.57 and 1.1 cm$^2$/s, and the activation energies are 258 and 273 kJ/mol respectively [39]. The same principle of increasing the grain size to decrease the effective diffusion coefficient was applied and found to be very effective in reducing hydrogen diffusion in electroplated sulfamate Ni [37].

Grain growth to decrease the effective Cr interdiffusion coefficient in the Ni-plating by decreasing the grain boundary contribution via increasing the Ni-plating grain size is likely to have a greater impact at low temperatures where the difference between the lattice diffusion
coefficient and the grain boundary diffusion coefficient is greater, grains tend to be smaller, and grain growth would otherwise not occur rapidly [29, 46].

**Grain Boundary Engineering**

In addition to controlling grain boundary diffusion by controlling grain size, diffusion may also be controlled by controlling the distribution of grain boundary types. Low energy boundaries; generally defined as those with a grain misorientation of 15° or below, have lower grain boundary energies due to their less open structure [29]. Diffusion along low energy boundaries occurs at a slower rate than diffusion along higher energy boundaries, shifting the grain boundary diffusivity much closer to that of the bulk [47, 48]. The many nuances of GBE are described in reference [48].

GBE requires thermomechanical processing based on either the strain annealing method or the strain recrystallization method [48]. Strain recovery annealing imposes a series of low to moderate strains (6-7%) followed by annealing that induces recovery as opposed to recrystallization [48]. Strain recrystallization involves higher degrees of cold work (≥30%) and higher temperature anneals (>0.4T_Melt) to induce recrystallization [48]. Strain recrystallization GBE has been found to be more effective in enhancing the grain boundary character distribution and allowing finer control of the final grain size [48]. Lehockey et al. was able to GBE cast Ni (99.99%) to increase special grain boundaries (Σ≤29) from 13% to 66% by reduction in thickness by rolling of 60% followed by anneal at temperatures between 950°C and 1150°C for between 1 and 15 minutes [49]. The prospect of grain boundary engineering the Ni-plating is promising because smaller initial grain sizes have been shown to produce a higher frequency of low energy boundaries [50].

### 2.8 C/Alloy Interactions in Molten Salts

The potential and severity of an interaction between alloys and graphite exposed to molten fluoride salts is a concern for any scheme which proposes to utilize such combinations. Schemes
proposed that may encounter this issue include molten salt fueled reactors (reactor core is graphite) and molten salt cooled reactors such as the AHTR (TRISO fuel particles encased in graphite compacts). Additionally, PyC/SiC coated C/SiSiC composites have been proposed for use as a heat exchanger material on the cold side of a heat transport loop between a high temperature nuclear reactor and a H₂ production plant [51].

The Gibbs free energy of formation of metal fluorides from the alloy constituent elements can be used to determine the most stable fluoride compounds (Fig. 2.2.1-1). These elements can be expected to be selectively attacked in an alloy by any oxidative component in a molten fluoride salt [8]. Likewise, the Gibbs free energy of metal carbides from the alloying elements can be used to determine the elements most likely to form carbides. For most of the high temperature alloys tested, Cr is the most active of the primary metal components and can be expected to be selectively attacked by any oxidative component in the salt [8]. Cr also has a large carbide formation energy, which would also make it susceptible to forming carbides.
The type of reaction that will occur between alloys and graphite will vary depending on the salt conditions as ascertained from current industrial experience with molten salts. In the Hall-Héroult Al extraction process, the molten salt mixture (primarily cryolite, Na$_3$AlF$_6$, with alumina, Al$_2$O$_3$, added) can interact with the graphite container material and form graphite intercalation compounds and cyanide in the graphite pot liners [52]. A non-cyanide carburizing process has also been described [53] that relies on a chloride salt mixture and a blend of selected graphite particles that are dispersed in the salt by mechanical agitation [53]. Molten salts are also used for heat treatment baths due to the ability to rapidly and uniformly heat parts [54]. Graphite rods may be used to rectify chloride heat treatment baths by reducing metal oxide corrosion products present in the bath to metals that adhere to the rods [55]. The metals may then be scraped off and the rods reused [55].
I. Ozeryanaya [56] has summarized, for molten salt heat treatment baths, multiple corrosion processes which can result in the dealloying of elements that are susceptible to forming multiple oxidation species in the salt and can alloy with the container material if alloy elemental constituents are more electropositive. Likewise, graphite may also take part in such processes if it is soluble in the salt and can form carbides with the elements with multiple oxidation states [56]. Pure FLiNaK is known to stabilize the Cr$^{3+}$ and Fe$^{3+}$ oxidation states, and the primary valence state of Cr metal in FLiNaK is Cr$^{3+}$ [8].

I. Ozeryanaya [56] found that chemical attack, in chloride salt heat treatment baths, could occur by what he referred to as non-electric transfer. Electronegative metals (i.e. Cr) in the tool alloys would dissolve into the salt with a low oxidation state (i.e. Cr$^{2+}$) and would transfer to electropositive metals in the container alloys by a simultaneous oxidation (Cr$^{3+}$) and reduction (Cr$^{0}$) provided the metals could form alloys with each other as exemplified in Equation 2.8-1 [56].

\[
3\text{Cr}^{2+} \leftrightarrow 2\text{Cr}^{3+} + \text{Cr(Fe)_{alloy}} \tag{Equation 2.8-1}
\]

According to I. Ozeryanaya [56], non-electric transfer increases with increasing: temperature, salt convection, and surface area of the electronegative metal. Graphite can also take part in non-electric transfer provided that the metals can form carbides as exemplified in Equation 2.8-2 and Fig. 2.8-2 [56].

\[
3\text{Cr}^{2+} \leftrightarrow 2\text{Cr}^{3+} + \text{Cr(C)_{carbide}} \tag{Equation 2.8-2}
\]
Fig. 2.8-2. Schematic of non-electric transfer described by I. Ozeryanaya, as applied to the Fe-Ni-Cr/graphite/FLiNaK system.

2.9 Electrochemistry

A real time high temperature diagnostic, capable of determining quantitative, trace amounts of corrosion species in the molten salt has been investigated. Details of an electrochemistry literature survey performed as part of this research can be found in the Appendix of this thesis, and a brief description is provided in this section.

Voltammetry is an electroanalytical method in which information about an analyte is obtained by measuring the current between a working and counter electrode as the potential of the working electrode is varied. Information about the analyte of interest may then be obtained by analyzing the current as a function of voltage; the resulting graph of current as a function of voltage is called a voltammogram. Voltammograms taken at different times during a corrosion test can indicate when certain species are increasing in concentration in the solution. If properly calibrated for specific elements, the species that is increasing in concentration can be identified. For Fe-Ni-Cr alloys the primary species will be chromium, but other elements can also be identified and quantified.
ORNL intended to use inline electrochemical, voltametric analysis of MSR fuel salt in every major installation and many minor facilities of the MSR program [57, 58]. The electrochemical analysis was needed for redox control and estimates of corrosion product ion concentrations [58]. Most of voltametric work performed during the MSR program was concerned with determination of oxidation states, suitable electrode materials, and basic electrochemical characteristics of specific elements [59].

Three container materials were referenced by ORNL that appeared to behave satisfactorily for electrochemical work; glassy carbon [60], Pyrolytic boron nitride [58], and graphite [61]. Mamantov noted that glass and quartz could not be used as container materials because trace H₂O impurities in the salt would result in the formation of HF that would attack the container [62].

**Three Electrode Setup**

A three electrode setup is commonly used for electrochemical measurements; utilizing 1) a working electrode (WE), 2) a reference electrode (RE), and 3) a counter electrode (CE). The three electrode setup is necessary so that the current applied to the working electrode does not polarize the RE [63]. The current flows and is measured between the working and counter electrode and the voltage is measured between the working and reference electrode (which has no flowing current) [63].

**Working/Counter Electrodes Materials**

WE and CE can be made from a variety of materials. A WE must provide high signal to noise ratios and a reproducible response [64]. Other factors affecting the choice of a WE and CE include: potential window of application, electrical conductivity, surface reproducibility, mechanical properties, cost, availability, and toxicity [64]. ORNL has tested a large number of materials as working electrodes in molten fluoride salts, including: Ni [65], Pt [58], Pd [58], Ir [58, 59], pyrolytic graphite [58, 61], Cu [58], Au [58], Ag [58], Re [58], and Ta [58].
In every solution, there will be a potential window in which voltammetric and galvanic measurements may be taken. In general the nobler the electrode material used the wider the potential window. For Pt electrodes used in molten fluorides, at high anodic potentials (with respect to the Ni/Ni(II) couple), Pt itself will be oxidized. At sufficiently high cathodic potentials alkali metals in fluoride salts such as lithium or potassium are evolved, and may plate and/or alloy with the WE [62]. More detail on the material choices and electrochemistry setup may be found in the thesis by D. Ludwig [66].

**Reference Electrodes**

For systems that are applying an external potential to the WE, it is necessary to use a RE with a constant potential, where the potential difference that drives the current would apply to the WE and CE. There has been several RE designs used in molten salts. The most simplistic electrode (not a true RE) used as a reference would be an inert metal wire (often platinum) immersed in the sample salt. While this scheme would allow for a potential reference point which would not have any current running through it that could lead to polarization, this type of potential reference is not as stable as a true RE and has been termed a quasi-reference electrode (QRE). With QRE’s, as the solution being tested varies in composition, so does the potential. Nonetheless, Mamantov used platinum as a QRE in molten fluorides noting that: the current passing through the QRE was extremely small ($\leq 10^{-8}$ A) when used in the 3-electrode system and under most conditions the potential of the QRE remained remarkably constant ($\pm 10$ mV) [62].

A true reference electrode would prevent the miss-assignment of elemental oxidation peaks that can occur due to abrupt changes in potential of a quasi-reference electrode due to changing redox conditions or polarization, and would vary far less than a QRE in stable solutions [60]. A literature review of reference electrodes in molten fluorides may be found in the appendix, but because they were not used extensively in work reported herein, will not be expounded upon here.
Anodic Stripping Theory

Among the quantitative voltametric techniques, anodic stripping voltammetry (ASV) is among the best suited for quantitative, trace analysis due to its preconcentration step [19, 24]. Fig. 2.9-1 details the main steps in anodic stripping voltammetry. In anodic stripping voltammetry, the working electrode is held at a potential negative enough to reduce the metal cation of interest, depositing it on the electrode. After a sufficient amount of time (long enough to deposit a sufficient amount of metal to get a decent signal to noise ratio), the potential is then swept to a more positive potential. The anodic potential sweep is termed the stripping step since the metal that was previously deposited is now oxidized, and in doing so, gives off an electron current that is read by an ammeter. In electrochemistry, the electrode where oxidation is occurring is said to be the anode. There are various methods of sweeping the potential; this work focused on the most simplistic stripping method, linear stripping. A cleaning step include after each measurement ensures that the working electrode surface is free of metals that could give interferences.

![Diagram of anodic stripping voltammetry](image)

**Fig. 2.9-1.** Potential of the working electrode as a function of time for anodic stripping voltammetry.
EMF Data

Several potential measurements for reduction reactions were found in the literature, but only one was found at the temperature of interest, and it was for NaF-KF (40-60 mole percent) eutectic, and none of the studies covered all the elements of interest present in the superalloys under study. Table 2.9-1 shows the most complete emf data table found for FLiNaK at 750°C, other tables found that were less complete or for other fluoride salts may be seen in Appendix E.

Table 2.9-1. EMF series for transition metal ions in molten FLiNaK at 750°C (1023K) in reference to the standard potential of a Ni^{2+}/Ni couple that was set to zero. *Known to be potentials of irreversible couples. (Source: [67])

<table>
<thead>
<tr>
<th>Half cell reaction</th>
<th>Standard potential (E_{1/4} volts vs. standard Ni^{2+}/Ni electrode, 1 mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al^{3+} + 3e^- = Al</td>
<td>-1.5</td>
</tr>
<tr>
<td>Ta^{2+} + 2e^- = Ta</td>
<td>-1.26*</td>
</tr>
<tr>
<td>Cr^{2+} + 2e^- = Cr</td>
<td>-1.13*</td>
</tr>
<tr>
<td>Ta^{4+} + 3e^- = Ta^{2+}</td>
<td>-1.03</td>
</tr>
<tr>
<td>Nb^{+} + e^- = Nb</td>
<td>-1.03*</td>
</tr>
<tr>
<td>Nb^{4+} + 3e^- = Nb^{+}</td>
<td>-0.754</td>
</tr>
<tr>
<td>Cr^{4+} + e^- = Cr^{2+}</td>
<td>-0.69</td>
</tr>
<tr>
<td>Fe^{2+} + 2e^- = Fe</td>
<td>-0.512</td>
</tr>
<tr>
<td>Fe^{3+} + e^- = Fe^{2+}</td>
<td>-0.21</td>
</tr>
<tr>
<td>Nb^{5+} + e^- = Nb^{4+}</td>
<td>-0.11</td>
</tr>
<tr>
<td>Ni^{2+} + 2e^- = Ni</td>
<td>0</td>
</tr>
</tbody>
</table>
3 Experimental

3.1 Procurement and Processing of Materials

The process to find suitable alloys for a molten salt heat transfer loop consisted of several steps. A literature survey was first employed to learn the basic mechanisms of alloy corrosion in molten salts in general and particularly those in molten fluoride salts. Next, a review of the literature from previous molten fluoride salt corrosion tests was conducted, and the resulting recommendations were taken into account. Finally, discussion with other researchers and research into the proposed alloy properties was instigated before finalizing the alloys ultimately selected for molten salt compatibility tests.

Based on discussions with research groups at the Oak Ridge National Laboratory and University of California, Berkeley it was decided that corrosion testing should include as many materials as possible that have been qualified by ASTM codes for use at the high temperatures envisioned for the intermediate heat transfer loop since these would be of immediate interest to the NGNP program. An advanced high temperature reactor (AHTR) working group developed a list of several promising alloys, their expected behavior in molten fluoride salts, and the ASTM sections for which they are codified [68]. From this list, the alloys tested by NASA and recommendations from ORNL, seven candidate alloys for molten fluoride salt environments were selected for the salt exposure experiments; some code-certified for high-temperatures and others recommended from previous studies [2, 68, 69]. Additionally, a nearly pure Ni-alloy and PYC/SiC coated and uncoated C/SiSiC composite were selected; the Ni alloy because of its known dissolution resistance in molten FLiNaK, and the composites because they are potential heat exchanger materials for the hydrogen plant side of the heat transport loop.

Seven alloys were selected for the molten salt tests. The alloys include Hastelloy-N, Hastelloy-X, Haynes-230, Incoloy-800H, Nb-1Zr, and Ni-201. Additionally, a Ni-plated coupon
of Incoloy-800H and a Ni-plated Fe-Ni-Cr alloy were also tested. Hastelloy-N, Hastelloy-X, Haynes-230, and Nb-1Zr were selected, based on past experience, from an initial candidate list of potential alloys for a molten salt heat transfer loop [69]. Additionally, Incoloy-800H, Hastelloy-N, Haynes-230, and Hastelloy-X have been identified as potential candidate materials for various aspects of the Advanced High Temperature Reactor (AHTR) concept [68]. Hastelloy-N was the alloy of choice in the Molten Salt Reactor Experiment (MSRE), and proved to have superior compatibility with the molten fluoride-graphite system at temperatures up to 650°C [25]. Additionally, Ni-201 is one of the noblest alloys in regards to compatibility with molten fluoride salts, though it has inadequate high temperature strength. Finally, Ni-electroplated Incoloy-800H was selected because of the high resistance of dissolution of Ni in molten fluoride salts and the high temperature strength of Incoloy-800H. The Ni-plated Fe-Ni-Cr model alloy was used to investigate diffusion and dissolution of Fe, Ni, and Cr without the interference of trace constituents and secondary phases. It was deemed that if the electroplating approach is demonstrated to be feasible, then this approach would have tremendous commercial potential for optimizing molten salt side corrosion and air-side oxidation resistance.

**Hastelloy-X:**

The Hastelloy-X was obtained from High Temp Metals as 0.076” thick sheet. It was solution heat treated at 1177°C. It was received in a cold rolled, annealed condition and had an ASTM grain size of 4.

| Table 3.1-1. Composition (weight %) of Hastelloy-X provided by the manufacturer. |
|----------------------------------|------|------|------|------|------|------|------|------|------|------|------|
| Hastelloy-X                      |      |      |      |      |      |      |      |      |      |      |      |
| Cr                                | 21.34|      |      |      |      |      |      |      |      |      |      |
| Mo                                | 8.76 |      |      |      |      |      |      |      |      |      |      |
| W                                 | 0.4  |      |      |      |      |      |      |      |      |      |      |
| Al                                | 0.08 |      |      |      |      |      |      |      |      |      |      |
| B                                 | 0.0026|     |      |      |      |      |      |      |      |      |      |
| S                                 | 0.001|      |      |      |      |      |      |      |      |      |      |
| P                                 | 0.22 |      |      |      |      |      |      |      |      |      |      |
| Ti                                | 0.01 |      |      |      |      |      |      |      |      |      |      |
| Fe                                | 19.29|      |      |      |      |      |      |      |      |      |      |
| C                                 | 0.059|      |      |      |      |      |      |      |      |      |      |
| Co                                | 1.39 |      |      |      |      |      |      |      |      |      |      |
| Ni                                | 47.5 |      |      |      |      |      |      |      |      |      |      |
| Si                                | 0.58 |      |      |      |      |      |      |      |      |      |      |
| Mn                                | 0.54 |      |      |      |      |      |      |      |      |      |      |
Hastelloy-N:

The Hastelloy-N was received from ORNL as 0.054” thick sheet. Only data pertaining to its elemental composition was provided.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Al</th>
<th>Si</th>
<th>Cu</th>
<th>S</th>
<th>V</th>
<th>Ca</th>
<th>Mg</th>
<th>P</th>
<th>Ti</th>
<th>Fe</th>
<th>C</th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy-N</td>
<td>6.31</td>
<td>16.11</td>
<td>.06</td>
<td>&lt;.01</td>
<td>0.38</td>
<td>0.01</td>
<td>0.003</td>
<td>.02</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.006</td>
<td>&lt;.01</td>
<td>4.03</td>
<td>.03</td>
<td>.15</td>
<td>72.17</td>
<td>0.53</td>
<td>&lt;.01</td>
</tr>
</tbody>
</table>

Ni-201:

The Ni-201 was obtained from High Temp Metals as 0.078” thick sheet. High temperature metals in turn obtained it from Mitsubishi Materials Corporation. It was received in a cold rolled, annealed condition. It had an ASTM grain size of 6.5.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Ti</th>
<th>C</th>
<th>Co</th>
<th>Cu</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-201</td>
<td>99.4</td>
<td>.19</td>
<td>.09</td>
<td>.05</td>
<td>.02</td>
<td>.02</td>
<td>.02</td>
<td>&lt;.01</td>
<td>.001</td>
</tr>
</tbody>
</table>

Incoloy-800H:

The Incoloy-800H was obtained as 0.25” thick plate from Rolled Alloys Inc. The prior thermo-mechanical history of Incoloy-800H involved hot rolling followed by a high temperature anneal (1176°C+-25°C for 1 h per inch thickness + 2 h), and descaling. The average ASTM grain size was 3.5.
Table 3.1-4. Composition (weight %) of Incoloy-800H as provided by the manufacturer.

<table>
<thead>
<tr>
<th>Incoloy-800H</th>
<th>Cr</th>
<th>P</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>C</th>
<th>Cu</th>
<th>Ni</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.42</td>
<td>0.014</td>
<td>0.50</td>
<td>0.57</td>
<td>45.26</td>
<td>0.069</td>
<td>0.42</td>
<td>31.59</td>
<td>0.76</td>
<td>0.001</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Haynes-230:

The Haynes-230 was obtained from High Temp Metals as 0.078” sheet. It was received cold rolled and annealed and had an ASTM grain size of 5.

Table 3.1-5. Composition (weight %) of Haynes-230 as provided by the manufacturer.

<table>
<thead>
<tr>
<th>Haynes-230</th>
<th>Cr</th>
<th>Mo</th>
<th>P</th>
<th>Si</th>
<th>La</th>
<th>S</th>
<th>W</th>
<th>B</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>C</th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.5</td>
<td>1.22</td>
<td>0.005</td>
<td>0.38</td>
<td>0.013</td>
<td>&lt;0.002</td>
<td>14.11</td>
<td>0.006</td>
<td>0.32</td>
<td>&lt;0.01</td>
<td>1.8</td>
<td>0.1</td>
<td>0.27</td>
<td>59</td>
<td>0.51</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Nb-1Zr:

The Nb-1Zr was obtained from ORNL as 0.188” plate. ORNL obtained this alloy from Cabot Supermetals. To produce this alloy at Cabot, a 2500 lb ingot was electron beam and arc cast melted. The ingot was machined and press forged to a 4.00” thick slab. It was then annealed at 1300°C for 2 hours. The 4” plate was then rolled to 0.3” plate and annealed at 1250°C for 2 hours, then rolled to 0.188” thick plate. The plating was received in 37% cold worked condition.

Table 3.1-6. Composition of Nb-1Zr as provided by ORNL.

<table>
<thead>
<tr>
<th>Nb-1Zr</th>
<th>O</th>
<th>Mo</th>
<th>Al</th>
<th>Be</th>
<th>Co</th>
<th>Cr</th>
<th>W</th>
<th>Si</th>
<th>Fe</th>
<th>N</th>
<th>C</th>
<th>B</th>
<th>Ti</th>
<th>Hf</th>
<th>H</th>
<th>Ta</th>
<th>Ni</th>
<th>Nb</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>130 ppm</td>
<td>&lt;30 ppm</td>
<td>&lt;20 ppm</td>
<td>&lt;10 ppm</td>
<td>&lt;20 ppm</td>
<td>&lt;30 ppm</td>
<td>&lt;50 ppm</td>
<td>&lt;35 ppm</td>
<td>46 ppm</td>
<td>22 ppm</td>
<td>&lt;2 ppm</td>
<td>&lt;40 ppm</td>
<td>51 ppm</td>
<td>&lt;3 ppm</td>
<td>1200 ppm</td>
<td>25 ppm</td>
<td>99.05 ppm</td>
<td>0.95 w%</td>
<td></td>
</tr>
</tbody>
</table>

Inconel-617:

The Inconel-617 was obtained from High Temp Metals as 0.06” sheet. It was received cold rolled and annealed and had an ASTM grain size of 3.5.
Table 3.1-7. Composition (weight %) of Inconel-617 as provided by the manufacturer.

<table>
<thead>
<tr>
<th>Inconel-617</th>
<th>Cr</th>
<th>Mo</th>
<th>P</th>
<th>Si</th>
<th>S</th>
<th>B</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>C</th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.1</td>
<td>9.58</td>
<td>0.002</td>
<td>&lt;0.1</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>1.05</td>
<td>0.4</td>
<td>1.0892</td>
<td>0.08</td>
<td>12.4</td>
<td>52.93</td>
<td>0.0609</td>
<td>0.0137</td>
</tr>
</tbody>
</table>

Fe-Ni-Cr Model Alloy:

The Fe-Ni-Cr model alloy was obtained from Sophisticated Alloys Inc. as a 0.5”x6”x1.25” bar. The main requirements for the metallurgy of this alloy was that it not exceed 0.01% C (weight %), and be a ternary Fe, Ni, Cr alloy with the Fe-Ni-Cr composition similar to Incoloy 800H. The alloy was made by vacuum induction melting, then cast and hot isostatically pressed into the bar shape.

Table 3.1-8. Composition (weight %) of the model alloy as provided by the manufacturer.

<table>
<thead>
<tr>
<th>Fe-Ni-Cr Model Alloy</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46.93</td>
<td>31.92</td>
<td>21.14</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

C/SiSiC Composites:

The C/SiSiC Composites were made by the Institute of Structures and Design, German Aerospace Center (DLR), utilizing an experimental process that has been described in a separate paper [51]. The C/SiSiC composites were formed by a Si melt infiltration process into a base carbon fiber material to convert the matrix carbon into SiC and to fill residual porosity [51]. Some carbon fibers were retained to reinforce the ceramic. The Si melt infiltration was performed in a furnace at ~1650°C under a pressure of ~1 mbar with a holding time of 45 min [51]. The C/SiSiC composites coupons were fabricated and cut from flat plates [51]. Wet chemical analysis found the elemental composition of the ceramic as: SiC = 69 m.% (59 vol.%), Si = 19 m.% (22 vol.%), and C = 12 m.% (19 vol.%) [51]. The carbon fraction remained mostly
in form of the carbon fibres that were retained in the microstructure. Chemical vapor deposited (CVD) pyrolytic C (PyC) and SiC coatings were applied by Hyper-Therm High-Temperature Composites, Inc., on several of the composite coupons. The C/SiSiC composites were first coated in SiC, followed by an overlayer of PyC.

### 3.2 Mechanical Properties of Alloys

An important metric used to select alloys for the molten salt tests was the alloys’ high temperature strength (Fig. 3.2-1). Pure Ni is not practical as a structural material, and was investigated to give a “calibration” mark for a material that should be resistant to dissolution in a pure FLiNaK salt and for comparison to the Ni-plated Incoloy-800H coupons. The Fe-Ni based alloy Incoloy-800H is not as strong as the Ni-based alloys but it is less expensive. The refractory based alloy Nb-1Zr is weaker than the superalloys at low temperatures, but is stronger at higher temperatures.

**Fig. 3.2-1. Ultimate tensile strength as a function of temperature of the alloys selected for corrosion tests** (sources: [70], [71], [72], [73], [74], [75], [76])
Another important metric used to determine high temperature suitability of an alloy is its creep properties. Table 3.2-1 presents stress rupture data for three different temperatures and stresses for Inconel-617, Haynes-230, Hastelloy-X, Incoloy-800H, and 304 stainless steel (arbitrarily chosen for comparison). The superalloys shown have much longer creep rupture times than 304 stainless steel. Furthermore, Inconel-617 and Haynes-230 have dramatically higher creep rupture times than the other superalloys. Hastelloy-N has creep rupture times similar to Hastelloy-X [74].

Table 3.2-1. Stress rupture data of several relevant alloys. *Values approximated from graph. (Source: [75], [76])

<table>
<thead>
<tr>
<th></th>
<th>760°C/103 MPa</th>
<th>871°C/31 MPa</th>
<th>982°C/14 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel-617</td>
<td>20 000*</td>
<td>30 000*</td>
<td>7 000*</td>
</tr>
<tr>
<td>Haynes-230</td>
<td>8 200</td>
<td>6 500</td>
<td>5 000</td>
</tr>
<tr>
<td>Hastelloy-X</td>
<td>900</td>
<td>5 000</td>
<td>2 100</td>
</tr>
<tr>
<td>Incoloy-800H</td>
<td>130</td>
<td>1 200</td>
<td>920</td>
</tr>
<tr>
<td>304 Stainless Steel</td>
<td>10</td>
<td>100</td>
<td>72</td>
</tr>
</tbody>
</table>

3.3 Alloy Metallurgy

Hastelloy-X:

Hastelloy-X is a solid solution strengthened, face centered cubic superalloy [28]. Hastelloy-X may get additional dispersion strengthening from carbide formation to a limited extent and more so from indirect means such as stabilizing grain boundaries from shear [28]. In Hastelloy-X, Co, Cr, Fe, Mo, and W are the primary solid solution strengtheners. W, Ti, and Mo can form MC precipitates. Cr can form M₇C₃, but it is a rare phase in superalloys. Cr, W, and Mo can form M₃C₆. Mo and W can form M₆C, which is usually randomly distributed, with some solubility for Cr [77]. With both Al and Ti present, it is possible that some of the strengthening fcc γ’ precipitate (Ni₃Al or Ni₃[Al, Ti]) or the detrimental η phase (Ni₃Ti) may form at elevated temperatures. The Al and Cr present in the alloy provide for good oxidation resistance, and the
boron present improves creep properties and increases rupture strength [28]. Given the elemental composition and the extended time at high temperatures, it is also possible that the detrimental rhombohedral μ, hexagonal laves, and tetragonal σ phases may develop [77].

**Hastelloy-N:**

Hastelloy-N is a Ni based face centered cubic solid solution strengthened superalloy. Mo is the primary solid solution strengthener, followed by Cr and Fe. Cr and Mo are the most likely elements to form carbides (M$_{23}$C$_6$) due to their relatively high concentrations. Additionally, Mo may form MC and M$_6$C, whereas Cr may form M$_7$C$_3$. Cr is the primary element for oxidation resistance [28]. It is possible that the detrimental hexagonal Laves phases and tetragonal σ phases may develop based on variations within the nominal composition range [77].

**Ni-201:**

Ni-201 is a commercially pure Ni grade [28]. It has a slightly tighter requirement for C content than Ni-200. Ni-200 should not be used above 315°C due to embrittlement from the precipitation of graphite in the temperature range of 425°C to 650°C [28]. Ni-201 may be used at higher temperatures. Ni-201 is primarily used in corrosive media, particularly in reducing environments [28].

**Incoloy-800H:**

Incoloy-800H is a solid solution strengthened, face centered cubic superalloy [28]. Incoloy-800H is widely used because it does not form the embrittling, tetragonal σ phase after prolonged exposure to temperatures above 649°C [78]. Cr is the major solid solution strengthener; Ni and C are the primary austenite stabilizers [28]. Ti forms globular, irregular shaped metal carbides (MC) of variable composition found within the grains as well as at grain boundaries [77]. Cr may also form higher order metal carbides such as Cr$_{23}$C$_6$. The addition of phosphorus promotes the precipitation of carbides. Al also retards the formation of the η phase (Ni$_3$Ti) that can form intergranularly as acicular plates in a Widmanstatten pattern [77]. Although Incoloy-800H is not
primarily precipitation strengthened, Al, Ni, and Ti still form some of the fcc $\gamma'$ precipitate ($\text{Ni}_3\text{Al}$ or $\text{Ni}_3[\text{Al}, \text{Ti}]$), and if the $\gamma/\gamma'$ mismatch is high, extended exposure above 700°C may cause the undesirable hexagonal $\eta$ phase to form [77]. The unfavorable Laves ($\text{Fe}_2\text{Ti}$) phase and $\sigma$ ($\text{FeCr}$) phase may also form [25].

**Haynes-230:**

Haynes-230 relies primarily on Cr and W for solid solution strengthening, and to some lesser extent Mo, Fe, and Co [28]. It is also strengthened by carbides. W and Mo can form MC. Cr may form M$_2$C$_3$. Cr, Mo, and W may form M$_2$C$_6$. Mo and W may also form M$_6$C [28]. The Cr and Al provide for good oxidation resistance [28]. It is possible that the detrimental rhombohedral $\mu$, hexagonal Laves phases and tetragonal $\sigma$ phases may develop based on variations in composition within the nominal composition range of these alloys [77].

**Nb-1Zr:**

Nb has the lowest melting point (2468°C) of the five major refractory alloys [28]. It is stable in most corrosive environments, with the exception of hydrofluoric acid [28]. Nb is usually fabricated near its recrystallization temperature, 1095°C to 1370°C [28]. Almost all the Nb alloys are solid solution strengthened with either: Zr, Ti, Hf, Ta, or W [28]. Nb-1Zr is resistant to corrosion from sodium vapor at high temperatures and pressures and is used extensively in molten metal systems at temperatures ranging from 980°C to 1205°C [28]. Nb begins to oxidize in air at temperatures above 425°C [28]. However, silicide coatings have been developed that allow for Nb alloys to be used at temperatures up to 1610°C [28]. C can be absorbed readily into this alloy if the C potential is high enough, forming brittle surface layers prior to diffusion into the bulk material [77]. Nb can become embrittled across its entire cross section by the incorporation of a few hundred ppm C, O, N, or H [77].
**Inconel-617:**

Inconel-617 is a solid solution strengthened, Ni-Cr-Co-Mo face centered cubic superalloy [76]. It is notable for having high temperature strength and exceptional corrosion resistance in a wide range of environments [76]. Solid solution strengthening comes from Co and Mo [76]. The high Ni and Cr content provide good corrosion resistance in oxidizing and reducing media, and the Al and Cr provide oxidation resistance at high temperatures [76]. Inconel-617 possesses very high creep rupture strength and a thermal expansion lower than most other austenitic alloys [76]. Co based superalloys may develop some additional precipitation strengthening from carbides (Cr$_7$C$_3$, M$_{23}$C$_6$), but not from any known intermetallic phases [53].

