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# ELECTROCHEMICAL CORROSION BEHAVIOR OF NICKEL ALLOYS IN SULFATE-

## CONTAINING MOLTEN SALTS AT 700 °C

A Dissertation in

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by

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## ABSTRACT

Hot corrosion on nickel based alloys has been the focus of extensive research due to their applications in high temperature operations such as gas turbines, petrochemical, and fossil fuel power engines. The demand for good mechanical and corrosion-resistant properties in construction materials for high temperature components has led to the development of several nickel-based superalloys. While these novel alloys are well known to exhibit sufficient mechanical properties, they lack corrosion resistance. As a result, components in high temperature processes do not exhibit the necessary degree of durability. During operation, the combustion zone in high temperature engines contains contaminants including sulfur (S) and sodium chloride (NaCl), which enter due to contamination in oil and polluted air. As a result, molten sulfate salts (e.g.  $Na_2SO_4$ ,  $K_2SO_4$ ) are formed within the combustion zone, which accelerate degradation reactions on metallic surfaces. To provide higher stability against the corrosive effect of alkali sulfates, a protective metallic coating is applied over the components in these high temperature environments. Corrosion behavior of metallic coatings is reported in the literature using burner-rig tests, exposure tests, and thermodynamic calculations; however, a fundamental study on the electrochemical corrosion behavior of nickel-based alloys has yet to be performed. Therefore, this dissertation aims to provide an outlook on the corrosion properties of nickel-based metallic coatings in corrosive environments.

Specifically, an electrolyte composition – LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) was used to elucidate the corrosion reactions at 700 °C. During molten sulfate induced corrosion (hot corrosion), metal elements undergo oxidation reactions (e.g. Ni  $\rightarrow$  Ni<sup>2+</sup> + 2e<sup>-</sup>) coupled with the reduction of SO<sub>4</sub><sup>2-</sup> ions. To further our understanding of the corrosion properties of metallic coatings, it is important to investigate the reduction mechanism of SO<sub>4</sub><sup>2-</sup> ions in hot corrosive environment. In a three electrode electrochemical cell configuration, sulfate ions were observed to undergo reduction reactions at sufficiently large negative overpotentials (< –1.1 V vs. Ag/Ag<sup>+</sup>) under inert argon atmosphere. It was found that  $SO_4^{2-}$  ion reduction reactions produce elemental sulfur (S) and sulfide (S<sup>2-</sup>) species, with charge-controlled, sluggish kinetics. Cyclic voltammograms remained invariant on switching the argon atmosphere to O<sub>2</sub>-0.1%(SO<sub>2</sub>+SO<sub>3</sub>), suggesting that electrochemical reduction potential of  $SO_4^{2-}$  ions is not dependent on the gaseous environment. However, the open circuit potential became more positive by ~0.60 V upon switching the argon atmosphere to oxidizing O<sub>2</sub>-0.1%(SO<sub>2</sub>+SO<sub>3</sub>) gas, implying the presence of stronger oxidants [O<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>] which can be coupled with the metal corrosion reactions during the hot corrosion processes.

To evaluate the corrosion behavior of nickel alloys in  $SO_4^{2-}$  ion containing solutions, electrochemical measurements with pure nickel in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> solution were performed under gaseous atmospheres of inert argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%(SO<sub>2</sub>+SO<sub>3</sub>). In inert argon, nickel corrosion developed an adherent NiO passive layer, resulting in a decreasing trend in open circuit potentials, and a low corrosion rate (~0.26 mA/cm<sup>2</sup>). In oxidizing atmospheres, Ni rapidly degraded due to the instability of NiO, which formed a dispersed NiO-NiS<sub>x</sub> phase, and showed significantly higher corrosion rates (7–12 mA/cm<sup>2</sup>).

With the baseline behavior of pure nickel established, oxygen active elements (e.g. Al, Cr) were alloyed with nickel to substitute the NiO passive layer with Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. Hot corrosion studies with  $\beta$ -NiAl (BCC phase) demonstrated a strong corrosion resistance under inert gaseous environment due to the formation of an adherent and protective alumina scale. However, oxidizing gaseous atmospheres led to localized damages in the alumina layer. Particularly, in the SO<sub>2</sub>-SO<sub>3</sub> containing environment, the Al<sub>2</sub>O<sub>3</sub> layer showed several cracks, which led to a corrosion rate ~35 times higher in comparison to that under inert argon. Upon the addition of 5 at% Cr in  $\beta$ -NiAl, the passive layer consisted of a bi-layer structure: pure Al<sub>2</sub>O<sub>3</sub> on the alloy surface and Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> solid solution on the outer part. The lower corrosion current densities of the Ni-Al-Cr alloys

compared to  $\beta$ -NiAl under pure O<sub>2</sub> as well as O<sub>2</sub>-0.1%(SO<sub>2</sub>+SO<sub>3</sub>) environments suggested the beneficial effect of Cr addition in  $\beta$ -NiAl.

Considering the fact that Cr addition in  $\beta$ -NiAl improves the corrosion resistance, Cr content was varied in Ni-Al-Cr alloys. It was observed that a small fraction of Cr is sufficient to improve the integrity of passive layer  $[Al_2O_3-Cr_2O_3]$  under a pure O<sub>2</sub> environment. Moreover, corrosion current densities decreased with higher Cr content in Ni-Al-Cr alloys [β-NiAl: 0.78 mA/cm<sup>2</sup>, NiAl-10Cr: 0.30 mA/cm<sup>2</sup>], In general, the corrosion properties of Ni-Al-Cr alloys improved with increasing content of Cr in hot corrosive environments containing pure  $O_2$ . To elucidate the effect of sulfur oxides in corrosion behavior of Ni-Al-Cr alloys, similar measurements were performed under a  $O_2$ -0.1% (SO<sub>2</sub>+SO<sub>3</sub>) environment. It was observed that Cr addition helps in repassivating the damaged sites on alloy surfaces. However, the repassivation time was dependent on Cr content. With increasing Cr, the recovery time decreased. Furthermore, corrosion potential measurements in SO<sub>2</sub>-SO<sub>3</sub> containing environments demonstrated an increasing trend of stability up to Cr = 5 at%; with any more addition of Cr reducing the magnitude. In agreement with the passivation stability predicted by corrosion potentials, Ni-Al-Cr alloys with Cr = 5 at% showed the least corrosion current density (~0.09 mA/cm<sup>2</sup>), which was approximately two orders of magnitude lower in comparison to  $\beta$ -NiAl. As a result, NiAl-5Cr is considered a prime composition for further enhancement of Ni-Al-Cr alloys in SO<sub>2</sub>-SO<sub>3</sub> containing hot corrosive environments.

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## Chapter 1

## **Introduction and Thesis Organization**

Corrosion in an ambient environment is a commonly observed type of materials degradation, which affects our day-to-day life in a profound manner. This form of degradation is primarily governed by the reaction of metallic element(s) with atmospheric species, e.g. moisture (H<sub>2</sub>O) and oxygen (O<sub>2</sub>) [1]. Rusting of steel based alloys is a common example of this kind of degradation at ambient temperatures, but metals also deteriorate in high temperature environments. For example – oxidation of electrical heating elements, burning of the tungsten filament in light bulbs, and tarnishing of cooking-ware, are temperature dependent degradations. Taking into account the role of temperature in degradation reactions, corrosion can be broadly classified into two categories – (i) aqueous corrosion and (ii) high temperature corrosion. While aqueous corrosion has a more significant influence in our day-to-day lives, corrosion at high temperature is closely related to numerous industrial environments, e.g. metal casting, high temperature furnaces, and power generating systems.

Scientific research on aqueous corrosion can be traced back to 1675, when Robert Boyle (1627-1691) published two articles: "Of the Mechanical Origin of Corrosiveness" and "Of the Mechanical Origin of Corrodibility" [2,3]; however, high temperature corrosion is a more recent focus in the scientific community. A literature search on this subject traces back the beginning of this research in 1913 with oxidation studies on tungsten by Langmuir [4], describing the reaction of tungsten vapor with nitrogen forming WN<sub>2</sub> compound. In general, metals exposed to high temperature under oxidizing gases such as O<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, and CO<sub>2</sub>, undergo oxidation reactions and form a metal oxide layer on their surface.

Following Langmuir's research, wider attention was paid to the oxidation kinetics and mechanisms of metal alloys in oxidizing environments at high temperature. Several notable studies include the discovery of the parabolic rate law of oxidation by Tammann [5], Pilling and Bedworth [6], with the mechanism being elucidated by Dunn [7,8]. A significant contribution towards the understanding of metal oxidation was made by Wagner starting in 1933, when he published his studies explaining the nucleation, growth, and diffusion kinetics of oxide scales [9–11]. Wagner's work became a stepping stone for the subsequent progress in this field and development of numerous alloys for high temperature applications.

