University of Nevada, Reno

Evaluation of the Corrosion Behavior of High Nickel Alloys in Molten Nitrate Salt for Solar Thermal Applications

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

by

Keenan O'Neill

Dr. Dev Chidambaram/Thesis Advisor

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We recommend that the thesis prepared under our supervision by

Keenan O’Neill

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Evaluation of the Corrosion Behavior of High Nickel Alloys in Molten Nitrate Salt for Solar Thermal Applications

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Master of Science

Dev Chidambaram, Ph.D.  
Advisor

Leslie Mushongera, Ph.D.  
Committee Member

Miles Greiner, Ph.D.  
Graduate School Representative

David W. Zeh, Ph.D., Dean  
Graduate School

December, 2020
Abstract

Increasing population and standard of living around the world has placed significant demand on the production of electricity. The use of fossil fuels for energy production is not a sustainable practice as fossil fuels cannot be quickly replenished. Renewable energy resources are sources of energy that are not depleted when harvested such as solar, wind, hydroelectric, and geothermal power. Concentrated solar power (CSP) involves harnessing the heat energy of sun and generally stores this heat energy to continue energy production after the sun has set. This process of thermal energy storage allows efficient storage of energy without the use of batteries. Intermittency of energy production would be significantly reduced using molten salts as a heat transfer fluid in a CSP plant that utilized a thermal energy storage system.

Efficiency is an important factor in the consideration of any process and would be paramount to successfully implementing CSP plants to generate energy from sunlight. A significant barrier to the implementation of this source of renewable energy is stable container materials that can withstand the high heat required for increased efficiency and aggressive corrosion of molten salts. Exposure studies are a common way of testing the corrosion behavior of a material in situ but require the temperature of the molten salt to be maintained throughout the duration of the experiment which can be thousands of hours. Accelerated corrosion testing utilizing electrochemistry was utilized to screen five materials tested in this study – UNS N06230, UNS N06025, UNS N06617, UNS N06625GR1, and UNS N06625GR2 – for further testing through evaluation of
electrochemical behavior. The surface morphology of the samples was studied using scanning electron microscopy. The surface oxide chemistry and structure were analyzed using X-ray diffraction, energy dispersive spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy for three of the samples.

Electrochemical evaluation of the five materials gave an indication of good corrosion resistance in this medium. All tested samples had current densities on the order of $10^{-4}$ A/cm$^2$. UNS N06230 exhibited the lowest average corrosion current density at 0.225 mA/cm$^2$. UNS N06625GR1 exhibited the highest average corrosion current density at 0.431 mA/cm$^2$. Corrosion potential of samples ranged from -66.2 mV vs. Pt to -227 mV vs. Pt. The morphology of the samples surfaces was studied using scanning electron microscopy which showed the formation of a surface film on all samples. Cross-sectional analysis was performed using focused ion beam (FIB) scanning electron microscopy. Pseudopassivity was indicated by the polarization curve of UNS N06625GR1 and was supported through Raman and XPS scans. Raman spectra indicated the formation of a nickel oxide on the surface with varying levels of chromium and iron present. EDS data indicated increases in the oxygen content on the surface of all samples. Raman spectra paired with XPS suggested the formation of various nickel-chromium-iron spinels on UNS N06625. These results show that UNS N06625 has the potential to be a material for use in solar-thermal plants.
Acknowledgements

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Chapter 1: Overview

1.1 Global Energy Usage

As society progresses and the standard of living rises around the world, the impact of harvesting and burning fossil fuels on the environment becomes more profound. The Environmental Protection Agency has reported that global carbon emissions from the burning of fossil fuels has increased nearly tenfold from the 1950s to 2010 (1). For just the United States on the same timeline, energy consumption has more than doubled with a significant portion of the energy consumed being from fossil fuels such as petroleum, coal, and natural gas. It is suggested that the burning of fossil fuels and the subsequent release of CO$_2$ into the atmosphere has a negative impact on the climate and aids in global warming (2). Since the early 2000’s, the use of coal as a means of producing energy has steadily declined but has been replaced by a steady increase in the use of natural gas and a significant increase in the use of crude oil for energy production (1). These sources of energy are still fossil fuels and will release CO$_2$ and other pollutants when burned. The use of renewable energy has seen some increase since the early 2000’s but still is not near the level of natural gas and crude oil. In the U.S., there are federal and state level targets for increasing renewable energy supported by federal tax credits to help supplement the use of these energy sources. It is projected by the United States Energy Information Administration that energy production from crude oil and coal will decrease in the future while energy production from dry natural gas and renewables will increase with renewables nearly doubling by 2050 (1). This increased focus on renewable energy makes pursuing more efficient, easily implemented forms of renewable energy a valuable
strategy for energy producers. As renewable energy becomes more desirable, research into creative and innovative methods becomes paramount to the implementation of renewable energy collection.

1.2 Concentrated Solar Power

Various forms of renewable energy exist, such as wind, hydroelectric, geothermal, and solar, and historically, hydroelectric has made up a majority of the renewable energy generated (3). However, solar power as a means of energy production has grown over eleven times from 2010 to 2019 whereas wind energy has only grown slightly less than three times over the same time period (1). Solar energy is also projected to more than triple in energy generation from 15% in 2019 up to 46% in 2050. The most commonly known means of generating electricity from solar power is the use of photovoltaic cells that use the photons present in sunlight to create a current through specific semiconductors. This allows for energy to be generated from sunlight, but energy cannot be generated if the sun is not shining. The materials used in solar panels also tend to be expensive which, when paired with their inability to produce energy when the sun is not shining, limits their use and requires energy storage systems such as load leveling batteries for continuous generation of energy. Concentrated solar power (CSP) is a means of generating electricity using the heat generated by sunlight instead of direct conversion of photons to electricity as in solar cells. The first industrial CSP plant was established in California in the 1980’s known as the Solar Electric Generating Systems plant and had nine different systems (4). Since then, CSP has seen considerable growth with 69 different plants being developed in 2018. CSP is generated mainly through three different
collector designs: parabolic trough collectors, Sterling dish systems, and CSP towers. All three designs utilize similar mechanisms: reflection of sunlight using curved mirrors, a central receiver for collecting heat, sunlight tracking, and a heat transfer fluid (HTF). These systems utilize curved mirrors that have a focal point at the location of the receiver to ensure maximum concentration of the light rays on the receiver. The mirrors are generally equipped with a motor and a sunlight tracker to ensure the maximum amount of sunlight is reflected. These mirrors, known as heliostats, allow the concentrated sunlight to heat the receiver to very high temperatures depending on the type of system used. The two most commonly used systems are the parabolic trough and power tower systems.