**Fe-Ni-Cr Model Alloy:**

The Fe-Ni-Cr model alloy coupons used for corrosion testing were electrical discharge machined to a thickness of 0.06” from the 0.5”x6”x1.25” bar stock. The model alloy had a very large grain structure, much larger than any of the other alloys. In the coupons that were etched, most grains were larger than the coupons thickness. Due to the very high purity of the model alloy, the only secondary phases that might form would be sparse carbides.

**3.4 Ni Electroplating**

The literature and thermodynamic data indicate that Ni is relatively immune from attack in molten fluoride environments; however by itself, Ni lacks the strength for use as a structural material or for piping and other heat exchange equipment at the temperature of interest. Therefore it was desirable to examine the possibility of using a Ni coating on a high temperature alloy, maintaining the advantages of a high temperature strength of alloy with the added benefits of low corrosion of the Ni coating on the molten salt side. Most Ni-plating is performed for decorative purposes, and only requires thin coatings, whereas a thicker coating of at least 40 µm is desirable for the molten salt corrosion work. Furthermore, there are two common methods of plating Ni; electroless Ni-plating, and electroplating.
The two most widely used methods for electroplating Ni are the Watts Ni and Ni sulfamate processes. The Ni sulfamate process was developed after the Watts process and is widely used because it develops low internal stresses in deposits, has high rates of deposition, and has superior throwing power [79]. Since the Ni sulfamate process is so widely used, and since it can deposit a very pure Ni coating, this process was chosen for the Incoloy-800H and model alloy coupons. It should be noted that the all-sulfamate process may ultimately need to be qualified and codified for coating the insides of piping.

3.5 Mo Plasma Spray Coating

At the temperature of interest (850°C), interdiffusion of Cr and Fe in the Ni-plating is a long term issue. This inherent limitation of Ni led to a search for another plating material that would prove compatible with the base alloy and corrosion resistant in molten salts while possessing orders of magnitude lower diffusion coefficients of Cr and Fe.

Thermodynamically, and as a major component in Hastelloy-N, Mo has demonstrated good molten salt corrosion resistance [4]. In our research, Mo and W enriched phases in Hastelloy-N, Hastelloy-X, and Haynes-230 were observed to resist dissolution attack, pointing towards the possibility of using a refractory metal or alloy for a corrosion resistant barrier in molten fluoride salts [9]. Mo is promising based on diffusion data as well; Cr and Fe tracer diffusion coefficients (Fig. 3.5-1), extrapolated from higher temperature data, are 2 to 3 orders of magnitude smaller than those in Ni [39]. Mo, like Ni, has a relatively low solubility in FLiBe, and this behavior may translate to FLiNaK [80].
3.5-1. Cr diffusion coefficients in Ni and in Mo as a function of inverse absolute temperature. (Source: 39)

3.6 Coupon Preparation

After sheets, plates, or bar stock of the alloys were procured they were either sheared mechanically, cut by electrical discharge machining (EDM), or cut by a laser process into rectangular test strips (32 mm width, 13 mm height, 1-2 mm thick) with a hole cut or drilled in the center for fixturing to the central graphite rod, as shown in Fig. 3.6-1. The model alloy had the same general dimensions but did not have a fixturing hole. When the Ni-plated model alloy coupons were exposed to FLiNaK, they were suspended with a Ni-wire. The alloy coupons were metallographically polished in order to facilitate accurate post-exposure analysis. Three coupons per crucible were exposed to FLiNaK, one was mounted and used for pre-corrosion analysis, and one was used for an oxidation test. Nb-1Zr proved especially difficult to polish. Coupons of Incoloy-800H and the model alloy were ground using up to 600 grit sand paper in preparation for Ni-plating, after which they were not polished prior to salt exposure.
Fig. 3.6-1. A) Coupon dimensions used for corrosion tests, the coupons were between 1 and 2 mm in thickness, and B) cut and polished corrosion test coupons of 800H (shown here as an example).

3.7 Microstructures of as-Received Coupons

After polishing, one coupon of each alloy was mounted in cross-section in a conductive bakelite mount for optical microscopy and SEM analysis. The coupons were then ground progressively with SiC paper starting with 320 grit sand paper and progressively moving down to 1200 grit, followed by final polishing step using a 1 μm diamond paste. Following this the coupons were etched using the etchants under conditions listed in table 3.7-1. After the coupons were etched, they were examined using optical and scanning electron microscopy and their microstructure was characterized using energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD). The Ni-plated coupons were etched using the etchant used for Ni-201 alloy.
Table 3.7-1. List of etchants and etching times for each alloy for microstructural analysis.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Etchant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy-X</td>
<td>Swab for 24 minutes.</td>
</tr>
<tr>
<td></td>
<td>ASTM 66 etchant</td>
</tr>
<tr>
<td></td>
<td>30 mL 50% HF</td>
</tr>
<tr>
<td></td>
<td>15 mL HNO₃</td>
</tr>
<tr>
<td></td>
<td>30 mL HCl</td>
</tr>
<tr>
<td>Hastelloy-N</td>
<td>Swab for 6 minutes.</td>
</tr>
<tr>
<td></td>
<td>ASTM 66 etchant</td>
</tr>
<tr>
<td>Ni-201</td>
<td>Swab Ni etch for 30 minutes</td>
</tr>
<tr>
<td></td>
<td>1 part HNO₃ (nitric acid)</td>
</tr>
<tr>
<td></td>
<td>1 part C₂H₄O₂ (acetic acid)</td>
</tr>
<tr>
<td>Incoloy-800H</td>
<td>Use fresh etchant for 5 minutes</td>
</tr>
<tr>
<td></td>
<td>ASTM 66 etchant</td>
</tr>
<tr>
<td>Haynes-230</td>
<td>Swab for 36 minutes.</td>
</tr>
<tr>
<td></td>
<td>ASTM 66 etchant</td>
</tr>
<tr>
<td>Inconel-617</td>
<td>Swab for 30 minutes.</td>
</tr>
<tr>
<td></td>
<td>ASTM 66 etchant</td>
</tr>
<tr>
<td>Nb-1Zr</td>
<td>Swab on for 1 minute.</td>
</tr>
<tr>
<td></td>
<td>Use ASTM 66 etchant.</td>
</tr>
</tbody>
</table>

Hastelloy-X:

Hastelloy-X had many Mo enriched precipitates. It is likely that these are intermetallic phases, but carbides could not be ruled out; however they have not yet been able to be identified as one or the other. TEM analysis of the Mo enriched regions would likely be necessary to determine whether or not they are carbides, but was not performed because they did not appear to be influential to Cr dissolution.

Hastelloy-N:

Hastelloy-N also had many Mo enriched precipitates. It is likely that they are an intermetallic phase but again carbides cannot be ruled out. Like the Mo enriched particles in Hastelloy-X, the Mo enriched particles in Hastelloy-N did not appear to be influential to Cr dissolution in FLiNaK.

Ni-201:

No precipitates were found in the Ni-201 coupon using SEM or EDS. No phases other than Ni were found using XRD. The structure consisted of equiaxed grains.
Inconel-800H:

Ti nitrides and carbides were found sparingly in precorrosion analysis of the Incoloy-800H. Unlike the Hastelloy alloys, EDS scans of the carbide precipitates could positively identify excess C in the precipitates over that of the base alloy. The Ti nitrides are likely a byproduct of the manufacturing process.

Haynes-230:

Haynes-230 had W enriched particles that were oriented in the direction of rolling, and were likely primary carbides. Like the Mo enriched particles in the Hastelloy alloys, the W enriched particles in Haynes-230 did not appear to influence Cr dissolution in FLiNaK.

Nb-1Zr:

The Nb-1Zr had grains oriented in the direction of rolling as expected from its 37% cold work. Like the Ni-201, no precipitates could be found in Nb-1Zr using SEM or EDS, and no other phases could be identified using XRD.

Inconel-617:

The Inconel-617 had Mo enriched precipitates that were oriented in the direction of rolling and were likely primary carbides. The occasional Ti nitride was also observed. Like the Mo enriched particles in the Hastelloy alloys, they did not appear to be influential to Cr dissolution in FLiNaK. The Ti nitrides are likely a byproduct of the manufacturing process.

Fe-Ni-Cr Model Alloy:

The Fe-Ni-Cr model alloy had a very large grain structure. Most grains were larger than the thickness of the coupons and were usually about 1 mm to 3 mm in diameter. Because of this large grain structure, there were far fewer grain boundaries present than in any other coupon. Because the model alloy had no other elements besides Fe-Ni-Cr and C, there were no other precipitates found, besides the rare carbide precipitate.
**C/SlSiC Composite:**

The C/SlSiC composite had a heterogeneous composition. From SEM and EDS, there were regions detected that were pure Si, pure C, and SlSiC. The pure C was mostly in the form of C fibers [51]. Pores up to 4μm in diameter were also observed in the composite (although most were much smaller), likely formed by agglomeration of the resin used in the production process [51].

**Ni-Plated Incoloy-800H:**

Three separate alloy batches were electroplated; two different heats of Incoloy-800H and a model Fe-Ni-Cr alloy similar in Fe, Ni, and Cr composition to Incoloy-800H. The alloy coupons were prepared using 600 grit SiC paper prior to plating, then Ni-plated using the sulfamate Ni electroplating process at a commercial firm (Southwest United Industries Inc.) in Tulsa, Oklahoma. This surface roughness was necessary to promote adhesion of the plating to the substrate alloy. A coupon from each Ni-plating batch was cross-sectioned and characterized. A coating ~45 μm was requested and the minimum coating thickness was found to fulfill this requirement for the three batches. The Ni-plating from the first two batches had an uneven coating thickness. As seen in Fig. 3.7-1, the thickness near the fixturing hole was the thinner (~64 μm) than near the edges (~175 μm). The third plating batch was very uniform in thickness (~80 μm).
Fig. 3.7-1. A) SEM image photomontage of the Ni-plated incoloy-800H cross-section showing differing thicknesses of the Ni-plating. The above coupon was cut in half at the hole region, and the image shows the bottom half of that cross-section, with the top being where the hole for fixturing the coupon would be. B) Etched SEM image of as-received Ni-plate showing Ni grains.

The as received Ni grain size was very small (~90 nm); characteristic of sulfamate Ni electroplating. It was necessary to use XRD line broadening analysis utilizing the Scherrer equation (Equation 3.7-1) to reliably determine grain size because the Ni grains were too small to determine the size from conventional etching and SEM procedures (Fig. 3.7-1B). The XRD data (Fig. 3.7-2) had a large [2 0 0] peak present for the peak at 2θ value of 51.8, which according to M. Byun et al. is characteristic of sulfamate Ni electroplate with a fiber texture component [81]. A computer software program, STOE WinXPOW was used to solve the Scherrer equation for the
[2 0 0] peak, and was calibrated using Ni-201 XRD data. This method estimated a Ni grain size of ~90 nm.

$$\beta = \frac{K \cdot \lambda}{L \cdot \cos(\theta)}$$

where

$\beta$=integral peak width

$K$=size factor (varies with shape, assumed to be 1)

$\lambda$=wavelength

$L$=volume averaged particle size

### Equation 3.7-1

![Graph A](image1.png)

**A** Precorrosion Ni-plated Incoloy-800H XRD data. **B** Precorrosion Ni-201 XRD data.

**Mo-Plated Incoloy-800H:**

Several Incoloy-800H coupons were coated in Mo with a plasma spray process at a commercial firm (Thermal Spray Technologies, Inc., Sun Prairie WI) for testing. The coupons were characterized by SEM and EDS after the Mo-coating was applied. The Mo-plasma spray coating was inconsistent in thickness on different edges of the coupons because the plasma spray process is ‘line of sight.’ Additionally, the fixturing hole was not directly sprayed and therefore
sparsely coated, alloy remnants from clamping the coupons were left on the Mo coating, and structures similar to cracks could be seen on corners (none found that went all the way through from surface to substrate). Oxides and S contaminants were also detected in the coating cross-section by EDS.

![Image](image_url)

**Fig. 3.7-3.** SEM of cross-sectioned Mo-thermal sprayed coupon. A) circle of gap region between edges. It is apparent from the Mo overlap that the top edge of the cross-sectioned coupon was sprayed prior to the sides. B) Poor coverage of fixturing hole region.

There was a significant amount of oxides detected in the Mo-plating using EDS analysis because Mo plasma spray coating was performed in ambient conditions. M. Laribi et al. has reported XRD data that shows the dominant oxide in Mo thermal spray is MoO₂, however according to Y. Wan et al., small amounts of MoO₃ can also be expected [82, 83]. MoO₃ is liquid at 795°C and this could lead to greater mobility of this constituent, however MoO₂ remains solid up to 1927°C [84].

**CVD PyC and SiC Coating On C/SiSiC Composite:**

The CVD PyC and SiC coated C/SiSiC composite had the same substrate microstructure as the uncoated composite. The SiC layer varied from ~50 µm to 80 µm, whereas the PyC coating was a fairly uniform thickness of ~4 µm.
Cr diffusion pathways and loss mechanisms as well as methods to improve the protection provided by the plating through modification of diffusion pathways were studied with a series of diffusion annealing treatments. Diffusion anneals utilized samples from all three Ni-plating batches, but the majority of the samples were from the Ni-plated model alloy (batch-3). The diffusion anneals were over the temperature range of 600°C to 1200°C, for between 30 minutes and 2000 h. The experimental setup for the heat treatments of the Ni-plated alloy coupons required enclosing the coupons in quartz ampoules under a He cover gas, as shown in Fig. 3.8-1. The study of mechanisms such as Cr diffusion in the ampoules was more convenient than those that could be obtained with the molten salt exposure apparatus. However, the study of mechanisms related to Cr dissolution still required exposure to molten salts.
Fig. 3.8-1. A plated coupon encapsulated in a quartz ampoule back-filled with He and a Ta foil to absorb residual oxygen.

It has been shown by Chen et al. that Cr interdiffuses with Ni via substitutional diffusion [85], and that this occurs via a vacancy related process [29]. Likewise, grain boundary diffusion has also been found to be mediated by vacancies as well [85]. There is very little diffusive interaction between Cr, Fe, and Ni atoms and from tracer diffusion measurements it has been shown that $D_{\text{Ni}} : D_{\text{Fe}} : D_{\text{Cr}} = 1:1.2:2$ over the temperature range of ~950°C-1275°C in a wide range of Fe-Ni-Cr alloys [31, 32, 86].

Effective interdiffusion coefficients were determined from the diffusion annealed coupons. A solution to the diffusion equation (Equation 2.7.2-7) for a distributed source of infinite extent (Equation 2.7.2-10) was fitted to concentration data obtained by EDS, and $D_{\text{eff}}$ was determined by a least squares fit. It has been found that concentration dependence of Cr interdiffusion coefficients exists but is quite small [41]. For more accurate and somewhat more rigorous Cr interdiffusion calculations, the Matano-Boltzmann method could be used. As can be seen in Fig. 3.8-2A, this method (utilizing Equation 2.7.2-10, not the Matano-Boltzmann method) often resulted in overestimation of Cr concentrations at the front of the Cr penetration profile.
3.9 Ni-Plating GBE and Secondary Recrystallization

Thermomechanical processing of the Ni-plating was investigated to determine if it could reduce diffusion of Fe, Cr, and Ni, lead to better understanding of the issues pertaining to void formation, and improve the mechanical robustness. Because of the strong dependence on the effective diffusion coefficient on grain size and grain boundary type, the priority was to increase grain size while minimizing Cr diffusion into the Ni-plating and to decrease the ratio of high energy boundaries to low energy boundaries.

A screening operation was undertaken to determine whether the strain recrystallization annealing GBE method or the strain recovery annealing GBE method was more effective in reducing the effective Cr diffusion rate before finalizing a method of thermomechanical processing prior to a FLiNaK exposure test. Due to the small initial grain size, a grain growth heat treatment (GGHT) for the electroplated Ni was undertaken on all coupons prior to any GBE work, that would allow for an easier initial grain boundary characterization via electron backscatter diffraction orientation imaging microscopy (EBSD OIM). Sulfamate Ni electroplating recrystallizes at relatively low temperatures followed by rapid grain growth. The
low recrystallization temperatures and rapid grain growth is due to the melting point and high purity of the Ni-plating [44], the small initial grain size [29, 87], and a large stored elastic distortion energy in the plating from a large density of crystalline lattice defects (like dislocations and twins) from the plating process [45, 88]. The distortion energy is released with annealing as the density of crystalline defects decrease [88]. The purity effect on recrystallization can be quite large; R. Bassard et al. suggest that impurities pinned the grain boundaries and inhibited the normal recrystallization process [42]. The recrystallization activation energy for sulfamate Ni-plating is much smaller than for Watts Ni-plating as well as wrought Ni (table 3.9-1); recrystallization activation energies decrease with cold working [45].

Table 3.9-1. Recrystallization activation energies of sulfamate and Watts Ni electroplate, and wrought Ni. (Source: [45])

<table>
<thead>
<tr>
<th>Type of Ni</th>
<th>Activation Energy kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfamate</td>
<td>54</td>
</tr>
<tr>
<td>Watts</td>
<td>200</td>
</tr>
<tr>
<td>Wrought Ni-60% deformation</td>
<td>290</td>
</tr>
<tr>
<td>Wrought Ni-20% deformation</td>
<td>320</td>
</tr>
</tbody>
</table>

The recrystallization of sulfamate Ni-plating begins at the substrate interface [45]. The nucleation driving force is thought to be greatest at the substrate-plating interface due of lattice misfit stress [45]. Through experimentation, a heat treatment schedule was determined that would grow the grains until the Ni-plating would be between 3-5 grains thick (1200°C for 1 min). The new grain size was ~23 microns (Fig. 3.9-1A). There are two primary concerns about the effectiveness of GBE of the Ni-plating for the purpose of decreasing Cr diffusion. First, the overall effect from grain boundary engineering of the Ni-plating will be blunted by the desire to maintain grains that are as large as possible, which will suppress the low energy grain boundaries influence on the bulk Ni-plating properties [48]. Second, low energy boundaries may randomize
at high temperatures due to increasing atomic mobility. Both effects could potentially lead to random boundaries forming short circuit paths for Cr diffusion through the plating.

Two general types of GBE were found in the literature, strain recovery annealed GBE (hereafter referred to as recovery-GBE) and strain recrystallization annealed GBE (hereafter referred to as recrystallization-GBE). Both methods were screened, with annealing times and temperatures estimated from suggestions for Ni-201 from reference [77]. The recrystallization-GBE started with GGHT sample, the Ni-plating thickness was reduced ~60% with cold rolling, then the coupon was annealed at 950°C for 15 min. The recrystallization-GBE (Fig. 3.9-1B) resulted in a grain size of ~71 µm. The recovery-GBE started with a GGHT coupon, the Ni-plating thickness was reduced by 5%, then the coupon was annealed at 750°C for 5 minutes; this process was then repeated 4 times. The recovery-GBE (Fig. 3.9-1C) resulted in a grain size of ~28 µm. It should be noted that after cold working, any recrystallization and grain growth is termed secondary recrystallization, and is used synonymously with the term abnormal grain growth [89].
Fig. 3.9-1. SEM image thermal and mechanically processed samples etched with the Ni-201 etchant described in Table 3.7-1. Smaller grains appear near Ni surface in all images. A) Grain growth heat treatment. B) Recrystalization-GBE. C) Recovery-GBE.

The recrystalization-GBE coupons had a more uniform plating structure than the recovery-GBE coupons. Error from the thickness measurements (micrometer accuracy, and plating variation) likely had a larger impact for the 5% deformations because the measurement error would take up a larger percentage of the measurements.

The coupons were subjected to a diffusion anneal at 700°C for 217 h to test the efficacy of the GGHT and GBE processes. 700°C was chosen as the test temperature, because at this temperature grain boundary diffusion accounts for a larger proportion of the effective diffusion coefficient than at 850°C. The results of the screening will be discussed more in the discussion
section, but the recrystallization-GBE appeared to give more consistent results and a slightly lower measured diffusion coefficient.

It was expected that the ratio of twin and low energy boundaries would increase from the GBE, verification via EBSD was difficult due to the large grains and consequently small # of grain boundaries that could be mapped using OIM at any one time. From the EBSD scan data collected, the Ni-plating possessed a higher percentage of low energy boundaries than would be expected from a polycrystal with a random microtexture, no special orientation, and uniform grain size (~11%). Furthermore, the GBE did not appear to significantly alter the number of low energy boundaries pre or post anneal (Table 3.9-2).

Table 3.9-2. Percentage of twin and low energy boundaries as a percentage of total boundaries in the Ni-plating. *large variation in grain deformation due to thickness differences during rolling. ** small number of boundaries, lots of noise.

<table>
<thead>
<tr>
<th>Coupon</th>
<th>Pre-Anneal %</th>
<th>Post-Anneal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGHT</td>
<td>35</td>
<td>37</td>
</tr>
<tr>
<td>SRRA-GBE</td>
<td>-</td>
<td>35*</td>
</tr>
<tr>
<td>SROA-GBE</td>
<td>38</td>
<td>33**</td>
</tr>
</tbody>
</table>

It was decided to proceed with the recrystallization-GBE process due to the grain uniformity that should translate into more uniform measured diffusion coefficients, and the larger grain sizes obtained through secondary recrystallization. Also, the additional strain from the rolling lowered the recrystallization energy, allowing for large grains to be formed more rapidly at high temperature, with less diffusion occurring than from heat treatment alone. In recent literature recrystallization-GBE has been noted to be more effective than recovery-GBE [48].

An oriented, fiber texture is seen with XRD (Fig. 3.9-2) on prepared coupons in grains with sulfamate Ni electroplating [90]. The Ni-plating, given the recrystallization-GBE thermomechanical processing, possessed an XRD pattern more like that of a cold-rolled and
annealed Ni-201 coupon. Henceforth, due to the ineffectiveness of the GBE, the recrystallization GBE process will be referred to as the secondary recrystallized modified Ni-plating.

![XRD data graphs](image)

**Fig. 3.9-2.** A) GBE XRD data B) precorrosion Ni-201 XRD data. C) precorrosion Ni-plated 800H (batch 1) XRD data.

### 3.10 Salt Procurement and Transfer Setup

The design and setup of the glove box, associated apparatus, and procedures necessary to minimize contamination of the salts were complex and necessitated significant engineering for the successful completion of this study. Much of this necessary engineering is detailed in Appendix B of this thesis, and for brevity, only the key components of direct relevance to the corrosion experiments are discussed here.

Based on discussions with ORNL about the importance of the role of salt composition and purity on corrosion, it was decided to procure the FLiNaK salt from Electrochemical Systems Inc., a spin-off company from ORNL located in Oak Ridge, TN. The company had previously provided salts for ORNL and other research programs. Contact with this company was established and 18 kg of FLiNaK, purified by a hydrofluorination purification process, was supplied in a sealed Ni vessel (Fig. 3.10-1A). The FLiNaK reservoir was 14 inches tall and 12 inches wide.
970 g of unpurified FLiNaK was also procured from Idaho National Laboratory (INL) (Fig. 3.10-1B). This nonhydrofluorinated FLiNaK salt was made from high purity ingredients. The INL FLiNaK was heated in a stepwise fashion while being purged with dry Ar gas (to remove additional H$_2$O) prior to melting into the FLiNaK eutectic. The smaller batch of salt from INL was used for comparison with the hydrofluorinated salt to study the importance of hydrofluorination on corrosion.
About one kilogram of salt was made at the UW in a similar fashion as that made at INL (Fig. 3.10-1C). It was made in a graphite crucible, and after cooling the surface of the salt in contact with the graphite crucible retained graphite on it.

In addition to the FLiNaK salts, a KCl-MgCl₂ salt was also used. This salt was made in a large 316 stainless steel canister in a glovebox. The salt was heated in a stepwise fashion, and then contacted with a Mg rod to remove metallic impurities by reduction that were more noble than Mg. The salt was then cooled to room temperature and crushed into manageable chunks. Parts of the salt near the Mg rod where found to be dark in color and had 1% Fe (as determined by neutron activation analysis). The least discolored salt volume was selected by visual inspection, and used for the salt exposure tests discussed here.

A system designed to pump the correct amount of salt into each salt exposure capsule (the salt exposure capsules will be discussed in the next section) inside the glove box was necessitated since the FLiNaK salt obtained from ECS Inc. was a monolith in large Ni container. The design schematic for the system used is shown in Fig. 3.10-2. The system consisted of a large Ni FLiNaK reservoir surrounded with a large cylindrical heater. The FLiNaK in the reservoir would be heated to 600°C before being pumped into the capsules. The capsules were also heated up to 600°C to reduce thermal shock on the graphite crucible and alloy specimens while pumping the molten FLiNaK into the capsules. The filling process (from heating up of the capsules to cooling back to room temperature) took about one day per capsule. After the capsules were filled with the FLiNaK, the filling hole in the lid of the stainless steel capsule through which the FLiNaK was pumped was welded shut while still at 600°C. When enough capsules for an experimental run were filled with FLiNaK and sealed, they were placed in the controlled-atmosphere, high-temperature furnace for testing.
3.11 Molten Salt Exposure Capsule Design

A simplified, cost-effective molten salt exposure capsule design was finalized based on discussions with Dr. Dane Wilson of ORNL (Fig. 3.11-1). It was the third design iteration; the previous ones may be viewed in the appendix along with a more lengthy description of the experimental setup. Design III used high-density graphite containment for the molten salt. A corrosion cell similar to that shown in Fig. 3.11-1, but where the graphite was replaced by Incoloy-800H was used for three exposure tests as well. For one Ni-plating salt exposure test, an all Ni-crucible setup was constructed, shown in Fig. 3.11-2.

Graphite was chosen as the main test container material after an extensive literature search of container materials for molten fluoride salts used by other researchers. The relatively low costs and ease of machining of graphite made it an attractive choice as a container material. Graphite is
fully compatible with molten fluorides up to very high temperatures [6]. However, if the graphite pore size were too large, the frozen salt would stick in the crucible after the salt cooled, making it hard to remove the salt post testing [91]. The POCO graphite used in the present study was grade AXZ-5Q1, had an average particle size of 5µm and a pore size of 0.7 µm [92]. Additionally, because purity of the salt was a concern, the graphite was purified (total ash range 5ppm or less) [93]. Experience with FLiBe from the MSRE indicated that with the small pore size it would have been less likely that the salt would infiltrate the graphite [25].

A separate crucible would be used for each corrosion test. The FLiNaK salt was introduced into crucibles in one of two methods; in the first method the molten salt would be pumped into the corrosion capsules through a hole nominally 1/4” in diameter in the stainless steel and graphite lids while in the glove box. This was done for all initial alloy screening capsule tests, except for Inconel-617. The second method of filling the capsules with FLiNaK was used on all other capsules; in this method salt chucks were introduced into the crucibles containing the test coupons before the crucible was welded into its stainless steel air boundary. The salts were kept in an Ar environment at all times, and the welds for the stainless steel air boundary crucible also occurred inside of the glove box once the salts had been introduced.
Fig. 3.11-1. Schematic illustration of the final molten salt exposure capsule design, for the static corrosion tests which was successfully used in the present study.

The filling process for salt procured from ECS, Inc., was as follows. First, the machined graphite pieces were cleaned with methanol ultrasonically using three, five minute steps to avoid pitting of the graphite (per manufacturer’s instructions). Following this the graphite pieces were cleaned ultrasonically in distilled water using three, five minute steps. The graphite crucibles and associated graphite components were then baked at 1000°C, for 8 hours (time at temperature picked arbitrarily) in an Ar atmosphere furnace to remove moisture. Following this, the crucibles were removed from the furnace and immediately stored under vacuum. When the time came to seal the graphite crucibles in the stainless steel capsules, the graphite crucibles were removed from the antechamber. Out of the antechamber three test alloy coupons were inserted as shown in Fig. 3.11-1 after being attached to the graphite rod with graphite screws, and the crucible was sealed with a graphite lid by setscrews, made from stainless steel. The capsule was then placed
back in the glove box. The lids of the stainless steel capsule and graphite crucible both had a hole to allow the molten salt to be pumped in. The fill holes were lined up during welding with a guide rod made from 1/8” tubing. The graphite capsule was welded into the stainless steel capsule. This process was repeated until all the capsules for a given run were welded.

When all the capsules were welded, the next step was to introduce FLiNaK salt. For this, the capsules were placed in the capsule heater. The weighing scale was turned on and an initial weight was recorded. The capsule and ECS FLiNaK reservoir were then heated up to 600°C and the transfer tube up to 500°C. When the temperatures stabilized, nominally 0.7 kg of the FLiNaK salt was pumped in the capsules. A scale placed under the capsule heater determined when the correct mass of molten salt had been introduced in the crucible. Once 0.6 kg had entered the crucible, the pressure inside the reservoir was equilibrated with the glove box, and the transfer line was blown out with Ar. The leftover salt remaining in the transfer tube would drain into the crucible or back into the FLiNaK reservoir. If enough FLiNaK had not been transferred over, the process was repeated until at least 0.7 kg was transferred with the mass of salt transferred being recorded. This critical mass of FLiNaK was necessary to ensure submersion of all three coupons in the molten salt. The system was calibrated such that the salt would not completely cover the top coupon until the entire capsule was heated up to about 800°C if 0.66 kg of FLiNaK was in the crucible, but would cover the coupons as long as the salt was molten (454°C) if 0.7 kg or more was added. The salt transfer tubing spigot was then removed from the crucible and the insulation around the top of the capsule heater partially moved to the side. The welding grounding cable was placed on the top of the capsule, grounding the capsule to the glove box, and the hole on the top of the stainless steel capsule was TIG welded shut. After the hole of the corrosion capsule was welded shut, the capsule heater was shut off and the capsule was allowed to cool before being removed. Just prior to removal, the final mass of the capsule was recorded. This filling process was repeated until all the capsules for a test run were filled with salt and sealed. After the
capsules were sealed, they could be removed from the glove box. Since the corrosion capsules were sealed at 600°C, the internal corrosion capsule pressure during testing at 850°C would be about 1.7 atm versus 5.1 atm if sealed at 20°C.

When it was time to start the corrosion tests, up to four corrosion capsules were placed in an Ar atmosphere controlled, high temperature furnace. The furnace was heated up to 700°C at 60°C/h and then up to 850°C at 30°C/h (ramp rates arbitrarily picked) and held at that temperature for 500 h. After the required 500 h exposure time for the corrosion experiments, the temperature would be lowered to 500°C, which took about 3 h. With the furnace at 500°C the Ar flow was increased to 50 scfh and the water flow to the door was maintained at its maximum in an attempt to cool the inside of the furnace and the silicone seal on the furnace door immediately before opening the door to the retort. This attempt to cool the interior and door of the furnace prior to opening it was performed to lower the temperature of the initial hot gas that would rise out of the furnace upon opening, which could potentially damage the silicone o-ring door seal.

The corrosion capsules, now at 500°C, were inverted with a large pair of tongs to allow the salt to drain into the upper portion of the crucible away from the alloy coupons, and placed outside the furnace. The capsules were placed back inside the furnace once all the crucibles were inverted, and the furnace was allowed to cool down to room temperature. In this design, the crucible height must be large enough and the coupons placed low enough, so that the salt would completely drain off the surface of the test coupons when inverted. Once the capsules had cooled down to room temperature, the crucibles were opened using a CNC mill that cut around the corrosion capsule beneath the weld and what would have been the bottom of the graphite crucible prior to inversion. Following removal of the stainless steel and graphite caps the alloy coupons were removed for detailed analysis. Salt samples from the exposures were also analyzed for alloying constituents [66].
A Ni crucible (Fig. 3.11-2) was used to test the effectiveness of modified Ni-plating in reducing Cr dissolution in FLiNaK. The Ni crucible was made from a Ni-201 tube welded to a Ni-201 sheet, using Weld Mold 700, 99% Ni filler for joining. A Ni wire was used to hold the coupons (99.98% Ni). Besides the difference in construction, the Ni crucible was treated in a similar manner as the other test crucibles. The Ni crucible salt exposure tests were also performed at 700°C, for 500 h.