## **1.1 Hot Corrosion**

Metal corrosion by surrounding oxygen can be significantly different when additional oxidizing species are present on the metal surfaces. For instance, metal corrosion under molten metal sulfates (e.g. Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub> [12]) is an accelerated form of metal degradation known as hot corrosion, which severely damages aircraft engines, marine turbines, petrochemical and power plants, and ore refineries. In these systems, the efficiency of the process is often improved with increasing operating temperature; hence, there is a demand for more stable and corrosion resistant material in the construction of such improved high temperature systems.

Petroleum feed carries an inevitable sulfur contaminant, which during combustion, generates sulfur oxides including sulfur dioxide (SO<sub>2</sub>) and sulfur trioxide (SO<sub>3</sub>). These gaseous species react with alkali halides (e.g., NaCl) present in the marine air as contaminants to form alkali and/or alkaline metal sulfates (e.g., Na<sub>2</sub>SO<sub>4</sub>). Such environmental conditions within the combustion zone lead to catastrophic degradation of metal surfaces [13].

Corey, Cross, and Reid reported the role of alkali sulfates in metal corrosion, documenting their observations on corrosion inside a low carbon steel boiler [14]. Further, Satz affirmed that Na<sub>2</sub>SO<sub>4</sub> is a precursor for metal sulfide inclusions near the fire-side surface of mercury boilers [15].

The idea that  $Na_2SO_4$  is a corrosive salt in high temperature environments was further reinforced by Sykes and Shirley [16] as well as Buckland, Gardiner, and Sanders [17]. Elaborating on the corrosive nature of  $Na_2SO_4$  salt on metal surfaces, Simons *et al.* [18] performed crucible tests on a stainless steel 310 surface in  $Na_2SO_4$  and proposed reduction reactions of  $Na_2SO_4$ . This was when researchers around the world developed curiosity about the corrosive effects of sulfate ions in high temperature applications.

#### **1.1.1 Types of Hot Corrosion**

Depending on the physical state of Na<sub>2</sub>SO<sub>4</sub>, hot corrosion studies have been categories in two temperature regimes.

## i) High temperature hot corrosion (Type I)

Hot corrosion above melting point of Na<sub>2</sub>SO<sub>4</sub> ( $T_m = 884$  °C) is referred to as high temperature hot corrosion, also known as Type I hot corrosion. Broadly, corrosion within the range of 900–1000 °C fall within the scope of this category.

#### ii) Low temperature hot corrosion (Type II)

Below the melting point of Na<sub>2</sub>SO<sub>4</sub>, a temperature region ~ 650-750 °C falls in the study of low temperature hot corrosion, also known as Type II hot corrosion. Even though this regime considers the solid state of Na<sub>2</sub>SO<sub>4</sub> for metal corrosion, the corrosive salt in a practical environment consists of low melting alkali halides (e.g. NaCl) and sulfate mixtures. For example, the eutectic composition of Na<sub>2</sub>SO<sub>4</sub> and NaCl melts at 620 °C, indicating a molten phase of Na<sub>2</sub>SO<sub>4</sub>. Additionally, SO<sub>4</sub><sup>2-</sup> species may come from other salts such as K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub> etc.

#### **1.2 Importance of Investigating Hot Corrosion**

While the effects of hot corrosion may not be as evident in our daily lives as aqueous corrosion, it can lead to catastrophic events that endanger human life. From a long list of hot corrosion induced accidents, two recent nearly fatal incidents are stated here.

### Incident #1

### Information Source: The Aviation Herald [19]

On July 12, 2014, flight TP-85 from Lisbon (Portugal) to Sao Paulo Guarulhos (Brazil) with 232 passengers on board experienced engine failure immediately after take-off at 3000 ft. in the air [20], which required the aircraft to dump its fuel at 5000 ft. Fortunately, the plane was able to land safely back at Lisbon's airport.

After two years of investigation, Portugal's GPIAA reported that low temperature hot corrosion (Type II) assisted in causing a crack in the high pressure turbine stage. Among the possible causes that led to this severe event was high sulfur content in air-fuel, sand, and salt coming from the maritime environment.

The same report also stated that from 2006 to 2014, there were approximately 13 incidents of this kind in GE made CF6-80E1A engines. Out of these 13, 11 occurred due to low temperature hot corrosion damaging the turbine blades.

#### Incident # 2

#### Information Source: The Guardian [21]

In 2016, the Japanese airline ANA experienced failure of three engines developed by Rolls-Royce for Boeing 787 Dreamliners. The first failure happened in February, during a flight from Kuala Lumpur to Tokyo. Similar failures took place in two other flights in March and August. As a result of these concerning events, ANA cancelled 18 domestic flights and kept 4 Boeing 787 Dreamliners grounded. Post-failure analysis of these engines indicated corrosion and cracking of turbine blades as the cause of failure, which led to the expensive decision to refurbish 100 Rolls-Royce engines.

### **1.3 Construction Alloys of High Temperature Components**

High temperature engines such as aircraft turbines, marine turbines, and other petrochemical engines endure aggressive environments during operation. In such locations, metallic components experience high mechanical stresses necessitating mechanical properties including strength, toughness, machinability, formability, and weldability in the development of new alloys. Nickel and cobalt-based alloys have been known to deliver suitable mechanical properties. However, due to relatively higher ductility and lower cost of nickel alloys as compared to cobalt based compositions, major focus is given to the development of new-generation nickel based systems. In the construction of turbine blades and similar components, nickel alloys are used where L1<sub>2</sub> phase is the primary lattice. Here, nickel and aluminum/titanium elements are arranged in an FCC lattice where Ni occupies face centered positions and with Al, Ti on the corners. An example of such an alloy system is 'Inconel', a family of nickel based superalloys. A member of this family – Alloy 600 contains the composition as given in Table 1 [22].

Table 1-1. Elemental composition of Alloy 600 from Inconel family of nickel superalloys [22].

Element	wt%
Ni	72
Cr	14 - 17
Fe	6.0 - 10
Mn	1.0
Cu	0.5
Si	0.5
С	0.15
S	0.015

Characterizations of these alloys revealed suitable mechanical properties required during the operation of gas turbines; however, they often lack in corrosion resistance. When exposed to hot corrosive environments, these alloys undergo surface degradation and consequently lose the attractive mechanical properties. Without compromising with the inherent properties of substrate composition, a new metallic composition exhibiting strong corrosion resistance is required to be used as surface coating.

#### **1.4 Metallic Coatings for Hot Corrosive Environments**

Considering that metals in oxidizing environments have the tendency to be oxidized, the protective behavior of metallic coatings is dependent on the parent alloy composition as well as the developed oxide scale. Therefore, for efficient coatings performance, a stable oxide layer exhibiting good corrosion resistance is desirable. In other words, surface engineering of these components is directed towards the growth of a slow growing, dense, and thermodynamically stable oxide scale. Most of the engineering alloys are primarily composed of iron, nickel, and/or cobalt. When these alloys contain elements such as aluminum, chromium, and silicon, they develop an oxide scale of alumina, chromia, and silica, respectively. During the formation of these oxide scales, the substrate is depleted with respect to oxide scale forming element(s). Therefore, in order to form a durable passive scale, a sufficient amount of oxide scale forming elements are required to be incorporated during the coating alloy development.

#### 1.4.1 Coating Types

On a broad scale, there are three types of metallic coatings in use. A brief description is as follows [23].

## i) Diffusion Coatings

Diffusion coatings are employed by surface enrichment of structural alloys by aluminum, chromium, silicon, or a combination of these elements. Usually, a  $\sim 60 \ \mu m$  thick layer of these elements is applied on the superalloy substrate.

## ii) Overlay Coatings

Overlay coatings are applied as a separate metallic layer having a composition of M-Cr-Al-Y, where M stands for nickel or cobalt or a combination of these two. These type of coatings are required to have a balance of oxidation, corrosion resistance, and mechanical properties such as ductility comparable to the substrate.

## iii) Thermal Barrier Coatings (TBCs)

TBCs are an extended form of diffusion or overlay coatings. TBCs are usually applied to insulate superalloy substrate from heat diffusion. In TBCs, the substrate is first covered with a bond coat which is applied by enrichment with an oxide scale former (diffusion coating) or by application of metallic layer with M-Cr-Al-Y composition (overlay coating). This bond coat is further coated with a ceramic layer, usually using partially yttria stabilized zirconia.

The focus of research in this dissertation is motivated towards the fundamental understanding of diffusion and overlay coatings. Therefore, a further discussion on thermal barrier coatings has been skipped and a detailed discussion on diffusion and overlay coatings is provided in Chapter 2. In order to acquire an understanding of metallic coatings in hot corrosive environments, a comprehensive outlook on the reduction behavior of  $SO_4^{2-}$  species is very important. There are several reports available in the literature on this subject; however, due to the complex speciation behavior of sulfur bearing species, conflicting findings have been reported in

the literature. As a result, an exact reduction mechanism remains a debatable subject. Chapter 3 of this thesis reports the reduction mechanism of molten sulfate species at 700 °C. Additionally, toward understanding the mechanisms of corrosive environments within gas turbines, the role of gaseous species ( $O_2$ ,  $SO_2$ ,  $SO_3$ ) in reduction reactions has been discussed.