Figure 1: The two most common forms of CSP plant are given with the CSP tower on the left and the parabolic trough system on the right (5).

Parabolic trough systems are more modular and smaller-scale than the power tower system and therefore cannot reach temperatures more than about 550°C. Power towers, however, have a significantly larger field of heliostats and are able to reach temperatures in excess of 2000°C. Solar power towers are also not limited to a modular structure and produce energy proportional to the amount of mirrors reflecting and
concentrating sunlight to the central chamber. The heat generated through the concentrated sunlight is transferred to a HTF that is then used in a Rankine cycle that transfers thermal energy to mechanical energy through a steam cycle. The Rankine cycle typically consists of a number of reservoirs where water is heated by the HTF into steam. This hot steam is then run through a steam turbine to generate energy. Some systems utilize a secondary steam chamber that is also heated with less of the HTF to increase the amount of thermal energy absorbed and transformed into electricity. After moving through the turbine, the steam will go through a condenser and be returned to a storage tank where it will then be run through the system again. Generally, CSP towers will be equipped with a system for storing hot HTF to be transferred to the Rankine cycle as well as a tank for storing the cooled HTF that has already released its heat energy to the cycle. The HTF in the cool reservoir will be pumped back into the heating chamber in the receiver and the process is repeated continuously. This type of system is known as a thermal energy storage (TES) system which allows a CSP plant to store heated HTF in a reservoir to supply heat as long as there is salt remaining. This hot HTF can be supplied to more than one water reservoir to create multiple levels of heating and provide energy even when the sun has set. A potential TES system with a CSP tower is given in Figure 2.
1.3 Molten Salt and Corrosion

The HTF is critical to the efficiency of a CSP plant as it is what transfers the collected thermal energy into the Rankine cycle. The property that most directly relates to capacity of energy stored is the HTF’s maximum operating temperature as this controls the amount of thermal energy the HTF can store at a given time. In addition to requiring a high operating temperature, the HTF should also be able to move easily through the system and should be able to transfer heat quickly. Having low viscosity and good thermal conductivity are qualities that are necessary for a HTF to be used effectively in a system with TES capabilities. The HTF should also not undergo reactions within the operation temperature, specifically reactions that generate a gas. Excessive gas buildup in the receiver or the piping to the Rankine engine may result in leaks or ruptures in the system that would release the HTF to the surrounding environment. The nature of a TES
system requires a material with a good heat capacity so that more heat can be stored in the material. Finally, having a low melting point is also an important characteristic of a HTF that is generally only a concern with molten salts. Some commonly used HTF are thermal oils and molten salts. Thermal oils cannot operate at significantly high temperatures and therefore reduce the energy generated by a CSP plant unless the HTF is placed under pressure to avoid evaporation. Molten salts are very diverse in chemistry and have varying maximum operating temperatures, melting points, viscosities, etc. A commonly used salt in commercial CSP plants is a mixture of potassium nitrate and sodium nitrate in a 40:60 wt% blend, respectively (4). This is commonly referred to as solar salt and has good properties such as a higher operating temperature than water or thermal oil with a relatively low melting point. A significant disadvantage to using molten salts is that this HTF is highly corrosive due to the high concentration of ions present and the high temperatures involved (4). Corrosion is a significant concern for these types of systems because the container material for the receiver, transfer pipes, and TES tanks must all be able to store the HTF without failing. Failure in this type of system would release high-temperature molten salt to the surrounding environment, posing a safety and an environmental concern. There is some insight into the corrosion mechanism of this mixture that involves the breakdown of the nitrate anion into nitrite and oxygen gas (7). This then allows for oxygen to react with the metal ions present and form oxides which can then potentially react with the oxide layer to reform the nitrate anion. While reactions and subsequent oxide formation can be predicted, the form of corrosion cannot be accurately anticipated and therefore the corrosion mechanism must be understood experimentally.
1.4 Corrosion Testing

Testing samples for corrosion in molten salts generally involves in situ testing where the samples are placed in a furnace with the molten salt at a given temperature and submerged in the salt. Known commonly as exposure testing, these samples are often left in this environment at the given temperature for a certain predetermined period of time ranging anywhere from tens to thousands of hours. Corrosion layers are then characterized to understand the surface chemistry, morphology, and corrosion mechanisms. Overall amount of mass lost/gained will yield a corrosion rate and a better understanding of the corrosion behavior of a given sample in that media.

The corrosion behavior of pure nickel has been tested over a 12 hour time period in one study that reported a parabolic increase in the mass of nickel during the exposure duration indicating the formation of a protective NiO layer that inhibited corrosion (8). Nickel was determined to still allow ion transfer through the oxide layer with significantly lower diffusion rates. A separate study on nickel, titanium, nickel-based alloys, and alumina-forming and aluminized alloys reported that pure nickel undergoes severe intergranular corrosion at 565°C in this media (7). This study reported that aluminized alloys and aluminum were very resistant to corrosion in this environment likely due to the formation of alumina. Other studies have corroborated the resistance of alumina-forming alloys in this medium (9, 10). Chromium is a common corrosion-inhibiting alloying element present in many high-temperature alloys. A study conducted on several alloys containing chromium found that chromium was likely to be selectively leached from the alloy and noted that other studies have reported chromium dissolution in this media (11, 12).
Exposure tests yield direct information on the corrosion behavior of samples tested and can be used to anticipate the corrosion resistance and suitability of a given sample for use in the testing environment. However, due to the length of these experiments and the fact that samples must be maintained at a specific temperature, these tests require significant energy costs and time to yield results. Corrosion testing must be conducted, however, as a material’s behavior cannot be accurately predicted without prior testing. Electrochemical corrosion testing is a means by which materials can be quickly tested to gain insight into a material’s corrosion properties without conducting an extensive exposure test. The results from these experiments have been demonstrated to relate to exposure study results in aqueous media (13) and have been utilized in several studies to indicate corrosion behavior and resistance (11, 14-16).