Fig. 3.11-2. The all Ni experimental setup for the 700°C, 1000 h, unmodified Ni-plated model alloy and modified Ni-plated coupons. A) The setup without the coupons, B) the setup with the coupons, the modified Ni-plated coupon is on the bottom, C) system assembly. The Ni wires were cut off and folded down prior to the stainless steel lid being welded on.

3.12 Removal of Salt from Coupons (Post-Corrosion)

Despite inverting the corrosion capsules at 500°C and allowing the molten FLiNaK salt to drain away from the coupons, a small but significant amount of salt stuck to the coupons upon cooling. Kirillov and Fedulov used a technique that involved washing coupons in a 1M solution of aluminum nitrate, a solvent for lithium fluorides, followed by washing in distilled water and alcohol [94]. This technique was effective in removing salt from coupons after a corrosion capsule test performed with FLiBe [94].
A method similar to that used by Kirillov and Fedulov [94] was used for the FLiNaK exposure tests. First, the alloy coupons were cleaned ultrasonically in their own individual beaker of 1 M Al(NO$_3$)$_3$ for 2, 5 min. periods, next the coupons were cleaned ultrasonically in 1, 5 min. interval in distilled water, followed by ultrasonic cleaning in acetone for 5 min. The coupons were then placed on Kimwipe tissues and allowed to dry before being weighed.

The chloride based KCl-MgCl$_2$ salt readily dissolves in water. For the salt exposure tests utilizing this chloride salt, the aluminum nitrate cleaning step was not used, and two rinse steps with water were performed prior to the acetone step.

Fig. 3.12-1. The top three coupons after molten salt corrosion tests but before cleaning and the same three coupons are shown on the bottom after cleaning. The cleaning procedure was consistently employed before weight measurements.

### 3.13 Electrochemistry

For anodic stripping voltammetry (ASV) experiments, initial room temperature tests to determine Cu concentrations in an aqueous 1 M KCl solution were undertaken with Pt WE and CE, and saturated calomel RE (SCE). A good correlation between integrated current and Cu concentration was obtained. This test was performed to increase familiarity with the ASV technique.
Pt was ultimately chosen as the primary electrode material because Pt is one of the most common metal electrodes used in stripping analysis, has a high melting point, and is chemically inert. Pt wire has been shown to be a suitable quasi reference electrode (QRE) in FLiNaK [62] and has been used as the WE and CE in our experiments and by other researchers in molten fluorides [62]. Initial voltametric tests were undertaken using the experimental apparatus shown in Fig. 3.13-1.

A fixed surface area of the working electrode would result in better correlations between peak currents and concentrations, while facilitating electrochemical analysis. Aluminum oxide was used for insulating the electrodes in FLiNaK. The electrodes for these initial fluoride based tests are shown in Fig. 3.13-2. A working electrode with a fixed surface area was manufactured by
drilling a hole in aluminum oxide bisque, inserting a platinum wire, then holding the aluminum oxide bisque and platinum at 1700°C for 12 h to allow for the aluminum oxide bisque to shrink down around the platinum wire. Because the melting point of Pt is ~1769°C, the Pt was amenable to being compressed due to softening, resulting in a very good seal between the Pt and the alumina. The surface of the working electrode is shown in Fig. 3.13-3 after being cut with a diamond saw and polished using diamond paste.

Fig. 3.13-2. Photograph of the three platinum electrodes encapsulated in alumina.

Fig. 3.13-3. SEM image of the interface between the platinum and aluminum-oxide showing a clean interface.
4 Results

4.1 Molten Salt Exposure Weight-Loss Results

The mass loss from all the alloy coupons exposed to molten salt (reported and discussed in an earlier work [9]) is summarized in Table 4.1-1. For the Fe-based and Ni-based alloys, corrosion generally increased as Cr and C content increased. The measured weight-loss for the Nb-1Zr was the greatest of all the alloys tested. This abnormally high weight gain for Nb-1Zr alloy was attributed to acceleration due to graphite (crucible material) which is discussed in detail in a later section. Although graphite accelerated the corrosion of other alloys, longer-term tests (500 h, 1000 h, and 2000 h) in other crucible materials (Incoloy-800H and Ni-201) showed that the mechanism of corrosion in these alloys was similar in graphite and non-graphite crucibles.

Weight-loss measurements tabulated in Table 4.1-1 were taken upon completion of the testing for all corrosion tests immediately after cleaning procedures to remove residual salts from the coupons. Several coupons detached from the central rod in the crucibles prior to completion of the tests, but were readily retrieved for analysis. The following coupons detached during testing in the graphite capsules while being exposed to ECS FLiNaK: two Ni-plated Incoloy-800H coupons, one Hastelloy-N coupon, and one Haynes-230 coupon. Circumferential cracks were observed on the graphite crucibles after being cut open for the following alloys: Hastelloy-X, Hastelloy-N, and Ni-201. It seems likely that the circumferential cracks of the graphite crucibles occurred after they were inverted upon freezing of the salt as evidenced by the lack of salt observed on the exterior of the graphite crucible pieces that were accessed during the coupon removal process. Therefore, it was concluded that the cracking of the graphite did not influence the corrosion tests. No deviations in expected behavior were seen in the detached coupons or in the coupons retrieved from cracked crucibles.
Table 4.1-1. Average alloy mass-loss per area for various materials after exposure to molten FLiNaK salt. Unless stated otherwise, the salt used was ECS FLiNaK, the exposure time was 500 h and the exposure temperature was at 850˚C. *Only one coupon exposed so there is no standard deviation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mass-loss/Area (mg/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-1Zr</td>
<td>139.0±40.9</td>
</tr>
<tr>
<td>Ni-201</td>
<td>0.0±0.5</td>
</tr>
<tr>
<td>Hastelloy-N</td>
<td>2.3±0.2</td>
</tr>
<tr>
<td>Hastelloy-X</td>
<td>13.2±0.4</td>
</tr>
<tr>
<td>Inconel-617</td>
<td>29.7±2.8</td>
</tr>
<tr>
<td>Haynes-230</td>
<td>51.4±1.2</td>
</tr>
<tr>
<td>Incoloy-800H</td>
<td>28.6±2.6</td>
</tr>
<tr>
<td>Incoloy-800H (INL FLiNaK)</td>
<td>20.7±2.2</td>
</tr>
<tr>
<td>Incoloy-800H (UW FLiNaK)</td>
<td>24.7±1.0</td>
</tr>
<tr>
<td>Incoloy-800H (UW KCl-MgCl₂)</td>
<td>10.8±0.2</td>
</tr>
<tr>
<td>Ni-Plated Incoloy-800H</td>
<td>1.7±2.0</td>
</tr>
<tr>
<td>Mo-Plated Incoloy-800H</td>
<td>Coupons could not be weighed</td>
</tr>
<tr>
<td>C/SiSiC</td>
<td>Coupons could not be weighed</td>
</tr>
<tr>
<td>CVD PyC-SiC C/ SiSiC</td>
<td>Coupons could not be weighed</td>
</tr>
<tr>
<td>C/ SiSiC (UW KCl-MgCl₂)</td>
<td>-5.2*</td>
</tr>
<tr>
<td>CVD PyC-SiC C/ SiSiC (UW KCl-MgCl₂)</td>
<td>-0.18±0.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Incoloy800H Capsule</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Incoloy-800H</td>
<td>0.15±0.22</td>
</tr>
<tr>
<td>Incoloy-800H (1000 h)</td>
<td>0.28±0.02</td>
</tr>
<tr>
<td>Incoloy-800H (2000 h)</td>
<td>0.66±0.01</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Ni-201 Capsule (700˚C, 1000 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Plated Fe-Ni-Cr Model Alloy</td>
</tr>
<tr>
<td>Modified Ni-Plated Fe-Ni-Cr Model Alloy</td>
</tr>
</tbody>
</table>

4.2 Salt Analysis for Cr Detection

Samples from the four salt batches (INL, ECS, and two UW made salts) and from all 8 capsule tests were taken for analysis using wet chemistry methods as well as neutron activation analysis (NAA) at the University of Wisconsin Nuclear Reactor (UWNR). The wet chemistry analysis included ICP-OES, ICP-MS, ion chromatography, moisture, and total C, N, and S tests performed at the University of Wisconsin Soil and Plant Analysis laboratory.
The accuracy of the salt analysis performed at the UW Soil and Plant Analysis Laboratory was found to be unreliable, likely due to the poor solubility of FLiNaK in the agent used by the laboratory to dissolve the samples (nitric acid). NAA was found to provide a more accurate analysis (Table 4.2-1 and 4.2-2). The methodology of the NAA can be found in the thesis by D. Ludwig [66]. Salt sample analyses by NAA were performed in triplicate.

Table 4.2-1. Cr content of the salts before the corrosion tests as determined by Neutron Activation Analysis (NAA) (Source: [66])

<table>
<thead>
<tr>
<th>Salt</th>
<th>Cr Content (weight ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECS FLiNaK</td>
<td>4.02 ± 0.49</td>
</tr>
<tr>
<td>INL FLiNaK</td>
<td>2.95 ± 0.51</td>
</tr>
<tr>
<td>UW FLiNaK</td>
<td>8.18 ± 0.85</td>
</tr>
<tr>
<td>UW KCl-MgCl₂</td>
<td>13.23 ± 0.72</td>
</tr>
</tbody>
</table>

Table 4.2-2. Cr content found in the salt after corrosion tests and the corresponding alloys tested as determined by NAA. Unless otherwise noted, the salt was ECS FLiNaK. (Source: [66])

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crucible</th>
<th>Time (h)</th>
<th>Cr Content (weight ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-201</td>
<td>Graphite</td>
<td>500</td>
<td>3.59 ± 0.21</td>
</tr>
<tr>
<td>Ni-plated Incoloy-800H</td>
<td>Graphite</td>
<td>500</td>
<td>77.29 ± 3.94</td>
</tr>
<tr>
<td>Hastelloy-N</td>
<td>Graphite</td>
<td>500</td>
<td>52.55 ± 2.67</td>
</tr>
<tr>
<td>Hastelloy-X</td>
<td>Graphite</td>
<td>500</td>
<td>327.40 ± 17.08</td>
</tr>
<tr>
<td>Haynes-230</td>
<td>Graphite</td>
<td>500</td>
<td>259.12 ± 13.09</td>
</tr>
<tr>
<td>Incoloy-800H</td>
<td>Graphite</td>
<td>500</td>
<td>371.85 ± 20.91</td>
</tr>
<tr>
<td>Inconel-617</td>
<td>Graphite</td>
<td>500</td>
<td>338.02 ± 18.30</td>
</tr>
<tr>
<td>Incoloy-800H (INL FLiNaK)</td>
<td>Graphite</td>
<td>500</td>
<td>324.62 ± 16.68</td>
</tr>
<tr>
<td>Incoloy-800H (UW FLiNaK)</td>
<td>Graphite</td>
<td>500</td>
<td>206.22 ± 10.74</td>
</tr>
<tr>
<td>Incoloy-800H</td>
<td>Incoloy-800H</td>
<td>500</td>
<td>99.78 ± 5.08</td>
</tr>
</tbody>
</table>

4.3 Post FLiNaK Exposure Microstructures of Uncoated Alloys

Following surface characterization on a field emission scanning electron microscope (SEM), the coupons were cross-sectioned, and mounted. An extensive survey of the alloys and their corrosion behavior in FLiNaK was undertaken, and is summarized here. From the surface
characterization undertaken, it has been noted that the surfaces of all the alloys containing Cr were depleted of this element. For the alloys that contained Mo and W (Haynes-230, Inconel-617, Hastelloy-N and Hastelloy-X), nodules enriched with these refractory metals were observed on the surface.

4.3.1 Ni-201

Ni-201 was largely immune to dissolution attack by FLiNaK. However, the grain boundaries appeared to be elevated in relation to the grains (Fig. 4.3.1-1A). Other changes seen in the Ni-201 from its pre-exposure state were mostly related to the high temperature effects, such as grain growth.

![Surface](image1.png)  ![Cross-section](image2.png)  ![Surface](image3.png)

**Fig. 4.3.1-1.** Ni-201 was largely immune to attack from FLiNaK (shown unetched). A) Surface, B) Cross-section.

4.3.2 Incoloy-800H

EDS point scans (20 kV) of the surfaces of Incoloy-800H coupons after FLiNaK exposure tests confirmed the dealloying of Cr. Averaged EDS point scans of the surface (Table 4.3.2-1) of a coupon exposed to the salt show the removal of active alloying elements Cr, Mn, Ti, and Al, but Ni and Si are enriched.
Table 4.3.2-1. Comparison of the chemical composition in weight % of the surface of Incoloy-800H before and after corrosion testing as determined by EDS and *given by the manufacturer.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Mn</th>
<th>Ti</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Exposure Incoloy-800H*</td>
<td>42.3</td>
<td>31.6</td>
<td>20.4</td>
<td>0.80</td>
<td>0.60</td>
<td>0.50</td>
<td>0.13</td>
</tr>
<tr>
<td>Average EDS of 800H in ECS Salt</td>
<td>56.4</td>
<td>40.2</td>
<td>2.22</td>
<td>--</td>
<td>--</td>
<td>0.18</td>
<td>1.02</td>
</tr>
</tbody>
</table>

The surface of the Incoloy-800H was depleted in Cr down to about 2 %, and correspondingly enriched in Fe and Ni. The surface of the Incoloy-800H was also the only FLiNaK exposed coupon that had pitted (Fig. 4.3.2-1). EDS of the pits revealed they were enriched in Fe and depleted in Ni and Si in comparison to the general surface. Fe enrichment and/or Ni depletion was greater for larger pits. Al, Ti, Mn, and Cr all have more negative Gibb’s free energies of formation for their respective fluorides compared to Fe and Ni (Al being the most negative, followed by Ti, Mn, and Cr), and can be expected to be dealloyed selectively in relation to the more noble alloy matrix, as was discussed in section 2.2.1.

Fig. 4.3.2-1. A) Plan view SEM image of Incoloy-800H exposed to ECS FLiNaK coupon, B) higher magnification image showing pits on the surface of Incoloy-800H.

The grain boundaries in a cross-sectioned, mounted, and polished Incoloy-800H coupon showed voiding caused by the loss of Cr through dissolution (Fig. 4.3.2-2A). In the Cr EDS x-
ray map of an Incoloy-800H cross-section (Fig. 4.3.2-2B), it can be seen that the surface is severely depleted in Cr while the grains further from the surface are less depleted of Cr. Evidence of $\gamma'$ phase (Ni$_3$Al) was also observed in sample cross-sections within grains near the sample surface (not shown).

![Fig. 4.3.2-2. A) FESEM of cross-section (~1mm thick) of FLiNaK exposed Incoloy-800H, and B) Cr EDS x-ray map.](image)

### 4.3.3 Hastelloy-X

Hastelloy-X had visible grain boundary attack for a depth of at least 300 µm (Fig. 4.3.3-1). EDS point scans of the cross-sectioned sample shown in Fig. 4.3.3-2 and displayed in Table 4.3.3-1, were taken of the Hastelloy-X in the alloy matrix (point 1) as well as at the Mo enriched points in the grain boundary region (point 2) and within the grain (point 3). It can be seen that the alloy matrix near the attacked grains has been depleted in Cr. Mo enriched precipitates were found throughout the Hastelloy-X corrosion coupons and especially at the grain boundaries. EDS analysis of the Mo rich precipitates have shown that they have a low concentration of Cr and Fe compared to the Ni matrix and that the Mo/Ni atomic ratio was near one. Mo intermetallic compounds have been found by M. Streicher in Hastelloy alloys, after exposure of the alloys to
temperatures ranging from 650°C to 1200°C, who identified as them [Ni, Fe, Co]3[W, Mo, Cr]2 or μ phase; the intermetallic precipitates found in the present study are likely the same phase [10].

Fig. 4.3.3-1. SEM images of Hastelloy-X after corrosion tests in molten FLiNaK salt at 850°C. A) surface plan view, and B) cross sectional image.

Fig. 4.3.3-2. Mo enriched precipitates in a cross-sectional view of unetched Hastelloy-X.
Table 4.3.3-1. EDS point scans (weight %) of Mo enriched precipitates and alloy matrix. From points shown in Fig. 4.3.3-2.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Exposure Hastelloy-X</td>
<td>21.34</td>
<td>19.3</td>
<td>47.53</td>
<td>8.76</td>
</tr>
<tr>
<td>Point 1</td>
<td>5.05</td>
<td>26.4</td>
<td>59.45</td>
<td>4.38</td>
</tr>
<tr>
<td>Point 2</td>
<td>0.74</td>
<td>7.94</td>
<td>36.32</td>
<td>42.9</td>
</tr>
<tr>
<td>Point 3</td>
<td>7.04</td>
<td>11.0</td>
<td>36.08</td>
<td>37.8</td>
</tr>
</tbody>
</table>

4.3.4 Hastelloy-N

Hastelloy-N (6% Cr by weight) experienced minor corrosion compared to the Cr-rich alloys. Hastelloy-N experienced uniform Cr depletion for a depth of about 50 microns (Fig. 4.3.4-1 and Fig. 4.3.4-2B), and did not appear to experience significant grain boundary attack in contrast to the Cr rich alloys. Precipitates enriched in Mo were observed in Hastelloy-N (Fig. 4.3.4-1), and appeared to be concentrated at the grain boundaries (Fig. 4.3.4-2C). The Mo/Ni ratio was near one like the precipitates found in Hastelloy-X.

Fig. 4.3.4-1. Mo-enriched precipitates in unetched Hastelloy-N appear white in color in the SEM images A) surface plan view, and B) cross-sectional image.
4.3.5 Haynes-230

The surface of Haynes-230 was depleted in Cr and enriched in Ni with a mostly Ni layer present on the surface (Fig. 4.3.5-1A). Haynes-230 experienced dramatic grain boundary attack throughout its cross-section (Fig. 4.3.5-1B). Haynes-230, which contains about 14 weight percent W, had precipitates similar to those found in the Hastelloy-X and N alloys but with W as a primary constituent. The precipitates were found predominantly in the grain boundary regions. The W enriched precipitates in Haynes-230 are primarily W and Ni as seen by Fig. 4.3.5-2, with low concentrations of other elements.
Fig. 4.3.5-2. A) Grain boundary corrosion and W enriched precipitate in unetched Haynes-230. B) EDS line scan over the precipitate with the white arrow in A), note that the Cr level on the sides of the precipitate was still depleted in Cr from the initial alloy Cr level because the precipitate resided in a grain boundary region that underwent Cr dissolution attack. The base alloy surrounding the precipitates that resided on grain boundaries, as seen for several of the precipitates in A), was attacked by Cr dissolution.

4.3.6 Inconel-617

Inconel-617 had formed a thin Ni-Co rich layer at the surface (Fig. 4.3.6-1). As determined by EDS, the film consisted almost entirely of Ni (~72% atomic), and Co (~15% atomic). Like the other alloys with refractory based alloying additions, the refractory element, Mo in this case, formed a Mo enriched precipitate.

Fig. 4.3.6-1. Inconel-617 surface, showing a Ni-Co surface layer.
In Inconel-617 the grain boundary region and surface were dealloyed of Cr as seen in earlier alloys. The grain boundaries appeared to have connected open space, in contrast to the apparently unconnected grain boundary voiding seen in Incoloy-800H and Hastelloy-X. It appeared that FLiNaK was able to permeate the grain boundary network as inferred from Na EDS x-ray maps (20 kV) of Inconel-617 (Fig. 4.3.6-2). Evidence of η phase Ni₃Ti (not shown) was also observed in sample cross-sections within grains near the sample surface.

Fig. 4.3.6-2. A) Inconel-617 mounted cross-section showing surface and grain boundary attack, B) EDS x-ray map showing Na (and therefore FLiNaK) penetration into the grain boundary regions of the alloy. The darker regions represent higher Na concentrations.

4.3.7 Nb-1Zr

Nb-1Zr was predicted to have no visible chemical attack based on the results from the NASA studies mentioned earlier; however it had by far the highest weight-loss of all the alloys tested. The majority of weight-loss may have occurred during the ultrasonic cleaning step as mentioned in section 4.1, and after cleaning the samples appeared heavily attacked (Fig. 4.3.7-1). There are several plausible explanations for the alloy behavior observed. First, graphite from the fixturing rod could have diffused into and embrittled the Nb-1Zr. Next, a galvanic couple could have
formed between the graphite rod and the alloy, and third, contaminants from the FLiNaK or graphite rod could have been absorbed into and embrittled the alloy. The first possibility was tested using a graphite capsule test with Nb-1Zr without salt, and produced no measurable weight-loss. When cross-sectioned and investigated under an SEM, no secondary phases were found (Fig. 4.3.7-2A). However, when a fracture surface of a post-exposure coupon was investigated, it was found that the grains appeared to partition into many “flakes” in contrast to less corroded regions (Fig. 4.3.7-2B).

![Fig. 4.3.7-1. The Nb-1Zr coupons post corrosion testing were heavily corroded and brittle. The top most coupon, A) initially appeared to be the least corroded, and the bottom coupon, C) the most heavily corroded.](image1)

![Fig. 4.3.7-2. Nb-1Zr was heavily embrittled, but its cross-section microstructure did not show any precipitates or imply any formation of different phases, particularly carbide phases. A) shows a cross sectioned coupon. B) Shows the fractured surface from the lowest coupon from the coupon shown in Fig. 4.3.7-1C.](image2)
4.4 Post KCl-MgCl₂ Exposure Microstructure of Uncoated Incoloy-800H

The surface of the Incoloy-800H coupons exposed to KCl-MgCl₂ (Fig. 4.4-1) at 850°C were much less pitted than the surface of the coupons exposed to the FLiNaK salt. The EDS data obtained for the surface of the chloride exposed coupon was similar to that obtained for the fluoride exposed coupons, in that the surface was depleted in Cr to ~2%.

![SEM of the surface of the Incoloy-800H coupon exposed to molten KCl-MgCl₂.](image)

As displayed in Fig. 4.4-2, the loss of Cr through dissolution was less severe for the KCl-MgCl₂ exposed coupons as was the grain boundary Cr depletion compared to the FLiNaK exposed Incoloy-800H coupons. Many oxides, such as Al₂O₃ are stable in chloride salts; Al₂O₃ can be seen in Fig. 4.4-3B within the grain boundaries of the exposed coupons where Cr has been removed (Fig. 4.4-3C).
4.5 \textit{C/SiSiC and PyC/SiC Coated Composites}

The molten FLiNaK and KCl-MgCl$_2$ exposures of C/SiSiC composites and CVD PyC and SiC coated C/SiSiC composites yielded similar results in regards to chemical attack and the effectiveness of the CVD PyC coating to prevent attack by the molten salt. The results for the FLiNaK exposure tests have been discussed in depth elsewhere [51]. The coupons exposed to FLiNaK and KCl-MgCl$_2$ fractured into many pieces, all of which could not be retrieved for the FLiNaK exposed samples, making weight-change data unreliable in FLiNaK (Fig. 4.5-1 and Fig. 4.5-2).
Figure 4.5-1. Composites exposed to molten FLiNaK at 850°C for 500 h. A) Uncoated C/SiSiC composite, B) and C) CVD PyC and SiC coated C/SiSiC composites.

Fig. 4.5-2. A) and B) CVD PyC coated C/SiSiC composite coupons. B) fractured coupon. C) fractured uncoated C/SiSiC composite.

All the composites appeared to be prone to fracture. The high fracture rate was likely due to the heat treatments alone; two of the six coupons being coated fractured during the high temperature CVD process according to the company that applied the CVD coating (Hyper-Therm High-Temperature Composites, Inc.). Weight-change data was obtained for the KCl-MgCl₂ exposed coupons. It was found that the uncoated coupon gained weight, whereas the coated coupons gained much less (Fig. 4.5-3). There was still an avenue for chemical attack of the coated coupons however due to fracture.
Fig. 4.5-3. Weight-gain per area of the coated and uncoated C/SiSiC composites after exposure to KCl-MgCl$_2$ at 850°C for 500 h in a graphite crucible. The coated coupons experienced much less weight-gain than the uncoated coupon.

Similar attack was found on the uncoated FLiNaK and KCl-MgCl$_2$ salt exposed C/SiSiC composites (Fig. 4.5-4 and Fig. 4.5-5). In the KCl-MgCl$_2$ salt exposed coupon, it was found that a Mg and Si oxide had formed in regions of the surface (Fig. 4.5-5 and Table 4.5-1).

Figure 4.5-4. A) Cross sectional SEM images of the uncoated C/SiSiC composite after exposure to molten FLiNaK 850°C for 500 h with depleted silicon and B) showing severe corrosion attack along the SiC grains and inter phase boundaries. (Source: [51])
Fig. 4.5-5. Plan view of the uncoated C/SiSiC composite exposed to KCl-MgCl₂ for 500 h at 850°C.

Table 4.5-1. EDS Analysis of points shown in Fig. XX. In Atom %.

<table>
<thead>
<tr>
<th>EDS Point</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.5</td>
<td>33.68</td>
<td>26.7</td>
<td>26.1</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>36.23</td>
<td>1.0</td>
<td>62.3</td>
</tr>
</tbody>
</table>

For both coupons, the CVD PyC/SiC coatings had prevented corrosion of the base Si where the PyC coating had maintained integrity. Fig. 4.5-6 shows a SEM of the surface of a PyC/SiC coated C/SiSiC coupon where the coating had been damaged from preparations to fixture the coupon for testing. It can be seen that the PyC region had remained unattacked.

Fig. 4.5-6. CVD PyC/SiC coated C/SiSiC coupon surface near the fixturing hole region post KCl-MgCl₂ exposure. The fixturing holes had to be redrilled prior to corrosion testing, which partially fractured the coating in regions such as that shown above, where the PyC coating is apparent, as is the attacked SiC coating region and underlying C/SiSiC substrate.
4.6 Graphite/Alloy Interaction in FLiNaK

Due to the construction of the graphite crucible in which the alloy/molten salt exposure test occurred, the alloy coupons were in intimate contact with graphite (fixturing rod and fixturing screws were made of graphite). Therefore, conditions that are necessary to facilitate galvanic corrosion are present, in that the alloys and graphite are likely far apart on the galvanic series (there is no known galvanic series data in FLiNaK), and the alloys and graphite are in electrical contact by the molten salt electrolyte. Because the molten salt is highly conductive, it is able to spread the corrosion over a large area of the less noble alloy, which would mask the otherwise tell tale signs of galvanic corrosion (i.e. the corrosion at the junction of the alloy and the graphite did not appear worse than elsewhere on the alloy) [95]. If galvanic corrosion were occurring, the small area of the anodic coupon (nominally 8 cm² per coupon), in comparison to the large area of the cathodic graphite crucible (nominally 250 cm²), could lead to a large corrosion driving force [95].

Therefore, in addition to the alloy samples, the graphite fixturing rods and crucibles were also analyzed. A grey film found on some of the graphite rods to which the coupons were fixtured was evidence of an interaction between graphite and the test alloy. The graphite components were analyzed extensively using SEM, EDS, XRD, XPS, and RBS techniques.

The film was most prevalent on the graphite fixturing rods from the Incoloy 800H, Haynes-230, and Inconel-617 coupon salt exposure tests. Fig. 4.6-1 shows the contrast between a fixturing rod (with a grey film) from a salt exposure with a high Cr alloy and the fixturing rod from a low Cr alloy (that did not have a visible film present).
Fig. 4.6-1. A grey film was visible on the high Cr alloy rods from the tests that experienced the most severe corrosion in contrast to the graphite rods from the no and low Cr alloy containing crucibles. A) Incoloy-800H (20% Cr by weight), B) Hastelloy-N (6% Cr by weight).

Some of the salts also had a darker appearance than others shown in Fig. 4.6-2. A possible reason for this could be graphite and therefore carbides contaminants in the FLiNaK salt. The primary Cr fluorides expected in the FLiNaK, CrF2 and CrF3 are greenish in color, and should result in a salt with that color upon freezing. I. Ozeryanaya et al. has described a process by which carbon or graphite material in molten NaCl may absorb ions and acquire a charge that in turn stabilizes the colloidal particles of carbon [96]. It is hypothesized a similar process may have been responsible for the grey coloration of the salt in Fig. 4.6-2A.

Fig. 4.6-2. A) The salt in the graphite crucible that contained the Haynes-230 had a grey color after corrosion testing, possibly due to suspended graphite or carbide particles in the salt. B) This was in contrast to other salts that appeared a bright white (Nb-1Zr test capsule).
Immediately upon removal from the graphite crucible it was seen that the refractory alloy Nb-1Zr coupons appeared to be coated in a black coating (Fig. 4.6-3). The Nb-1Zr coupons were the only ones that appeared to develop a black coating similar in coloration to the graphite rod.

Fig. 4.6-3. Nb-1Zr immediately after removal from graphite corrosion capsule, prior to cleaning and weighing.

The graphite rods were sectioned into pieces and a region immediately adjacent to the alloy coupons was prepared for quantitative analysis. The Cr rich film (Fig. 4.6-4) present on the coupon rod from the Incoloy-800H crucible on average contained about 1:3 ratio of Fe:Cr, as shown in Table 4.6-1 (for Incoloy-800H the Fe:Cr ratio is about 2:1). Films present on the graphite fixturing rods from other high Cr alloy molten salt exposures were primarily Cr enriched and had negligible concentrations of other elements. EDS does not provide for a reliable, quantitative C determination due to C contamination from the environment (called adventitious C).
Fig. 4.6-4. SEM of Cr-rich film on graphite fixturing rod from Incoloy-800H containing crucible tests.

Table 4.6-1. EDS point corresponding to number 1 in Fig. 4.6-4. Data in atomic %.

<table>
<thead>
<tr>
<th>EDS Point</th>
<th>C</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>57.9</td>
<td>32.2</td>
<td>9.4</td>
</tr>
</tbody>
</table>

As seen in Fig. 4.6-5, the Cr and Fe were present as a surface film on the Incoloy-800H coupon fixturing rod and did not penetrate deeply into it. The thickness of the Cr rich layer varied between graphite rods. The film was thickest for the Incoloy-800H coupon fixturing rod (~15 µm), thinner for the Haynes-230 coupon fixturing rod (~5 µm), and thinnest for the Inconel-617 coupon fixturing rod (~2 µm). As seen previously, Haynes-230 had the greatest weight-loss/area, followed by Inconel-617, and Incoloy-800H. The thickness of the films on the graphite rods therefore does not correlate directly with the weight-loss/area.
Fig. 4.6-5. SEM on graphite central fixturing rod from (A) Incoloy-800H corrosion experiments with a ~15 micron thick carbide layer. EDS x-ray mapping of elemental B) Cr, and C) Fe, show the elements are concentrated on the surface and do not penetrate into the graphite.

XRD analysis of the film on the graphite fixturing rods detected Cr$_7$C$_3$ from the molten salt exposures of Incoloy-800H, Haynes-230, and Inconel-617. The XRD data from the Incoloy-800H matches the XRD data card for Cr$_7$C$_3$ (Fig. 4.6-6), except for a peak shift of a few degrees, thought to be from the 1:3 Fe:Cr atomic ratio. XRD analysis of Haynes-230 and Inconel-617 coupon rods also indicated Cr$_7$C$_3$ peaks, but with no misalignment. In the case of Inconel-617, an additional peak was present that corresponded with Cr$_3$C$_2$. 
XPS detected multiple C peaks (Fig. 4.6-7), with one at 282.7 eV that is associated with carbide formation [97]. While not shown, the XPS data from the Cr 2p$_{3/2}$ and 2p$_{1/2}$ peaks and from the Fe 2p$_{3/2}$ peak also closely match XPS data from M. Detroye et al. for (FeCr)$_7$C$_3$ [98].
Fig. 4.6-7. XPS data from the Cr rich film found on the graphite rod that was used to fixture the Incoloy-800H coupons. The sample was progressively sputtered with Ar, followed by sampling of the electron binding energy, leading to a decreasing peak from adventitious C contamination and increasing peaks from the graphite rod and carbide.