Subsequently, nickel corrosion is introduced in Chapter 4. Addition of aluminum and chromium in nickel alloys leads to the formation of alumina and chromia layer(s), respectively, on the metal surface. Considering the fact that a slow growing passive scale is required for a durable protection in hot corrosive environment, passivation by alumina scale has been evaluated by performing electrochemical studies with  $\beta$ -NiAl phase in molten sulfate electrolyte. It was observed that the growth of alumina scale under oxidizing gases is also accompanied by localized damages. Additionally, alumina based passivation is vastly impacted under the presence of SO<sub>2</sub>-SO<sub>3</sub> species. In such environment, Cr addition in  $\beta$ -NiAl has been observed to enhance the corrosion resistance.

The beneficial effect of chromium in Ni-Al-Cr based ternary alloys observed by electrochemical measurements was in good agreement with the available reports in the literature [23,24]. However, the focus of previously reported studies has mainly remained in the type I hot corrosion regime. Furthermore, fundamental studies informing the corrosion properties of nickel alloys under varying content of chromium are sparse [25]. Chapter 5 reports electrochemical studies performed on Ni-Al-Cr ternary alloys in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte with the varying content of chromium. Subsequently, effect of SO<sub>2</sub>-SO<sub>3</sub> gases on the Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> scale stability has been investigated. Immersion tests were also performed at 700 °C to corroborate electrochemical observations.

## Chapter 2

## High Temperature Alloys and Their Performance in Molten Sulfates Containing Corrosive Environments

#### 2.1 Background of Corrosion-resistant Metallic Coatings

In the early 1970s, Talboom [26] studied several cobalt based quaternary alloys by varying Al between 12–20 wt%, Cr between 20–40%, and yttrium level at 0.5 wt% for coating applications to counter hot corrosion, and concluded that Co-Cr-Al-Y (60.5-25-14-0.5 wt%) alloy provided the most corrosion resistant behavior. Since then, there has been an extensive research dedicated to cobalt based alloys for their applications in the hot corrosive environments [27–32]. During the successive progress in this field, it was established that the nickel and cobalt based alloys exhibit similar corrosion properties. In efforts to reduce the cost of corrosion resistant coatings, nickel based alloys obtained significant development due to relatively lower cost of nickel in comparison to that of cobalt. Furthermore, nickel alloys exhibit higher ductility in comparison to cobalt alloys [23,24,33]. Chemical compositions of few important corrosion resistant nickel alloys are given in Table 2-1 [34,35].

During the exposure of nickel alloys to the hot corrosive environment, the corrosion rate is primarily governed by (i) alloy composition, (ii) microstructure of alloy, (iii) thermodynamic stability of passive film, (iv) sulfate salt deposits, (v) surrounding gases, and (vi) operating temperature [24,36]. These alloys, when employed in the hot corrosive environment, develop an oxide scale which is primarily responsible for imparting resistance against corrosive species such as  $SO_4^{2-}$ ,  $O_2$ , and sulfur oxide gases. For example, pure nickel in a sulfate environment develops a NiO passive layer containing Ni<sub>3</sub>S<sub>2</sub> phase [37,38]. This passive layer on the nickel surface further limits the corrosion by reducing the reaction between nickel and corrosive species. Therefore, new compositions of nickel alloys must form a protective passive layer against the corrosive species.

Allow	Composition (wt%)												
Апоу	Ni	Со	Cu	Мо	Cr	Fe	W	Mn	Si	С	Al	Ti	Oth.
600	76		0.2		15.5	8		0.5	0.2	0.08			
625	61			9	21.5	2.5		0.2	0.2	0.05	0.2	0.2	3.6 (Na+ Ta)
690	58		0.5		29	9		0.5	0.5	0.05			
725	57			8	21	7.5		0.35	0.2	0.03	0.35	1.5	3.5 (Nb)
U-700	Bal	18.5		5.1	15						4.3	3.5	
U-500	Bal	18.5		4	18.5						3	3	
R-77	Bal	15		4.2	14.6						4.3	3.35	
R-80	Bal	10		4	14		3.8				3	5	
IN-713	Bal			4.1	12.5						6.1	0.8	2 (Cb)
IN-100	Bal	15		3.0	10						5.5	4.7	1 (V)
IN-738	Bal	8.5		1.75	16		2.6				3.4	3.4	1.75 (Ta)
IN-792	Bal	9		2	12.5		4				3.3	4.4	3.6 (Ta)
Hast-X	Bal	1.5		9	22		0.6						18 (Fe)
Ni-50Cr	Bal				50								
Ni-2541	Bal				25						4		1(Y)

Table 2-1. Some compositions of nickel alloys commonly used in the hot corrosive environment [34,35].

In general, the mechanism of hot corrosion on alloy surfaces is similar to that for high temperature oxidation of metal. However, unlike oxidation, hot corrosion takes place in the additional presence of molten sulfate deposits. Therefore, prior to the discussion on sulfate induced corrosion of nickel alloys, it becomes imperative to discuss the oxidation behavior of alloys at high temperature. The following section will describe the high temperature oxidation of engineering alloys and their governing mechanisms. Subsequently, the role of sulfate ions in the accelerated degradation of nickel alloys will be highlighted based on the literature.

### 2.2 Thermodynamic and Kinetic Understanding of Metal Oxidation at High Temperatures

Metal alloys (M), when exposed to oxidizing species such as pure  $O_2$  gas, undergo an oxidation reaction forming a metal oxide. If the metal has the tendency to release 'n' electrons, the oxidation reaction can be given by reaction 2-1:

$$2M + n/2 O_2 (g) \rightarrow M_2O_n$$
 Reaction 2-1

The spontaneity of the above reaction can be estimated by the formation energy ( $\Delta G_f^o$ ) of metal oxides. As an example, thermodynamic properties such as enthalpy of formation, entropy change, and Gibbs energy of formation for the growth of alumina at several temperatures are given in Table 2-2. Since the Gibbs energy of formation is negative, growth of alumina is an exothermic process and occurs spontaneously.

Figure 2-1 shows the trend of Gibbs energies as a function of temperature for the oxidation of some common engineering metals [39]. Utilizing these plots, other thermodynamic parameters such as the formation enthalpy ( $\Delta H_f^o$ ) and the change in entropy ( $\Delta S_f^o$ ) can be estimated using Equation 2-1.

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o$$
 Equation 2-1

T (°C)	Enthalpy Change,	Entropy Change, ΔS	Gibbs Energy of	
I ( C)	ΔH (kJ/mol)	(J/mol-K)	Formation, $\Delta G$ (kJ/mol)	
600	-1673.082	-310.580	-1401.900	
700	-1693.879	-332.859	-1369.957	
800	-1692.948	-331.950	-1336.716	
900	-1691.902	-331.018	-1303.568	
1000	-1690.753	-330.079	-1270.513	

Table 2-2. Enthalpy of formation, change in entropy, and Gibbs energy of formation for the growth of alumina passive layer on aluminum surface during oxidation at high temperatures [39].



Figure 2-1. Ellingham diagram calculated for the formation of metal oxides on several engineering elements from 500  $^{\circ}$ C to 2000  $^{\circ}$ C.

The intercept of  $\Delta G_f^o$  on y-axis at 0 K and the slope  $d\Delta G_f^o/dT$  provide the formation enthalpy ( $\Delta H_f^o$ ) and change in entropy ( $-\Delta S_f^o$ ), respectively. The slope  $d\Delta G_f^o/dT$  includes a negative sign on the entropy term. Therefore, a negative slope in the  $\Delta G_f^o$  vs. T plot (Ellingham diagram) indicates an increase in entropy during the course of oxidation and vice versa. These thermodynamic quantities can be used to assess the feasibility of metal oxidation in an oxidizing environment at a given temperature. From Figure 2-1, it is evident that the Gibbs energy of formation for alumina is substantially negative than most other oxides. Therefore, alumina-based passivation is considered one of the most stable protections in oxidizing environments.

In practical oxidizing environment, the activity of oxygen may deviate from unity, affecting the growth of metal oxides. In other words, the formation of metal oxides and their stability depends on the oxygen partial pressure in the gaseous environment. Employing the thermodynamic relation

$$\Delta G_f = \Delta G_f^o + RT * lnK$$
 Equation 2-2

,where K is the reaction constant for the equilibrium of metal oxidation reaction, partial pressures of oxygen are calculated and the results are shown in Table 2-3. It is clear that the oxygen partial pressure required to oxidize these elements is exceptionally low. In practice, the oxygen pressure in contact with metallic coatings is several orders of magnitudes higher, resulting in an inevitable growth of passive oxide scale.