While the use of electrochemical corrosion testing does give a representation of the corrosion behavior of a sample in a specific environment, it is not adequate as a standalone test for implementing the use of the tested material. Many different factors exist when understanding corrosion, such as passivation, pitting, intergranular corrosion, and selective leaching, some or all of which may not be represented in such short exposure experiments. However, the use of electrochemical corrosion testing as a screening process is invaluable to prevent significant time and energy waste on a material that has poor resistance in a given environment. Therefore, the use of electrochemical corrosion testing as a screening process is a good way to identify which materials should be approved for exposure testing. This thesis aimed to study the corrosion behavior of four different nickel-base alloys in the molten solar salt as a screening process. Further, the sample surfaces were characterized to understand the corrosion performance and to
determine which alloys were promising to be selected for long term testing. The following sections of this thesis are a direct copy of a manuscript submitted to the Journal of the Electrochemical Society. This is the revised version that has been modified after addressing the comments from two anonymous reviewers.
Chapter 2: Introduction

2.1 Concentrated Solar Power

Energy demands around the world continue to grow steadily with increases in population and development. This growing energy demand is increasing emphasis on methods of generating energy (17). Fossil fuels are the primary source of energy production, but their burning produces CO₂ which accounts for ~81% of all U.S. greenhouse gas emissions (18, 19). The atmospheric pollution from fossil fuel sources has created a worldwide initiative for the use of more sustainable energy sources, such as geothermal, hydroelectric, wind, and solar energy. Intermittent sources of energy such as wind and solar require a secondary energy storage system to provide energy consistently throughout the day like baseload energy sources. One source of sustainable energy that has gained increased interest in recent years is concentrated solar power (CSP) with thermal energy storage (TES) as it does not require a secondary energy storage system. CSP involves collecting energy from the sunlight and transferring it into a TES medium. CSP plants utilize many different designs – parabolic troughs, dish Sterling engines, and solar power towers – but the energy generated comes from reflecting light from the sun onto a central point (20). The central point contains a heat transfer fluid (HTF) that distributes its heat to a Rankine cycle steam generator to generate electricity (20). This process is more efficient at providing energy throughout a day than the photovoltaic cells used in solar panels due to the fact that the energy harnessed can be stored in the form of thermal energy in a heat storage medium for use at later times when the sun is not shining (21). The heat storage medium requires specific characteristics to be effective, such as a
high boiling point, a low melting point, high heat capacity, high thermal conductivity, and a higher operating temperature than currently available heat transfer media (22).

2.2 Heat Transfer Fluid

Until recent years, the most common TES media was steam or thermal oils, but molten salt mixtures are able to reach higher operating temperatures than both water-based fluids and thermal oils (22, 23). This higher operating temperature increases the theoretical thermodynamic efficiency of the heat engine system according to Carnot’s efficiency. A common molten salt heat transfer medium currently in use for solar thermal applications is the solar salt blend, a mix of 3:2 NaNO$_3$:KNO$_3$ (24). A significant issue with using molten salts as a HTF is the corrosive effect of the molten salts at high temperatures which limits the container materials that can be used for these systems. The corrosion behavior of service alloys is especially important in plants that generate energy throughout the day due to thermal cycling of the HTF that can affect the tank materials even more. Since corrosion is not easily modelled or predicted, direct corrosion testing in the solar salt medium is required to understand the behavior of specific materials in these systems.

In addition to solar thermal systems, similar molten salts are used in other applications such as in the heat-treatment of alloys. A molten nitrate salt, called Drawsalt, is used for solution treatment of aluminum alloys (25). Molten nitrate salts have also been employed for heat treatment of carbon and low-alloy steels due to the temperature range at which molten nitrate salts can operate. In a process called martempering, steels undergo an interrupted quenching process where they are cooled rapidly to just above the
martensite formation temperature and are held there for a period of time before being cooled to room temperature (26, 27). Molten salt are also used to heat workpieces as it avoids thermal shock by reducing the initial heat flux into the workpiece (28). These applications will also benefit from the studies conducted here on identifying new corrosion resistant materials.

2.3 Types of Testing

A common way to test the corrosion resistance of a material in a given environment is by exposure testing. Various materials, such as ferritic and stainless steels, nickel and nickel-chromium alloys, and high-temperature alloys have been the subject of extensive exposure studies in molten nitrate salts similar to solar salt (10, 11, 29-40). Exposure testing yields direct information about a material’s performance through gravimetric analysis and corrosion layer analysis, but exposure studies are expensive and require lengthy testing periods to provide more accurate data. It is far more beneficial to use accelerated electrochemical testing as a screening process to evaluate materials to determine whether a material is a suitable candidate for use in a specific environment. Results from accelerated electrochemical testing have been successfully related to exposure experiment results in aqueous systems making them a good screening process (13). The molten solar salt medium is not as stable as aqueous systems because of their high temperature, high ion concentration, and the added instability resulting from nitrate ion decomposition at high temperatures into nitrite and various nitrous oxides (NOx) (14, 30, 41, 42). Nevertheless, it has been shown that the information obtained
from electrochemically accelerated corrosion tests in molten nitrate salts can relate effectively to results obtained from long-term exposure tests (11, 14).

2.4 Summary of Testing

Potentiodynamic polarization has been conducted on various iron-based alloys of varying degrees of corrosion resistance, and in these alloys it is shown that a scale mainly composed of iron oxides and sodium iron oxides is developed (11, 12, 43). It has also been demonstrated that preferential leaching of chromium is a frequent issue in high-chromium metals such as stainless steels and nickel-chromium alloys (11, 39, 44-47). In various studies conducted, nickel-based high-chromium alloys generally outperform ferritic alloys, but the alloys reported to be most resistant to corrosion in solar salt are those with high aluminum content in addition to chromium or those coated with aluminum (9, 35, 37, 43). Two out of the five materials tested herein contain greater than 1 wt% aluminum, but it is unknown at this time whether the aluminum content plays a role in corrosion resistance in solar salt at 500°C. In this study, four high-chromium, nickel-based alloy samples were studied using potentiodynamic polarization to screen these materials for long-term exposure studies. Surface chemistry of these alloys were then studied to understand the surface chemistry and correlate it to the observed corrosion behavior.
Chapter 3: Experimental

3.1 Samples

Five different materials – UNS N06230, annealed (Alloy 230); UNS N06025, solution annealed (VDM Alloy 602CA®); UNS N06617, solution annealed (VDM® Alloy 617); UNS N06625GR1, annealed (VDM® Alloy 625 Grade 1); and UNS N06625GR2, solution annealed (VDM® Alloy 625 Grade 2) were used in this study. The certified compositions of these materials are listed in Table 1. Only one entry is given for alloys UNS N06625GR1 and UNS N06625GR2 as they are the same alloy, UNS N06625, with different heat treatments. The GR1 and GR2 suffixes refer to the following heat treatments: GR1 was annealed per ASTM B443 Grade 1 requirements at 950 to 1,050 °C (1,742 to 1,922 °F), and GR2 was solution annealed per ASTM B443 Grade 2 requirements at 1,080 to 1,160 °C (1,976 to 2,120 °F). The samples reported in this study were tested in their as-received state with a final sanded surface preparation of 120 grit for consistency between samples.
Table 1: The chemical composition of the four alloys is shown below in weight percent.