The graphite crucible underwent the same reactions as the graphite fixturing rod; however, because the fixturing rod was in closer proximity to the samples, much more of the corrosion products deposited on the fixturing rods than the crucible walls. EDS was not sensitive or precise enough to reliably detect Cr in the graphite crucible wall. Therefore, Rutherford backscatter spectroscopy (RBS) was used to determine the concentration of Cr as a function of depth into the graphite crucible, in a high Cr alloy that did not show the same gray layer on the central graphite rod (Hastelloy-X). Cr was detected and decreased with depth (Fig. 4.6-8), albeit at much lower concentrations (starting at near 5 atom % and decreasing to near zero within the first 1 to 2 microns).
4.7 Mo-Plating as a Cr Diffusion Barrier

4.7.1 Diffusion Anneals

To verify the Mo-plating adhesion and to experimentally determine the diffusion properties of elements in Mo, coupons were annealed at 850°C, for 500 h, and 1000 h, in the same sealed quartz ampoule setup discussed in section 3. Heat treatment results (Fig. 4.7.1-1), demonstrate that the Mo-plating adhered to the base alloy, no cracks penetrated the entirety of the substrate, and Cr and Fe diffusion were greatly reduced compared to that in the Ni-plating.

Submicron grains developed and oxygen from oxides in the Mo-plating reacted with Cr at the alloy/Mo interface during the heat treatments. For the coupon that under went the 500 h, 850°C heat treatment; the Cr oxide layer that developed at the 800H/Mo interface was about 2 µm in thickness (Fig. 4.7.1-1B). In general, as annealing time was increased (at 850°C), the Mo layer...
consolidated, voids coalesced, and the Cr oxide interlayer increased in thickness (Fig. 4.7.1-1C). Cr became depleted in the substrate near the Mo-plating interface as it formed the Cr oxide. From the EDS data in Fig. 4.7.1-2, it was surmised that the Cr oxide was present as Cr$_2$O$_3$. The Gibbs free energy of formation of Cr$_2$O$_3$ from the reactions

$$3\text{MoO}_2 + 4\text{Cr} \rightarrow 2\text{Cr}_2\text{O}_3 + 3\text{Mo} \quad \text{Equation 4.7.1-1}$$

and

$$\text{MoO}_3 + 2\text{Cr} \rightarrow \text{Cr}_2\text{O}_3 + \text{Mo} \quad \text{Equation 4.7.1-2}$$

show that both are thermodynamically favorable; Cr$_2$O$_3$ formation results in a more negative Gibb’s free energy of formation than MoO$_2$ or MoO$_3$ formation at 850°C.

![Fig. 4.7.1-1. Cross-sectioned Mo plasma sprayed Incoloy-800H coupons. The Mo-coating is about 160 µm thick. A) As received microstructure, B) After 500 h at 850°C in He, C) After 1000 h at 850°C in He.](image)
Fig. 4.7.1-2. A) Mo-plated Incoloy-800H showing the formation of a Cr oxide interlayer after a 500 h, 850°C, heat treatment. B) EDS line-scan over the Cr oxide in A (arrow).

4.7.2 FLiNaK Exposure

Mo-plated samples underwent the same FLiNaK exposures as the unplated coupons (graphite capsule, 500 h, 850°C). After testing, it was seen that the Mo-plating delaminated from the substrate and was non-protective of the underlying substrate resulting in Cr dissolution from the substrate and a large weight-loss per area. The exact cause of the delamination was not immediately apparent, and would require further investigation to pinpoint. The delamination could have been due to incomplete coating, cracks in Mo-plating at edges, differing thermal expansion coefficients of Mo and the Incoloy-800H, formation of Cr oxide at the Mo/800H interface leading to stresses there, brittle intermediate Fe-Mo phases [99], or all/some combination.

Because the Mo-plating delaminated, the underlying Incoloy-800H had the same general appearance and characteristic Cr dealloying as the uncoated Incoloy-800H. Mo/substrate interdiffusion was found to have occurred in some locations despite the Cr oxide barrier (Fig. 4.7.2-1). Mo enriched particles were found on the surface of the Incoloy-800H (Fig. 4.7.2-1A) and Cr, Fe and Ni were found on the surfaces of the Mo plating (Fig. 4.7.2-1B and Fig. 4.7.2-1C), as seen from the EDS point scans in Table 4.7.2-1.
Fig. 4.7.2-1. Incoloy-800H surface after the FLiNaK exposure and Mo-plating had delaminated. B and C) Plan-view SEM of Mo-plating outer and inner surfaces, respectively, showing EDS point scan regions.

Table 4.7.2-1. EDS point scans corresponding to numbers in SEM images from Fig. 4.7.2-1. Atomic %.

<table>
<thead>
<tr>
<th>EDS Point</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.23</td>
<td>3.08</td>
<td>13.38</td>
<td>34.89</td>
<td>34.57</td>
</tr>
<tr>
<td>2</td>
<td>1.23</td>
<td>2.30</td>
<td>42.31</td>
<td>52.00</td>
<td>1.82</td>
</tr>
<tr>
<td>3</td>
<td>10.54</td>
<td>3.44</td>
<td>36.23</td>
<td>1.80</td>
<td>46.56</td>
</tr>
<tr>
<td>4</td>
<td>6.73</td>
<td>3.68</td>
<td>42.37</td>
<td>2.60</td>
<td>44.12</td>
</tr>
<tr>
<td>5</td>
<td>12.37</td>
<td>2.30</td>
<td>15.20</td>
<td>26.43</td>
<td>43.63</td>
</tr>
<tr>
<td>6</td>
<td>6.99</td>
<td>2.69</td>
<td>39.06</td>
<td>10.72</td>
<td>40.30</td>
</tr>
</tbody>
</table>

Fe, Ni, and Cr were found on the surfaces of the Mo-plating, with Ni exclusively found in large quantities on the inside face of the Mo-plating (Fig. 4.7.2-2). The relative position of the Ni can be explained by its low solubility in FLiNaK; the only way it could have gotten into the plating was through interdiffusion. Fe and Cr however could dissolve into solution, and redeposit on the more electropositive Mo surface. This phenomenon has been found to occur between electronegative metals and electropositive containers in heat treatment salts [56].
The experiments on Mo-coating, combined with the observation of stable Mo-based precipitates in certain alloys after molten salt corrosion tests indicate that surface treatment to enrich the surface with Mo may be generally beneficial to protect alloys from molten FLiNaK corrosion.

4.8 *Sulfamate Ni Electroplating as a Cr Dissolution Barrier*

4.8.1 **Diffusion Anneals to Investigate Diffusion Pathways**

Cr will eventually diffuse through the Ni-plating to the surface, and once at the surface it may be removed via dissolution if the salt is at an oxidizing redox potential compared to the surface chemistry of the alloy [8]. To gauge the expected time until Cr would diffuse to the surface of the Ni-plating, a series of diffusion anneals over a range of temperatures was undertaken so that the effective Cr interdiffusion coefficient could be calculated as a function of temperature. The diffusion anneals were undertaken in He filled quartz ampoules due to the simplicity of the design and the increased speed at which the coupons could be evaluated. The Ni-plated coupons were
cross-sectioned after the diffusion anneals, and EDS linescans for Cr, Fe, and Ni were taken across the diffusion zones at the substrate/plating interface to determine the Cr concentration profiles. Effective Cr interdiffusion coefficients were then calculated by a least squares fit as mentioned in the experimental section. It has been recommended that a minimum of 3-5 linescans be used to get an averaged diffusion coefficient to reduce error [41]. For this work, a minimum of 5 to 7 linescans (over different regions of the plating) were used to determine the effective Cr interdiffusion coefficients. Subsequently, a single effective Cr interdiffusion coefficient was determined by averaging from the multiple Cr interdiffusion coefficients for each temperature investigated (Table 4.8.1-1). The averaged effective Cr interdiffusion coefficient as a function of inverse temperature is shown in Fig. 4.8.1-1, the error bars represent the standard deviation of the 5-7 independently calculated Cr interdiffusion coefficients, and the points represent the averaged Cr interdiffusion coefficient value. Diffusion anneal times were initially limited so that Ni-plating could be considered semi-infinite in thickness [100], i.e.

\[
\text{thickness} > 10\sqrt{D_{Cr}^\text{eff} \cdot t}.
\]

\textbf{Equation 4.8.1-1}

In general, it is found that the grain boundary diffusion contribution becomes significant below \(~0.75-0.8\ T_{melt}\ \text{(in K)}\) [29]. Grains are smaller at lower temperatures, and there is a greater relative cross-sectional area of the grain boundary through which an element may diffuse [29]. In FCC metals the activation energy for grain boundary diffusion is about half that of lattice diffusion (due to the more open structure of the grain boundary) so grain boundary diffusion rates increase less rapidly than lattice diffusion rates with temperature [29, 39]. The contributions from grain boundary diffusion are negligible at high temperatures, but dominate at low temperatures [29].
Fig. 4.8.1-1 shows a graph of the effective Cr interdiffusion coefficient as a function of inverse temperature of Ni-plated 800H (batch-2), a Ni-plated model alloy (batch-3), and B. Million et al.’s Cr tracer diffusion data (10.1% Cr, 78.7% Ni), that is valid for lattice diffusion. Additionally, exponential curves of best fit are shown for the Ni-plated Incoloy-800H and B. Millions data. The change in slope of the curve around 0.75-0.8 T_{melt} (for Ni: 1000°C-1100°C) corroborates the observation that grain boundary diffusion becomes important below this temperature [29]. In diffusion studies of electroplated Cr on electroplated Ni, grain boundary diffusion of Cr through Ni was found to be significant between ~600°C-1000°C [101]. The slope change occurs because grains are smaller at lower temperatures and there is a larger grain boundary area through which Cr may diffuse, and also because the difference between the lattice diffusion coefficient and the grain boundary diffusion coefficient decreases as temperatures increase [29, 85]. As grain size increases with temperature the total grain boundary area decreases. If the measurement was only of lattice diffusion the slope of the line would be constant until ~600°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Calculated Cr Interdiffusion Coefficient (cm²/s)</th>
<th>Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>9.5E-13 ± 3.5E-13</td>
<td>7</td>
</tr>
<tr>
<td>750</td>
<td>1.4E-12 ± 3.4E-13</td>
<td>5</td>
</tr>
<tr>
<td>800</td>
<td>3.2E-12 ± 1.2E-12</td>
<td>8</td>
</tr>
<tr>
<td>850</td>
<td>2.9E-12 ± 1.2E-12</td>
<td>14</td>
</tr>
<tr>
<td>900</td>
<td>9.8E-12 ± 2.4E-12</td>
<td>23</td>
</tr>
<tr>
<td>950</td>
<td>1.6E-11 ± 6.0E-12</td>
<td>21</td>
</tr>
<tr>
<td>1000</td>
<td>2.3E-11 ± 9.3E-12</td>
<td>37</td>
</tr>
<tr>
<td>1050</td>
<td>6.0E-11 ± 1.3E-11</td>
<td>125</td>
</tr>
<tr>
<td>1100</td>
<td>7.6E-11 ± 4.7E-12</td>
<td>59</td>
</tr>
<tr>
<td>1150</td>
<td>2.2E-10 ± 3.4E-11</td>
<td>63</td>
</tr>
<tr>
<td>1200</td>
<td>4.7E-10 ± 5.2E-11</td>
<td>111</td>
</tr>
</tbody>
</table>
Fig. 4.8.1-1. Calculated Cr interdiffusion coefficient in Ni electroplate, plotted with higher temperature Cr tracer diffusion data from B. Million et al. [32].

4.8.2 Grain Growth to Reduce the Effective Cr Interdiffusion Rate

Grain growth was investigated to mitigate Cr diffusion because increasing grain size would lower the contribution of grain boundary diffusion to the overall effective Cr interdiffusion rate. Specifically, this involved heating the sample up to 1200°C for 1 min, followed by mechanical deformation of the Ni-plating thickness to ~60% by cold rolling, then annealing at 950°C for 15 min. The modified plating coupons were then tested in a He environment at 700°C for 217 h and 1000 h, and at 850°C for 500 h. Additionally, one modified and unmodified coupon were exposed to FLiNaK at 700°C for 1000 h. The coupons were cross-sectioned and polished after the He and salt exposures, and the effective Cr interdiffusion rates were estimated from EDS line-scan data (Table 4.8.2-1). It must be noted that because the kinetic regime was solidly in the B kinetic regime for the modified coupons (to be discussed more in the discussion section), the calculated effective Cr interdiffusion data provided an approximate but usable estimate of Cr diffusion rates. The grain sizes reported in table 4.8.2-1, were determined post diffusion anneal
for the unmodified Ni-plating, and from a single representative sample for the modified plating prior to diffusion annealing. The point during processing at which the grain size was measured is shown in the flowchart in figure 4.8.2-1.

Table 4.8.2-1. Effective Cr interdiffusion data estimated from Cr concentration curves obtained from EDS line-scans. *Measured post diffusion anneal for unmodified plating, measured from single modified plating pre-diffusion anneal. **Plating exhibited multiple grain size zones.

<table>
<thead>
<tr>
<th>Processing</th>
<th>Anneal Time (h)</th>
<th>Anneal Temperature (°C)</th>
<th>Grain Size* (µm)</th>
<th>Approximate Effective Cr Interdiffusion Rate (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>217</td>
<td>700</td>
<td>7</td>
<td>9.5E-13 ± 3.5E-13</td>
</tr>
<tr>
<td>Modified</td>
<td>217</td>
<td>700</td>
<td>71</td>
<td>2.3E-13 ± 5.8E-13</td>
</tr>
<tr>
<td>Unmodified</td>
<td>1000</td>
<td>700</td>
<td>8</td>
<td>5.2E-13 ± 1.7E-13</td>
</tr>
<tr>
<td>Modified</td>
<td>1000</td>
<td>700</td>
<td>71</td>
<td>6.2E-13 ± 1.1E-13</td>
</tr>
<tr>
<td>Unmodified</td>
<td>500</td>
<td>850</td>
<td>17</td>
<td>1.4E-12 ± 7.4E-13</td>
</tr>
<tr>
<td>Modified</td>
<td>500</td>
<td>850</td>
<td>71</td>
<td>3.2E-12 ± 2.8E-12</td>
</tr>
</tbody>
</table>

**FLiNaK Exposed**

| Unmodified | 1000 | 700 | ** | 1.7E-13 ± 6.7E-14 |
| Modified   | 1000 | 700 | 71 | 9.2E-14 ± 9.1E-14 |
Fig. 4.8.2-1. The grain size was measured post diffusion anneal for the unmodified samples. The grain size was measured post processing, but pre-diffusion anneal for the modified plating samples.

The modified Ni-plating may be seen in Fig. 4.8.2-2 after plating deformation and the recrystallization anneal. It can be seen that the thermomechanical processing resulted in the production of a plating structure usually about one grain thick, with occasional regions on the surface of the plating having smaller grains.
Fig. 4.8.2-2. Modified Ni-plating (after grain growth), prior to diffusion studies.

The etched microstructure of the modified plating is shown after the diffusion annealing at 700°C for 1000 h, and 850°C for 500 h in He in Fig. 4.8.2-3. Note: the Ni-plating etch is ineffective on etching Ni with virtually any Cr in it, so if a region etches, it is indicative that it is pure Ni. Cr diffusion to the surface of the Ni-plating through grain boundaries is evident in Fig. 4.8.2-3 due to the raised (less etched) grain boundaries and unetched surface region. The Cr diffused preferentially along the grain boundaries to the surface region of the alloy, where the Cr was able to diffuse into smaller grains via lattice diffusion. The Cr grain boundary diffusion was also verified using EDS analyses. It is apparent that there was increased lattice diffusion of Cr from the grain boundaries into the grains for the coupons exposed to 850°C for 500 h (Fig. 4.8.2-3B).
Fig. 4.8.2-3. A) Modified Ni-plating after diffusion annealing at 700°C for 1000 h, B) Modified Ni-plating after diffusion annealing at 850°C for 500 h. Both etched using the Ni-201 etchant in Table 3.7-1.

The smaller grain structure of the etched unmodified Ni-plating diffusion annealed in He at 700°C for 1000 h, and 850°C for 500 h is shown in Fig. 4.8.2-4.
The etched microstructure of the modified and unmodified Ni-plating is shown after exposure to FLiNaK at 700°C for 1000 h in Fig. 4.8.2-5. It is apparent that the microstructure of the unmodified Ni-plating exposed to FLiNaK is different than the microstructure of the coupons exposed to He, in that the grains near the substrate interface grew larger than the grains in the He exposed coupon, whereas the grains near the surface of the plating appeared to remain closer in size to the He exposed coupons. In the modified Ni-plating exposed to FLiNaK, the grain boundary Cr diffusion apparent in Fig. 4.8.2-3 is not obvious.

The FLiNaK exposed coupons (both modified and unmodified Ni-Plating) incurred a slight weight-gain, but the weight gain was less for the modified plating coupon. The modified and unmodified coupons exposed to FLiNaK at 700°C for 1000 h in the Ni crucible both experienced weight-gain, whereas the unmodified Ni-plated coupons exposed to FLiNaK at 850°C for 500 h
in the graphite crucible experienced weight-loss. However, the modified Ni-plated coupons gained half as much weight as the unmodified plating when exposed to FLiNaK (700°C, 1000 h).

Fig. 4.8.2-5. A) Modified Ni-plating exposed to FLiNaK at 700°C for 1000 h, B) Unmodified Ni-plating exposed to FLiNaK at 700°C for 1000 h.

4.9 Alloy Air Oxidation Studies

As discussed earlier, the dissolution resistance of Fe-Ni-Cr alloys in pure molten fluorides can usually be correlated to the Cr content of the alloy, with more dissolution as Cr content increases. However, a minimum Cr content is also required for oxidation resistance on the outside of air exposed piping. Therefore, a compromise in Cr content must be made, or a way to reduce Cr dissolution in FLiNaK must be implemented, for any piping that is simultaneously exposed to both molten salt and air. Alternatively, an oxidation resistant coating could be applied to the piping exterior. The Cr content in Hastelloy-N was chosen as the minimum (~8 atomic % Cr) that would still protect against excessive oxidation on the air-exposed side at the maximum envisioned temperature of molten salt reactors.
Although extensive data likely exists on the oxidation resistance of all the alloys chosen, it was desirable to corroborate the oxidation resistance of the specific heats of the investigated alloys. Six alloys and Ni-plated Incoloy-800H were tested for air-oxidation resistance at 850°C for 500 h in a tube furnace that was open to air on one side.

Shortly after starting the oxidation test (~30 min), it could be seen that the Nb-1Zr appeared to “puff up” on the edges. By the next day, this coupon had split in half, swollen enough to break the wire suspending it, and fallen to the base of the tube heater (Fig. 4.9-1A). It did not appear that the Nb-1Zr coupon was in contact with any of the other coupons, so it was decided to continue with the test, leaving the Nb-1Zr coupon in place until the completion of the testing.

![Fig. 4.9-1. A) The Nb-1Zr coupon completely oxidized early in the oxidation test leaving a yellow, brittle structure, B) The oxidized Ni-plating readily flaked off of the Ni plated Incoloy-800H coupon. By the time this photo was taken, a large portion of the Ni-plating had flaked off of the side photographed.](image)

The results from the air oxidation test confirmed expectations (Fig. 4.9-2). The Nb-1Zr performed worst, which was predicted since it is well known to oxidize rapidly. The Ni-201 was the second worst performer; this was also expected because it did not have any Cr in it which is necessary for high temperature oxidation resistance. Likewise, the Ni-plating on the Ni-plated Incoloy-800H coupon oxidized and after the test the oxidized plating flaked off when stress was
applied (Fig. 4.9-1B). For this reason, the weight gain data may be underestimated for the Ni-plated Incoloy-800H coupon. The rest of the oxidation results were consistent for high temperature oxidation resistant alloys. It could be suspected that an Fe superalloy would be more prone to oxidation than a Ni one; however this was not guaranteed due to the differences in Cr content between the alloys. Thus the application of Ni-plating on only the inner surface (salt side) of a piping on a high Cr alloy would be a cost-effective solution to independently optimize against molten salt corrosion on the inner side and air oxidation on the outer side of the piping.

![Weight Gain Data Chart]

**Fig. 4.9-2.** Weight gain data after air oxidation tests of various alloys. The alloys that did not have Cr in them all experienced severe weight gain. The superalloys that had Cr in them for oxidation protection and solid solution strengthening performed better.

4.10 Electrochemistry as a Corrosion and Compatibility Diagnostic

4.10.1 Anodic Stripping Voltammetry

Salt obtained from the Haynes-230 salt exposure at 850°C, for 500 h, was used to verify the viability of the ASV method for determination of corrosion products in FLiNaK. Several peaks
were identified (Fig. 4.10.1-1) in the voltammograms obtained from anodic stripping analysis in the used salts. In order to identify the exact species responsible for each peak and rule out other possibilities, more experiments would be necessary which involve only one species to positively match peaks and concentrations to oxidation potentials and current (respectively). Work on this was undertaken for Cr and Fe, and was reported in the thesis of D. Ludwig [66].

Fig. 4.10.1-1. Voltammogram from anodic stripping voltammetry in molten FLiNaK containing corrosion impurities using a 15 second plating step, a scan rate of 100 mV/s during the stripping step, followed by a 10 second cleaning step. Each peak likely represents a different chemical species and is likely a corrosion product formed by the corrosion of Haynes-230 in molten FLiNaK.

The initial electrochemistry tests ran from a potential from -1.5 to 3 V versus a platinum quasi-reference electrode. It was later determined from these tests and from a review of the literature two things: 1) that platinum oxidizes at potentials more positive than 1.5 V versus the
platinum quasi-reference electrode (Fig. 4.10.1-2), and that aluminum oxide is not stable in molten fluorides as determined by a decrease in aluminum oxide surface area. Furthermore, chromium was noted to deposit on the aluminum oxide electrodes over time (it is not known at this time whether the chromium was deposited as a fluoride or as an oxide, but both species possess a green appearance) as shown in figure 4.10.1-3.

Fig. 4.10.1-2. Oxidation of the counter electrode and working electrode material can be seen in these light micrographs.

Fig. 4.10.1-3. Likely chromium deposit on aluminum oxide electrodes exposed to FLiNaK.
4.10.2 Potentiometry

Potentiometry of several alloys versus a Ni-Ni(II) RE was also investigated. In potentiometry, the potential is measured between two electrodes. The WE in this case was shaped like a flag and was a small square of alloy tack welded onto a Ni-wire. While initial results were promising (Fig. 4.10.2-1), time and material constrains did not allow for further investigation. From the potentiometry, Ni-201 was found to be the most cathodic, and Hastelloy-X the most anodic of the 4 alloys tested. Hastelloy-N was in between the Hastelloy-X and Ni-201. Less expected was the position of Incoloy-800H in comparison to Hastelloy-X and Ni-201; since Hastelloy-X has similar Cr content, yet much higher Fe content than Hastelloy-X, it was expected to have a more cathodic potential. Verification of all alloys (and especially Incoloy-800H) potentials would be needed for further analysis.

![Graph showing potentiometry results for several alloys versus a 10% Ni-Ni(II) RE in FLiNaK at 650°C.](image-url)

Fig. 4.10.2-1. Potentiometry results for several alloys versus a 10% Ni-Ni(II) RE in FLiNaK at 650°C.
5 Discussion

5.1 General Alloy Corrosion Behavior

5.1.1 Weight-loss Per Area Correlation with Initial Alloy Cr Content

The literature has suggested a correlation between weight-loss of austenitic Ni and Fe-Ni based alloys and Cr content. In experiments performed by NASA in fluoride salts, a general increase of attack with increasing Cr level was observed. It is pertinent to determine if the molten salt exposed alloy weight-loss/area data is also correlated with Cr content. Ni-plated Incoloy-800H is not considered here since it is not completely known how the Ni-plating influenced the Cr levels of the base alloy and to what extent the diffusion of Cr into the Ni-plating would affect this correlation. Fig. 5.1.1-1 shows a reasonable correlation between weight-loss/area and the initial alloy Cr content.

![Graph showing weight-loss per area correlation with initial alloy Cr content](image)

Fig. 5.1.1-1. The weight-loss per area approximately correlates to the initial alloy Cr content.
5.1.2 Cr in Post-Exposure Salt Correlation with Initial Alloy Cr Content

Fig. 5.1.2-1 plots the Cr content in the FLiNaK salt (ppm weight) for each Fe-Ni and Ni-based alloy exposure (Table 4.2-2) as a function of initial alloy Cr content. Again, there appears to be a reasonable correlation between the Cr content in the salt and the initial Cr content of the alloy. According to research from ORNL, for FLiNaK containing 2.5% (mole %) uranium tetrafluoride, the equilibrium content of Cr in the salt at 600°C is ~1100 ppm by weight, and at 800°C, ~2700 ppm [8]. It is expected that for non-fuel bearing salts, the equilibrium content would be somewhat lower [8].

![Graph showing correlation between Cr content in FLiNaK salt and initial Cr content in alloy.](image)

Fig. 5.1.2-1. Correlation between Cr in the salt after corrosion tests and the initial Cr content of the alloy.
5.1.3 Weight-loss Per Area Correlation with Initial Alloy C Content

Weight-loss per area was also correlated to the initial C content of the high Cr alloys (~20%-23% by weight). Fig. 5.1.3-1 shows weight-loss/area as a function of C content for several alloys with similar Cr concentrations. Due to the known tendency of Cr and C to form carbides at the test temperatures, the C in the alloys forms Cr carbides at the grain boundaries that are responsible for the weight-loss/area correlation and grain boundary Cr loss and void formation.

![Graph showing weight-loss per area versus weight % Carbon in Alloy]

Fig 5.1.3-1. Weight-loss per area correlates well with precorrosion alloy C content for the alloys that have similar Cr levels.

C already present in the alloys diffuses in the alloys and forms carbides at elevated temperatures. The primary carbide formed in the alloys of consequence is Cr carbide, Cr being a primary alloying constituent. In FLiNaK salt, Cr is the most corrosion prone alloying constituent for Fe-Ni-Cr alloys. It is noted that Ti will also form carbides that can concentrate at grain boundaries, but Ti is less than 1% for all the alloys exposed.

M. Streicher has shown that Hastelloy alloys can suffer from aqueous intergranular corrosion if the alloy is held between 650°C-1200°C for extended periods, due to carbide formation and to a
lesser degree, intermetallic phase formation [10]. The intergranular corrosion in aqueous solutions was found to decrease dramatically by the removal of C [10]. J. Jackson et al. exposed cast Fe-Ni-Cr alloys in molten salt heat treatment baths and concluded that intergranular corrosion along carbide networks was more responsible for mass loss than general surface attack [27]. Furthermore, Streicher found that carbides formed in Hastelloy alloys were of the (Cr, Fe)\textsubscript{23}C\textsubscript{6} variety [10]. Cr\textsubscript{23}C\textsubscript{6} usually forms at the grain boundaries, as the carbide in Fig. 5.1.3-2A demonstrates [77].

Streicher suggested that the grain boundary attack in aqueous solutions occurred due to galvanic action on the alloy surface between the anodic grain surface, and the cathodic carbide precipitates at the grain boundary (i.e. the carbides are protected, while the alloy adjacent to them is corroded) [10]. This cannot be the case for the alloys exposed to FLiNaK however, because post exposure, the Cr carbides have disappeared (this could still be the case for the refractory carbides seen in some alloys however). It appears that the carbides are being attacked by the FLiNaK, but this cannot occur in the alloy away from the surface if the voiding is unconnected. It is hypothesized that the Cr is concentrated at the surface of the alloy along the grain boundaries, and is dissolved into the salt as the salt/alloy/graphite system attempts to reach equilibrium. The Cr carbides that are not directly connected to the Cr carbide network will still be affected by the direct dissolution of the Cr carbides by the salt due to a higher concentration gradient, and therefore increased diffusion rates within the grain boundary. The faster diffusion pathways along the grain boundary networks than lead to depletion of Cr at the grain boundaries and void formation (Fig. 5.1.3-2B).

T. Chen et al., has shown that increasing C content (0.004 to 0.07 % by mass) and the resulting formation of M\textsubscript{23}C\textsubscript{6} at grain boundaries will lower the grain boundary diffusion rate of Cr over a wide temperature range (note: there was no Cr removal mechanism in his study), but has little effect on bulk diffusion [85]. This demonstrates that increased C content does not lead
to increased grain boundary diffusion by itself. The structure of the carbides at the grain boundary however, may become more connected with increasing C content, and this increase in connectivity of the Cr carbides that are attacked directly by the FLiNaK is hypothesized to be the fundamental origin of the correlation between the weight-loss per area and the C content for the high Cr alloys.

In Inconel-617 and Haynes-230, the grain boundary region appeared to have connected open space, in contrast to the apparent unconnected voiding seen in Incoloy-800H and Hastelloy-X. EDS x-ray maps had shown Na in the GB region of Inconel-617, indicating that FLiNaK was able to permeate the grain boundary network. If FLiNaK can penetrate the grain boundary regions then the alloys can be expected to be depleted of Cr at a much faster rate due to the increased area of attack and shorter distances that the Cr would need to diffuse in the alloy to reach the FLiNaK.

It is speculated that the apparent connected intergranular void structure of Inconel-617 and Haynes-230 may have arisen from a more connected Cr carbide structure (possibly a Cr carbide film) due to the higher C content of these alloys; however this has not been investigated in depth, and a prolonged heat treatment and SEM/EDS analysis would be required support this hypothesis.
To prove this increase in connectivity of Cr carbides leading to increased grain boundary corrosion, observation of the evolution of the carbide network with increasing carbon content must be further investigated. An extended heat treatment of the high Cr alloys at 850°C without salt exposure, and observation of the increasing connectivity of the Cr carbides with C content could validate this hypothesis.

### 5.1.4 Nb-1Zr Behavior

As shown earlier, a black coating was formed on the Nb-1Zr coupons, and while it seems likely that carbides may have formed directly on the surface of the Nb-1Zr coupons, no attempt has been undertaken to prove this since it would have been outside of the scope of this work. The Nb-1Zr became severely embrittled, with one coupon breaking in half upon removal from the fixturing rod, and furthermore during a cleaning step to remove salt more transfer of the alloy and the corrosion products into the cleaning solution occurred indicating that the alloy was mechanically disintegrating. Zr is more electronegative than Cr and known to react in non-electrical transfer in a method similar to that mentioned previously which results in the formation of ZrC, and Nb and its alloys are known to be embrittled by low levels of impurities such as C [56, 102]. Fig. 5.1.4-1 shows the fracture surface of a Nb-1Zr coupon. It can be seen that the alloy microstructure developed a “flaky” structure. This transition likely led to the brittle behavior seen after corrosion tests.
Fig. 5.1.4-1. Nb-1Zr was heavily embrittled, the fracture surface from a coupon that fractured during removal from the graphite holder after exposure to FLiNaK, appeared to have formed brittle flaky layers.

5.1.5 Alloy Corrosion in Alloy Crucibles

The weight-loss measured from the Incoloy-800H coupons in the Incoloy-800H capsule were miniscule in comparison to the tests in the graphite capsules (Fig. 5.1.5-1). This difference in weight-loss highlights the increase in corrosion of the alloy coupons due to graphite promoting Cr de-alloying from the coupons by removing Cr from solution.
The Cr content determined by NAA in the graphite capsule test was 372 ± 21 ppm Cr compared to 99.8 ± 5.1 ppm Cr in the Incoloy-800H capsules (500 h). A comparison with the graphite crucibles is complicated by the possibility that Cr carbides could have been in suspension in the salt. If graphite is partially soluble or present in solution as a colloid, then the Cr FLiNaK solubility determined by NAA may appear to be much larger than it actually is due to the nature of the measurement (i.e. Cr may have reacted to form carbides with some of the colloidal graphite and remained suspended in solution).

5.2 FLiNaK Salt Purity and KCl-MgCl₂ Salt Investigation

The weight-loss/area for the Incoloy-800H coupons in the FLiNaK obtained from ECS and INL, and the salt made at the UW-Madison were similar (Fig. 5.2-1). It was observed that the Incoloy-800H coupons exposed to the salt that went through the most stringent purification process (described in more detail in Appendix E) had the most weight-loss in comparison to the
salts that were made by mixing high purity ingredients and heating in a stepwise fashion (the FLiNaK salt from INL and the FLiNaK salt made at the UW). The corrosive attack on the FLiNaK exposed coupons was similar, a comparison of attack on Incoloy-800H from the hydrofluorinated salt and the INL prepared salt can be found in appendix C. Furthermore, the KCl-MgCl₂ salt exposed coupons had ~2-3 times less weight-loss, and much less variance between coupons than the FLiNaK exposed coupons.