Reduction of the thermodynamic energy is a prerequisite for the initiation of passive scale formation. However, the subsequent growth of the oxide scale is limited by the developed oxide layer. Wagner [9] proposed that the metal oxidation initiates through the chemisorption of  $O^{2-}$  on the pristine metal surface, which subsequently develops an electric field on the metal surface to ionize the metal atoms which leads to the formation of metal oxide. After initial growth of the oxide layer on the alloy surface, subsequent growth is controlled by the outward diffusion of metal cations  $(M^{n+})$  and electrons (e<sup>-</sup>), and the inward diffusion of oxygen anion (O<sup>2-</sup>) through the oxide layer. A schematic of the diffusion of charged species (ions and electrons) through a passive oxide layer is shown in Figure 2-2.

Table 2-3. Minimum partial pressure of oxygen  $(P_{O_2})$  required for the oxidation of engineering elements at various temperatures [39]

Reaction(s)	Partial pressure of $O_2$ , $P_{O_2}$ (atm)						
	$T = 500 \ ^{\circ}\mathrm{C}$	<i>T</i> = 1000 °C	<i>T</i> = 1500 °C	$T = 2000 \ ^{\circ}\mathrm{C}$			
$2Al + 3/2 O_2 \rightarrow Al_2O_3$	2.57 * 10 <sup>-65</sup>	1.69 * 10 <sup>-35</sup>	1.79 * 10 <sup>-22</sup>	3.28 * 10 <sup>-15</sup>			
$2Cr + 3/2 O_2 \rightarrow Cr_2O_3$	1.39 * 10 <sup>-42</sup>	1.05 * 10 <sup>-22</sup>	$4.70 * 10^{-14}$	3.79 * 10 <sup>-9</sup>			
$Si + O_2 \rightarrow SiO_2$	8.39 * 10 <sup>-53</sup>	8.96 * 10 <sup>-29</sup>	2.74 * 10 <sup>-18</sup>	3.38 * 10 <sup>-12</sup>			
$Ni + \frac{1}{2}O_2 \rightarrow NiO$	1.67 * 10 <sup>-23</sup>	5.48 * 10 <sup>-11</sup>	1.47 * 10 <sup>-5</sup>	0.0234			
$\text{Co} + \frac{1}{2} \text{O}_2 \rightarrow \text{CoO}$	5.59 * 10 <sup>-25</sup>	1.35 * 10 <sup>-12</sup>	3.59 * 10 <sup>-7</sup>	3.40 * 10 <sup>-4</sup>			
$Fe + \frac{1}{2}O_2 \rightarrow FeO$	1.24 * 10 <sup>-29</sup>	$1.40 * 10^{-15}$	1.41 * 10 <sup>-9</sup>	2.45 * 10 <sup>-6</sup>			
$Ti + O_2 \rightarrow TiO_2$	5.18 * 10 <sup>-55</sup>	4.77 * 10 <sup>-30</sup>	3.60 * 10 <sup>-19</sup>	3.87 * 10 <sup>-13</sup>			



Figure 2-2. A schematic illustrating the growth mechanism of passive oxide layer on the metal surface in oxidizing gaseous environment at high temperature.

Since, the subsequent growth of the passive layer depends on the movement of charged species through the existing layer, the thickness of the grown passive film becomes a limiting factor. Therefore, the growth rate will be inversely proportional to the thickness of the passive layer [40]. If at a given time (t), the oxide scale thickness is y, then

$$\frac{dy}{dt} = \frac{k}{y}$$
 (k: a proportionality constant) Equation 2-3

On integration, 
$$y^2 = 2^k k^k t$$
 + constant Equation 2-4

Initially, at t = 0, the thickness of oxide layer was 0. Therefore,

$$y^2 = k_p * t$$
 (on replacing 2\*k with another constant,  $k_p$ ) Equation 2-5

The coefficient  $k_p$  is known as the parabolic rate constant.

Wagner established that an ideal (protective) passive layer grows under diffusioncontrolled kinetics, showing a parabolic trend of passive scale thickness as a function of time. Under an environment containing oxidizing species such as oxygen, nitrogen, sulfur, and chlorine, the extent of metal oxidation can be assessed by oxide scale thickness or the weight gain measurements at various time-intervals. Since weight gain is proportional to the oxide scale thickness, Equation 2-5 can be rewritten as

$$W^2 = k_p * t$$
 Equation 2-6

Where, W is the weight gain per unit surface area of the exposed specimen in time t. Based on the weight gain measurements, the fraction of passive scale forming metal element(s) in oxide phase can also be evaluated. The parabolic rate constants ( $k_p$ ) determines the durability of the alloy. Therefore, a passive scale with a lower parabolic rate constant provides greater durability.

Equation 2-6 describes metal oxidation at a fixed temperature well. However, when varying the surrounding temperature, the parabolic rate constant  $(k_p)$  is described by the Arrhenius equation as below.

$$k_p = A * \exp(-\frac{\Delta E_a}{R*T})$$
 Equation 2-7

Where, *A* is pre-exponential factor,  $E_a$  is activation energy, *R* is the ideal gas constant and *T* is temperature in K. The associated variables in Equation 2-7 such as  $E_a$ , *A* and  $k_p$  can be calculated by using this equation at different temperatures [40].

Metal alloys containing aluminum develop an alumina scale with thickness of 1-20  $\mu$ m. After an initial growth, alumina layer behaves as a barrier to further alumina development, which in turn reduces the growth rate of the passive scale. Figure 2-3 shows parabolic rate constants for the growth of various oxide scales over a wide temperature range [24]. Commonly used alloys in a high temperature regime are primarily based on nickel, cobalt and/or iron. Based on thermodynamic formation energies of metal oxides [Figure 2-1], it is evident that when these alloys contain aluminum, chromium, and/or silicon, they undergo the preferential formation of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and/or SiO<sub>2</sub> on the alloy surface. Since, alumina growth has a small magnitude of parabolic rate constant, alumina based passive layer is desirable to counter oxidation reactions.



Figure 2-3. Parabolic rate constant for the growth of common passive oxide scales in oxidizing environments at various temperatures [24]

### 2.3 Metal Oxidation in Sulfate Containing Environment – Hot Corrosion

Hot corrosion is an accelerated form of metal oxidation at high temperatures. Metal alloys exposed to sulfate containing environments undergo oxidation due to air as well as sulfate ions. As described in Section 1.1 [Chapter 1], high temperature applications including the combustion of oil/gas introduces sulfur oxides e.g. SO<sub>2</sub> and SO<sub>3</sub>. These gaseous species form alkali sulfates when reacting with ingested marine or polluted air which usually contain NaCl as contaminant. For example, industrial gas turbines located in the vicinity of ocean air were found to exhibit the presence of several alkali/alkaline sulfates such as Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, CaSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> as listed in Table 2-4 [12]. Based on their relative fractions, it is also evident that Na<sub>2</sub>SO<sub>4</sub> is the primary salt present in the turbine engine.

Constituent	Composition (wt%)	Composition (mol%)
Na <sub>2</sub> SO <sub>4</sub>	56.50	54.68
$K_2SO_4$	6.97	5.50
$CaSO_4$	14.85	15
MgSO <sub>4</sub>	21.73	24.82

Table 2-4. Composition of typical metal sulfates present in industrial gas turbines [12]

Several studies have been reported in the literature on the corrosion behavior of nickel alloys [23,24,37,38,41–44]. For example, a mechanistic framework for the corrosion behavior of nickel alloys was developed by performing oxidation and hot corrosion studies with pure nickel [37,38,41]. It was established that nickel specimens coated with Na<sub>2</sub>SO<sub>4</sub> (~0.5 mg/cm<sup>2</sup>) underwent accelerated corrosion, forming nickel oxide (NiO) and nickel sulfide (NiS<sub>x</sub>) phases in O<sub>2</sub> environment at 1000 °C. Over a period of 90 mins, nickel hot corrosion showed a weight gain of approximately 3.5-5.5 mg/cm<sup>2</sup>, whereas nickel oxidation (without Na<sub>2</sub>SO<sub>4</sub>) showed less than 1.5 mg/cm<sup>2</sup> during the same period of time [38]. Further comparison between these two degradation processes also showed that the nickel oxidation led to the formation of a dense NiO layer, whereas the NiO-NiS<sub>x</sub> layer under Na<sub>2</sub>SO<sub>4</sub> was porous.

Besides Na<sub>2</sub>SO<sub>4</sub>, hot corrosion reactions are also influenced by the chemistry of surrounding gases. For example, inside the turbine combustor, nickel alloy are exposed to O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and sulfur oxides (SO<sub>2</sub> and SO<sub>3</sub>). Luthra [28] reported that sulfur oxides react with the passive oxide layer on nickel alloys forming low melting temperature eutectic compositions. For example,

NiO layer on nickel surface will form NiSO<sub>4</sub>–Na<sub>2</sub>SO<sub>4</sub> ( $T_{eutectic} = 670$  °C) upon exposure to sulfur oxides. As a result, the passive layer becomes less protective. Further effect of SO<sub>2</sub>-SO<sub>3</sub> gases on nickel corrosion was studied by Lillerud & Kofstad [41] and Gheno & Gleeson [37]. It was observed that nickel coated with a thin layer of Na<sub>2</sub>SO<sub>4</sub> ( $2.8 \pm 0.5 \text{ mg/cm}^2$ ) showed ~15 µm thick NiO passive layer under air and ~60 µm thick NiO layer under O<sub>2</sub>-0.1%(SO<sub>2</sub> + SO<sub>3</sub>) environment at 700 °C [37]. Based on these studies, it is clear that the nickel alloys developing NiO passive scale will undergo accelerated corrosion due to the presence of sulfur oxides within high temperature processes, such as indusrial gas turbines.