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>UNS N06230</th>
<th>UNS N06025</th>
<th>UNS N06617</th>
<th>UNS N06625GR1/2</th>
</tr>
</thead>
<tbody>
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<td>Ni</td>
<td>REM</td>
<td>62.0</td>
<td>54.28</td>
<td>61.17</td>
</tr>
<tr>
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<td>-</td>
<td>8.6</td>
<td>8.5</td>
</tr>
<tr>
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<td>-</td>
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<td>-</td>
<td>11.4</td>
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</tr>
<tr>
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<td>2.2</td>
<td>1.07</td>
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</tr>
<tr>
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<td>0.1</td>
<td>0.42</td>
<td>0.20</td>
</tr>
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<td>0.01</td>
<td>0.05</td>
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</tr>
<tr>
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<td>25.7</td>
<td>22.3</td>
<td>21.6</td>
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<tr>
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<td>9.4</td>
<td>1.42</td>
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</tr>
<tr>
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<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>-</td>
<td>0.0002</td>
<td>-</td>
</tr>
<tr>
<td>As</td>
<td>-</td>
<td>-</td>
<td>&lt;0.001</td>
<td>-</td>
</tr>
<tr>
<td>Bi</td>
<td>-</td>
<td>-</td>
<td>&lt;0.00003</td>
<td>-</td>
</tr>
<tr>
<td>Ta</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3.2 Materials and Methods

The five different materials were evaluated using potentiodynamic polarization tests in a 3:2 by weight NaNO₃:KNO₃ mixture. The sodium nitrate and potassium nitrate used in this study were of ACS Reagent grade and purchased from VWR and Amresco, respectively. A 3:2 by weight NaNO₃:KNO₃ mixture was used for all experiments. The preparation procedures for these salts and the experiments below have been described in previous publications that included drying for a 24-hour period to reduce water content of the salts (11, 29). The salt was melted in an alumina crucible in a furnace that was heated
to 500°C in a fume hood for each experiment. All potentiodynamic polarization experiments and open circuit potential (OCP) analyses were conducted in a three-electrode setup using a Gamry Reference 600 potentiostat that was controlled using the Gamry software. A coiled UNS N06625 wire was used as the counter electrode for each experiment, and a platinum wire was used as a pseudo-reference electrode mirroring previous studies (11, 29). A schematic of the furnace and electrode assembly is provided in Figure 3.

Figure 3: The schematic of the setup used for this study. Briefly, the experimental setup consisted of suspending the three electrodes (WE: working electrode, RE: reference electrode, and CE: counter electrode) in molten 3:2 by weight NaNO₃:KNO₃ salt mixture.
Before electrochemical testing, all electrodes were cleaned with deionized water, followed by a rinsing with acetone, and finished with a rinse of isopropanol before being dried either in air or with compressed air. Prior to potentiodynamic analysis, OCP was monitored for 1.25 hours which was the average time required for the variation to be less than ±15 mV from the average. Following OCP measurement, potentiodynamic polarization was conducted with a scan rate of 5 mV/s with a range of -0.5V to 1V vs. OCP. This scan rate and potential range were chosen based on previous work with similar metals in this molten salt blend (11, 29). The tests were conducted using duplicates. The samples were rinsed post-testing with deionized water to remove any remaining salt residue. The area of each sample exposed to the molten salt medium was measured post-experiment (uncertainty of ±0.25mm$^2$) to establish the current density.

Morphology of the sample surfaces was studied using backscattered and secondary electron (BSE and SE) detectors of a FEI Scios Dual-Beam scanning electron microscope (SEM). During imaging studies, energy dispersive spectra (EDS) were also obtained. Samples were cross-sectioned using the Ga$^+$ focused ion beam (FIB) in the FEI Scios dual-beam SEM. Micrographs and EDS line scans were taken of the cross-section. Samples were analyzed using X-ray diffraction (XRD) using a Rigaku SmartLab 3kW X-Ray Diffractometer. Raman spectra from the samples’ surfaces were also collected using a Thermo Scientific DXR Raman that was equipped with a 10mW, 532nm laser. Sample surfaces were also analyzed using X-ray photoelectron spectroscopy (XPS) to understand the chemistry of the sample surfaces. A PHI model 5600 Spectrometer was utilized for XPS studies.
Chapter 4: Results

4.1 Polarization Results

Electrochemical tests were conducted to evaluate the corrosion resistance and corrosion behavior of each alloy. The results of the potentiodynamic polarization tests for each alloy are shown in Figure 4. The corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) were determined by the Tafel extrapolation method and are provided in Table 2. These values were compared to values obtained from similar studies and are reported in Table 3 (11, 31). Similar to most other studies in molten salts, a Pt pseudo-reference was used in this study and thus the reported potentials are relative to the Pt pseudo-reference electrode (11, 29, 48-50).

The lowest average corrosion current density was 0.225mA/cm$^2$ for alloy UNS N06230, and the highest average corrosion current density was 0.431mA/cm$^2$ for alloy UNS N06625GR1. These values correspond well to values reported for other nickel-based, corrosion-resistant alloys and are comparable to that of stainless steels. UNS S31600 and UNS N08810 exhibited corrosion current densities of about 0.1mA/cm$^2$ and 0.154mA/cm$^2$, respectively, under similar experimental conditions (11).

Table 2: The average corrosion current density ($i_{corr}$) and the corrosion potential ($E_{corr}$) are shown below for each sample.

<table>
<thead>
<tr>
<th></th>
<th>UNS N06230</th>
<th>UNS N06025</th>
<th>UNS N06617</th>
<th>UNS N06625GR1</th>
<th>UNS N06625GR2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{corr}$(mA/cm$^2$)</td>
<td>0.225</td>
<td>0.397</td>
<td>0.348</td>
<td>0.431</td>
<td>0.244</td>
</tr>
<tr>
<td>$E_{corr}$(mV) vs. Pt</td>
<td>-214.5</td>
<td>-114.4</td>
<td>-66.2</td>
<td>-148.2</td>
<td>-227.0</td>
</tr>
</tbody>
</table>
Table 3: A comparison of the corrosion current density and corrosion potential between various samples is shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (mV) vs. Pt</th>
<th>$I_{\text{corr}}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNS N06230</td>
<td>-214.5</td>
<td>0.225</td>
</tr>
<tr>
<td>UNS N06025</td>
<td>-114.4</td>
<td>0.397</td>
</tr>
<tr>
<td>UNS N06617</td>
<td>-66.2</td>
<td>0.348</td>
</tr>
<tr>
<td>UNS N06625GR1</td>
<td>-148.2</td>
<td>0.431</td>
</tr>
<tr>
<td>UNS N06625GR2</td>
<td>-227.0</td>
<td>0.244</td>
</tr>
<tr>
<td>UNS S31600</td>
<td>-139.3</td>
<td>0.100</td>
</tr>
<tr>
<td>UNS N08810</td>
<td>-214.2</td>
<td>0.154</td>
</tr>
<tr>
<td>UNS G41300</td>
<td>-171.9</td>
<td>0.200</td>
</tr>
<tr>
<td>NiCr25FeAlYB</td>
<td>~ -25.0</td>
<td>~2.000</td>
</tr>
</tbody>
</table>
Figure 4: Potentiodynamic polarization scans obtained at a scan rate of 5mV/s from the five different samples evaluated in this study are shown. Additionally, the samples showing the lowest and highest current density in this study are shown against the results for UNS S31600. A: UNS N06230; B: UNS N06025; C: UNS N06617; D: UNS N06625GR1; E: UNS N06625GR2.
4.2 Polarization Discussion