![Weight Loss/Area (mg/cm²)](image)

**Fig. 5.2-1.** The FLiNaK salt exposed coupons had more corrosion and greater variance in weight-loss compared to the KCl-MgCl₂ exposed coupons. All tests performed in graphite capsules, at 850 °C, for 500 h.

The surface of the coupon exposed to the KCl-MgCl₂ was much less pitted than the surface of the coupons exposed to the FLiNaK salt. The EDS data obtained for the surface of the chloride exposed coupon was similar to that obtained for the fluoride exposed coupons, in that the surface was depleted in Cr to ~2%. As implied by the weight-loss/area data and displayed in Fig. 5.2-2, the loss of Cr through dissolution was much more severe for the FLiNaK exposed coupons as was the grain boundary Cr depletion.
Fig. 5.2-2. EDS x-ray maps of Cr distribution in cross-sectioned A) FLiNaK exposed Incoloy-800H, and B) in KCl-MgCl₂ exposed Incoloy-800H.

The observation of Al₂O₃ within the grain boundaries of the KCl-MgCl₂ exposed coupons is also promising because it points towards the possible inclusion of larger amounts of Al in the metallurgy of chloride salt compatible alloys and presents a new possible coating path that may be investigated. Al is a common alloying element that is added for high temperature oxidation resistance, and for precipitation hardening in some of the highest temperature superalloys. Turbine blade manufacturers often rely on Al rich coatings to reduce corrosion, so a large amount of literature on Al rich coatings is available (diffusion aluminide coatings are used to protect 80% to 90% of all aircraft turbine blades) [103]. The effect of the oxides that formed at the grain boundary is not known, Al₂O₃ may decrease Cr grain boundary diffusion in a similar fashion as T. Chen et al. has shown to occur for Cr due to grain boundary Cr carbides [85].

5.3 C/SiSiC Composites and PyC/SiC Coating for Corrosion Prevention

As shown in Fig. 5.3-1A, the cross-sectioned, uncoated C/SiSiC coupon had a corrosion layer ~40 µm in thickness, whereas the cross-sectioned, PyC/SiC coated composite had no visible attack (Fig. 5.3-1B). Furthermore, as seen previously with the FLiNaK exposed coupons, the pure Si regions (light colored regions in the micrographs in Fig. 5.3-1) appeared to be selectively
attacked. The reason for the selective Si attack is likely the same given for the attack of the composites in the FLiNaK salt (reported in ref. [51]), namely that the Si has a higher corrosion potential in the chloride. In FLiNaK, the Gibb’s free energy of fluoride formation per F₂ molecule (ΔGₚₚ) is more negative for the Si phase than the SiC phase and the more negative the ΔGₚₚ for a particular phase, the more this phase can be expected to be attacked by dissolution. Furthermore, at 850°C, the ΔGₚₚ of SiF₄ is more negative than for SiF₂, so it is therefore likely that SiF₄ is the more stable phase in FLiNaK salt. The same energetic argument just given for corrosion in FLiNaK holds for the KCl-MgCl₂ salt as well.

![Diagram of composite microstructures](image)

**Fig. 5.3-1.** Post-corrosion coated and uncoated C/SiSiC composite microstructures from KCl-MgCl₂ exposure at 850°C for 500 h.

### 5.4 Graphite/Alloy Interaction in FLiNaK

The graphite capsules and fixturing rods appeared to accelerate the corrosion of the alloys by removing Cr from the solution. This would have left the FLiNaK more basic than it otherwise would be, and therefore more corrosive. Carbides formed in Hastelloy alloys have been found to be of the (Cr, Fe)₂₃C₆ variety [10], whereas those found on our graphite rods were identified as Cr₇C₃. The formation of Cr₇C₃ carbides from Cr₂₃C₆ carbides is thermodynamically favorable at
850°C, that is, the change in Gibbs free energy of formation from the Cr carbide change from Cr$_{23}$C$_6$ to Cr$_7$C$_3$ results in a negative change in Gibbs free energy; specifically,

\[ 7\text{Cr}_{23}\text{C}_6 + 27\text{C} \rightarrow 23\text{Cr}_7\text{C}_3 \]
\[ \Delta G_{\text{FF}} < 0 \]  \hspace{1cm} \text{Equation 5.4-1.}

While the Cr$_{23}$C$_6$ carbides present in the alloy did not themselves transform into Cr$_7$C$_3$, the fact that the overall reaction is favorable indicates that there is a potential driving force from one to the other. While it is fairly easy to make a thermodynamic argument for the formation of Cr$_7$C$_3$ from Cr$_{23}$C$_6$, the explanation for the Cr transport to the graphite surface and subsequent carbide formation is less straightforward. The reaction of CrF$_3$ with Cr is also thermodynamically favored leaving CrF$_2$ as product, i.e.

\[ 2\text{CrF}_3 + \text{Cr} \rightarrow 3\text{CrF}_2 \quad \text{and} \quad 46\text{CrF}_3 + \text{Cr}_{23}\text{C}_6 \rightarrow 69\text{CrF}_2 + 6\text{C} \]
\[ \Delta G < 0 \]  \hspace{1cm} \text{Equation 5.4-2.}

But thermodynamically, the reactions occurring with the graphite are not thermodynamically favored without some other driving force, i.e.

\[ 3\text{CrF}_2 \rightarrow 2\text{CrF}_3 + \text{Cr} \quad \text{and} \quad 21\text{CrF}_2 + 3\text{C} \rightarrow 14\text{CrF}_3 + \text{Cr}_7\text{C}_3 \]
\[ \Delta G > 0 \]  \hspace{1cm} \text{Equation 5.4-3.}

It has been mentioned previously that Cr$^{3+}$ is stabilized in FLiNaK and has been found to be the dominant chemical state in solution [8]. It is speculated that this tendency to stabilize the 3+ cation state is what allows the reactions in equation 5.4-3 to occur in the basic molten FLiNaK salt.
For a thermodynamic equilibrium between the salt, crucible, and alloy to be established, the activity of the salt, crucible, and alloy must equalize. The thermodynamic equalization is an activity difference driven process and occurs by the removal of Cr from the alloy into solution forming Cr$^{2+}$ and from the removal of some of the Cr$^{2+}$ from solution forming a Cr metal layer on the graphite (see Fig. 5.4-1). This requires the conversion of some of the Cr$^{2+}$ to Cr$^{3+}$ in solution because the graphite is noble and does not donate electrons for the reduction of Cr$^{2+}$ to Cr. Once the Cr is deposited it then reacts with the graphite ($\Delta G < 0$); the Cr$^{3+}$ in solution would then transport back to the surface of the coupon further allowing for dissolution of Cr from the alloy coupon.

In the particular case of Cr forming a Cr layer on the graphite, the Cr metal layer proceeds to react with the graphite, forming Cr carbides. This changes the activity of the solid and allows for further depletion of the Cr in the salt causing corrosion to continue. The creation of Cr$^{3+}$, from the reduction of Cr$^{2+}$, creates an oxidizing agent that transports back to the alloy surface of the coupon and accelerates the Cr dissolution.

Fig. 5.4-1. Schematic of non-electric transfer applied to the Fe-Ni-Cr/graphite/FLiNaK system.
5.5 Mo-Plating Delamination and Potential as a Diffusion/Dissolution Barrier

The plasma sprayed Mo-plating delaminated from the 800H coupons and for this reason it was non-protective. The delamination could have been caused by: incomplete plating (allowing for substrate attack), oxides in Mo-plating from plasma spray process (performed in air) and increasing corrosiveness of salt, porosity in Mo-plating allowing some salt in infiltrate into Mo-coupon interface (followed by attack on Cr and possibly expansion/contraction of salt during melting/freezing), concentrating of Cr as an oxide at the Mo-800H interface followed by infiltration and attack by FLiNaK, or increased stress at the oxide layer due to different thermal expansion coefficients of Mo and 800H from room temperature to 850°C (thermal linear expansion coefficient $\alpha_{800H} = 1.4\%$ and $\alpha_{Mo} = 0.5\%$ so that $\alpha_{800H} / \alpha_{Mo} \sim 3$) [104]. To determine the root cause of the failure, a more in depth investigation of the Mo-plating is needed. While plasma spray Mo-plating as applied to the coupons was ineffective, Mo as a plating material could potentially still be used if the root cause of delamination could be found. The dissolution resistance of Mo and the low Cr and Fe diffusion rates in it are promising.

5.6 Ni-Plating Microstructural Control to Reduce Diffusion/Dissolution

5.6.1 Calculation of Cr Diffusion Parameters in Ni-plating

Lattice Diffusion Parameters

Below ~1100°C, grain boundary diffusion becomes significant, at 1100°C and above, the concentration profiles in the Ni-plating again became smooth, and fit well to the extended initial distribution solution to Fick’s second law. The grain size at this temperature was also very large, approximately the thickness of the Ni-plating, so when EDS linescans were taken across the plating, it was always measuring interdiffusion through single grains. Because the diffusion of Cr in single grains was being measured, the calculated effective Cr interdiffusion coefficients from 1100°C and above were effectively the lattice interdiffusion coefficients.
The lattice interdiffusion coefficient activation energy and pre-exponential factor may be calculated for the high temperature data (above ~0.8T_{Melt}=1100°C) by fitting the effective Cr interdiffusion coefficient data points to an Arrhenius diffusion relation (Fig. 5.6.1-1 and Table 5.6.1-1). When compared to work by others, it is seen that the activation energy matches well, however the pre-exponential term is significantly larger.

![Graph](image)

**Fig. 5.6.1-1.** An Arrhenius diffusion relation was fit to the high temperature data to determine the lattice diffusion activation energy and pre-exponential factor.

**Table 5.6.1-1.** Pre-exponential factors and activation energies for lattice and grain boundary diffusion coefficients. *Smithells lattice term was from Cr tracer diffusion in Ni data. (source: [39]) **T. Chen et al., from Cr tracer diffusion in Ni-16Cr-7Fe (mass%) with 0.004% C. Grain boundary values calculated assuming δ=0.5 nm. (source: [85])

<table>
<thead>
<tr>
<th>Diffusion Component</th>
<th>Pre-exponential Factor (cm²/s)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice (this work)</td>
<td>41</td>
<td>310</td>
</tr>
<tr>
<td>Lattice*</td>
<td>1.1</td>
<td>273</td>
</tr>
<tr>
<td>Lattice**</td>
<td>5.1 (+2.8, -1.8)</td>
<td>286 ± 4.1</td>
</tr>
<tr>
<td>Grain boundary (this work)</td>
<td>0.008</td>
<td>120</td>
</tr>
<tr>
<td>Grain boundary**</td>
<td>0.0096 (+0.0076, -0.0042)</td>
<td>203 ± 5.2</td>
</tr>
</tbody>
</table>

**Grain Boundary Diffusion Parameters**

The Hart equation (equation 2.7.2-5) can be used to determine the grain boundary diffusion coefficient, and has previously been used to determine the grain boundary diffusion coefficient of
H in Ni-plating and Cu in sulfamate Ni-plating [36, 37, 45]. Using Hart’s equation (equation 2.7.2-5), the effective Cr diffusion coefficients from Table 4.8.1-1, parameters for $D_i$ calculated above, and grain size data from those specific diffusion data points, it is possible to calculate the grain boundary diffusion coefficients for data below ~850°C (assuming the grain boundary width, $\delta$, is 0.5 nm and the segregation coefficient, $s$, is 1) [30, 34, 35, 36, 37]. Above 850°C, the effective diffusion length of Cr (~12 µm) on the right hand side of the Matano plane (into the Ni-plating) started to become smaller than half the grain size, so this data was not used as it was believed it would not incorporate many grain boundaries. The grain boundary diffusion coefficients were calculated for diffusion data between 850°C and 700°C and are plotted in Fig. 5.6.1-2. The pre-exponential factor and activation energy for grain boundary diffusion was then determined by an Arrhenius fit and reported in Table 5.6.1-1. In most metals, the ratio of grain boundary activation energy over the lattice activation energy is expected to be about 0.4 to 0.6 [30], and the ratio obtained from this research was about 0.39.

![Fig. 5.6.1-2. The grain boundary diffusion coefficient calculated using the Hart equation.](image)

**Kinetic Regime and Reliability of Diffusion Parameters**

In section 2.7.2, it was mentioned that in the A kinetic regime, Hart’s equation may be used to determine both the grain boundary and bulk diffusion coefficients. This is because in the A
kinetic regime, the grain size is generally small enough, and the lattice diffusion length long enough, so that the concentration profile data from diffusion anneals appears smooth, and may be fit well to the extended initial distribution solution to Fick’s second law (equation 2.7.2-10). In the B regime, though, the diffusion profiles become more convoluted due to the increased role of grain boundary diffusion, and the fits of the concentration data to the extended initial distribution solution to Fick’s second law are usually poor due to the peaks in concentration at the grain boundaries. Therefore, in the B regime, the experimental diffusion profile may not fit the error function solution to the diffusion equation (equation 2.7.2-10). However, literature suggests that the transition from the A to the B regime may not necessarily be well-defined, mostly due to scatter in grain size in polycrystals [105].

As seen in Table 5.6.1-2, all the volume diffusion lengths, \((D_0t)^{0.5}\), obtained using extrapolated bulk diffusion coefficients (from this research) and used to extract the grain boundary diffusion coefficients are smaller than the grain size and the resulting \(\Lambda\) values are all above 2, so the diffusion anneal data that was used for calculating the effective diffusion coefficients did not clearly belong in the A kinetic regime. However, the concentration profile data was found to be quite smooth, so it is believed that the lower temperature profile data may still be used to give an approximation of the grain boundary diffusion coefficients from the effective Cr interdiffusion coefficient data obtained from the fits. The comparable values obtained from this research with that found in the literature appear to bear this out, however, it is noted that the conditions of the diffusion anneals and times were not ideal. The non-ideal diffusion times came about due to the desire to maintain the semi-infinite slab approximation necessary for diffusion couple data, which was constrained by the Ni-plating thickness (equation 4.8.1-1). To obtain data that was clearly in the A kinetic regime, longer diffusion times would have been required, which would have increased the diffusion lengths beyond that allowable for
the semi-infinite slab approximation, and would have increased complexity of the fitting
equations used to extract the effective Cr diffusion coefficient.

Table 5.6.1-2. Calculated Ni-plating diffusion data. Value used for \( D_t \) extrapolated from
1100°C. \( \delta \) is the assumed grain boundary width, \( d \) is the grain size, and \( \Lambda \) is the kinetic
parameter of the \( \Lambda \) regime.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>( \delta ) (( \mu )m)</th>
<th>( (D_t)^{0.5} ) (( \mu )m)</th>
<th>( d ) (( \mu )m)</th>
<th>( \Lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.0005</td>
<td>0.3</td>
<td>7</td>
<td>23</td>
</tr>
<tr>
<td>750</td>
<td>0.0005</td>
<td>0.6</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>800</td>
<td>0.0005</td>
<td>0.8</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>850</td>
<td>0.0005</td>
<td>1.8</td>
<td>14</td>
<td>8</td>
</tr>
</tbody>
</table>

There also likely exists a systematic error in the calculated lattice and grain boundary
diffusion coefficients, in that grain growth during the diffusion anneal was assumed not to
significantly bias the effective Cr interdiffusion coefficient towards faster than actual diffusion
rates. In fact there would have been more grain boundary diffusion early on because the grains
were much smaller, before the growth rate decreased and the grain sizes stabilized. By using
Hart’s equation with a fixed grain size (the post diffusion anneal grain size displayed in Table
5.6.1-2), this initial grain boundary diffusion component was not accounted for. The overall
significance of this error is assumed to be small, but at this point is unknown. As mentioned in
section 2.7.3, J. Katz et al. found no difference in the measured Cu interdiffusion coefficient
between 100 h and 10 h by 600°C, but did find a difference at lower temperatures (the effective
Cu interdiffusion coefficients were determined for sulfamate Ni-electroplate in much the same
manner as Cr was for this present study, and the diffusion parameters of Cu in Ni are similar to Cr
in Ni) [36].
5.6.2 Calculation of Grain Growth Parameters in Ni-plating

The empirical grain size relationship (equation 2.7.3-2) was fit to grain size data taken as a function of time for temperatures between 600°C and 1200°C, and values for $K'$ and ‘$n$’ extracted at each temperature from the data fits. An example of this is shown in Fig. 5.6.2-1, for 700°C, and the compiled values for several temperatures are shown in Table 5.6.2-1. The grain size was determined by a linear intercept method on etched coupons. Issues that were not considered that could possibly impact the measurements were that as Cr diffuses into the Ni-plating the grain growth behavior will likely change, and grain growth would be influenced by other factors such as grain surface energy and no longer follow normal grain growth models as the grain size approached the thickness of the plating [89].

Fig. 5.6.2-1. Grain growth of Ni at 700°C for 1 h, 217 h, 500 h, and 1000 h, a power fit used to derive $K'$ and ‘$n$’. 

$R^2 = 0.8521$
Table 5.6.2-1. Grain growth parameters $K'$ and ‘n’.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>$K'$ (µm)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>2.5</td>
<td>0.06</td>
</tr>
<tr>
<td>700</td>
<td>4.2</td>
<td>0.08</td>
</tr>
<tr>
<td>800</td>
<td>4.6</td>
<td>0.21</td>
</tr>
<tr>
<td>850</td>
<td>8.7</td>
<td>0.19</td>
</tr>
<tr>
<td>1000</td>
<td>21</td>
<td>0.31</td>
</tr>
<tr>
<td>1100</td>
<td>52</td>
<td>0.15</td>
</tr>
<tr>
<td>1200</td>
<td>140</td>
<td>0.38</td>
</tr>
</tbody>
</table>

It has been shown in literature that for grain growth in films, normal grain growth may slow and eventually stop once the grain size becomes comparable to the film thickness; this phenomenon is called the specimen thickness effect [89]. The ratio of the average grain size to Ni-plating thickness (assuming an 80 µm thick Ni-plating as determined in section 3.7) used for determining the grain size parameters ranged from about 4% to about 55% for the 600°C to 1200°C data, respectively. To avoid interference from the specimen thickness effect, it was decided to use data in Table 5.6.2-1 from 600°C to 850°C (arbitrarily choosing the 850°C, 35% thickness ratio as the cutoff point) for the determining the functional nature of grain growth parameters with temperature.

The values for $K'$ and n from Table 5.6.2-1 were plotted as functions of inverse temperature (Fig. 5.6.2-2) and temperature (Fig. 5.6.2-3), respectively. From the plotted values of n and $K'$, temperature dependent functions were derived. Because $K'$ is known to be Arrhenius, it was fit to an Arrhenius equation, and $K_0$ and $Q_{0n}$ were determined.
Fig. 5.6.2-2. \(K'\) as a function of inverse temperature. The data is fit to an Arrhenius relation for the data from 850°C and below.

Table 5.6.2-2. Parameters for \(K'\).

<table>
<thead>
<tr>
<th>Temperature Range (C)</th>
<th>(K_0) (µm)</th>
<th>(Q_0n) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600-850</td>
<td>290</td>
<td>35</td>
</tr>
</tbody>
</table>

‘\(n\)’ is known to be temperature dependant, but the functional dependence was not known, a linear fit was arbitrarily applied to the ‘\(n\)’ values for different temperatures. The values of the linear fit are shown in Table 5.6.2-3. As discussed in the background section, theoretically, ‘\(n\)’ should equal 0.5, but in practice ‘\(n\)’ is often much lower and only approaches 0.5 in pure metals and/or at high temperatures [29]. The values for ‘\(n\)’ reported are slightly lower than expected if the trend had followed the results of M. Chauhan et al., who had found ‘\(n\)’ increasing from ~0.05 to ~0.16 from ~100°C to 420°C respectively in nanocrystalline Ni sheet (~25 nm average grain size) [43]. However, M. Chauhan did not report the processing method used to obtain their nanocrystalline sheet, so the data may not be directly comparable.
Fig. 5.6.2-3. Exponent ‘n’ as a function of temperature for Ni. The data is fit to the data from 850˚C and lower.

Table 5.6.2-3. Parameters for ‘n’ for the equation \( n = mx + b \).

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>m</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>600-850</td>
<td>0.62E-4</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

5.6.3 Modeling Diffusion in Ni-Plating

A time and temperature dependent model of the effective Cr interdiffusion coefficient based on the Hart equation (equation 2.7.2-5) was constructed by adding the functional dependencies on temperature and time for grain growth (Equation 2.7.3-2) in sulfamate Ni-plating and lattice and grain boundary diffusion (Equation 2.7.2-1).

\[
\tilde{D}_{\text{Cr}}^{\text{eff}}(t,T) = \frac{Q_0}{k_BT^{m+b}} D_{0,gb} e^{\frac{Q_0}{k_BT}} \left( 1 - \frac{Q_0}{k_BT^{m+b}} \right) \frac{Q_0}{k_BT} e^{-\frac{Q_0}{k_BT}} \quad \text{Equation 5.6.3-1}
\]

With this model of the effective Cr interdiffusion coefficient, the time dependence of the effective Cr interdiffusion coefficient can be investigated and allow for theoretical predictions.

The expanded Hart equation (Equation 5.6.3-1) is plotted against time and temperature and
overlaid on the effective Cr interdiffusion coefficient data in Fig. 5.6.3-1 as a metric to examine how well the model matched up with the experimentally derived data. The average percent difference from the model and the data was ~35%, with a total propagated error of ~15%. With the D(t, T) model, predictions can be readily made for given times and temperatures and the effects of increased initial grain size could readily be investigated. Because above 850°C the grain size becomes a significant ratio of the Ni-plating thickness, and thin film effects causing abnormal grain growth are encountered, the square grain assumption and grain growth can be expected to deviate from the model at about this point. The model essentially assumes infinite plating thickness.

![Fig. 5.6.3-1. The diffusion model plotted against experimental data.](image)

The time functionality of the effective diffusion coefficient for several temperatures was investigated for temperatures from 600°C through 900°C, and is plotted in Fig. 5.6.3-2. In this plot, the calculated diffusion coefficients were divided by the effective Cr inter diffusion coefficient calculated using the Hart equation with the grain size fixed at initial measured grain size (90 nm). Despite temperature differences the initial drop-off in the effective Cr interdiffusion coefficient is rapid, but then tends to stabilize.
Fig. 5.6.3-2. The diffusion model was used to determine the change in the diffusion coefficient over time. The diffusion coefficient was divided by an initial diffusion coefficient calculated using the initial Ni-plating grain size of 90 nm.

5.6.4 Secondary Recrystallization Grain Growth to Decrease Cr Diffusion

The Cr interdiffusion coefficient model indicated that as grain size increases, the effective Cr interdiffusion coefficient should decrease. The effectiveness of the grain size increases from the plating modification via thermomechanical processing was found to be minimal using the techniques employed in this research. For the times and temperatures used, the Cr diffusion in the modified Ni-plating was within the B kinetic regime, where only information about $\delta D_{gb}$ (or $s\delta D_{gb}$, but for this research it was assumed $s=1$) may be reliably extracted [30]. That being said, the methods used were still able to provide meaningful estimates for the effective Cr diffusion coefficient, although with a large amount of variance.

It was demonstrated in section 4.8.2 and displayed in Table 4.8.2-1 that increasing grain size did not appear to have a large effect in altering the effective Cr interdiffusion rates of the He exposed coupons. Because the grain size was on the order of the Ni-plating thickness, the modification of the Ni-plating may have decreased the number of low energy boundaries that would have been encountered by Cr diffusing along the grain boundary in a Ni-plating that was
many grains thick, thereby allowing for Cr diffusion along higher energy boundaries to dominate the diffusion of Cr to the surface.

### 5.6.5 Cr₂O₃ as a Potential Diffusion Barrier

Due to the relatively large Cr diffusion rates in Ni at temperatures above 600°C, Ni-plating by itself may not be an effective long-term protective strategy to prevent Cr loss at the temperatures of interest (~850°C) in oxidizing salt conditions. During the course of this study it was observed that some of the Incoloy-800H samples had an interlayer of Cr₂O₃ between the alloy and the Ni-plating. SEM analysis showed that this Cr₂O₃ interlayer dramatically reduced diffusion of Cr, Fe, and Ni between the substrate and the Ni-plating. Fig. 5.6.5-1 shows resulting EDS linescans taken of the Ni-plated coupon post diffusion anneal over a section of the Ni-plated coupon with and without the oxide interlayer. It can be seen that where the oxide layer is present, the Cr oxide interlayer effectively slowed Cr diffusion into the Ni-plating, and where the Cr oxide was not present, Cr diffusion into the Ni-plating proceeded unhindered.

Data for the effective Cr diffusion coefficient in Cr₂O₃ at 850°C is not readily available, but A. Sabioni et al. determined the effective diffusion rate of Fe in Cr₂O₃ films formed on a Ni₇₀Cr₃₀ alloy to be 7.7x10⁻¹⁶ cm²/s at 800°C, and 8.9x10⁻¹⁵ cm²/s at 900°C, and for bulk diffusion of Cr in single crystal Cr₂O₃ at 1200°C to be 1.0 x10⁻¹⁸ cm²/s and the ratio of D traged/Dl~10⁴ for Cr diffusion in polycrystal Cr₂O₃ [106, 107]. If the same trend held for Cr as for Fe, those rates would be about 4 orders of magnitude lower than the Cr diffusion rates observed in the Ni-plating, and from the higher temperature Cr in Cr₂O₃ diffusion data, it appears that the diffusion rates could be even lower. This observation provides avenues for practical solutions to mitigating corrosion of high Cr alloys in molten fluoride salts. For example, the alloy could be initially heated to form a thin layer of Cr₂O₃ prior to Ni-plating.
5.6.5-1. SEM images and EDS line-scans from the same diffusion annealed Ni-plated Fe-Ni-Cr model alloy sample, but taken over different zones, A) where an oxide interlayer acted as a diffusion barrier and B) where the oxide layer was not present. C) The Cr diffusion zone for A) and B), and oxygen from the Cr oxide in A).

5.6.6 Ni-Plating Response in FLiNaK

Unmodified Plating

Ni-plated Incoloy-800H coupons were tested under similar conditions as the unplated alloy tests [9] (850°C for 500 h in graphite crucibles) and was highly successful in reducing weight-loss/area through Cr dissolution from the underlying alloy exposed to FLiNaK (Fig. 5.6.6-1).
The surface of the FLiNaK exposed, Ni-plated Incoloy-800H coupons were devoid of the pitting seen on the unplated Incoloy-800H coupons, although EDS scans of the surface detected concentrations of Cr and of Fe of several percent. The inherent variations in Ni-plating thickness were utilized effectively to shed more light on the mechanisms of Cr dissolution, particularly void formation at the grain boundaries. When the cross-sectioned FLiNaK exposed Ni-plated Incoloy-800H coupons were examined, a characteristic, thickness dependent void structure was found. The differing thicknesses of Ni-plating are affected differently by bulk and grain boundary diffusion and Cr dissolution in FLiNaK (at 850°C after 500 h).

An understanding of the origin of the void structure and its impact on Cr diffusion are necessary to understand the nature of the Cr dissolution processes and the role of the Ni-plating microstructure. To increase understanding, the Ni-plated coupons that had been exposed to FLiNaK at 850°C for 500 h were examined in detail using SEM and EDS.

For the 850°C, 500 h, FLiNaK exposed unmodified Ni-plating, where the Ni-plating was much thicker than the effective Cr penetration depth (as determined by EDS), Cr diffusion to the surface though the grains of the Ni-plating did not occur. Voids were found in the Ni-plating, but
were concentrated at the grain boundary; the bulk Incoloy-800H appeared largely unaffected (Fig. 5.6.6-2). Voids along the Ni-plating grain boundaries were seen throughout the Ni-plating at all thicknesses, but were dominant in the thick Ni-plated regions due to the absence or lower concentration of voids formed due to bulk or other short circuit Cr diffusion/dissolution phenomena.

![Image](image_url)

**Fig. 5.6.6-2.** A) SEM, B) EDS line scan showing the Cr distribution through the Ni-Plating after the 850°C, 500 h, FLiNaK exposed. In this region the Ni-plating was ~175 μm thick.

Where the Ni-plating was slightly thinner than the effective penetration depth for Cr in the Ni, a void layer formed in the Ni-plating parallel to the surface, ~25 μm in the plating as measured from the plating surface (Fig. 5.6.6-3A). The parallel voids in the intermediate thickness plating are likely caused by a combination of grain boundary and bulk diffusion, although the exact progression that leads to the void lines would require more research.

In Fig. 5.6.6-3C it can be seen that Fe has built up at the FLiNaK/Ni-plating interface as evidenced by the line scan. The diffusion of Cr (and Fe to a lesser extent) through the Ni-plating would likely be problematic over long term use. Cr has a slightly higher diffusion coefficient than Fe in Ni [32], but when Fe and Cr reach the surface of the Ni-plating, the Cr is dissolved to a larger extent than the Fe.
Fig. 5.6.6-3. A) Ni-plating post FLiNaK corrosion, cross-section SEM. B) Cr EDS x-ray map of A. C) EDS line scan showing the Cr distribution through the 850°C, 500 h, FLiNaK exposed, Ni-plated 800H coupon. In this region the Ni-plating was ~80 µm thick. D) Similar magnifications of Haynes-230 exfoliating a film.

It has been found that grains in the near-surface region remain smaller than subsurface grains from FLiNaK exposures and after thermomechanical processing. Furthermore, in FLiNaK, abnormal grain growth affects the Ni-grains on the interior of the plating, leaving in effect a three zone plating, seen for the 700°C for 1000 h FLiNaK exposed coupons in Fig. 5.6.6-4.
The unmodified Ni-plating in Fig. 5.6.6-4 appeared to have formed larger grains than expected close to the substrate (Fe-Ni-Cr model alloy). The increase in grain size could have been caused by exposure to the FLiNaK. It has been seen in TZM coupons exposed to LiF-BeF₂-ThF₄-UF₄ (68-20-11.7-0.3 mol %) at 1100°C for 1011 h, that the alloy exposed to the salt partially recrystallized (while coupons not directly exposed to the salt had not) and this was attributed to the leaching of Ti and Zr from the alloy by the salt [23]. For the Ni-plating, trace impurities may have been leached from the grain boundary region allowing for abnormal grain growth; however why the grains near the surface appeared to not experience this same phenomenon is not conclusively known.

Because recrystallization begins at the substrate/plating interface, the grains can be expected to be larger near this interface, if grain growth was still occurring. However, from unmodified Ni-plating exposed to He at 700°C for 1000 h, the grain size is more uniform and much smaller (~8 µm). It is clear that whatever was arresting grain growth in the He cover gas exposed coupons was not present in the FLiNaK exposed coupons. It is also interesting that the growth of
the inner grains exceeds that of the surface grains, pointing to the stored strain energy
overweighing the loss of pinning elements through dissolution as a driving force for grain growth.

For the intermediate thickness plating, exposed to FLiNaK at 850°C for 500 h (Fig. 5.6.6-5A), the voids appear to build up at the location of the interface (~20 µm in from the surface) found between the large grains and the smaller surface grains seen in the 700°C, 1000 h FLiNaK exposed Ni-plated coupon (Fig. 5.6.6-4). It may also be significant that bulk diffusion appears to have reached the surface in this region. The lines of interconnected porosity, in the 850°C 500 h FLiNaK exposed coupons, may be related to a similar small grain/large grain interface region.

An SEM image from a thicker Ni-plating region (Fig. 5.6.6-5B) shows what appear to be large grains covered in parts near the surface with a layer of Ni also about 20 µm thick, about the same thickness as that in the region of the Ni-plating in Fig. 5.6.6-5A that appears to be in the process of exfoliating.