#### 2.4 Role of Oxygen Active Elements in Nickel Alloys

Since the NiO passive layer on nickel (or nickel alloys) is porous and undergoes a dissolution reaction in the hot corrosive environment, oxygen active elements are added in nickel alloys to develop more stable passive layer. Due to high thermodynamic stability, slow growth kinetics, and compact lattice structure, alumina based passivation on nickel alloys provides an improved resistance against corrosive species [23,24]. Therefore, gas turbine components, which are typically constructed using nickel alloys, are coated with a thin layer of aluminum using various methods such as pack cementation, slurry cementation, chemical vapor deposition (CVD), and metallizing [23]. During the aluminizing process, aluminum from the source is deposited on the substrate alloy and diffuses inwards forming a Ni-Al intermetallic phase. A Ni-Al binary phase diagram is shown in Figure 2-4 [45]. A beta-nickel aluminum binary phase is an intermetallic material which includes the crystallographic distribution of Ni and Al atoms in BCC (CsCl) lattice. This binary phase exhibits a high melting point ( $T_m = 1638$  °C) and does not change phases over a wide range of temperatures. Therefore, this composition is known for its significant corrosion resistance properties in the high temperature corrosive environments. During exposure to oxidizing

and hot corrosive environments, a slow growing alumina scale forms on the alloy surface because of the slow diffusion of aluminum from the bulk metal toward the alloy surface.



Figure 2-4. Nickel-aluminum binary phase diagram depicting the phase behavior from 400  $^{\circ}$ C to 1800  $^{\circ}$ C [45]

Similar to pure nickel, hot corrosion studies have been performed with samples containing  $\beta$ -NiAl phase [36,46–48]. Gheno *et. al.* [47] reported that  $\beta$ -NiAl coated with a thin layer of Na<sub>2</sub>SO<sub>4</sub> (2.8 ± 0.5 mg/cm<sup>2</sup>) showed the formation of an alumina passive layer after hot corrosion. However, the alumina scale exhibited localized damages which led to the internal oxidation of the bulk  $\beta$ -NiAl [48,49]. Hot corrosion studies with  $\beta$ -NiAl in O<sub>2</sub>-0.1% (SO<sub>2</sub>-SO<sub>3</sub>) showed scattered nodules of NiO and NiAl<sub>2</sub>O<sub>4</sub> phases of varied size (~85 µm). During the localized damage in an alumina film, the underlying alloy is directly exposed to corrosive species [SO<sub>4</sub><sup>2–</sup>, O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>], which leads to subsequent corrosion.

Typically, metal alloys and ceramics have significantly different lattice parameters. For example, alumina grows in a hexagonal lattice (a = 4.785A and c = 12.991A) [50] whereas  $\beta$ –NiAl is a CsCl type lattice (a = 2.88A) [51]. While eliminating this lattice mismatch is difficult, the impact can be significantly reduced by maintaining a thin passive layer. A scale thickness around 1-20 µm has been found to exhibit stable interfacial behavior. Considering these constraints, growth of alumina scale on metal alloys is desirable. However, during the localized damage, repassivation of the metal surface becomes a critical step. Usually, regrowth of alumina on damaged sites of  $\beta$ -NiAl is a slow process, which makes  $\beta$ -NiAl susceptible to continuous corrosion. Therefore,  $\beta$ -NiAl is alloyed with other elements such as Cr, Co, and Pt to facilitate faster alumina growth [52,25,46–49].

Malik *et. al.* [53] and Nicholls *et. al.* [42] reviewed a wide range of alloy compositions for coating applications in hot corrosive environments. It was realized that chromium rich compositions have strong corrosion resistance to the sulfate containing environment [27,53].  $\beta$ -NiAl based alloys with added Cr demonstrate a shorter duration of transient oxidation, suggesting the faster regrowth of alumina on damaged sites. Giggins and Pettit [52] suggested that Ni-Al-Cr alloys in oxygen containing surrounding, undergo preferential oxidation of Cr, forming a Cr<sub>2</sub>O<sub>3</sub> layer. Over continued growth of Cr<sub>2</sub>O<sub>3</sub>, the partial pressure of oxygen at the alloy *vs.* chromia interface decreases to stop its subsequent growth. However, due to the lower requirement of oxygen for alumina formation [Table 2-3, Figure 2-1], aluminum reacts with residual oxygen and forms an alumina layer beneath the chromia. The diffusivity of Cr with respect to Al in Ni-Al-Cr alloys is higher, which gives these alloys the ability to quickly diffuse chromium and form a Cr<sub>2</sub>O<sub>3</sub> layer in the event of localized damage in the passive film. As a result, addition of Cr in  $\beta$ -NiAl improves the corrosion resistance. A representative sketch reproduced from Novak's work [54] depicting the performance of alumina forming alloys in hot corrosive environment is shown in Figure 2-5.


Figure 2-5. Generic behavior of nickel and cobalt based alloys in hot corrosive environments (reproduced from Novak's work [54])

Nickel alloys when combined with aluminum improve corrosion resistance, as evident from Figure 2-5. However, further addition of Cr is required to obtain higher resistance in aggressive hot corrosive environments such as within the combustion zone in gas turbines. To improve the passivity of alloy surface, oxygen-active elements e.g., Y, Si, Ta, or Hf [55–58] are also added to the alloy. During the growth of the passive oxide scale, these elements segregate at the oxide scale-alloy interface. Such segregation inhibits the outward movement of cations through the oxide scale and strengthens the integrity of the passive layer. Further discussion on the role of reactive elements in nickel based alloys has been given in Chapter 6.

#### 2.5 Chemical Stability of Passive Scales in Molten Sulfate Environment

After the growth of passive oxide layer on the alloys surface, sulfate species are in contact on the passive scale. Thus, chemical reactivity between passive scale and Na<sub>2</sub>SO<sub>4</sub> solution influences the stability and corrosion resistance of nickel alloys. Rapp [59–61] suggested that the chemical solubility of surface oxides (e.g. NiO, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>) in molten Na<sub>2</sub>SO<sub>4</sub> can be utilized to predict the stability of passive layer. The chemistry of molten Na<sub>2</sub>SO<sub>4</sub> can be described by the following equilibrium reaction.

$$Na_2SO_4 = Na_2O + SO_3(g)$$
 Reaction 2-2

Based on the activities of Na<sub>2</sub>O and/or SO<sub>3</sub>(g), Rapp [59] defined the basicity and acidity of Na<sub>2</sub>SO<sub>4</sub> molten phase in terms of  $a_{Na_2o}$  and  $a_{SO_3}$ . For example, a sulfate salt with high  $a_{Na_2o}$  or low  $a_{SO_3}$  is basic in nature or vice versa. Corresponding to Na<sub>2</sub>SO<sub>4</sub> acid-base chemistry, the solubility behavior of various metal oxides such as NiO, Co<sub>3</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> etc., were measured as shown in Figure 2-6. For a stable passive layer, a minimum solubility in Na<sub>2</sub>SO<sub>4</sub> is required. Metal oxides such as NiO and Co<sub>3</sub>O<sub>4</sub> are basic in nature and exhibit low solubility in basic sulfate electrolyte. On the other hand, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> are acidic in nature and retain a low solubility in acidic sulfate environment. Corrosive environments within most of the high temperature turbines exhibit a sulfate chemistry, which corresponds to the low solubility range of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> phases. Therefore, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> based passive layers are desirable for hot corrosive applications.



Figure 2-6. Solubilities of common metal oxides in fused  $Na_2SO_4$  electrolyte solution at 1200 K [59–62]

# 2.6 Electrochemical Aspects of Hot Corrosion Reactions

The hot corrosion of nickel alloys involves the liberation of electrons at the reaction site, which react with the surrounding species to form corrosion products [9]. For example, in sulfate

induced degradation, alkali sulfates (e.g.  $Na_2SO_4$ ) dissociate to their ionic form ( $Na^+$  and  $SO_4^{2-}$ ) and react with metal elements (e.g. nickel). Hot corrosion depends on two electrochemical reactions, known as cathode and anode half-cell reactions. During the corrosion process, the metal element tends to lose electrons (anode reaction) and corrosive species such as  $O_2$ ,  $SO_3$ ,  $SO_4^{2-}$  consume them (cathode reaction) as follows [63].

$$M \rightarrow M^{n+} + n e^{-}$$
Reaction 2-3 $X + n e^{-} \rightarrow Y$ Reaction 2-4

where X denotes the participating corrosive species and Y is the corresponding reduced phase.