The polarization curves for the alloys tested in this study do not show any clear region of passivation. Therefore, based on the polarization curves, it is unlikely that these alloys are passivating during these tests. There is a region of pseudo-passivity in the UNS N06625GR1 sample indicated by a small section of the curve having a slope that is negative which agrees with prior studies on alloys with similar compositions (38). However, the decrease in current density with increasing potential is not significant enough to indicate stable passivation and is thus referred to as pseudopassive (51, 52). UNS N06230 had the highest corrosion resistance based on its corrosion current density (0.225 mA/cm²) which may correlate to this being the only alloy with tungsten as a component. However, solution annealed UNS N06625GR2 had very similar corrosion current density at 0.244 mA/cm². It has been proposed that the presence of tungsten in the alloy leads to the formation of salt-soluble tungstates that result in increased corrosion (33). However, the results from this study did not provide a correlation between tungsten and corrosion rates.

Corrosion current density is not the only indicator of corrosion resistance. Alloy UNS N06625GR1 had the largest average Tafel slope. An exposure study that tested UNS N06625 and various stainless steels showed that UNS N06625 formed a stable nickel-iron-oxide scale and underwent a lower magnitude of mass change (47). These results correlate with the relatively higher corrosion resistance of UNS N06625 in this salt. It is unknown how these alloys compare to aluminized alloys which generally exhibit a lower level of corrosion than other alloys in the solar salt off-eutectic (35, 37). The corrosion behavior of chromium-containing alloys such as stainless steels has been
studied extensively in this medium; it has also been frequently observed, including in prior studies by the authors, that chromium ionizes and leaches out from the bulk alloy when exposed to molten nitrate salts (11, 34, 39, 45, 47). It should be noted that the corrosion current densities observed in this study are in agreement with corrosion current densities observed for other nickel alloys and are amongst the lowest for bulk alloys observed in this study (53, 54). While, the Solar Energy Technology Office of the U. S. Department of Energy has set a year 2030 corrosion rate target goal of 30µm/year, studies have yet to identify a bulk alloy capable of achieving that corrosion rate on short-term studies. Given that reported corrosion current density in solar nitrate salt under similar conditions have been on similar order (38) and even higher such as 10^{-3} \text{ A/cm}^2 \text{ (54, 55), and corrosion rates of } \sim 300 \mu\text{m/year (56). This study reports corrosion current densities of in the range of } 10^{-4} \text{ A/cm}^2 \text{, which can be approximated to corrosion rate in the range of } \sim 250 \mu\text{m/year, based on assumptions. It should be noted that the corrosion rate calculated from accelerated corrosion studies should not be compared with long term exposure studies which enable a material to develop a passive film and does not polarize the material to high potentials. Thus, the corrosion current densities observed in this study are at the lower end of corrosion current densities that have been reported and thus makes all of these alloys potential candidates for molten nitrate salts.}

4.3 Surface Analysis and Discussion

The samples were cleaned and imaged before and after the potentiodynamic polarization testing. The photographs of the samples prior to and post-testing are shown in Figure 5 with the submerged end on the bottom half of each sample. The top and bottom halves of
the samples show corrosion due to vapor and immersion, respectively. The first two samples from the left on each image are duplicate samples (post-testing) and the third sample in each image is that of an untested control (pre-exposure). Several similarities exist in the visual appearance of the materials that were tested. Four distinctly colored corrosion layers were observed on the samples: violet, blue, gray, and gold. These colors can be seen with varying presence on every tested sample. UNS N06230, UNS N06617, UNS N06625GR1, and UNS N06625GR2 seem to have all four of these colors, while UNS N06025 was observed to have a gold colored oxide film. Thus, while the images show that all samples underwent some level of tarnishing and film formation, it should be noted that the UNS N06625 samples (under both heat treatment conditions) appear to be visually least tarnished.
Figure 5: The post exposure samples (two duplicates on the left) are shown along with their unexposed control on right for each material. The samples were exposed to molten salt on the bottom. A: UNS N06230; B: UNS N06025; C: UNS N06617; D: UNS N06625GR1; E: UNS N06625GR2.

Micrographs of the sample surface obtained from secondary electron microscopy show the morphology of the sample surface before and after corrosion testing. As all
samples had similar surface morphology prior to testing, one sample image was given to represent pre-testing morphology. Images obtained from other samples are provided in supplementary information. The SE-SEM images show development of some oxide crystallites at 35kx magnification on the tested samples and are shown in Figure 6.

Figure 6: The SE-SEM images for five post-exposure samples and one as-received sample are shown above at 35000X. All as-received samples looked similar. The small, coarse shapes shown on the tested samples appear to be oxides. A: UNS N06230; B: UNS N06025; C: UNS N06617; D: UNS N06625GR1; E: UNS N06625GR2; F: as-received UNS N06625GR2.
EDS scans at 4kX magnification were performed on all samples with a general surface composition of nickel and chromium with small concentrations of other elements as provided in Table 4. It should be noted that the depth of analysis of EDS is large and may allow for signal from the base metal. Thus, while the EDS alone may not be used as conclusive evidence for determining stoichiometry, the differences observed between the surface film and the bulk metal can be used to understand the nature of the surface film.

The results for UNS N06625GR1 indicate that the surface composition was primarily nickel and chromium with lower concentrations of molybdenum, oxygen, niobium, and iron. The EDS scans for UNS N06625GR2 reveal similar results with slightly more chromium and nickel present. The elemental composition on the surface of UNS N06617 was similar to its bulk composition with nickel and chromium making up most of the surface layer with lower compositions of cobalt, oxygen, molybdenum, iron, and aluminum. The scans for UNS N06230 indicate a surface composed primarily of nickel and chromium with smaller concentrations of tungsten, iron, oxygen, and molybdenum. The EDS scans for UNS N06025 indicated nickel as the primary element on the surface with a smaller concentration of chromium. The presence of aluminum, iron, and oxygen was also indicated as well as lower concentrations of copper and carbon. The minor species observed in the EDS scan (K, Ca, N, Na) were likely due to impurities in the salt or salt that was still present on the sample.
Table 4: The elemental composition of the surfaces of the post-exposure samples as obtained from EDS is given below. Values are given in weight %.