![Fig. 5.6.6-5. A) Unmodified Ni-plating exposed to FLiNaK at 850°C for 500h, B) Thicker region of unmodified Ni-plating exposed to FLiNaK for 500 h.](image)
Vacancies are localized in the Ni-plating near the Ni-plating/salt interface as Ni atoms move to fill the surface lattice locations previously occupied by Cr atoms lost to the FLiNaK. When enough vacancies build up near the surface and reach a saturation limit, they conglomerate as voids. The voids are likely concentrated at the grain boundaries because Cr diffuses preferentially from the substrate through the Ni-plating along grain boundaries; and because of the difference in grain sizes, the voids may get concentrated at the large grain/small grain interface because this is where most of the diffusion is occurring.

Over time the connectivity of voids will likely lead to the formation of a film. Ni rich films were also found on Haynes-230 coupons exposed to FLiNaK (Fig. 5.6.6-3D), and similar films caused by interconnected porosity parallel to the surface have been described by A. Misra et al., after alloy exposure to molten fluoride salts [2]. Interconnected porosity has also been observed in other corrosion environments. For example, in 9CrODS oxidized by supercritical water, interconnected pores were observed in the alloy and oxide layers [108]. The pores were attributed to the outward flow of specific elements (Fe in this case), leaving vacancies that could not be replenished with other elements quickly enough [108].

If the Ni-plating is much thinner than the Cr penetration depth, then the Ni-plating may consolidate with heat treatment creating discontinuities between the Ni-plating grains. FLiNaK would then have direct access to the underlying alloy along the discontinuities, leading to grain boundary Cr depletion and general and grain boundary void formation in the Incoloy-800H (Fig. 5.6.6-6). Moderately increasing plating thickness however can easily prevent these discontinuities from forming.
Fig. 5.6.6-6. SEM image and EDS x-ray map of Cr in FLiNaK exposed, Ni-plated Incoloy-800H, coupon held at 850°C for 500 h. The void structure complicates diffusion modeling. A discontinuity in the Ni-plating is circled in (A).

Fig. 5.6.6-7. A) Coupon 8B, hole region. B) EDS line-scan showing that as Cr and Fe reach the Ni-plating/FLiNaK interface, the Cr is lost through dissolution to a larger extent than Fe.

Modified Ni-Plating

It was observed that for the FLiNaK exposed (700°C, 1000 h) modified Ni-plated samples, that voids appeared to correspond to the grain boundaries (Fig. 5.6.6-8), indicating that the short circuit diffusion of Cr through the grain boundary that had been seen in the heat treated only coupons, resulted in Cr loss and grain boundary void formation when exposed to molten FLiNaK. This result, bolstered by SEM evidence that appeared to show increased void formation at the grain boundaries in the 850°C, 500 h FLiNaK exposed coupons, supports the argument that grain
boundary diffusion of Cr through the Ni-plating and dissolution into the salt results in void formation in the Ni-plating grain boundaries.

Fig. 5.6.6-8. SEM micrograph of the FLiNaK exposed, recrystalization annealed GBE Ni-plating. Voids can be seen that appear to correspond to the grain boundaries, indicating that the short circuit diffusion of Cr through the grain boundary, seen in the heat treated only coupons, resulted in Cr loss and grain boundary void formation in the FLiNaK exposed coupons.

Fig. 5.6.6-9 shows the calculated diffusion coefficients for modified and unmodified Ni-plating diffusion annealed in He ampoules for 1000 h, and those exposed to FLiNaK for the same time and temperature. It is immediately apparent that FLiNaK exposure greatly affects the measured Cr interdiffusion coefficient. At this point, it is unknown why the FLiNaK exposure caused this large reduction in the effective Cr interdiffusion coefficient, but this reduction may be partly due to abnormal grain growth of the unmodified plating brought on by FLiNaK exposure and the large grain size of the modified plating increasing the grain size beyond that allowable for the method used to fit the interdiffusion rate (discussed earlier in section 5.6.1).
5.6.7 Voiding Replication Heat Treatments

To determine if the voids seen in the FLiNaK exposed Ni-plated 800H should be attributed to FLiNaK exposure or heat treatment effects, Ni-plated coupons were held at 850°C for 500 h in He filled ampoules. Diffusion can be modeled adequately in the absence of dissolution, however, once dissolution of Cr is considered, void formation must be introduced, and this leads to a much more complicated picture of diffusion. Defects such as free surfaces, grain boundaries, interfaces and dislocations are associated with a more open structure and the jump frequency of atoms migrating along these defects will be higher than in the lattice [29]. Vacancies (and eventually voids resulting from their coalescence) at the grain boundary region however would open up the boundary more, allowing for easier diffusion of Cr. For this reason void formation is deleterious for Ni-plating.

B. Jacobson and J. Silwa [46] found that the location of voiding during grain growth heat treatments (without molten salt exposure) coincided with migrating, high angle grain boundaries. As electroplated Ni grains grow, crystal defects and impurities are swept up along the grain boundaries [87], which leads to void formation in these interfaces [109]. In general, almost all Ni-plating decreases slightly in density after heating and voids may be found at the grain
boundaries [110]. It is often not clear whether the voids are gas bubbles from vaporized impurities, or cavities produced from the coalescence of excess vacancies [46]. Voids can be seen along grain boundaries in most recrystallized Ni platings, but have been found to occur less frequently for the sulfamate process [110]. Porosity introduced in Ni-plating along the grain boundaries during heat treatment can be detrimental because the openings provide a faster pathway for diffusion through the coatings [110].

To gauge how much of an influence the heat treatment had on void formation, Ni-plated coupons were heat treated under a He cover gas in quartz ampoules for the same thermal history as the 850°C FLiNaK exposed coupons (500 h). Fig. 5.6.7-1A and Fig. 5.6.7-1B show voids from the Ni-plating, A) having been exposed to FLiNaK, and B) only the heat treatment. It is evident from the heat treatment alone that the Ni-plating was prone to voiding. Due to this evidence, it is likely that the large number of voids seen in Fig. 5.6.7-1A and Fig. 5.6.7-1B were at least partially due to impurities or defects.

Fig. 5.6.7-1. A) Ni-plated Incoloy-800H exposed to FLiNaK, showing voiding. B) Ni-plated Incoloy-800H exposed to heat treatment with a He cover gas. Showing same voiding present in FLiNaK exposed coupon, indicating voiding was caused by impurities or excess vacancies.
An image editing/analysis program called MacBiophotonics ImageJ was used to calculate the void space at the grain boundary of the FLiNaK exposed and heat treated coupons (Table 5.6.7-1). The area fraction of voids in the Ni-plating was larger for the FLiNaK exposed coupon than for the heat treated coupon alone. Although the heat-treated-only coupon had similar grain boundary void localization as the FLiNaK exposed coupons (i.e. at grain boundaries); the surface area ratio of voids/bulk was lower. This implied that additional grain boundary voiding may come from Cr or other elements lost to the FLiNaK through grain boundary diffusion.

Table 5.6.7-1. The area fraction of voids in the Ni-plating was much larger for the FLiNaK exposed coupon than for the heat treated coupon alone. Obtained from 500x magnifications that included the substrate as well as the Ni-plating.

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Average Void Size (µm)</th>
<th>Area Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLiNaK</td>
<td>14</td>
<td>1.0</td>
</tr>
<tr>
<td>He</td>
<td>12</td>
<td>0.6</td>
</tr>
</tbody>
</table>

5.6.8 Estimated Ni-Plating Cr Penetration Times

For a first order approximation of the time until it can be expected to have Cr reach the surface of a 100 µm thick plating, the effective penetration depth estimation is used. The effective penetration depth can be determined once a diffusion coefficient is known. The effective penetration depth to the right of the Matano plane (into the Ni-plating) may be determined by [38]:

\[ x_{i,R} = \sqrt{2 \cdot D_{i,R} \cdot t} \]  

Equation 5.6.8-1

Once Cr has penetrated to the surface of the plating, Cr dissolution may occur under oxidizing salt conditions. The penetration depth was calculated, using the calculated effective Cr interdiffusion term from the aforementioned model (section 5.6.3) for 500 h because the diffusion
rates appear to be leveling off by that time (Table 5.6.8-1). It is noted that actual Cr diffusion will be slightly underestimated due to the assumption of a constant diffusion coefficient, and the underestimation will be larger for lower temperatures where the Ni-plating is still undergoing normal grain growth. Because the effective Cr interdiffusion coefficient is essentially a weighted average of the grain boundary and lattice Cr interdiffusion coefficients, Cr penetration to the surface along the grain boundary will likely have already occurred and its effects evident by the time the calculated penetration depth is achieved.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>Time till 100 µm penetration depth (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>41 000</td>
</tr>
<tr>
<td>700</td>
<td>18 000</td>
</tr>
<tr>
<td>800</td>
<td>9 800</td>
</tr>
<tr>
<td>850</td>
<td>7 200</td>
</tr>
<tr>
<td>900</td>
<td>4 800</td>
</tr>
<tr>
<td>1000</td>
<td>1 200</td>
</tr>
</tbody>
</table>

5.7 Electrochemistry as a Corrosion and Compatibility Diagnostic

The use of anodic stripping voltammetry for analysis of metal impurities in the salt was demonstrated, however further work is needed to assign the numerous oxidation peaks to elements and to demonstrate accuracy and precision. D. Ludwig (in conjunction with the author) worked on the determination of the Cr peaks, on the construction of a Ni/Ni(II) reference electrode, and several other aspects related to improving accuracy and precision of the technique and reported in his thesis [66].

The inability to find an insulator for increased control of the working electrode surface area is unfortunate, but is not a major detriment for use of the technique. Further work using the aluminum oxide as an insulator is currently being undertaken in chloride based salts, where the
aluminum oxide is stable and the issues encountered in fluoride based salts should not be seen. No major issues are foreseen that will preclude the use of ASV as an online corrosion diagnostic.

Potentiometry also demonstrated promising results, however due to the time and material constraints; its potential was not fully explored. It is recommended that this technique be investigated further as a means to rank alloys tendency to corrode in molten salts.
6 Conclusions and Recommended Future Work

6.1 General Corrosion Results and Alloy Compatibility with Molten FLiNaK

A number of high temperature Fe-Ni-Cr alloys of interest to the VHTR-NHI program, Ni-201, and Nb-1Zr were evaluated for their corrosion resistance in molten FLiNaK salt at 850°C for 500 h, using graphite crucibles. To ensure safety and salt purity, the graphite crucibles were encapsulated in stainless steel containments and experiments were performed under an Ar cover gas. Since the static corrosion capsules were held at isothermal conditions, corrosion from contaminate, and corrosion due to dissolution, driven by the solubility of the various alloying constituents in the initially basic molten salt, were the dominant corrosion mechanisms. The least noble primary alloying constituent of the Fe-Ni-Cr alloys, Cr, dissolved into the FLiNaK salt until such a point where thermodynamic equilibrium between the alloy, the fluoride salt, and the container material was established. The dissolution of Cr from the Fe-Ni-Cr alloys into the molten salt was particularly pronounced at the grain boundaries of the alloys.

It was found that the weight-loss per area of the exposed coupons correlated with the initial Cr content of the alloy. The Cr-content of the salt after corrosion tests correlated well with the initial Cr content of the corresponding alloys. In alloys containing 20 to 23% Cr, weight-loss per area for alloys also correlated well with the initial C content of the alloy due to the precipitation of Cr-carbide at the grain boundaries in the initial alloy microstructure. The Ni-201 alloy, a nearly pure Ni alloy, was very resistant to corrosion. The refractory alloy Nb–1Zr exhibited pronounced carburization, embrittlement and fracture which manifested as severe weight loss.

Void formation occurred in the alloys from Cr dissolution at the surface of exposed grains and at grain boundaries. Initiation of subsurface voids occurs by oxidation-reduction with impurities and dissolution of active alloy species, primarily Cr, into the molten salt. When the surface was depleted of Cr, Cr from the interior of the alloy diffused down the concentration
gradient to the surface. Diffusion occurred by a vacancy process and was essentially unidirectional, so an excess of vacancies built up in the near surface regions of the alloy. The vacancies precipitated into voids at areas of disregistry, principally at grain boundaries and impurities.

The compatibility of alloys with FLiNaK in the corrosion tests rank as follows: Nb-1Zr experienced the most weight-loss/area, followed by (in decreasing weight-loss/area) Haynes-230, Inconel-617, Incoloy-800H, Hastelloy-X, Hastelloy-N, and Ni-201. In alloys Hastelloy-X, Hastelloy-N, Inconel-617 and Haynes-230, Mo and W-rich precipitates were observed within the alloys and on their surfaces after corrosion tests, implying that these refractory metals are resistant to corrosion in molten fluoride salts. For alloy Inconel-617 and Haynes-230, a nearly pure Ni-Co and Ni layer, respectively, was created at the surface because of Cr dissolution from the surface. For the Fe-Ni-Cr and Ni-Cr based alloys investigated, the voids precipitated along the grain boundaries, and near the surface of the alloy samples. EDS data of Inconel-617, showed salt infiltration along the grain boundary network. It therefore is possible that some of the grain boundary Cr carbides were interconnected for the high Cr, high C alloys. This increasing connectivity of the grain boundary Cr carbides resulted in correlation of the weight-loss/area with C content for the high Cr alloys.

6.2 FLiNaK Salt Purity and KCl-MgCl₂ Salt Investigation

From the conditions used in the corrosion tests undertaken, hydrofluorination of the FLiNaK did not decrease Cr dissolution into the salt. This conclusion however takes into account the effects of graphite interaction that likely kept the salt at a more corrosive state than otherwise would be expected.

The alloys exposed to KCl-MgCl₂ had a much lower Cr dissolution rate (and hence less corrosion) than the alloys exposed to FLiNaK, and substantially less grain boundary attack.
6.3 **C/SiSiC Composites and PyC/SiC Coating for Corrosion Prevention**

In the uncoated C/SiSiC composites the pure Si regions were selectively attacked in both FLiNaK and KCl-MgCl₂. The CVD PyC/SiC coating was shown to be extremely effective in preventing corrosion attack of the underlying C/SiSiC composite. However, due to the observed interaction of Cr in solution with graphite in the alloy salt exposure tests, it is recommended that the compatibility of the potential piping alloy with the potential heat exchanger PyC/SiC coated C/SiSiC composite material be investigated.

6.4 **Graphite/Alloy Interaction in FLiNaK**

The graphite crucible accelerated the Cr dissolution process by way of forming Cr-carbide phases for the Cr-containing alloys. The enhanced corrosion rate induced by the graphite crucible and components provided an accelerated environment for evaluating the relative corrosion performance of various candidate alloys in a reasonable time. For Incoloy-800H exposed to FLiNaK in Incoloy-800H capsules, the Cr dissolution rate appeared to be linear up to at least 2000 h at 850°C. SEM evaluation of the Incoloy-800 samples from the two types of crucibles showed that the mechanism of corrosion for the two cases was largely identical.

It is believed that an acceleration of Cr dissolution in FLiNaK from high Cr alloys in graphite containers occurred due to interactions of Cr²⁺/³⁺ with the alloy, salt, and graphite. Cr dealloys from the samples and forms Cr fluorides in the salt; the Cr in the salt then deposits on the graphite from solution. This process continues until a thermodynamic equilibrium is established between the alloy, salt, and crucible. From neutron activation analysis (NAA), it was seen that the Cr content of the salt from a 500 h at 850°C exposure for Incoloy-800H in an Incoloy-800H crucible in FLiNaK was 99.8 ± 5.1 ppm, whereas it was 372 ± 21 ppm for the same alloy in a graphite
capsule, an increase in Cr dissolution from the alloy by a factor of ~3.5. The corrosion acceleration was likely promoted by FLiNaK’s tendency to sustain multiple oxidation states of Cr and the differences in chemical activities between the electronegative Cr in the alloy and the graphite capsule. A Cr$_7$C$_3$ film was identified on the graphite rod used to hold the Incoloy-800H coupons, and the salt from several corrosion tests had a grayish appearance pointing towards colloidal graphite and or carbide suspensions in the salt. The formation of carbides would lead to an increase in chemical activity had they not been formed and a metal film been present. In addition to carbide formation, the possibility of a galvanic couple as well as the formation of graphite intercalation compounds were also examined.

The compatibility of an alloy with graphite is related to the Cr content of the alloy and the ease with which Cr may be de-alloyed. Alloys with similar Cr contents can show dramatically differing compatibilities with graphite (i.e. weight-loss) because of the different rates of Cr dissolution from alloys into the FLiNaK and resulting carbide formation on the graphite. For example Hastelloy-X had a similar Cr content as Haynes-230, yet had less weight-loss and therefore Cr removal, likely due to its lower C content and therefore reduced presence of Cr carbides and a less interconnected grain boundary carbide structure. Because Hastelloy-X had less Cr dissolution into the salt than Haynes-230 (as determined by NAA), many of the features of graphite interaction seen in the other high Cr alloys, such as a visible Cr rich film on the fixturing rod and a dark salt coloration were not readily apparent.

### 6.5 Mo-Coating Delamination and Potential as a Diffusion/Dissolution Barrier

Based on the observation of Mo-rich precipitates in alloys Hastelloy-N, Hastelloy-X, and Inconel-617 after corrosion tests and the low diffusivity of Cr in Mo documented in literature, Mo plasma sprayed coatings were evaluated for compatibility with FLiNaK. High temperature, heat treatments in a He environment demonstrated the development of a diffusion bond between the coating and the substrate alloy. Mo plasma spray coatings delaminated from the substrate when
exposed to FLiNaK and for this reason they were non-protective. This delamination may be caused by porosity in the coating or the thermal mismatch between the coating and the substrate as it cools from the high temperature plasma spray deposition process. With alternate ways of incorporating Mo at the surface such as diffusional or electrochemical processes, the problem of delamination could be potentially eliminated.

6.6 Ni-Plating Microstructural Control to Reduce Diffusion/Dissolution

The Ni-plating applied to the Incoloy-800H coupon decreased Cr depletion in FLiNaK by an order of magnitude during testing at 850°C for 500 h. Nevertheless, Cr and Fe were still able to diffuse to the salt/Ni-plating interface through the Ni in the 850°C 500 h salt exposure tests. Once Cr reached the surface of the Ni-plating, dissolution ensued, with its accompanying effects of vacancy and void formation, leading to excess porosity in the Ni-plating primarily at the grain boundary. Therefore, while the Ni-plating was extremely successful in reducing Cr dissolution from the underlying alloy, Cr was found to have diffused through the Ni-plating, and the Ni-plating barrier likely has a useful lifetime depending on temperature, thickness, and microstructure.

6.6.1 Cr Diffusion, Ni Grain Growth, and Diffusion Model Development

Estimates for pre-exponential values and activation energies were made from diffusion data obtained from diffusion anneals of the Ni-plated alloy performed in He, and in general these estimates were in agreement with data in literature. Estimates for temperature dependant grain growth parameters ‘n’ and K were calculated by holding Ni-plated alloy samples isothermally at a range of temperatures for several exposure times and then fitting the observed grain sizes to an empirical time and temperature dependent grain size equation.

With the lattice, grain boundary, and grain growth parameters derived from the diffusion anneals, a model of the effective diffusion coefficient as a function of grain size (time dependant
for a given temperature) was formulated utilizing the expanded Hart equation. The model was successful in predicting the effective Cr diffusion rate in polycrystal Ni under normal grain growth conditions. However, FLiNaK exposure of the Ni-plating appears to alter normal grain growth mechanisms, making such a model limited in utility for predicting benefits from grain growth under conditions which appear to operate in FLiNaK exposed coupons. The likely cause of the abnormal grain growth is speculated to be from the removal of impurities into FLiNaK that would otherwise hinder boundary migration. Therefore, models must be developed in FLiNaK that includes the effects of the many factors that may arise from selective metal dissolution.

6.6.2 Secondary Recrystallization Grain Growth to Decrease Cr Diffusion

Below 1100°C, grain boundary diffusion contributes significantly to the effective Cr diffusion rate. Increasing the Ni grain size in the plating would therefore decrease the contribution of grain boundary diffusion to the apparent diffusion rate. Because of this dependence of the effective diffusion rate on grain size, multiple thermomechanical processes were studied to reduce the grain boundary diffusion contribution. Larger grains resulted in a lower Cr diffusion rate due to lower grain boundary contribution. Because of normal grain growth mechanisms and the difference between lattice and grain boundary activation energies, large grains were more protective against corrosion at lower temperatures where the grains grow much slower and where grain boundary diffusion occurs much more rapidly than lattice diffusion. However, once grain size approached the Ni-plating thickness, Cr diffused to the surface in a shorter time scale than through a more random grain boundary network with smaller grains. Large grains were therefore more protective than smaller grains, but the grain size should not be allowed to approach the thickness of the Ni-plating.
6.6.3 Ni-plating Response and Void Formation in Ni-Plating

It was found that some voiding in the Ni-plating occurs due to heat treatment alone and was likely caused by impurities or specific plating methods, so good quality control and optimization of the plating process to reduce impurities is needed to further enhance the effectiveness of the Ni-plating in mitigating corrosion. Grain boundary diffusion was also found to be significant and likely resulted in the void formation observed along the grain boundary of modified Ni-plating (thermomechanically processed to increase grain size) exposed to FLiNaK at 700°C for 1000 h, and increased voiding in unmodified Ni-plating exposed to FLiNaK at 850°C for 500 h. Therefore, the locations of voids in the Ni-plating provided insight into the Cr diffusion pathways that contributed to Cr dealloying.

6.6.4 Ni-Plating Cr Penetration Times and Cr$_2$O$_3$ as a Diffusion Barrier

The kinetics of Cr penetration through a 100 µm thick Ni plating was estimated for several temperatures based on the effective Cr interdiffusion data obtained from He diffusion anneals. Once Cr has penetrated the Ni-plating, it is possible for it to be dissolved if the salt is at an oxidizing potential.

The presence of a Cr oxide interlayer between the Ni-plating and the alloy substrate dramatically reduced diffusion of Cr, Fe, and Ni between the substrate and the Ni-plating. This provides a simple cost effective approach to further enhancing the efficacy of Ni-plating against corrosion in molten fluoride salts.

6.7 Electrochemistry as a Corrosion and Compatibility Diagnostic

High temperature electrochemistry of molten salts provides fundamental in situ information on cation dissolution in molten salts; additionally it can provide insights into the propensity for corrosion of various alloys in molten salts. Anodic stripping voltammetry can potentially
determine chemical concentrations in salts in real time. Potentiometry can also give an instantaneous indication of a base alloy’s or plating’s corrosion potential in a molten salt.

Anodic stripping voltammetry however requires that the individual oxidation potentials of species in the salt be known for quantitative analysis, so for this technique to be successfully used, the oxidation potentials and working curves of cations of interest must be known. For potentiometry to give an indication of an alloy’s corrosion susceptibility, it must be determined what potential is acceptable for an alloy in a molten salt. Usually the closer the alloys’ potentials, the more compatible they will be if placed in contact with each other in a molten salt. Testing more alloys using the potentiometry technique and comparing their potential to the results of direct salt exposure tests can indicate the usefulness of this technique and is recommended.
Appendix

A

FLiNaK Properties
**Dynamic Viscosity: \( \mu \)**

The dynamic viscosity of FLiNaK near its melting point is slightly more than 10 times that of water at STP. At 850°C, the temperature of the salt exposure experiments, it is about twice that of water at STP. Equation A-1 is valid for temperatures from 475°C to 875°C (plotted in Fig. A-1) [111].

\[
\mu(T) = \left( 5.0351 \times 10^{-13} \right) T^4 \cdot \left( 2.1034 \times 10^{-9} \right) T^3 \cdot \left( 3.3161 \times 10^{-6} \right) T^2 \cdot \left( 0.0023468 \right) T + \left( 0.63319 \right) \left( \text{kg/m-s} \right)
\]

**Equation A-1**

where

\( \mu(T) \) = dynamic viscosity  
\( T \) = temperature in Kelvin

**Fig. A-1.** Dynamic viscosity of FLiNaK salt as a function of temperature as plotted using equation A-1. For comparison, the viscosity of water at 25°C is about 0.001 kg/m-s.
Density: $\rho$

Equation A-2 may be used to calculate the density as a function of temperature, shown in Fig A-2 [112].

$$
\rho(T) = -0.73 \frac{\text{kg}}{\text{m}^3 \cdot \text{K}} \cdot (T - 273.15) + 2530 \frac{\text{kg}}{\text{m}^3}
$$

**Equation A-2**

where

$\rho(T) = \text{density as a function of temperature}$

$T = \text{temperature in Kelvin}$

Fig. A-2. Density of FLiNaK salt as function of temperature. From this correlation, one can expect to observe an increase in the volume of FLiNaK of about 14% from its melting temperature of 454°C up to 850°C.
Specific Electrical Conductivity: $k$

The electrical conductivity of FLiNaK has been measured and correlated to temperature from 494°C to 649°C (Fig. A-3) [113].

$$k(T) = 0.742 \frac{1}{\Omega \cdot m \cdot K} \cdot T - 447.4 \frac{1}{\Omega \cdot m}$$  \hspace{1cm} \text{Equation A-3}

where

$k(T)$ = specific electrical conductivity as a function of temperature

$T$ = temperature in Kelvin

![Figure A-3. Electrical conductivity of FLiNaK salt as a function of temperature.](image-url)
Appendix

B

Experimental Setup for Corrosion Testing
Experimental Setup for Corrosion Testing

The experimental setup consisted of the items, procedures and methodologies that would be used for the long-term corrosion tests. It was not obvious what the ideal container material would be, so an effort was made initially to find a container material that would impact the corrosion tests to the least extent possible. After a literature survey and consultation with other researchers, it was determined that carbon and Ni were the preferred container materials. Ni proved to be costly, and had a potential to participate in corrosion reactions during the tests. It was therefore decided that graphite with a small pore size be used as the container material, and to use an outer stainless steel air/pressure boundary.

There were several design iterations before the final design was conceived for the static corrosion capsules. Each iteration bringing about simplifications and improvements to the overall design. The design progressed from a complex two-pressure vessel system that would have tested six alloys simultaneously to a simplified crucible test that would test each alloy independently. Many calculations were performed to check the suitability of various designs, and eventually used for final design decisions.

Crucible Selection

A suitable material to use for the crucible had to be found before starting the design and construction of the static corrosion experiment. Many different materials have been used for containment of molten fluorides for corrosion testing (see Table B-1). Carbon-based containers quickly stood out as being the most inert material in respect to the fluorides. Recommendations from researchers at ORNL also had a major influence in the decision of container material. ORNL usually made the test crucibles from the same alloy as the coupons, and when it proved too difficult to do this, would use graphite or glassy carbon for a crucible [23]. Glassy carbon had the added benefit of making removal of the solid salt easier due to its non-wetting nature.
carbon however is much more expensive than purified graphite and was therefore removed from consideration.

Graphite was chosen as the container material after an extensive literature search of container materials used by other researchers studying molten fluoride salts. Ignoring the argon cover gas, the interfaces of the UW static corrosion experiment are limited to salt/coupon, salt/graphite, coupon/graphite. Graphite is fully compatible with molten fluorides up to very high temperatures [6]. However, if the graphite pore size were too large, the frozen salt would stick in the crucible after the salt cooled, making it hard to remove the salt post testing [91].
# Table B-1. Survey of the salt and container materials used in previous studies.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Temperature (°C)</th>
<th>Test Type</th>
<th>Containment</th>
<th>Problems/Purpose</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF-NaF-KF</td>
<td>800-550</td>
<td>Loop</td>
<td>Hastelloy-N</td>
<td>Cyclic dissolution and deposition process</td>
<td>[6]</td>
</tr>
<tr>
<td>LiF-19.5CaF2 NaF-27CaF2-36MgF2</td>
<td>797 &amp; 930</td>
<td>Static</td>
<td>Alumina Quartz</td>
<td>Alumina Leaked Quartz acted as catalyst</td>
<td>[2]</td>
</tr>
<tr>
<td>NaF-ZrF4-UF4 (~50-46-R) NaF-KF-LiF-UF4 (11-41-45-R)</td>
<td>550-900</td>
<td>Loops</td>
<td>Inconel, Ni-Mo alloys (at least 4, )</td>
<td>Cyclic dissolution and deposition process</td>
<td>[4]</td>
</tr>
<tr>
<td>LiF-NaF-KF</td>
<td>600</td>
<td>Static</td>
<td>Graphite crucible in quartz containment (now using Ni)</td>
<td>Majority of salt climbed out of graphite crucible into quartz tube. Graphite crucible made melt black.</td>
<td>[114]</td>
</tr>
<tr>
<td>20 of them, all Tmelt&gt;100° C</td>
<td>&gt;727</td>
<td>Static</td>
<td>Graphite crucibles, and Pt cups with boron nitride powder for sticking</td>
<td>Salts stuck to Pt cups</td>
<td>[115]</td>
</tr>
<tr>
<td>LiF-NaF-KF</td>
<td>500</td>
<td>Static</td>
<td>High density graphite crucible</td>
<td>None mentioned</td>
<td>[116]</td>
</tr>
<tr>
<td>2LiF-BeF2</td>
<td>500,600,700, 800</td>
<td>Static with Ar Bubbling</td>
<td>Ni and glassy carbon crucibles</td>
<td>Crucible choice differed with test environment</td>
<td>[117]</td>
</tr>
<tr>
<td>LiF-BeF2-ZrF4-ThF4-UF4 (70-23-5-1-1)</td>
<td>588-688</td>
<td>Loop</td>
<td>304 SS loop</td>
<td>---</td>
<td>[118]</td>
</tr>
<tr>
<td>LiF-BeF2-ThF4-UF4 (68-20-11.7-0.3)</td>
<td>540-650</td>
<td>Loop</td>
<td>316 SS loop</td>
<td>---</td>
<td>[118]</td>
</tr>
<tr>
<td>LiF-BeF2 (66-34)</td>
<td>525-650</td>
<td>Loop</td>
<td>316 SS loop</td>
<td>Be rod decreased corr. Rate from 8 to 2 µm/yr</td>
<td>[118]</td>
</tr>
<tr>
<td>LiF-NaF-KF</td>
<td>600</td>
<td>Loop</td>
<td>Carbon loop with Mo diaphragm</td>
<td>Leaks from joints, failure of heating elements, freeze valve difficulties</td>
<td>[119]</td>
</tr>
<tr>
<td>LiF-BeF2</td>
<td>500</td>
<td>Static</td>
<td>304 L SS (sealed vessel)</td>
<td>Vacuum welded, very little corrosion</td>
<td>[119]</td>
</tr>
<tr>
<td>LiF-BeF2</td>
<td>800 &amp; 1100</td>
<td>Static</td>
<td>316 L SS (cylindrical)</td>
<td>CrC7 coated carbon coupon</td>
<td>[119]</td>
</tr>
<tr>
<td>LiF-BeF2</td>
<td>800 &amp; 1100</td>
<td>Static</td>
<td>Hastelloy N (cylindrical)</td>
<td>CrC7 coated carbon coupon</td>
<td>[119]</td>
</tr>
<tr>
<td>LiF-BeF2</td>
<td>800 &amp; 1100</td>
<td>Static</td>
<td>Molybdenum (cylindrical)</td>
<td>Mo2C coated Mo supports</td>
<td>[119]</td>
</tr>
<tr>
<td>LiF-BeF4</td>
<td>493-649</td>
<td>Loop</td>
<td>316 SS</td>
<td>Be addition decreased corr.</td>
<td>[20]</td>
</tr>
<tr>
<td>LiF-BeF2-ThF4-UF4</td>
<td>704-566</td>
<td>Loop</td>
<td>Hastelloy N-m</td>
<td>4 separate loops built to determined alloy modifications</td>
<td>[20]</td>
</tr>
<tr>
<td>LiF-BeF2-ThF4-UF4</td>
<td>704-566</td>
<td>Loop</td>
<td>Inconel 601</td>
<td>Investigated metal plate-out on graphite</td>
<td>[20]</td>
</tr>
<tr>
<td>LiF-BeF2-ThF4-UF4</td>
<td>1100</td>
<td>static</td>
<td>TZM</td>
<td>Investigated TZM alloy</td>
<td>[23]</td>
</tr>
</tbody>
</table>
Design I and Design II

The main components for design I of the corrosion experiment consisted of two large stainless steel vessels, a Ni and a glassy carbon crucible for containing the salt, and two double-ball-valve setups that would have allowed for electrode insertion and salt sampling. Additionally, flow would be induced in the experiment by bubbling argon gas into the FLiNaK in the glassy carbon crucible. A schematic illustration of the first design is shown in Fig. B-1. The design consisted of two vessels, a Ni vessel in which the salt would be melted and a glassy carbon corrosion test vessel. Provisions were also made for introducing electrodes for cyclic voltammetric studies. The voltammetric studies would provide on-line information on the effects of dissolution of the alloy constituents in the salt. Design 1 was abandoned because it was thought that placing the coupon crucible in an argon-filled glove box would provide similar results and greatly simplify the engineering involved. Other challenges involved finding high temperature valves for FLiNaK and seals between glassy carbon and Ni, as well as the high material-salt contact area.
Fig. B-1. The experimental setup for design 1. On the left is the fill crucible, on the right is the glassy carbon crucible containing the molten salt inside of a containment vessel.