Interestingly, the anode half-cell reaction is usually predictable. For example, the electrochemistry of pure nickel corrosion indicates the anode half-cell reaction is Ni  $\rightarrow$  Ni<sup>2+</sup> + 2e<sup>-</sup>. Conversely, the reduction reaction(s) of sulfate ions in hot corrosive environment are more complex. Sulfate-induced hot corrosion has been widely studied in the literature. However, an understanding of the electrochemical properties of molten sulfates still remains incomplete. This is due to the complex speciation behavior of sulfur-bearing species (e.g., SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, S<sup>2-</sup>, SO<sub>3</sub> etc.) with a variety of proposed reaction pathways at high temperatures. For example, Liu and Johnson *et al.* suggested that sulfate ions (SO<sub>4</sub><sup>2-</sup>) can be directly reduced to elemental sulfur (S), sulfite (SO<sub>3</sub><sup>2-</sup>), and/or sulfide (S<sup>2-</sup>) ions [64,65]; whereas Burrows and Wrench *et al.* concluded that sulfate ions are not directly reducible species in molten salts [66,67]. In addition, several reduction reactions involving SO<sub>3</sub> were also proposed under an oxidizing O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> atmosphere. Sequeira and Shores *et al.* suggested that SO<sub>3</sub> molecules can be reduced into S<sup>2-</sup> and/or SO<sub>2</sub> [68,69]; Park and Rapp proposed that pyrosulfate ions (S<sub>2</sub>O<sub>7</sub><sup>2-</sup>) are first formed from the equilibrium reaction of:

$$SO_4^{2-} + SO_3 = S_2O_7^{2-}$$
 Reaction 2-5

and further reduced into  $SO_4^{2-}$  and  $SO_3^{2-}$  [70]. Therefore, it is evident that the reduction reactions of sulfate ions during the alloy degradation are still unsettled in the literature due to the complex speciation of sulfur bearing species.

## 2.7 Objective of the Current Work

The hot corrosion of nickel based alloys has been widely studied using popular methods such as the exposure test and burner-rig test, and corroborated with thermodynamic stability calculations of corrosion products. However, the available literature on the electrochemical corrosion of nickel alloys [35,71–75] remained focused on complex engineering alloys with compositions similar to given in Table 2-1. In order to strengthen our understanding of the hot corrosion behavior of nickel alloys, a fundamental knowledge on the role of individual elements of the alloy compositions is required but currently not available.

Electrochemical studies rely on the interfacial kinetics of metallic systems in the corrosive environment and can be directly correlated with other methodologies, e.g. burner-rig test [35]. An electrochemical understanding of hot corrosion can provide a fundamental view of metal degradation in sulfate containing environments. In addition, due to the high sensitivity of electrochemical measurements, a relatively short time in comparison to the other methodologies is required to assess the corrosion behavior of a given alloy. Therefore, electrochemical measurements can be applied as an initial screening on a large batch of alloys, and thus provide economic benefits in the development of new alloy compositions for coating applications. This dissertation strives to build a fundamental electrochemical understanding towards the corrosion behavior of nickel alloys in the hot corrosive environment. Specifically, efforts have been made to understand the role of passive scale forming elements (aluminum and chromium) in nickel alloys to counter corrosion in gas turbines under type II (650–750 °C) corrosion mechanism. First, an understanding of the reduction behavior of sulfate (SO<sub>4</sub><sup>2–</sup>) ions was developed by performing electrochemical measurements in molten sulfate salt at 700 °C. Then, the influence of gaseous species (O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>) on the reduction of sulfate ions and/or their participation in corrosion reactions has been studied [Chapter 3]. Within the perspective of building an understanding towards the passive protection provided by alumina and chromia layers in hot corrosive environment, the effect of aluminum and chromium addition in nickel has been investigated by electrochemical methods. The electrochemical corrosion behavior of  $\beta$ -NiAl has been studied to contrast with pure Ni. Further, effect of Cr addition in  $\beta$ -NiAl to improve alumina based passivation has been explored. To corroborate electrochemical findings, immersion tests were performed in parallel and corrosion morphologies were interpreted in terms of possible degradation reactions [Chapter 4]. Moreover, the corrosion resistance of Ni-Al-Cr alloys was understood by varying Cr content under different environments of pure O<sub>2</sub> and O<sub>2</sub>-0.1%(SO<sub>2</sub>+SO<sub>3</sub>) gases. The observed corrosion behavior has been explained on the basis of alloy microstructure, integrity of passive scale, and electrochemical corrosion potentials and resistance [Chapter 5].

# Chapter 3

# Electrochemical Studies of Molten Sulfates in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C

## **3.1 Introduction**

Aggressive chemical and thermal environments found in industrial and marine gas turbines are well known to accelerate the degradation of materials in hot section components. The liquidstate dissociation of metal sulfates, e.g.:

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$$
 Reaction 3-1

suggests that the degradation of alloys will proceed through interfacial electrochemical reactions at the alloy/molten sulfate interface. Thus, understanding the electrochemical behavior of corrosive molten sulfate is important in the study of sulfate-induced hot corrosion reaction mechanisms as well as in evaluating alloy performance under molten sulfate environments. Some of the previous studies on the electrochemical reduction reactions of sulfur-bearing species are summarized in Table 3-1, including the electrolyte system and the temperature of investigation. It is evident, that a wide range of  $SO_4^{2-}$  ion reduction reactions have been reported [64,65,70]. Also, few reports suggested that direct reduction of sulfate ions was not possible and the involvement of  $SO_3$  species in the reduction mechanism was suggested [68–70]. Notably, Burrows and Hills [66] and Wrench and Inman [67] reported that sulfate ions are non-reducible species.

Reactions	Electrolyte	<i>T</i> (°C)	Ref.
Direct sulfate ion (SO <sub>4</sub> <sup>2-</sup> ) reduction			
(a) $SO_4^{2-} + 2e^- \rightarrow SO_3^{2-} + O^{2-}$	Li <sub>2</sub> SO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub>	625	[64]
	Li <sub>2</sub> SO <sub>4</sub> -Na <sub>2</sub> SO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub>	550	[65]
(b) $SO_4^{2-} + 6e^- \rightarrow S + 4O^{2-}$	Li <sub>2</sub> SO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub>	625	[64]
	Li <sub>2</sub> SO <sub>4</sub> -Na <sub>2</sub> SO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub>	550	[65]
(c) $SO_4^{2-} + 8e^- \rightarrow S^{2-} + 4O^{2-}$	Li <sub>2</sub> SO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub>	625	[64]
	$Na_2SO_4$	900	[70]
(d) sulfate ions are not reducible	Li <sub>2</sub> SO <sub>4</sub> -K <sub>2</sub> SO <sub>4</sub>	625	[66]
	NaCl-KCl-Na <sub>2</sub> SO <sub>4</sub>	750	[67]
<b>Reduction reactions involving SO<sub>3</sub></b>			
(e) $SO_4^{2-} = SO_3 + O^{2-}$			
$SO_3 + 2e^- \rightarrow SO_2 + O^{2-}$	Na <sub>2</sub> SO <sub>4</sub> / Na <sub>2</sub> SO <sub>4</sub> -NaCl	900	[68]
$\mathrm{SO}_3 + 8\mathrm{e}^- \longrightarrow \mathrm{S}^{2-} + 3\mathrm{O}^{2-}$			
(f) $S_2O_7^{2-} + 8e^- \rightarrow SO_4^{2-} + S^{2-} + 3O^{2-}$			
$SO_3 + 2e^- \rightarrow SO_2 + O^{2-}$	Na <sub>2</sub> SO <sub>4</sub>	900	[69]
$SO_3^{2-} + 6e^- \rightarrow S^{2-} + 3O^{2-}$			
(g) $SO_4^{2-} + SO_3 = S_2O_7^{2-}$	N. 60	000	
$S_2O_7^{2-} + 2e^- \rightarrow SO_4^{2-} + SO_3^{2-}$	Na <sub>2</sub> SO <sub>4</sub>	900	[70]

Table 3-1. Summary of reduction reactions in sulfate system reported in the literature, including the electrolyte system and the temperature [64–70].

In order to accurately understand the role of sulfate ions in hot corrosive environment, an exact reduction mechanism of sulfate ions becomes very important. This work specifically investigated the electrochemical behavior of molten sulfates at 700 °C, in particular, sulfate reduction reactions which will be coupled with the metal oxidation reactions in hot corrosion process. In this study, sodium sulfate (5–15 mol%) was dissolved into eutectic LiCl-KCl (59-41 mol%,  $T_{\text{eutectic}} = 353$  °C) to observe the characteristic reduction waves of the sulfate system using cyclic voltammetry in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolytes. These measurements were conducted under two different gaseous atmospheres of inert argon and oxidizing O<sub>2</sub>-0.1% SO<sub>2</sub> to contrast the electrochemical behavior of molten sulfates. Reaction products derived from sulfate reduction under constant potentials were also characterized. Other proposed reactions involving sulfite (SO<sub>3</sub><sup>2-</sup>) and pyrosulfate (S<sub>2</sub>O<sub>7</sub><sup>2-</sup>) ions were examined within the context of thermal stability of these species at temperatures above 700 °C.