<table>
<thead>
<tr>
<th>Element</th>
<th>UNS N06230</th>
<th>UNS N06025</th>
<th>UNS N06617</th>
<th>UNS N06625GR1</th>
<th>UNS N06625GR2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>46</td>
<td>42</td>
<td>36</td>
<td>33</td>
<td>36</td>
</tr>
<tr>
<td>Cr</td>
<td>27</td>
<td>30</td>
<td>26</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
<td>11</td>
<td>3</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>W</td>
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<tr>
<td>Mo</td>
<td>3</td>
<td>-</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>O</td>
<td>9</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>5</td>
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<tr>
<td>C</td>
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<td>-</td>
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<tr>
<td>Cu</td>
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<td>-</td>
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<tr>
<td>Si</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

Three of the samples, namely UNS N06230, UNS N06625GR1, and UNS N06625GR2, were cross-sectioned and imaged using FIB-SEM and the micrographs of the cross-section for these samples are given in Figure 7. As discussed in subsequent sections, UNS N06625 (GR1 and GR2) appear to be the better suited for the conditions studied here. UNS N06230 has been well studied in this environment and was thus used.
to compare the performance of UNS N06625. Thus, these three samples underwent more
detailed examination. The oxide layer on UNS N06230 does not appear to be a complete
oxide as seen in the SEM micrographs. One area imaged in Figure 5 did have some oxide
formation in a localized area about 4µm across where the oxide thickness was 986nm.
The composition of this area as indicated through an EDS map was mainly oxygen and
iron but appears to be depleted of chromium. The oxide layer formed on UNS
N06625GR1 seemed to vary significantly from 150nm up to 1.7 microns. The EDS map
indicates a surface composition of mostly oxygen and nickel with some iron present.
Chromium appears to be more concentrated in the bulk than on the surface of this sample.
The thickness of the oxide layer on UNS N06625GR2 was relatively consistent and
ranged between 600 and 800nm. The EDS line scan data, provided in Figure 5, indicates
a composition of nickel, sodium, and oxygen in the oxide layer with smaller levels of iron
and chromium. Sodium and oxygen content decreased rapidly towards the bulk of the
sample, whereas chromium and nickel content increased. Niobium content decreased
from the oxide layer into the bulk metal of the sample. It should be noted that these
surface films were formed after polarization studies and should not be considered as
indicative of the long-term behavior of the samples.

The corrosion behavior of nickel in eutectic NaNO₃:KNO₃ mixtures has been
studied previously, and it has been shown that nickel passivates with a nickel oxide layer
that can still allow transfer of Ni²⁺ (8). Nickel-based alloys have also been shown to
develop layers formed primarily of nickel oxides (31, 38, 42, 44, 46, 47). The
rhombohedral shape of the oxides seen in the SE-SEM images of the tested samples
resembles similar SEM images of a nickel oxide that developed on UNS N06690 exposed
to pressurized water reactor simulated water (57). The crystallites also approximate those found on UNS N06230 and UNS N06625 in an exposure experiment of the same salt medium (33).

The XRD patterns obtained from the samples are shown in Figure 8. Due to the short exposure time of the samples to the molten salt, the corrosion layer was exceedingly thin. Thus, the XRD patterns of only the matrix of the sample were observed in each case and the XRD did not detect the presence of a surface film, likely due to the surface film being very thin.
Figure 7: SEM images from the cross-sections obtained using FIB milling are shown for UNS N06230 (A); UNS N06625GR1 (D); and UNS N06625GR2 (E). The surface layer is not complete on UNS N06230 and vary in thickness on UNS N06625GR1 and is relatively consistent on UNS N06625GR2. The line scan data for UNS N06625GR2 (bottom image) indicates highest levels of oxide, sodium, iron, and niobium in the outer surface which decreases rapidly towards the bulk. Chromium and nickel follow a reverse trend.
Figure 8: XRD patterns obtained from the surface of the samples showed, for all samples, only the pattern of nickel with orientations noted at the top of the figure. Thus, the oxide film on the surface was too thin for XRD studies. A: UNS N06230; B: UNS N06025; C: UNS N06617; D: UNS N06625GR1; E: UNS N06625GR2.

The Raman spectra of each exposed alloy is shown in Figure 7. The results for the Raman spectra on UNS N06230 had features at 575 cm\(^{-1}\) and 700 cm\(^{-1}\) with the feature at 575 cm\(^{-1}\) being considerably larger than the feature at 700 cm\(^{-1}\). These features may be representative of NiCr\(_2\)O\(_4\), but the results for UNS N06230 seem to be shifted by about 25 wave numbers from the spectra for NiCr\(_2\)O\(_4\) which has features at 550 cm\(^{-1}\) and 675 cm\(^{-1}\) (58, 59). The Raman spectra for UNS N06617 exhibited features at 550 cm\(^{-1}\) and 675 cm\(^{-1}\) which can be attributed to NiCr\(_2\)O\(_4\). The Raman spectra for UNS N06025 exhibits three clear features near 330, 470, and 710 cm\(^{-1}\) which corresponds fairly well to the Raman spectra for NiFe\(_2\)O\(_4\) (58-60). The Raman spectra for UNS N06625GR1 and UNS N06625GR2 both showed features (700 cm\(^{-1}\), ~580 cm\(^{-1}\)) corresponding to
NiFe$_2$O$_4$, but these samples also had a feature (700 cm$^{-1}$) that could potentially be attributed to Nb$_2$O$_5$ (58, 59, 61, 62). In conjunction with the EDS line scan shown in Figure 5, it may be ascertained that Nb is present on the surface of UNS N06625GR2, and that it may be present as Nb$_2$O$_5$. It is unclear whether molybdenum is present in the oxide layer as no molybdenum was observed through Raman spectroscopy. The Raman spectra for UNS N06025 corresponded well to previous results for NiFe$_2$O$_4$ with several matching features (58-60).