A schematic illustration of design II is shown in Fig. B-2. Design II would also involve a glassy carbon crucible, but it would be housed in a glove box with an argon cover-gas. This design was abandoned after discussions with researchers at ORNL, who pointed out that even sub ppm levels of oxygen in the argon-cover gas could cause significant contamination over the 1000 h exposure period initially planned for the corrosion tests. After discussion with ORNL, it was decided not to test different alloys simultaneously because it would be difficult to isolate corrosion mechanisms. Moreover, because the voltametric experiments would introduce more components in direct contact with the salt, it was decided that voltametric experiments would be investigated separately.
Fig. B-2. Schematic illustration of second design explored for the static corrosion test cell. The alloy coupons would be lowered into the molten salt once the molten salt reached temperature and removed upon completion of testing.

Calculations

Many calculations were performed to ensure the reliability and success of the molten salt exposure experiments. These calculations included: heat transfer calculations for estimation of salt temperature during temperature ramp-up and to estimate the glove box heat load, estimation of internal stresses on the corrosion capsule at temperatures of up to 1000°C under varying pressures, salt height calculations, graphite and stainless steel thermal expansion, and corrosion time estimations based on data from other researchers.

Temperature Ramp Simulations

Finite element heat transfer simulations of the temperature profiles of the outer wall of the corrosion cell and the salt during temperature ramp-up were made using the computer software program FEHT (Fig. B-3). The FEHT analysis was performed to allay concern that the alloy
coupons may take a significant amount of time to experience the experimental temperatures of interest inside the graphite and stainless steel capsules. One hour was given for the oven to ramp up to 1000°C from room temperature. From this figure it can be seen that within about two hours the temperature of the coupons inside of the capsule would approach that of the furnace if the furnace was ramped up from 20°C to 1000°C in the first hour. Convection in the molten salt and argon inside the crucible were neglected for these calculations, so they are likely conservative.

![Fig. B-3. Finite Element Heat Transfer (FEHT) simulations showing the temperature of the outer walls of the containment and the salt during temperature ramp-up.](image)

Several correlations were used to determine suitable heat transfer coefficients for use in FEHT. After inputting functions for the temperature dependent heat transfer coefficients for the lid and the sides, the ambient fluid temperature (surrounding argon gas temperature) was allowed to vary in time. Other properties such as thermal conductivities, densities, and specific heats were either found in FEHT or through a literature search. Because the bottom of the capsule was directly contacting the furnace retort, it was assumed to have the same temperature as the retort.
Both the functions for the heat transfer coefficients for the top of the stainless steel crucibles as well as for the sides were found in the Handbook of Heat Transfer Fundamentals [120]. For \( \text{Ra} \leq 10^5 \) use of the laminar Nusselt number is appropriate. For the top of the lid, equation B-1 was used to find the Nusselt number that in turn was used to find the heat transfer correlation:

\[
\text{Nu}_L = \frac{1.4}{\ln\left(1 + \frac{1.4}{\text{Nu}_T}\right)}
\]

\textbf{Equation B-1}

where

\[
\text{Nu}_T = 0.835 \cdot C_L \cdot \text{Ra}^{\frac{1}{7}}
\]

\[
C_L = \frac{4}{3} \cdot \frac{0.503}{\left[1 + \left(\frac{0.492}{\text{Pr}^{\frac{9}{16}}}\right)^{\frac{2}{3}}\right]}
\]

\[
\text{Pr} = \frac{C_p \cdot \mu}{k}
\]

\[
\text{Gr} = g \cdot \beta \cdot (T_{\text{fluid}} - T_{\text{wall}}) \cdot L^3
\]

\[
\text{L} = \frac{A}{P}
\]

\( A \) = area of capsule top

\( P \) = capsule perimeter

\( C_p \) = specific heat

\( \mu \) = dynamic viscosity

\( v \) = kinematic viscosity

\( \beta \) = volumetric expansion coefficient

\( k \) = thermal conductivity

\( g \) = acceleration due to gravity

A similar correlation, equation B-2, was used to find the heat transfer coefficient for the edge of the corrosion capsule:
\[ \text{Nu}_{C} = \frac{0.9 \cdot \xi \cdot \text{Nu}_p}{\ln(1 + 0.9 \cdot \xi)} \]

\[ \text{Equation B-2} \]

where

\[ \xi = \frac{2 \cdot \frac{L}{D}}{\text{Nu}_T} \]

\[ \text{Nu}_p = \frac{2.8}{\ln\left(1 + \frac{2.8}{\text{Nu}_T}\right)} \]

\[ \text{Nu}_T = C_L \cdot \text{Ra}^{\frac{1}{3}} \]

\[ C_L = \frac{4}{3} \cdot \frac{0.503}{\left[1 + \left(\frac{0.492}{\text{Pr}}\right)^{\frac{9}{8}}\right]^{\frac{16}{9}}} \]

\[ \text{Ra} = \text{Gr} \cdot \text{Pr} \]

\[ \text{Pr} = \frac{C_p \cdot \mu}{k} \]

\[ \text{Gr} = g \cdot \beta \cdot \left(\frac{T_{\text{fluid}} - T_{\text{wall}}}{\nu}\right) \cdot L^3 \]

L = cylinder height
D = capsule diameter
C\( _p \) = specific heat
\( \mu \) = dynamic viscosity
\( \nu \) = kinematic viscosity
\( \beta \) = volumetric expansion coefficient
k = thermal conductivity
g = acceleration due to gravity
Fig. B-4. (a) is a basic schematic of the finite element heat transfer (FEHT) model, a slice is shown with the radial axis of symmetry on the left. The gray area is the stainless steel air boundary, the crosshatched area is the graphite, the green area inside near the bottom is the FLiNaK, and the blue area inside near the top is the argon gas. (b) shows the temperature distribution one hour after heating, when the ambient temperature has reached 554°C. The coolest region in the center has reached ~366°C and the hottest region on the bottom near the outside is near 554°C. After two hours, one full hour at temperature, there is virtually no temperature variation.

Glove Box Heat Load

The heat load inside the glove box was estimated to properly size the glove box heat exchanger. It was believed that there would be three cylindrical heaters of differing sizes in the glove box at the time of the calculation. Calculations were made for three different scenarios in which, two of the heaters were at 500°C, one of the heaters was at 800°C, and one of the heaters was at 1000°C. Conservative calculations led to a result of 800 watts needing removal from the glove box. However, if actions were taken such as covering the heaters with insulation, the amount of heat that would be needed to be removed from the glove box would decrease by at least 30%. The glove box heat exchanger has adequately cooled the glove box when all the heaters were left on for extended periods lasting several days in the present glove box.
configuration. The basic equations used were essentially variations of equation B-3, before the contributions from the sources were summed. Both the view factor and the emissivity were assumed to be one, which would give a conservative estimate.

\[ Q_T = Q_C + Q_R \]  

Equation B-3

where

\[ Q_C = h \cdot A \cdot (T_W - T_e) \]
\[ Q_R = F \cdot e \cdot \sigma \cdot A \cdot (T_W - T_e) \]

\( Q_T \) = total heat transferred to the glove box
\( Q_C \) = heat transferred to the glove box from convection
\( Q_R \) = heat transferred to the glove box from radiation

\( h \) = heat transfer coefficient between the glove box gas and the heater
\( A \) = heat transfer surface area
\( T_W \) = wall temperature
\( T_e \) = glove box ambient gas temperature
\( F \) = view factor
\( e \) = emissivity
\( \sigma \) = Stefan's Constant

**Hoop and Lid Stresses**

The hoop and lid stresses on the 304 stainless steel capsules were calculated to determine the optimal method of filling the capsules with salt. It was decided to fill the capsules and weld them shut at 600°C within the glove box, and perform the corrosion tests at 850°C. This method would lead to a hoop stress of about 420 kPa and a lid stress of 250 kPa, well within creep rupture limits. Initial plans had called for the crucibles to be filled at room temperature and tested at 1000°C. The hoop and lid stresses at 1000°C would have been 5.0 MPa and 3.0 MPa respectively and approaching the creep rupture limits of 304 stainless steel. Equation B-4 was used to calculate the hoop stress.
\[
\sigma_H = \frac{\Delta P \cdot R}{t}
\]  \hspace{1cm} \text{Equation B-4}

where

\( \sigma_H \) = hoop stress
\( \Delta P = P_1 - P_o \)
\( P_1 \) = inside pressure = \( P_1 \) or \( P_2 \)
\( P_o \) = outside pressure = 101325 Pa
\( t \) = wall thickness

The internal pressure was calculated using the ideal gas law

\[
P V = n R T
\]  \hspace{1cm} \text{Equation B-5}

where

\( P \) = internal pressure
\( V \) = internal volume
\( n \) = number of moles present
\( R \) = ideal gas constant
\( T \) = absolute temperature

Since the number of moles present and the gas composition did not change, one can simplify the calculation of internal pressure using a ratio as shown in equation B-6.

\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}
\]  \hspace{1cm} \text{Equation B-6}
where

\[ P_1 = \text{initial interior pressure} \]
\[ P_2 = \text{final interior pressure} \]
\[ T_1 = \text{initial temperature in Kelvin} \]
\[ T_2 = \text{final temperature in Kelvin} \]
\[ V_1 = \text{initial interior gas volume} \]
\[ V_2 = \text{final interior gas volume} \]

The initial and final temperatures were fixed and the volumes could be solved for using the initial volume of the crucible and the density temperature dependence of FLiNaK. Either the initial or final pressure could then be calculated.

Calculations were also performed to determine the vacuum necessary to weld the crucible at room temperature to obtain zero stress upon reaching the operating temperature of 1000°C (i.e. zero pressure difference between the inside of the corrosion capsule and the outside). Fig. B-5 shows the results pressure (1/5 atmosphere) and how pressure would vary as a function of temperature.
Fig. B-5. Calculation of Hoop stress up to 1000°C for 304 stainless steel outer containment, assuming the containment is evacuated to 1/5 atmosphere.

The stress on the lid was calculated using case 10a (equation B-7) in table 11.2 from Roark’s Formulas for Stress and Strain [121]. It is valid for a uniform pressure on a simply supported circular plate.

\[
\sigma_B = \frac{6 \cdot M_C}{t^2}
\]

Equation B-7

where

\(\sigma_B\) = Bending stress on lid
\(M_C\) = moment on the lid from a uniform pressure
\(t\) = thickness of the plate
When the circular plate has the pressure distributed uniformly over its entirety:

\[ M_C = \frac{q \cdot a^2 \cdot (3 + \nu)}{16} \]

**Equation B-8**

where

\( q \) = pressure  
\( a \) = outer radius  
\( \nu \) = Poisson's ratio

The Poisson’s ratio for 815°C was used because it was the closest available value that could be found.

**Height of FLiNaK**

The change in height of the FLiNaK salt with temperature was calculated several times before and during the experiment. Two calculations are worth noting. The first calculation regarding salt height in the graphite crucibles \( (H_{Crucible}) \) was to determine the salt mass needed in the corrosion capsules. The volume occupied by the coupons and the graphite screws was neglected, as was the milling and tapped holes in the graphite rod that aided in holding the coupons and the fixturing graphite screws.

\[ M = \rho \cdot V \]

**Equation B-9**

where
\[ \rho = -0.73 \cdot T + 2530 \]

\( T = \text{FLiNaK temperature} \)

\[ V = H_{\text{Crucible}} \cdot \left( \pi \cdot R_0^2 - \pi \cdot R_1^2 \right) \]

\( H_{\text{Crucible}} = \text{height of salt in crucible} = 3 \text{ inches (0.0762 m)} \)

\( R_0 = \text{graphite crucible inner radius} = 1.5 \text{ inches (0.0381 m)} \)

\( R_1 = \text{graphite sample holder rod radius} = 3/16 \text{ inches (0.004763 m)} \)

Initial calculations for the salt requirements to ensure complete immersion of coupons at 1000°C indicated that about 0.63 kg would be required per crucible test, but since the scale that is being used is accurate to within 0.1 kg; 0.7 kg would be used. For tests at 850°C, more FLiNaK would be necessary to cover the coupons (~0.66 kg), but again due to scale precision, 0.7 kg would be added. Fig. B-6 shows the mass needed as a function of temperature to ensure that the top coupon is covered by at least \( \frac{1}{4} \)” of FLiNaK.

Fig. B-6. Mass of FLiNaK required to completely cover the three test coupons, as a function of temperature.
It became necessary to determine the height of the FLiNaK inside the FLiNaK reservoir as a function of temperature up to 950°C. There was 18 kg of FLiNaK in the Ni-200 container; it had nominal internal dimensions of 11.5” (0.292 m) diameter and 13.5” (0.343 m) in height.

Equation B-10 was used to determine the maximum height obtained by the FLiNaK. The height of FLiNaK in the container as a function of temperature is shown in Fig. B-7.

\[ H(T) = \frac{M}{A \cdot \rho(T)} \]  

**Equation B-10**

where

- \( H \) = height of FLiNaK
- \( M \) = initial mass of FLiNaK
- \( \rho(T) \) = density of FLiNaK as a function of temperature
- \( A = \pi \cdot r^2 \)
- \( r \) = reservoir radius
Graphite/Stainless Steel Expansion

Because of the different thermal expansion coefficients between stainless steel and graphite, there was initially concern about using stainless steel screws to hold the graphite lid to the graphite crucible as well as keeping the graphite capsule inside the stainless steel capsule. The plan for the screws, crucible, and capsule was to provide a large enough tolerance so that the different expansion coefficients upon heating and cooling became a non-issue. To determine whether this would be an acceptable approach, the thermal expansion coefficients and changes in length were determined. The analysis used equation B-11 to determine the change in length of both the graphite and the stainless steel:

$$\beta = \frac{\delta}{L_1(T_f - T_i)}$$  

\text{Equation B-11}

where
\( \beta \) = thermal expansion coefficient
\( \delta \) = change in length
\( L_i \) = initial length
\( T_{f,i} \) = final and initial temperatures respectively

From this analysis it was found that the stainless steel capsule would expand 0.7 thousandths of an inch more than the graphite crucible and similarly for the screws. An adequate tolerance was given for the graphite capsules inside the stainless steel capsules, and for the stainless steel screws and graphite threads.

**Corrosion Exposure Duration**

The length of the molten salt exposures was chosen so that it could be expected that the majority of coupons would experience corrosion, but ideally not long enough were all the metals would have reached equilibrium with the salt long before the furnace was shut off. The former case would not present as much data for analysis and the latter case would waste time and electricity. It was initially desired for the crucible experiment to last 1000 h; however, upon further review the length of time was scaled back. The reasons for doing this were two fold. First, similar Russian research had shown that corrosion in molten salts curtailed dramatically in static systems after 200 h [122]. Moreover, based on other researchers results in open systems (in an inert atmosphere but with a replenished cover gas), as shown in Fig. B-8 and B-9, 500 h would produce sufficient corrosion to obtain meaningful analyses [2]. Furthermore, intergranular corrosion could be expected to be more severe, since in many cases more of the reactive alloy constituents such as Cr, Ti, or Al will be located there.
Fig. B-8. Corrosion depth as a function of exposure duration (100 hr and 500 hr) at 797°C in alumina crucibles under 1 atm of argon gas. The molten salt is LiF-19.5CaF$_2$. (Source: [2])
Experimental Preparations and Progress

After finalizing the design of the experiment, supplies were appropriated, preparations were made, several scoping experiments were conducted, and the static corrosion experiment was initiated. The majority of the early work was outfitting a glove box in which to transfer the salt and perform the work that required an inert atmosphere. Some time after work on the glove box started, graphite rods and cylinders for the corrosion capsules were obtained, and machining was initiated. The last major piece of equipment to be obtained was the controlled atmosphere furnace. Once all the major pieces were acquired and assembled, the salt exposures proceeded.

Insulation

The insulation and thermal shielding used to keep the glove box and working surfaces cool and the heated regions hot and uniform in temperature required several different materials and techniques. The capsule heater, ordered from Thermcraft, contained a fiberboard type insulation
attached around its circumference; fiberboard insulation was also used to insulate the top and bottom of both the capsule and FLiNaK reservoir heaters. Both heaters were then wrapped in another layer of Kaowool insulation before being wrapped in a fiber cloth insulation primarily to keep the glove box interior free from contamination from the Kaowool insulation. A glass cloth tape was used to hold the fiberboard insulation pieces together, and wire was used to compact and hold the Kaowool and fiber cloth to the exterior of the heaters.

Heat loss from the bottom of the capsule heater was a concern because it rested on a scale (needed to ensure the proper amount of FLiNaK was allocated to each corrosion capsule). The scale had a maximum operating temperature limit of 40°C. Fiberboard insulation and firebricks were placed under the capsule heater to reduce heat loss. The capsule heater and fire bricks were in turn placed on a metal sheet which was elevated from the scale using large nuts. The scale top then had a sheet of cloth insulation wrapped over it, and on top of that, Al foil was wrapped and taped to the sides of the scale top. These precautions would reduce the heat seen by the scale by reducing the direct conduction of heat from the firebricks to the scale and by allowing convective cooling of both the scale surface and the metal sheet on which the firebricks rested by the circulating glove box gas. A thermocouple was inserted under the cloth insulation, in contact with the metal scale top, and readings never reached above 40°C. Fig. B-10 shows the heat reduction method that was employed to reduce the temperature of the scale.
DAQ with LabVIEW

LabVIEW was used for measurements and automation as well as to perform and coordinate analyses, throughout the molten salt research. LabVIEW was used to record temperature data for the argon-atmosphere furnace and to record temperature, oxygen, and humidity data for the glove box as well as controlling the heaters therein. In the glove box, LabVIEW was used to control a SCR with a PID controller which in turn controlled both hemispheres of the FLiNaK reservoir heater. LabVIEW also controlled four other PID controllers which were used to control relays for both hemispheres of the capsule heater as well as the three tape heaters used for the transfer tubing. All the heater temperatures were controlled precisely. The SCR control usually did not vary more then a tenth of a degree as long as there was nothing being performed in the glove box, and the relay controlled heaters usually varied less then a degree.

Temperature Measurements

Type K thermocouples have 0.025°C resolution from -20°C to 1100°C, and were used for all parts of the experiment except for the controlling thermocouples used in the argon atmosphere furnace, which used the manufacturer provided type-N thermocouples [123].
Gas Environment

In most of the literature surveyed, an inert atmosphere (usually argon) slightly in excess of atmospheric pressure was used to prevent air intrusion and maintain purity (low moisture). Therefore the glove box was kept at a slight overpressure to ensure that flow was out of the glove box in case a leak was present. The argon atmosphere furnace had a constant argon gas sweep in the retort, a water-cooled silicone o-ring door seal, and a gas check valve located on the exit stream to prevent back-flow.

The argon atmosphere furnace used industrial grade argon or nitrogen for sweep gas. The purity in the argon atmosphere furnace was not as important as the glove box because it was used merely to prevent oxidation of the exterior of the corrosion capsules. The glove box used an industrial argon gas as the primary cover gas. The glove box also required an argon/hydrogen or nitrogen/hydrogen gas mixture to regenerate its Dry-Train (a gas contaminant filter always in use while the glove box was) that removed gas contaminants such as oxygen and water.

Glove Box

Due to the corrosive nature of contaminants in the FLiNaK salt, it was necessary to handle the FLiNaK in a glove box to prevent contamination. Fig. B-11 shows a photograph of the glove box at a distance showing several important components. Fig. B-12 shows the rear exterior of the glove box with other critical components.
Fig. B-11. Glove box front.

Fig. B-12. Glove box rear showing many key parts, including electrical boxes, feed-throughs, water chiller, and variacs.
Three electrical boxes were attached to the back of the glove box to house instruments as shown in Fig. B-12. The smaller electrical boxes, on the left and right of the large one, housed 120 V connections for the tape heaters, 240 volt connections for the cylindrical heaters and heat exchanger fans, and a welding lead. The large electrical box housed various electrical connections, an SCR, relays, and fuses. All the gas piping on the exterior of the glove box could be evacuated with the correct opening and closing of specific valves.

Fig. B-13 shows the glove box interior with the Plexiglas front removed. The glove box was used to take salt samples and fill the corrosion capsules with FLiNaK. Two cylindrical heaters and three wrap heaters were used in the glove box; the FLiNaK reservoir heater, capsule heater, and three tape heaters on the FLiNaK transfer tube. All the heat sources were wrapped in insulation, and the two cylindrical heaters that were used for the FLiNaK reservoir and capsule heater were placed on insulating fiberboards that were in turn placed on fire bricks placed on metal sheets that were elevated from the glove box base and scale by hexagonal nuts.
A heat exchanger was fabricated that consisted of two radiators on the front and two fans in the back to force the glove box gas over the radiators. Cooling water for the radiators was fed into the glove box through two feed throughs using ½” stainless steel tubing. The glove box heat exchanger, Fig. B-14, held the internal glove box temperature at or below 30°C while the capsule heater was kept at temperatures near 1000°C, and while the FLiNaK reservoir heater and capsule heater were at 600°C and the transfer tube was at 500°C for extended periods.
Fig. B-14. The glove box heat exchanger was located in the rear-upper portion of the glove box. Fans were mounted in the back of the heat exchanger enclosure to force the glove box air through the radiators.

The glove box had several penetrations welded into it for instrumentation, power, gas, and water. It had been leak tested and shown to provide an adequate air boundary. The majority of the feed-throughs were made in one of three ways. For the larger wiring feed-throughs, generally, a double male pipe coupler was bisected, the bottom portion was filled with an epoxy called VS-101, and the epoxy was allowed to harden. Once hardened, low tolerance holes for the wiring were drilled through the epoxy and the wires were fed into the feed through. The feed-throughs were then filled with more epoxy to make them airtight. For the smaller wired feed-throughs, machinists wax was used prior to the first epoxy use to keep the epoxy in a disk shape. After the epoxy hardened, most of the wax would be dug out and the remaining wax dissolved with acetone before the next step. Holes were then drilled into the epoxy and the wires placed through before the final epoxy. The feed throughs that were used for tubing relied on pipe/compression fitting couplers that put leak-proof compression fittings on the tubes.

The glove box had an integral online purifier called a “Dry-Train” that removed moisture to <2 ppm and kept the O₂ level to below 0.1 ppm with all the equipment inside of the glove box. The dew point was measured with a SHAW Moisture Meter. The SHAW moisture meter, model SDA, used a Red Spot Sensor, shown in Fig. B-15A. The sensor was placed in front of the Dry-Train intake fan and its measurable dew point range was from -20°C to -80°C.
The oxygen level was measured with an Alpha-Omega Series 3000 Trace Oxygen Sensor. The oxygen sensor was capable of measuring oxygen levels of 0.1-1000ppm (Fig. B-16). A gas pump for the sensor was located inside the glove box and continuously pumped the glove box gas through the sensor, located outside of the glove box. Stainless steel tubing connected the gas pump to the sensor on the glove box exterior. The sensor was an electrochemical cell acting as a transducer. The electrochemical cell used a lead anode, a gold plated cathode, and an electrolyte consisting of potassium hydroxide to determine the oxygen level inside the glove box [124]. It was very specific to oxygen provided that compounds that can oxidize lead were not present [124]. Halogens such as chlorine or fluorine may be able to oxidize lead [124]. The sensor had three ranges, 0-10/100/1000 ppm $O_2$, and would automatically switch between them. The accuracy was ±1% of full scale under standard operating conditions [124]. During normal operations, the oxygen meter readings would generally stay at zero, but if a negative pressure was induced inside the glove box, the measured oxygen levels would increase to about 1 or 2 ppm.

Fig. B-15. Dew-point sensor was located near the dry-train fan inlet, shown in (a) and (c). The signal from the sensor was read in LabVIEW and from the glove box moisture meter (b).
Creep/Oxidation Test/Validation

Once design III was finalized but prior to the decision to fill the crucibles with molten FLiNaK and seal at 600°C and perform tests at 850°C, stress and thermodynamic calculations had indicated that the 304 stainless steel would be near its creep rupture limits (4 to 5 bar), if held at 1000°C for 500 h. An important consideration in the design of the corrosion cell was the mechanical stability of the outer stainless steel capsule that constituted the boundary between the molten salt and the furnace atmosphere.

The stainless steel capsule was made from three separate 304L stainless steel pieces, a 4” ID cylinder 7” in length, and with a wall thickness of 0.237” and two end caps, ¼” in thickness. Welding was performed using five TIG passes using ER 308L, 0.0625” diameter filler rod. To allow for the contraction of air during cooling a small gap was left open that was eventually filled by the same method after cooling. The stainless steel capsule was then heated to 1000°C and held at this temperature for 500 h (temperature and time identical to initial planned corrosion tests). While the test was proceeding, a steel drum was placed over the heater to contain any blast fragments in case of capsule failure.
Despite considerable oxidation of the surface (a pile of oxide scales were removed from the capsule and heater after testing), the stainless steel capsule maintained its integrity in that there were no obvious cracks in the welds or in the cylindrical sections of the capsule or apparent yielding of the end-caps or the cylinder walls. Fig. B-17 shows a photograph of the successful test and stainless steel capsule after exposure at 1000°C for 500 h, in air.

Fig. B-17. Photograph of the oxidized stainless steel capsule and setup after exposure at 1000°C for 500 h, in air. A) shows the heater setup, B) shows the capsule and a pile of oxide scales that were removed from the capsule and the heater after testing. C) Shows the capsule after testing with the majority of the oxide scales removed. D) Shows the capsule that was tested after 500 hr at 1000°C on the left next to a capsule from a cancelled test that reached 1250°C (note that the capsule tested at test conditions showed no yielding).

To examine the presence and penetration of cracks in detail, the weld from the cylinder to the stainless steel top was sectioned, mounted, polished, and then examined under a scanning electron microscope (Fig. B-18 and B-19).
Maximum crack length was identified to be ~1500 µm and the oxide layer on the inner surface was about 20 µm in thickness. The total wall thickness prior to the test was 6020 µm (0.237”).

Fig. B-19. Crack images. SEM images of (a) oxide layer on the inner surface and (b) cracks emanating from the outer side of the stainless steel capsule (maximum crack length was measured at 1500 µm). No penetrating cracks could be found on the interior of the capsule sections analyzed.

Atmosphere Controlled Furnace

An atmosphere-controlled high-temperature furnace was acquired from CM Furnaces (Fig. B-20), it was a model 1216FL with an Inconel-601 retort. The furnace was equipped with argon atmosphere control and was fully sealable (except for the gas inlet and exit lines that also were
used to feed in thermocouple wiring). The furnace provided for steady state operation up to 1150°C with a multiple segment programmable control.

**Fig. B-20. Photograph of the argon-atmosphere box-furnace that was used for high temperature corrosion studies.**

Due to the nature of design III, it was necessary to invert the capsules at 500°C to allow for the molten FLiNaK to drain off of the alloy coupons within. Initially, it was unclear how difficult this step would be and how the furnace would handle being opened at this temperature. Prior to opening the furnace door, the operator who would be inverting the capsules put on heat resistant clothing and increased the water flow rate to the door and gas flow rate through the retort. These two steps were undertaken to decrease the gas temperature inside the retort prior to opening the furnace door so that the silicone o-ring seal on the door would not be damaged. The heat resistant clothing consisted of a helmet with face shield, aluminized trench coat, and fiber gloves. The furnace door was opened and swiveled away from the operator, who then could use tongs to grab the capsules, remove them from the retort and invert them before returning them to the retort. Once the capsules were inverted, the furnace door would be closed and the retort purged of air. The water and air flow-rates would then be decreased back to the normal operating conditions.
For all the corrosion tests, the identical furnace program, shown in Fig. B-22 through B-24, was used. Fig. B-22 shows the overall furnace profile. The initial part of the furnace program (Fig. B-23) would ramp the furnace to 750°C at 60°C/hour, followed by a ramp to 852°C at 30°C/hour. A furnace reading of 852°C corresponds to temperatures inside of the furnace retort of about 850°C. Once at 852°C, the furnace would dwell at that temperature for 500 h. After 500 h the program would step to 509°C, however it would take the furnace about 3 ½ h to approach this temperature as seen in Fig. B-24. Once at 500°C the door would be opened and the crucibles inverted. Fig. B-24 shows the interior thermocouples would record a momentary temperature drop when the door was opened, but the temperature would quickly go back to 500°C after the door was closed.
Fig. B-22. Test one temperature profile. Above is the temperature profile that was plotted from recorded furnace temperature data averaged from 4 interior thermocouples obtained during corrosion testing.

Fig. B-23. Two segment ramping temperature. The furnace temperature increased at 60°C/hr until 750°C, it then increased 30°C/hr until reaching 852°C.
Fig. B-24. After 500 h at 850°C, the furnace would ramp down to 500°C and hold at that temperature for about 8 h, long enough for the system to equilibrate at near 500°C, the crucibles to be flipped, and the system to re-attain 500°C. The temperature drop from the furnace door being opened to facilitate crucible flipping is apparent at about 542 h.

Graphite Procurement and Machining

Three sizes of graphite cylinders/rods were procured from POCO Graphite. Two graphite cylinders 4” diameter and 40” long, six 3/8” diameter and 40” long graphite rods and fifteen ¼” diameter and 25” long graphite rods were procured for the base stock for all the crucible components. The POCO graphite was grade AXZ-5Q1, had an average particle size of 5µm and a pore size of 0.7 µm [92]. Additionally, because purity of the salt was a concern, the graphite was purified (total ash range 5ppm or less) [93]. Experience with FLiBe from the MSRE indicated that with the small pore size it would have been less likely that the salt would infiltrate the graphite [25]. The graphite crucibles and rods were machined first on a lathe. Further machining involved; milling for the grooves for the alloy coupons, drilling the holes for
attachment, and manually taping the holes. The graphite screws for fixturing the test coupons on the central rod were prepared using a lathe. Fig. B-25 through B-27 show the final product.

**Fig. B-25.** Photograph showing graphite pieces for one crucible and alloy coupons.

**Fig. B-26.** Photograph showing alloy coupons and coupon rod inserted into graphite crucible.
As recommended by POCO Inc., all machined graphite parts were ultrasonically cleaned first in methanol and then in distilled water. To avoid pitting the graphite, POCO recommended no more than 5 minutes of continual exposure to ultrasonic methanol/water. The cleaning process involved 3, 5 minute steps of ultrasonic cleaning in methanol followed by 3, 5 min. ultrasonic sessions with water. After drying, the graphite was heated to 1050°C and held for 8 h (Fig. B-28) to further remove moisture and oxygen before adding FLiNaK.
Fig. B-28. The graphite was baked out at about 1050°C for eight hours to remove residual moisture locked in the graphite.

**Corrosion Capsule Assembly**

The alloy coupons were placed in the graphite crucibles just prior to final assembly. The graphite crucibles were then placed in the 304 stainless steel capsules and the lids of the capsules were welded on. Further description of the salt filling and encapsulation process may be found in the main thesis.

**Final Capsule Sealing**

After the corrosion capsules were assembled, and filled with FLiNaK, the hole on the top of the capsules was welded shut using ER308L filler as seen in Fig. B-29. The top pieces of insulation on the top of the capsule heater were moved to either side during welding to allow for a grounding connection between the capsules and the welder power supply.
Fig. B-29.  A) is a photograph of the final weld being made on the crucible to seal up the hole through which the molten FLiNaK was pumped. B) is a connection that was used to ground the crucible inside the heater so that it could be welded. The ground consisted of two copper blocks attached to an Al cable with stainless steel screws.