## 3.2 Experimental

## 3.2.1 Electrochemical Cell Components and Assembly

<u>Electrolytes</u>: Anhydrous LiCl (Alfa Aesar, Product No. 10515), KCl (Sigma Aldrich, Product No. 746436), and Na<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich, Product No. 238597) were weighed in appropriate quantities and mixed together inside argon-filled glovebox ( $O_2 < 0.5$  ppm). The dry mixture of LiCl-KCl or LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> was placed in an alumina crucible ( $60 \times 104$  mm or 39  $\times$  91 mm in diameter and height; McDanel Advanced Ceramics).

The dry, homogeneous reference electrolyte (LiCl-KCl-AgCl) was prepared by adding 1 wt% (0.39 mol%) of AgCl in LiCl-KCl eutectic composition. The mixed powder was poured into a quartz crucible (24 mm diameter and 14 cm height) and loaded in the vacuum-tight stainless steel chamber. The chamber was evacuated to less than 1.3 Pa, heated at 80 °C for 12 h, at 230 °C for 12 h under vacuum, purged with ultra high-purity argon three times, and heated at 700 °C for 3 h

for pre-melting under flowing argon atmosphere (~50 mL/min). The pre-melted reference electrolyte was ground into a fine powder for the preparation of reference electrode.

<u>Electrodes</u>: A reference electrode (RE) was constructed using a closed-end mullite tube (6.35 cm outer diameter, 4.78 mm inner diameter, and 45.7 cm length; Coorstek), which contained about 0.5 g of LiCl-KCl-AgCl electrolyte and a silver wire (1 mm diameter and 48 cm length) to establish a reversible Ag/Ag<sup>+</sup> half-cell potential at 700 °C. The open-end of the mullite tube was sealed with epoxy under inert argon atmosphere. A graphite counter electrode (CE) was fabricated in a cylindrical shape (9.5 mm diameter and 5 cm length) and connected to a stainless steel electrical lead (3.2 mm × 46 cm threaded rod in diameter and length).

Working electrodes (WEs) were selected among tungsten wire, platinum or glassy carbon rods (1 mm diameter). Tungsten WE was selected for the LiCl-KCl electrolyte because tungsten is immiscible with metallic lithium; however, platinum or glassy carbon (GC) can react with lithium to form intermetallic compounds (e.g., Li<sub>2</sub>Pt) during cathodic polarization. Platinum and glassy carbon WEs were used in the LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolytes because the tungsten WE was found to dissolve into the LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte during cathodic polarization. The Pt or GC rods were cut in 4 cm lengths, inserted into a graphite adapter (9.5 mm diameter and 2 cm length), and the adapter was connected to a stainless steel electrical lead. A schematic cell configuration and approximate electrode geometry are shown in Figure 3-1.

<u>Electrochemical cell assembly</u>: The electrochemical cell assembly was conducted inside an argon-filled glove box due to the hygroscopic nature of alkali-metal chlorides and sulfate. A three-electrode electrochemical cell was assembled by arranging the electrodes inside an alumina crucible that contained 30–70 g of the mixed electrolyte, and the cell was placed inside the stainless steel test chamber (Figure 3-1). Stainless steel baffle plates were installed to maintain a uniform temperature inside the test chamber. The sealed cap was designed to include seven ultra-torr fitting ports for insertion of electrical leads and a thermocouple. All the electrical leads were electrically isolated from the stainless steel chamber using alumina tubes (6.4 mm outer diameter, 4.8 mm inner diameter, and 30 cm length).



Figure 3-1. Schematic of experimental set-up for measurements of electrochemical properties in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte at 700 °C: (a) electrochemical cell configuration (top view) and approximate electrode geometry, and (b) test chamber assembly.

In experiments under oxidizing, reactive  $O_2$ -0.1%  $SO_2$  atmosphere, an alumina test chamber (10.5 cm inner diameter, 11.4 cm diameter outer diameter, and 43 cm length; Coorstek) was employed in place of the stainless steel test chamber. A platinum mesh (2.5 × 2.5 cm) was rolled and inserted into the gas inlet tube located inside the test chamber to facilitate an equilibrium partial pressure of  $SO_3$  according to:

$$\frac{1}{2}O_2(g) + SO_2(g) = SO_3(g)$$
 Reaction 3-2

The assembled test chamber was loaded into a crucible furnace (CC-12, The Mellen Company, Inc.) and evacuated to less than 1.3 Pa. The electrochemical cell inside the test chamber was dried using a similar procedure described for preparing the reference electrolyte to remove residual moisture from the cell components, and then heated at 700 °C under flowing argon. The cell temperature was recorded using K-type thermocouple enclosed in a closed-end quartz tube and thermocouple data acquisition board (NI 9211, National Instruments).

#### **3.2.2 Electrochemical Measurements**

Electrochemical signals were collected using a potentiostat-galvanostat (Metrohm, PGSTAT 302F). Once the electrochemical cell reached the target temperature 700 °C, the stability of reference electrodes was verified by measuring the potential difference between the two identical Ag/Ag<sup>+</sup> REs. The electrochemical measurements were performed when the potential difference between the two REs remained less than 5 mV. For measurements under oxidizing atmosphere, O<sub>2</sub>-0.1% SO<sub>2</sub> gas mixture (Airgas) was introduced at the flow rate of ~50 ml/min after a thermal steady-state was achieved. During the transition from argon to O<sub>2</sub>-0.1% SO<sub>2</sub> atmosphere, the open circuit potentials of the platinum WE were continuously monitored.

Cyclic voltammetry was conducted at scan rates of 10–100 mV/s using a tungsten WE in LiCl-KCl (59-41 mol%), and platinum or glass carbon WEs in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53-37-10 mol%). Prior to electrochemical measurements in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte, uncompensated solution resistance  $R_{\rm u}$  was estimated using electrochemical impedance spectroscopy (EIS) to correct

potential drop ( $I \cdot R_u$ ) in the measurements. As is typical for highly conductive molten salt electrolytes, a low solution resistance was obtained, typically less than 0.3  $\Omega$  [Figure A-1, Appendix A]. The nominal surface area of WEs was estimated to be 0.50 cm<sup>2</sup>, based upon the immersion depth of WEs in the electrolyte (1.6 cm). At selected potentials, separate electrolysis experiments were conducted in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolytes under constant potential control to obtain electrolysis products from sulfate reduction reactions for characterization.

### 3.2.3 Characterization of LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> Electrolyte

After the constant potential electrolysis, the electrochemical cell was cooled to room temperature and disassembled inside the glovebox. The electrolyte was isolated from the cell assembly for further characterization by scanning electron microscope (SEM, FEI Quanta 200) fitted with energy dispersive spectroscopy (EDS) for chemical analysis, and by X-ray diffractometer (XRD, PANalytical Empryean) over  $2\theta$  angles 20–70° with step size of 0.026°, dwell time per step of 200s, and scan rate of 0.033°/s for phase characterization. Finally, simultaneous differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were conducted using a thermal analyzer (STA 449, Netzsch Instruments). About 30–50 mg of powdered salt samples were loaded into an alumina crucible and data were collected during the heating cycle at a heating rate of 10 °C/min under 100 ml/min high-purity flowing Ar gas.

#### 3.3 Results and Discussion

#### 3.3.1 Electrochemical Reduction of Sulfate Ions under Inert Argon Atmosphere

Prior to the investigation into the electrochemical reduction behavior of sulfate ions, cyclic voltammograms were obtained in the eutectic LiCl-KCl to identify the electrochemical window and relevant faradaic processes using a tungsten WE at 700 °C under inert argon atmosphere. These voltammograms were commenced towards the cathodic region and concluded from anodic region (*i.e.* negative and positive potentials, respectively, *w.r.t.* open circuit potential of tungsten WE),

which showed negative current densities in forward scan and positive current densities in reverse scan. As shown in Figure 3-2(a) (dashed line), the electrochemical window of the LiCl-KCl was approximately 3.0 V at a scan rate of 100 mV/s and delimited by the decomposition reactions of LiCl: lithium metal reduction at -2.1 V vs. Ag/Ag<sup>+</sup> and chlorine gas evolution at +0.9 V vs. Ag/Ag<sup>+</sup>. At chlorine evolution potential, a small anodic wave preceding the linearly rising current region was also observed, which could be due to a passive WCl<sub>2</sub> layer formation on tungsten WE according to:

$$W + Cl_2(g) \rightarrow WCl_2, \quad \Delta_r G = -145.5 \text{ kJ/mol at } 700 \text{ }^{\circ}C \text{ [39]}$$
 Reaction 3-3







**(b)** 





Figure 3-2. Cyclic voltammograms at 700 °C under inert argon atmosphere: (a) a comparison between LiCl-KCl electrolyte using tungsten working electrode (WE), (dashed line) and LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte using platinum WE (solid lines) at scan rate of 100 mV/s, (b-c) comparisons between platinum and glassy carbon WEs in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte at scan rate of 100 mV/s, and (d) comparison at various scan rates of 10–100 mV/s using platinum WE.