Figure 9: Stacked Raman spectra for all five samples is shown above. Features marked with 1, 2, and 5 correspond to NiFe$_2$O$_4$. Features marked with 3 and 4 correspond to NiCr$_2$O$_4$. The potential feature for Nb$_2$O$_5$ is also located at position 1 on spectra D and E. Raman spectra obtained from samples UNS N06625GR2, UNS N06625GR1, and UNS N06025 are seen to be similar. A: UNS N06230; B: UNS N06025; C: UNS N06617; D: UNS N06625GR1; E: UNS N06625GR2.
The Raman results indicate a mixed Ni-Fe-Cr oxide present on every tested sample with varying compositions. It is reported that mixed metal oxides such as a nickel-iron-chromium oxide will have varying features due to specific metal cations occupying certain sites in the lattice (59). The position of features and their relative intensity can be changed due to varying levels of iron and chromium and their position in the lattice which influences the Raman shift. For UNS N06230, the presence of a layer made up of mostly nickel oxide is indicated by the main feature at about 500cm$^{-1}$ (58). The formation of an oxide layer mainly composed of nickel oxide on UNS N06230 in this medium is reported in literature (33). It is possible that chromium and iron are present in the initial oxide layer causing the formation of these secondary features and the similarity to spectra for a mixed NiFe$_x$Cr$_{2-x}$O$_4$ spinel (59). The Raman spectra for UNS N06617 closely resembles that of UNS N06230 which likely indicates an oxide layer with a similar composition. The Raman results for UNS N06025 resemble the Raman spectra for a spinel primarily composed of NiFe$_x$Cr$_{2-x}$O$_4$ given in literature (59).
oxide layer causing the formation of these secondary features and the similarity to spectra for a mixed NiFe\textsubscript{2-x}Cr\textsubscript{x}O\textsubscript{4} spinel (59). The Raman spectra for UNS N06617 closely resembles that of UNS N06230 which likely indicates an oxide layer with a similar composition. The Raman results for UNS N06025 resemble the Raman spectra for a spinel primarily composed of NiFe\textsubscript{2-x}Cr\textsubscript{x}O\textsubscript{4} given in literature (59).

Raman results for UNS N06625GR1 and UNS N06625GR2 are similar with slight differences in feature intensities. A feature that may correspond to niobium oxide was observed on Raman scans for both UNS N06625GR1 and UNS N06625GR2 which is supported by the presence of Nb observed in EDS scans on these samples. The presence of niobium in the oxide layer formed in this medium on alloys similar in composition to UNS N06625 has been reported in tests done on this alloy in a simulated supercritical water reactor (60). Further investigations need to be performed to understand whether Nb\textsubscript{2}O\textsubscript{5} forms due to the presence of oxygen at high temperatures and its effect on corrosion in this environment. It is unclear whether this oxide is resistant to corrosion or if it accelerates corrosion due to galvanic coupling as reported in literature on UNS N06625 in supercritical water (63). The EDS results for N06230 indicate the formation of an oxide of an undetermined composition. It has been reported that tungsten forms oxides at high potentials that were not reached in this experiment (64). Tungsten has also been reported to dissolve and form tungstates in this medium (46, 65). Further studies into the corrosion layer of UNS N06230 in this medium are required to better understand the influence of tungsten on corrosion of the samples. The iron concentration is indicative of an iron-nickel-chromium oxide forming on the surface. Aluminum and chromium in UNS N06025 have been reported to prevent metal dusting corrosion through the formation of
corundum (66). Corundum was not observed in the Raman spectroscopy data for this sample which may be due to the thinness of the oxide layer. The EDS data for UNS N06617 indicate small amounts of cobalt, molybdenum, and oxygen. Cobalt has been reported to prevent wear corrosion and erosion-corrosion in chromium-nickel alloys due to wear, but has not been reported to prevent corrosion in molten nitrate salts (67). Cobalt has been reported to be selectively leached from alloys similar to UNS N06617 in the solar salt medium at 600°C (68). Molybdenum has been reported to ionize and form molybdates in this medium (65). As discussed later, the presence of chromium was also fairly prominent in the XPS and EDS data on all samples, and this is likely due to chromium forming a spinel with nickel and iron. While it was not observed in the alloys tested in this study, the presence of molybdenum has been reported to accelerate intergranular corrosion in austenitic steels in a similar molten salt environment (69). It has been suggested that stainless steels may undergo intergranular corrosion due to sensitization in molten solar nitrate salts and intergranular cracking is observed in UNS N06625 during extension testing in the molten solar nitrate environment (45-47, 70). All of the alloys tested in this study were high-chromium, nickel-based alloys that may have undergone sensitization of chromium due to the temperature at which the study was conducted. It is well known that chromium forms carbides at grain boundaries at high temperatures; the formation of chromium carbides leads to depleted chromium in the areas adjacent to the grain boundary (71, 72). These chromium depleted regions lead to intergranular corrosion. Due to the short duration of the test, it is unlikely that intergranular corrosion can be directly observed. However, chromium has been reported to be soluble as a chromate ion in this medium which can yield to dissolution of
chromium into the molten salt (11, 30). While the salt was not tested in this study, our previous study conducted in the same environment has shown dissolution of Cr into the salt from Cr containing alloys, including UNS S31600 and UNS N08810 (11) in agreement with other results (30). Further studies with longer exposures are required to yield evidence of intergranular corrosion in these alloy samples.

A study conducted on the corrosion performance of UNS N06230 in a binary nitrate salt showed that it formed an outer layer of nickel oxide with 5 at.% sodium, and beneath this layer, another oxide layer with a significantly higher concentration of nickel was present (33). This inner layer of nickel oxide exhibited uniform corrosion by oxidation, which may explain the stable corrosion behavior of UNS N06230 in these experiments. In addition, one study conducted on the corrosion performance of UNS N06617 in the same salt mix showed that this alloy suffered pitting, chromium dissolution, and oxidation at the pitted region (68). It was also suspected by the study that chromium nitride formed under low oxygen partial pressure. The same study also reported that high-chromium alloys can form K$_2$CrO$_4$ along the grain boundaries, indicating intergranular corrosion in high-chromium, nickel-based alloys. The presence of potassium in small concentrations was indicated in the EDS scans performed on the samples, but no evidence of this compound was indicated through Raman analysis. In high-chromium steels such as UNS S31600, chromium forms carbides during sensitization (71). This process is less due to the salt mixture and more due to the high temperature environment related with these types of corrosion tests (45). This phenomenon does lead to enhanced corrosion as discussed earlier. The study conducted on UNS N06625 showed development of an oxide layer primarily composed of nickel,
oxygen, and iron, with small amounts of sodium present (47). This is similar to the results obtained from EDS scans conducted on UNS N06625GR1 and UNS N06625GR2. The aforementioned study on UNS N06625 also proposed that this alloy exhibits scale dissolution in the solar salt environment during polarization, but the study also reported lower level of corrosion compared to stainless steels and ferritic steels. This is contrary to the polarization curve data observed for UNS N06625GR1 and UNS N06625GR2 which indicates these samples did not undergo passivation during the polarization tests. However, as discussed earlier the sample does show pseudo passivation and thus has the ability to form a more protective oxide film with time. It is unknown what role aluminum and niobium play in the corrosion behavior of these alloys in the molten nitrate medium.