**Coupon Removal**

After the corrosion capsules cooled to below 40°C, they were removed from the furnace and the bottom sections cut off using a slitting saw on a CNC mill in two steps. The first step cut through the stainless steel canisters, and the second step cut through most of the graphite (the final breaking off of the graphite bottom was done with a screwdriver to minimize graphite dust inside the test crucible). After cutting off the bottom sections, the coupon rods were broken off and the coupons were removed and cleaned (cleaning step described in thesis). After the coupons had dried, they were weighed a second time before being placed in a desicator to await further analysis.
Fig. B-30. A) shows the initial cutting of the stainless steel capsule, B) shows the cutting of the graphite capsule, C) shows the corrosion capsule after having the stainless steel and graphite bottoms removed, and D) shows the section of graphite rod with the coupons still on.
Appendix

C

Molten Salt Exposure Data
**Coupon Prep**

Following surface characterization on a scanning electron microscope (SEM), the coupons were cross-sectioned, and mounted. First, the coupons were cross-sectioned using a large wafer diamond disk at slow speed with distilled water as lubricant; the water tray was scrubbed and rinsed out prior to filling. Next, the cross-sectioned coupons were mounted in either Buehler Konductomet or Buehler Probemet molding compound. The mounted coupons were then ground and polished, starting with about 600 grit SiC paper and finishing with 1 micron diamond paste on a disposable pad. After the cross-sectioned and mounted coupons were polished to a mirror finish they were cleaned of paste and mounting compound by first cleaning with micro-organic soap, followed by 5 minutes of ultrasonic cleaning in acetone, the cleaning with micro-organic soap and ultrasonic acetone treatment was then repeated twice. After the last ultrasonic cleaning in acetone the coupons were cleaned once more with micro-organic soap before being ultrasonically cleaned in water for five minutes.

**Incoloy-800H**

Three types of exposure tests were performed for the Incoloy-800H; 1) in hydrofluorinated FLiNaK obtained from Electrochemical Systems Inc., 2) in non-hydrofluorinated FLiNaK obtained from INL, and 3) a ‘blank’ test in which the coupons were placed in a crucible prepared in a manner similar to the first and second tests, but without the salt.

EDS point scans of the surfaces of Incoloy-800H coupons after corrosion tests confirmed the removal of alloying constituents in molten FLiNaK. Averaged EDS point scans of the surface (table C-1) of a coupon exposed to the salt show the removal of active alloying elements and EDS point scans of the coupon exposed to the same temperature conditions but without the molten salt show its chemical composition closely resembles the original composition of the alloy.
Table C-1. Comparison of the chemical composition of the surface of Incoloy-800H before and after corrosion testing. For comparison, compositions of the alloy heated in a blank capsule (without salt) is also shown.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Mn</th>
<th>Ti</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Heat Data</td>
<td>42.3</td>
<td>31.6</td>
<td>20.4</td>
<td>0.80</td>
<td>0.60</td>
<td>0.50</td>
<td>0.13</td>
</tr>
<tr>
<td>Average EDS of 800H (Blank Capsule)</td>
<td>44.4</td>
<td>32.4</td>
<td>17.4</td>
<td>0.59</td>
<td>0.81</td>
<td>4.38</td>
<td>0.05</td>
</tr>
<tr>
<td>Average EDS of 800H in ECS Salt</td>
<td>56.4</td>
<td>40.2</td>
<td>2.22</td>
<td>--</td>
<td>--</td>
<td>0.18</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Argon Exposed Incoloy-800H

The argon exposed coupons were put through identical conditions to the molten salt exposed coupons, with the exception that they were not exposed to FLiNaK salt and retained the argon atmosphere from the glove box. Upon removal of the coupons, portions of some of the coupons appeared to have oxidized slightly from what little oxygen was in the glove box before the corrosion capsule was sealed.

SEM of Plan View

The argon exposed coupon surfaces were concentrated in Al (table C-2) and either had similar or slightly less amounts of Cr than that from the pre-corrosion coupon.

Fig. C-1. SEM of coupon Incoloy-800H exposed to Ar in a blank capsule (plan view).
Table C-2. Composition of Incoloy-800H in weight percent corresponding to Fig. C-1.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average EDS of 800H (Blank Capsule)</td>
<td>2.75</td>
<td>14.14</td>
<td>0.54</td>
<td>46.40</td>
<td>35.97</td>
<td>0.22</td>
</tr>
<tr>
<td>Heat Data</td>
<td>0.5</td>
<td>20.42</td>
<td>0.76</td>
<td>45.26</td>
<td>31.26</td>
<td>0.42</td>
</tr>
</tbody>
</table>

**SEM of Cross-section**

Fig. C-2 shows two precipitates along a grain boundary. Point scans of the precipitates (table C-3) show that they are primarily Ti. Further analysis by EDS x-ray mapping showed them to be enriched in carbon in comparison to the surrounding material, implying that they were Ti carbides. Furthermore, the Ti carbides were located at a grain boundary. The grain boundary was enriched in Cr as seen as seen from EDS x-ray mapping also shown in Fig. C-2.

![Fig. C-2. SEM of cross-section of hole region of a coupon from a blank capsule. The coupon was unetched and exposed only to argon gas.](image)

**Table C-3. Composition of Incoloy-800H in weight percent corresponding to Fig. C-2.**

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Ti</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS Point 1</td>
<td>0.21</td>
<td>0.15</td>
<td>--</td>
<td>--</td>
<td>95.91</td>
<td>1.05</td>
<td>1.47</td>
<td>1.20</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>EDS Point 2</td>
<td>0.47</td>
<td>0.19</td>
<td>--</td>
<td>0.13</td>
<td>0.64</td>
<td>20.61</td>
<td>45.60</td>
<td>31.49</td>
<td>0.03</td>
<td>0.85</td>
</tr>
<tr>
<td>EDS Point 3</td>
<td>--</td>
<td>0.09</td>
<td>--</td>
<td>--</td>
<td>96.48</td>
<td>0.82</td>
<td>1.34</td>
<td>1.04</td>
<td>0.22</td>
<td>--</td>
</tr>
<tr>
<td>Heat Data</td>
<td>0.5</td>
<td>0.13</td>
<td>0.001</td>
<td>0.014</td>
<td>0.57</td>
<td>20.42</td>
<td>45.26</td>
<td>31.26</td>
<td>0.42</td>
<td>0.76</td>
</tr>
</tbody>
</table>

**INL FLiNaK Exposed Incoloy-800H**

The Incoloy-800H coupons that were exposed to the INL FLiNaK were heavily corroded in comparison to the pre-corrosion coupons and the argon exposed coupons. The corrosion was
primarily in the form of Cr depletion of the grain boundaries and surface grains. Various microstructural changes were also observed.

**SEM of Plan View**

The surfaces of the alloys exposed to the molten FLiNaK were heavily pitted as seen in Fig. C-3. The grain boundaries appeared preferentially attacked, making it easy to identify some of the grains. However, in some surface regions the grains were heavily pitted and the grain boundary could not be identified.

![Fig. C-3. SEM of plan view of unetched Incoloy 800H after exposure to (INL) FLiNaK. (B) is a higher magnification of (A).](image)

EDS point and line scans demonstrated that the Cr was depleted from the surface to about 2.5 weight percent and silicon was enriched to about 1 weight percent. The Ni/Fe ratio increased, likely due to the noble nature of Ni. Furthermore, the grain boundary that intersects with the surface was enriched in Fe in comparison to the grains.

**SEM of Cross-section**

As seen in Fig. C-4, voids are abundant along the coupon edges and collect along the grain boundaries. Within grains near the middle of the cross-sectioned specimen, the chemical
composition is similar to the original alloy heat data. EDS x-ray mapping further demonstrates the removal of Cr at the surface and along grain boundaries. As seen in the figure, Cr is depleted from the grain boundaries and near surface regions prior to being depleted from grains further in the coupon. The Cr depletion of the INL FLiNaK coupons along the grain boundaries is in contrast to the enrichment of Cr along the grain boundary seen in the argon exposed coupons which had undergone a similar heat treatment.

Fig. C-4. SEM and EDS x-ray map of unetched cross-section of INL exposed Incoloy-800H.

Fig. C-5 shows the near surface region. It appears that the smaller grains were more heavily attacked as is evident from the apparent number of voids seen in the smaller grains. An EDS line-scan (Fig. C-6) across the length of the cross-sectioned coupon further demonstrated that the surface was depleted in Cr, and that the Cr was likely first depleted along the grain boundaries prior to Cr diffusion from the grains into the grain boundary region. It was also evident that less Cr was depleted from the grain boundary region as depth into the coupon increased.
Fig. C-5. SEM and EDS x-ray map of unetched cross-section of INL exposed Incoloy-800H.

Fig. C-6. EDS line-scan of unetched Incoloy-800H exposed to INL FLiNaK.

A Ti carbide precipitate was found in a grain about 200 microns in from the coupon surface and is shown in Fig. C-7. EDS analysis (Fig. C-8) showed that it was enriched in Ti and carbon.
At high magnifications, needle-like formations were found near the edge regions of the coupon (Fig. C-9). EDS x-ray mapping showed that the precipitates were Al rich. In Fe-Ni and Ni based superalloys, precipitates rich in Al would be assumed to be the strengthening Ni$_3$[Al, Ti] $\gamma'$ phase. EDS line-scans show that the precipitates were enriched in Al and Ti, but they contained much more Fe than would be expected for a Ni$_3$[Al, Ti] precipitate. It was suspected
that the precipitates were the $\gamma'$ phase and that the line scans were detecting the alloy matrix underneath the precipitates.

Fig. C-9. SEM and EDS x-ray map showing Al locations in unetched Incoloy-800H (INL salt).

ECS FLiNaK Exposed Incoloy-800H

The coupons exposed to the hydrofluorinated FLiNaK experienced similar corrosion issues microstructurally as that of the coupons exposed to INL obtained FLiNaK.

SEM of Plan View

In general, the surfaces of the Incoloy-800H coupons exposed to hydrofluorinated FLiNaK appeared to be slightly more corroded than the surfaces of the coupons exposed to non-hydrofluorinated FLiNaK.
The same general trends observed for the surface of the coupons from the Incoloy-800H coupons in INL FLiNaK were also observed for the hydrofluorinated FLiNaK. The surface was depleted in Cr down to about 2 %, and correspondingly enriched in Fe and Ni. Furthermore, point scans of the pits in the surface revealed the same trend observed along the grain boundaries in the coupons exposed to INL FLiNaK, where the pits, like the previous grain boundaries, were enriched in Fe. The pitted regions also had much less silicon present in them in comparison to the surface. The line-scans in Fig. C-11 showed the change in surface composition between the pitted and non-pitted regions. It also appeared that the Fe enrichment and/or Ni depletion was more dramatic for larger pits.
SEM of Cross-Section

The grain boundaries were clearly visible due to voids conglomerating on them in the cross-sectioned coupon (Fig. C-12). EDS point scans showed that the composition within the grains in the central region of the coupon was similar to the composition prior to corrosion testing. An EDS line-scan revealed that the Cr depletion of this coupon was monodirectional, with the right surface experiencing the majority of the Cr depletion. This likely occurred because the left side was against the fixturing graphite rod, which masked the coupon. In the EDS x-ray map of Cr, it could be seen that the smaller grains were severely depleted in Cr while the larger grains were not.
Fig. C-12. SEM of unetched cross-section of Incoloy-800H coupon and EDS x-ray map.

Fig. C-13 shows a grain boundary junction between three grains near the center of the coupon. It exhibited an intricate microstructure, with several small precipitates, in addition to showing the Cr depletion more dramatically.

Fig. C-13. SEM of unetched cross-section of hole region of Incoloy-800H coupon and EDS x-ray map of cross-section (1,000x) exposed to ECS FLiNaK.

A line-scan across the grain boundary shown in Fig. C-13 (Fig. C-14), demonstrated the same Cr depletion as seen previously, however it was more apparent that the Cr depletion resulted in more of an increase in Ni than Fe than that seen on the surface.
Fig. C-14. EDS line-scan of unetched Incoloy-800H exposed to ECS FLiNaK. The line scan corresponds to the horizontal line in Fig. C-13.

The EDS line-scan shown in Fig. C-15 shows the Cr depleted region, for the small grains, extends into the surface about 150 µm.
Fig. C-15. SEM of unetched Incoloy-800H cross-section exposed to ECS FLiNaK.

Fig. C-16. EDS line-scan of unetched Incoloy-800H exposed to ECS FLiNaK that follows the red, horizontal line seen in Fig. C-15.
Appendix

D

Hydrofluorination Purification Method at ORNL
Chemical Processes in Purification by Hydrofluorination

Exposure of LiF and BeF containing molten salts to H₂O in air leads to hydrolysis as shown below (reaction moves primarily from left to right) [125]. Metal oxides in salts tend to have higher melting points than their corresponding fluorides [126]. Such that the oxide in a molten salt is often written as a solid [126]:

\[
\text{H}_2\text{O}(g) + 2\text{F}^-(d) \leftrightarrow \text{O}^{2-}(d) + 2\text{HF}(g)
\]

**Equation D-1**

**Notation: c=solid, d=dissolved, g=gaseous**

The order of increasing nobility of various metals depends on whether an oxide is present [126]. Mo, Cr, and Ni are more noble in the absence of an oxide [126]. In FLiBe, the reaction in equation D-1 (from left to right) leads to the precipitation of BeO [125]. Fe, Ni, Cr, and Mo (constituents in Hastelloy-N) oxides are mostly insoluble in FLiBe [126]. Many transition metals, such as Cr or Mo, in the oxide state in a salt are often at higher valence levels than as fluorides, which affect the redox potential of the salt and the salt’s equilibrium concentration of transition metals (i.e. Cr²⁺ and Mo³⁺) in solution [126].

The reverse of this reaction (equation D-1 from right to left), sparging with HF, is used as a purification treatment [125]. The hydrofluorination of MSRE fuel salt was shown to remove oxides to as low as ~ 60 ± 15 ppm oxides. In general, the ease of oxide removal by hydrofluorination increases with decreasing temperature and increasing partial pressure of HF [125]. HF was used extensively at ORNL as a reagent in its studies of molten fluorides and to remove oxides in molten fluorides [126]. Hydrofluorination was a critical step in the preparation of fluoride mixtures for the MSRE, which were prepared using a batch process (a layout of the process is shown in Fig. D-1) [127].
Fig. D-1. Fluoride production facility layout of operating level. (source: [127])

The MSRE salt preparation process proceeded as follows: starting materials were weighed and transferred to a melt down facility on vibratory conveyers, once in the meltdown facility, Be metal turnings were added to the melt to reduce structural metal impurities to their metallic states and the melt was sparged with He and H₂ at high flow-rates to remove insoluble carbon by entrainment [127]. For primary salt purification, the melts were initially sparged with a HF/H₂ gas mixture (1:10 vol. ratio), and oxides (present initially or formed by reaction of fluoride salts with water upon heating), were removed as water by the reaction shown in equation D-1. Measurement of HF concentration in the gas effluent was used for process control and was indicative of oxides remaining in the mixtures [127]. Fig. D-2 demonstrates the efficiency of this reaction (equation D-1); in about 30 minutes most of the oxides in FLiBe have been converted to fluorides and water.
Sulfides were removed from the melt (as H$_2$S) by reaction with HF, however sulfates had to first be reduced by hydrogen or added Be before removal by HF was effective [127]. Structural metal fluoride impurities (such as NiF$_2$ or FeF$_2$) would result in the depletion of Cr activity in Hastelloy-N and therefore were also removed for experiments [127]. Following HF treatment, the melts were sparged with H$_2$ alone at 700°C to reduce the fluoride metal impurities by the reaction [127]:

$$\text{H}_2 + \text{MF}_2 \leftrightarrow 2\text{HF} + \text{M}^0$$

\textbf{Equation D-2}

where

M=Fe, Cr, Ni, etc...
After H₂ treatment, the melt was sparged with dry He to remove remaining HF, and the melt was transferred to a storage container, passing through a sintered Ni filter along the way to remove entrained solids from the melt [127]. There appears to be some hold-up of HF (potentially as OH⁻ and F⁻) than would result from the small solubility of HF alone [126]. Primary process control was therefore thru analysis of process gas streams [127]. Secondary control was from filtered samples of the salt mixtures that were taken periodically [127].
Appendix

E

Electrochemistry Literature Survey
**Electrochemistry Theory**

The corrosion processes in molten fluoride salts are primarily electrochemical in nature. The electrochemical potential, $\mu_C$ in equation E-1, is defined as the change in free energy per unit species with everything else held constant [128]. The difference between the energy barrier for taking electrons from and giving electrons to the working electrode (that sets the solutions electrochemical potential) is equal to the chemical potential.

$$\mu_{\text{elec}}(e, \text{conductor}) = \left. \frac{\partial G}{\partial e} \right|_{T, p, \ldots}$$  \hspace{1cm} \text{Equation E-1}

where

$$\mu_{\text{elec}}(e, \text{conductor}) = \text{electrochemical potential}$$

For low concentrations, the activities of the ions are approximately their concentrations, so that the chemical potential may be written as E-2.

$$\mu_{\text{elec}} = \mu_{\text{elec}}^0 + k_B \cdot T \cdot \ln \left( \frac{[\text{Ox}]}{[\text{Redox}]} \right)$$  \hspace{1cm} \text{Equation E-2}

where

- $k_B$ = Boltzmann's constant
- $T$ = temperature
- $[\text{Ox}]$ = Oxidized species concentration (reducing agent)
- $[\text{Redox}]$ = Reduced species concentration (oxidizing agent)
Dividing the electrochemical potential by the number of electrons involved in the oxidation/reduction reactions gives the electrode potential, equation E-3.

\[
E = E^0 + \frac{k_B \cdot T}{n \cdot e} \cdot \ln \left( \frac{[\text{Ox}]}{[\text{Redox}]} \right) = E^0 + \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{[\text{Ox}]}{[\text{Redox}]} \right)
\]

Equation E-3

where

- \( E \) = electrode potential
- \( E^0 \) = standard electrode potential of the electrode couple
- \( R \) = gas constant
- \( F \) = Faraday’s constant

**Electrochemistry Literature Survey and Technical Review**

A large amount of electrochemical research in molten fluoride salts was undertaken by ORNL and others. A pinpointed review of some of that work will be reviewed here. In addition to calculating corrosion product concentrations, Mamantov noted that with platinum WE used in molten fluorides, diffusion coefficients of several corrosion products in FLiNaK may be calculated with the Randles-Sevcik equation [62].

**Reference Electrodes**

A true reference electrode is needed for comparing results from electrochemical tests with previous results and those from the literature. The majority of work reviewed from ORNL during the MSR program used a Ni/NiF\textsubscript{2} reference electrode. For this type of electrode, a Ni wire is inserted into a salt solution similar to the salt under study, but with a specific amount of NiF\textsubscript{2} salt added (the salt was usually saturated in NiF\textsubscript{2}). The wire and NiF\textsubscript{2} salt mixture would be kept in a separate container than the test salt, but ionically in contact with the salt. The ionic contact between the salts would be made through a porous membrane, salt bridge, or ionic conductor.
ORNL experimented with several different designs for Ni/NiF₂ RE. Ni/NiF₂ reference electrodes used by ORNL that relied on a porous membrane were made of thin walled hot pressed boron nitride for use from 500°C to 550°C, but it was found that above 550°C hot pressed boron nitride would deteriorate rapidly [129]. For higher temperatures, ORNL utilized a design with a single LaF crystal, shown in Fig. E-1. Single crystal LaF₃ acted as an ionic conductor between the NiF₂ salt mixture compartment and the melt under study [130]. The single crystal LaF₃ however proved to have severe limitations, in that it would crack and leak during thermal cycling [62].

![Fig. E-1. Ni/NiF₂, LiF-BeF₂ saturated with NiF₂, contained in single crystal LaF₃ (Source: [59])](image)

Kontoyannis eventually came up with a much more robust RE design with good reproducibility and hardiness, that involved a Ni²⁺/Ni couple reference electrode kept chemically separated yet electrically connected to the molten salt with a hollowed out graphite cylinder setup [131]. Kontoyannis used an isostatically molded rod of EK-90 graphite (total open porosity of 14% and pore size of 7 µm) coated with 30 µm of pyrolytic boron nitride deposited by the CVD
technique for electrical insulation [131]. Currently ORNL uses a derivative RE based on the work of Kontoyannis, and their setup is shown in Fig. E-2 [80].

Fig. E-2. ORNL electrode design. The reference electrode used at ORNL is shown on the left and in the middle. The reference electrode is made of graphite (UCAR ATJ grade and Ringdorff R6300), with pyrolytic coated with boron nitride by Advanced Ceramics to electrically isolate it. The working and counter electrodes are iridium wire. (Source: [80])

Linear Scan Voltammetry

Linear scan voltammetry was used by ORNL for some electrochemical analyses that did not require a high level of sensitivity. ORNL used LSV with carbon and inert metal electrodes to study Cr and other salt constituents in LiF-BeF$_2$-ZrF$_4$ and LiCl-KCl [58, 65, 132]. In linear scan voltammetry (LSV), the potential of the working electrode is varied linearly with time, and the resulting current is plotted against the linear potential change, creating a voltage-current graph called a voltammogram. The resulting current-voltage curve will follow a predictable pattern with the current reaching a diffusion limited maximum value (in most molten halide salts) that is directly proportional to the concentration of the electroactive ion or ions [60]. Linear plots of peak current vs. concentration were obtained from 0.02 to 1 V/sec at 500°C [65]. Relatively high
concentrations were estimated directly from the height of the LSV voltammetric wave (typically 20 ppm) in MSRE fuel salt and proposed coolant.

**Anodic Stripping Voltammetry**

To measure lower concentrations than those capable of being measured using linear scan voltammetry, ORNL proposed the use of stripping voltammetry [60]. Mamantov determined that anodic stripping voltammetry (ASV) in molten fluorides was more reproducible than cathodic stripping voltammetry (CSV) for in-situ-determinations and that ASV is particularly suitable for trace metal analysis [61, 62]. ASV was used to determine down to 1 ppm of Ni in FLiNaK, and 25 ppb Bi in LiF-BeF\(_2\)-ZrF\(_4\) [62, 132]. A proof of principle test was performed that demonstrated the linearity of the Cr peak with plating time and is shown in Fig. E-3 [59]. ORNL proposed to measure Cr with the ASV technique in coolant loops, but no evidence has been found that it had been demonstrated in a loop setting [133].

![Fig. E-3. Cr stripping current peaks with several plating time and a working curve for peak height and plating time. (Source: [59]).](image-url)
Technical Electrochemistry Issues encountered at ORNL and Their Solutions to Them

There are several known complications that can arise during any voltammetric measurement, and specifically ASV that may negatively affect quantitative measurements. The principle issues that affect all ASV measurements are contamination, intermetallic compound formation (between different analytes and an analyte and the WE), and overlapping stripping peaks [134]. These issues have been well documented and there are various strategies for minimizing their mal effect on measurements [134]. The following discussion will mostly concern specific issues encountered by ORNL with electrochemistry in molten salts.

Wetting Behavior

It is also well known that the surface tension of most liquids is at a maximum at an electrodes surface at zero charge, and decreases as the charge increases [64]. Furthermore, ORNL found that in LiF-BeF₂ salt soluble active metals cause the LiF-BeF₂ salt to become wetting if the salt was in an electrically conductive container [135].

Contaminated Melts

Contaminants may hide the signal from the element that is being searched for. Manning and Mamantov often used a fourth electrode (in addition to the typical three) to act as a cathode for purification of the melts by electrolysis [61]. This technique may be used to remove contaminants with a more anodic potential than the analyte of interest.

Oxygen and water are by far the most harmful contaminant. Saturation of several fluoride melts with oxides and water will lead to an over voltage passivation of the working electrode that would make it impossible to perform voltammetric measurements since the electrode surface would become non-conductive [62].

In the coolant salt test facility at ORNL, it was observed that a Ni film would form by mass transfer on electrically isolated electrodes, which were slightly cooled through conduction of heat through the electrical leads [58]. The Ni film was removed by holding the electrodes at anodic
potentials (to Ni) when not in use [58, 136]. The electrodes could not be cleaned
electrochemically immediately before each use because NiF₂, which is sparingly soluble, would
form a film on the electrodes that would block further current flow [136].

**Poor Baseline, LSV Specifics**

Corrosion product voltammagrams were obtained (Fig. E-4) in the coolant salt test facility,
but accurate corrosion product concentrations could not be obtained due to a poor baseline (the
same issue encountered by this author) [58]. Corrosion products were estimated from theoretical
equations (using voltammagrams similar to those in Fig. E-4) but were lower than those measured
by wet chemistry. ORNL partially attributed the difference between the estimated values from
the electrochemistry and those obtained from wet chemistry methods to the inability of the LSV
technique to measure insoluble species, such as free metals, in the salt [58].

---

**Fig. E-4** LSV voltammagrams of corrosion products in the coolant salt test facility at
ORNL on a gold electrode in fluoroborate salt. The results were obtained by holding at
anodic potentials $\geq 0.3$ V when not in use and using fast scan rates [136]. (Source: [58])
Changing Electrode Surface Area and Insulation to Fix Area of WE

At ORNL in the FCL-2b (forced convection loop), iridium electrodes were used to monitor the reduction of fuel in LiF-BeF₂-ThF₄ by Be additions [58]. Continuously changing temperatures and areas of the electrodes exposed to the molten salt made quantitative measurements difficult [58]. For removable inert electrodes, precise pretreatment and polishing greatly increase the reproducibility of results [64].

One way to ensure constant WE area is to have a well defined conductive area exposed to the salt by insulating the rest of the WE. Finding insulating materials that are stable in molten fluorides has historically been challenging. Hot pressed boron nitride was the most common insulator material in Mamantov’s experiments in molten fluorides and was used by him to fix the area of the working electrode (Fig. E-5) but hot pressed boron nitride is slowly penetrated by melts over time, and begins to deteriorate above 500°C [61, 62].

![Diagram of the shield tube](image)

**Fig. E-5.** By fixing the area of the working electrode, reproducibility of voltammograms can be increased and calculations can be made easier. (Source: [61])

Another way to fix the area of the working electrode that is contacted by the molten salt is to fix the salt height on the working electrode. ORNL investigated the use of a shield tube to reduce
the change in surface area and also salt convection [58, 136]. The shield tubes could also be purged of salt to provide fresh melt surface and keep floating material away from the electrode [58, 137].

**EMF Tables**

Standard electrode potentials have been determined for a variety of elements in many salt mixtures over a wide range of temperatures, and several pertinent ones are shown below.

**Table E-1. Half cell potentials in FLiNaK and MSRE fuel salt (LiF-BeF₂-ZrF₄) at 500°C in reference to the standard potential of a Ni²⁺/Ni couple that was set to 0.000. (Source: [59, 138])**

<table>
<thead>
<tr>
<th>Half cell reaction</th>
<th>Standard potential in FLiNaK (vs. Ni²⁺/Ni RE)</th>
<th>Standard potential in LiF-BeF₂-ZrF₄ (vs. Ni²⁺/Ni RE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be²⁺ + 2e⁻ =Be</td>
<td>-2.120</td>
<td>-2.120</td>
</tr>
<tr>
<td>Zr⁴⁺ + 4e⁻ =Zr</td>
<td>-1.742</td>
<td>-1.742</td>
</tr>
<tr>
<td>U⁴⁺ + e⁻ = U³⁺</td>
<td>-1.480</td>
<td>-1.480</td>
</tr>
<tr>
<td>Cr²⁺ + 2e⁻ =Cr</td>
<td>-0.701</td>
<td>-0.701</td>
</tr>
<tr>
<td>Cr³⁺ + e⁻ =Cr²⁺</td>
<td>-0.514</td>
<td>-0.514</td>
</tr>
<tr>
<td>Fe²⁺ + 2e⁻ =Fe</td>
<td>-0.390 -0.410</td>
<td>-0.200 0.166</td>
</tr>
<tr>
<td>Fe³⁺ + e⁻ =Fe²⁺</td>
<td>-0.200</td>
<td>0.166</td>
</tr>
<tr>
<td>Ni²⁺ + 2e⁻ =Ni</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**Table E-2. Standard electrode potentials in FLiNaK at 610°C in reference to the standard potential of a Ni²⁺/Ni couple that was set to 0.000. (Source: [19])**

<table>
<thead>
<tr>
<th>Half cell reaction</th>
<th>Standard potential (volts vs. standard Ni²⁺/Ni electrode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb³⁺ + e⁻ =Yb²⁺</td>
<td>-1.45</td>
</tr>
<tr>
<td>U⁴⁺ + 2e⁻ =U³⁺</td>
<td>-1.2</td>
</tr>
<tr>
<td>V⁴⁺ + e⁻ =V³⁺</td>
<td>-0.9</td>
</tr>
<tr>
<td>Eu⁴⁺ + e⁻ =Eu³⁺</td>
<td>-0.64</td>
</tr>
<tr>
<td>Ni²⁺ + 2e⁻ =Ni</td>
<td>0.000</td>
</tr>
</tbody>
</table>
Table E-3. Half cell potentials in 40NaF-60KF (mole %) eutectic salt at 850°C in reference to the standard potential of a Ni²⁺/Ni couple that was set to zero. (Source: [63])

<table>
<thead>
<tr>
<th>Half cell reaction</th>
<th>Standard potential (volts vs. standard Ni²⁺/Ni electrode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺ + 3e⁻ = Al</td>
<td>-1.5</td>
</tr>
<tr>
<td>Mn²⁺ + 2e⁻ = Mn</td>
<td>-1.04</td>
</tr>
<tr>
<td>Cr³⁺ + 3e⁻ = Cr</td>
<td>-0.7</td>
</tr>
<tr>
<td>Cr²⁺ + 2e⁻ = Cr</td>
<td>-0.07</td>
</tr>
<tr>
<td>Ni²⁺ + 2e⁻ = Ni</td>
<td>0</td>
</tr>
<tr>
<td>Fe³⁺ + 3e⁻ = Fe</td>
<td>0.12</td>
</tr>
<tr>
<td>Cu¹⁺ + e⁻ = Cu</td>
<td>0.48</td>
</tr>
<tr>
<td>Ag¹⁺ + e⁻ = Ag</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table E-4. EMF series for transition metal ions in molten FLiNaK at 750°C (1023K) in reference to the standard potential of a Ni²⁺/Ni couple that was set to zero. *Known to be potentials of irreversible couples. (Source: [67])

<table>
<thead>
<tr>
<th>Half cell reaction</th>
<th>Standard potential (E₁/4 volts vs. standard Ni²⁺/Ni electrode, 1 mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺ + 3e⁻ = Al</td>
<td>-1.5</td>
</tr>
<tr>
<td>Ta²⁺ + 2e⁻ = Ta</td>
<td>-1.26*</td>
</tr>
<tr>
<td>Cr²⁺ + 2e⁻ = Cr</td>
<td>-1.13*</td>
</tr>
<tr>
<td>Ta⁵⁺ + 3e⁻ = Ta⁺</td>
<td>-1.03</td>
</tr>
<tr>
<td>Nb⁺ + e⁻ = Nb</td>
<td>-1.03*</td>
</tr>
<tr>
<td>Nb⁴⁺ + 3e⁻ = Nb⁺</td>
<td>-0.754</td>
</tr>
<tr>
<td>Cr³⁺ + e⁻ = Cr⁺</td>
<td>-0.69</td>
</tr>
<tr>
<td>Fe²⁺ + 2e⁻ = Fe</td>
<td>-0.512</td>
</tr>
<tr>
<td>Fe⁺ + e⁻ = Fe⁺⁺</td>
<td>-0.21</td>
</tr>
<tr>
<td>Nb⁵⁺ + e⁻ = Nb⁴⁺</td>
<td>-0.11</td>
</tr>
<tr>
<td>Ni²⁺ + 2e⁻ = Ni</td>
<td>0</td>
</tr>
</tbody>
</table>
References


[114] G. Fakuda, Personal communiqué, University of California-Berkeley, Berkeley, CA, 2005