The XPS spectra obtained from UNS N06625GR1, UNS N06625GR2, and UNS N06230 after 1 min of Ar\(^+\) sputtering are shown in Figure 8. As can be seen, both UNS N06625GR1 and UNS N06625GR2, show a much higher ratio of O to Ni compared to UNS N06230. This is again indicative of a thicker or more complete oxide film formed on UNS N06625GR1 and UNS N06625GR2 compared to UNS N06230. Furthermore, the O1s spectra obtained from the three samples were peak-fit and are shown in Figure 9. It can be easily seen that the oxygen signal is very noisy on UNS N06230 further indicative of the thinner film. Peak-fit shows that the UNS N06230 surface consists of a significant amount of hydroxide and adsorbed water. In comparison, both UNS N06625GR1, UNS N06625GR2 surfaces consist primarily of oxide and much smaller amounts of hydroxide and almost negligible absorbed water. Hydration levels of a surface film is known to change (73) and also affect the corrosion behavior (74, 75). Deprotonation of such films may occur leading to the formation of an inner oxide film.
and a more hydrated outer gel-like film that have different ion selectivity (76, 77). Such a bipolar behavior has been described on iron, (76, 77) stainless steels, (78-80) and aluminum alloys (75, 81). It is hypothesized that such a bipolar behavior might occur on the surfaces of UNS N06625GR1 and UNS N06625GR2 as well, as they are Ni-Cr alloys. If such a behavior were to occur, it would explain the stronger oxide film observed upon sputtering (inner film) compared to hydrated film. This would also help explain the pseudopassive behavior observed in these alloys. In a study done on the long-term corrosion resistance of UNS N06625, a protective oxide film composed primarily of nickel, oxygen, and iron was formed which corresponds well to the observed Raman spectra of NiFe$_2$O$_4$ on UNS N06625GR1 and UNS N06625GR2 (47).

![Figure 10: Stacked XPS survey scan spectra are shown for the two samples of alloy UNS N06625 with spectrum E obtained from GR2 and spectrum D obtained from GR1 samples. A survey scan from UNS N06230 (spectrum A) is also shown for comparison. The most intense lines from the elements are labeled.](image-url)
Figure 11: Peak-fitted XPS O1s spectra obtained from the same three samples in Figure 6 namely, UNS N06230 (A, bottom), UNS N06625GR1 (D, center), and UNS N06625GR2 (E, top) are shown. Peaks labeled x, y and z refer to oxygen peaks from oxide, hydroxide and water. Both samples of alloy UNS N06625 have a more oxide-based and less hydrated surface films.
Chapter 5: Conclusions

Accelerated electrochemical testing was conducted on several alloys in the solar salt medium composed of a 3:2 by weight NaNO₃:KNO₃ mixture. All tested samples had corrosion current densities on the order of $10^{-4}$ A/cm². UNS N06230 (Haynes Alloy 230) exhibited the lowest average corrosion current density at 0.225mA/cm², and UNS N06625GR1 (VDM® Alloy 625 Grade 1) had the highest average corrosion current density at 0.431mA/cm². UNS N06625GR2 (VDM® Alloy 625 Grade 2) had the highest range of effective corrosion resistance based on the slope of the Tafel region. The corrosion current density for all tested samples were higher than that of UNS S31600 which may appear to be at odds with research indicating that nickel-based, high-chromium alloys are more corrosion resistant in this medium. However, the ability to form long-term passive protective films in the molten salt medium was not studied and it appears from the pseudopassive region that UNS N06625GR1 may possess the ability to passivate. The corrosion layer was too thin to be detected through XRD scan. The SE-SEM images show signs of a developing oxide layer at 35kx magnification on the samples that underwent potentiodynamic polarization. Raman spectra paired with XPS suggested the formation of various nickel-chromium-iron oxides and the potential formation of niobium oxide on UNS N06625GR1 and UNS N06625GR2. These results compare well to results from other research, but the role and behavior of niobium in these samples requires further study to be properly understood. While accelerated testing shows that all of the tested high nickel alloys performed at a similar level in molten nitrate salts, further work is necessary to fully understand the long-term behavior in this environment, especially to understand their ability to passivate.
Chapter 6: Future Work

As the use of accelerated corrosion testing is designed to be a method of preliminary screening for exposure testing, some future work that should be conducted involves exposure testing the samples screened in this study. Exposure testing should be focused on phenomena that were presented in this study. For UNS N06230, the influence of tungsten on the corrosion behavior of the sample should be explored. It would be beneficial to analyze the corrosion layer present on a long-term exposure study to observe whether tungsten was internally oxidized and formed soluble tungstates. The presence of tungstates in the salt could be confirmed through salt analysis in an inductively-coupled plasma optical emission spectrometer (ICP-OES). It would be likewise beneficial to see if UNS N06230 did develop a full oxide layer over the surface and whether the composition of the oxide layer was similar to what has been observed in literature.

Published literature on the performance of UNS N06025 in exposure testing in the 3:2 by weight NaNO$_3$:KNO$_3$ medium was not found in the literature search for this research. Therefore, exposure testing on this sample would undoubtedly yield relevant information on its performance and corrosion resistance. It is unclear at this time whether the surface is composed of a mixed NiFe$_x$Cr$_{2-x}$O$_4$ oxide and what the composition of that oxide is. It is also unclear if the relatively high aluminum content has any role in corrosion resistance or oxide layer formation.

UNSN06617 should likewise be analyzed as literature on its performance was sparse. The influence of cobalt should be further studied and salts should be analyzed for cobalt content. An exposure test would also yield information about whether potassium is forming an oxide with chromium as has been reported in prior literature.
Both grades of UNS N06625 should be studied further to better understand what role niobium has in the corrosion of these samples. Exposure testing and subsequent analysis of the oxide layer would reveal whether niobium oxide is forming and may yield information on its role in the corrosion performance of this alloy. Finally, UNS N06625 should be studied extensively using both exposure testing and post-exposure characterization as it appears promising for use in solar nitrate salts. It is very likely that the performance of UNS N06625 might be better than the well-studied UNS N06230, which is generally considered a standard for these environments.
References

54. J. Wang, Y. Jiang, Y. Ni, A. Wu and J. Li, Materials and Corrosion, 70, 102 (2019).
Appendix
This document contains the XRD and Raman data collected from the analyzed samples as well as the polarization curves and all SEM images captured.

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