Upon the addition of 10 mol% Na<sub>2</sub>SO<sub>4</sub> into the eutectic LiCl-KCl electrolyte, two additional reduction waves were obtained at the same scan rate within the electrochemical window using platinum WE [solid lines in Figure 3-2(a)]. The first reduction wave (thin solid line) started at -0.3 V vs. Ag/Ag<sup>+</sup> with a peak current density of -2.5 mA/cm<sup>2</sup>, and the second wave (thick solid line) started at -1.1 V vs. Ag/Ag<sup>+</sup> with a peak current density as high as -790 mA/cm<sup>2</sup>. In reversal scans of the second wave, the anodic peak current was substantially smaller and the anodic peak potential was widely separated from cathodic peak potential, suggesting that the reduction reactions are chemically irreversible.

Using a glassy carbon WE, voltammetric measurements were conducted over a similar potential range and compared with platinum WE [Figure 3-2(b) and 3-2(c)]. As shown in Figure 3-2(b), a strong reduction wave was observed at large overpotentials (E < -1.1 V vs. Ag/Ag<sup>+</sup>) for both glassy carbon and platinum WEs, confirming the direct reduction of sulfate ions independent of electrode materials. In contrast, the first reduction wave observed with platinum WE was absent from the glassy carbon WE [Figure 3-2(c)], suggesting that this reduction wave may originate from the pristine platinum surface oxides according to:

$$PtO_2 + 2e^- \rightarrow PtO + O^{2-}$$
 Reaction 3-4

 $PtO_2 + 4e^- \rightarrow Pt + 2O^{2-}$ .

The above redox reaction 3-5 of platinum oxides may explain the fading of the first reduction wave during multiple scans over a large potential range.

Voltammograms were also obtained at various scan rates of 10–100 mV/s using a platinum WE [Figure 3-2(d)]. As the scan rate increased, the reduction current density increased monotonically; however, the peak potentials were substantially shifted in the negative direction, indicating sluggish charge transfer kinetics of sulfate reduction reactions. It should be noted that during the reversal scan, several oxidation waves were observed possibly due to reaction products from sulfate reduction.

Briefly summarizing, voltammetric study suggests that the sulfate ions can be reduced in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte at sufficiently negative overpotentials (E < -1.1 V vs. Ag/Ag<sup>+</sup>) under inert argon atmosphere, and the sulfate reduction processes exhibit a high degree of irreversibility due to the chemically irreversible reactions and sluggish charge transfer kinetics. Reduction behavior of sulfate ions was also investigated by varying the electrolyte solutions, e.g. Li<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub> and NaCl-Na<sub>2</sub>SO<sub>4</sub>.Interestingly, the reduction wave corresponding to sulfate ions remained invariant [Figure A-2, Appendix A]

Reaction 3-5

### 3.3.2 Electrolysis and Characterization of Electrolysis Products

Constant potential electrolysis experiments in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (10 mol%) were conducted for 24 h under inert argon atmosphere to identify the reaction products associated with sulfate reduction, using a platinum WE. From voltammetric measurements, two electrode potentials were selected at -0.4 V vs. Ag/Ag<sup>+</sup> and -1.6 V vs. Ag/Ag<sup>+</sup>, before and after the onset of sulfate reduction wave at -1.1 V vs. Ag/Ag<sup>+</sup>. At E = -1.6 V vs. Ag/Ag<sup>+</sup>, a steady cathodic current density (~110 mA/cm<sup>2</sup>) was observed during electrolysis, but very little cathodic current density (less than 0.8 mA/cm<sup>2</sup>) was observed at E = -0.4 V vs. Ag/Ag<sup>+</sup> [Figure 3-3(a)].



**(a)** 



**(b)** 

Figure 3-3. Constant potential electrolysis at 700°C in inert argon atmosphere using a platinum working electrode (WE) for 24 h: (a) in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (10 mol%) at potential, E = -0.4 V and -1.6 V vs. Ag/Ag<sup>+</sup>, and (b) in various Na<sub>2</sub>SO<sub>4</sub> compositions (5–15 mol%) in eutectic LiCl-KCl at potential, E = -1.6 V.

The electrolysis experiments were also performed at varying Na<sub>2</sub>SO<sub>4</sub> concentrations of 5– 15 mol% at E = -1.6 V vs. Ag/Ag<sup>+</sup> [Figure 3-3(b)]. In all Na<sub>2</sub>SO<sub>4</sub> compositions, substantial cathodic current densities of 110–180 mA/cm<sup>2</sup> were measured consistently, but the current density was not specifically dependent on the sulfate concentration. Such a behavior may originate from the sluggish charge transfer reactions of the sulfate ions at the electrode-electrolyte interface, compared to the mass transport kinetics of sulfate ions in the electrolyte.

Upon the completion of electrolysis in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (10 mol%), the electrochemical cell was cooled to room temperature, disassembled inside the glovebox, and the electrolyte was

separated to examine the electrolysis products. The electrolyte held at E = -0.4 V vs. Ag/Ag<sup>+</sup> retained a pristine white color exhibiting the overlapped regions of oxygen and sulfur in SEM-EDS elemental maps [Figure 3-4(a)], but the electrolyte held at E = -1.6 V vs. Ag/Ag<sup>+</sup> exhibited yellow color, in particular, near the electrolyte surface. In the electrolyzed salt at E = -1.6 V vs. Ag/Ag<sup>+</sup>, a distinct pure sulfur phase was identified without overlapping with oxygen region, as shown in elemental mappings of sulfur and oxygen [Figure 3-4(b)].







**(b)** 





(c)





Figure 3-4. Characterization of the LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (10 mol%) electrolyte after electrolysis at (a) potential, E = -0.4 V vs. Ag/Ag<sup>+</sup>, (b) potential, E = -1.6 V and 700°C for 24 h: elemental X-ray mappings of sulfur and oxygen taken from the surface of the electrolyte, (c) thermal analysis (DTA/TGA) obtained from ~50 mg of the electrolyte at 10 °C/min under 100 ml/min flowing argon, and (d) X-ray diffraction pattern of the electrolyzed electrolytes at potential, E = -1.6V and -0.4 V as well as the pristine electrolyte, compared to the diffraction patterns of Na<sub>2</sub>S<sub>2</sub>, S<sub>6</sub>, Li<sub>2</sub>SO<sub>4</sub>, NaCl, KCl, and LiCl from crystal structure database [76–78].

The electrolyzed salt at E = -1.6 V vs. Ag/Ag<sup>+</sup> was further characterized by TG-DTA at a heating rate of 10 °C/min and four characteristic endothermic peaks were apparent at 102 °C, 130 °C, 350 °C, and 395 °C [Figure 3-4(c)]. The peak at 102 °C is associated with the evaporation of residual water molecules due to the hygroscopic nature of the electrolyte, accompanied by ~4% weight loss of the sample. The peak at 130 °C is thought to be related to the melting of sulfur ( $T_m$ ,

**(d)** 

 $_{\rm S}$  = 115 °C), evidenced by the presence of sulfur from chemical analysis with SEM/EDS. The last two peaks at 350 °C and 395 °C come from the solidus and liquidus temperatures of the electrolyte. These two transition temperatures agree with those of pristine electrolyte at 355 °C and 397 °C, respectively [dashed lines in Figure 3-4(c)].

Finally, the phases of the electrolyzed salt were analyzed using XRD in comparison with the pristine electrolyte [Figure 3-4(d)]. The pristine electrolyte was mainly composed of LiCl, KCl, NaCl, and Li<sub>2</sub>SO<sub>4</sub>. Notably, diffraction peaks of Na<sub>2</sub>SO<sub>4</sub> were absent due to the following metathetical reaction during the solidification:

Na<sub>2</sub>SO<sub>4</sub> + 2LiCl 
$$\rightarrow$$
 2NaCl + Li<sub>2</sub>SO<sub>4</sub>,  $\Delta_r G = -32.7$  kJ/mol at 700 °C [39] Reaction 3-6

The diffraction peaks of the electrolyte at E = -0.4 V vs. Ag/Ag<sup>+</sup> were in good agreement with the pristine electrolyte, indicating no substantial electrolysis products.

In contrast, the electrolyzed salt at E = -1.6 V vs. Ag/Ag<sup>+</sup> exhibited several additional characteristic peaks, marked with \* and # in Figure 3-4(d). While a thorough phase analysis of the electrolyzed electrolyte was not feasible due to complex diffraction peaks of several co-existing compounds, the overall diffraction pattern suggested the presence of S<sub>6</sub> (#) and Na<sub>2</sub>S<sub>2</sub> (\*) phases. Interestingly, Jaroudi *et al.* investigated the reactions between pure sulfur and Na<sub>2</sub>S using Raman spectroscopy at 75–450 °C, and determined the formation of Na<sub>2</sub>S<sub>2</sub> phase according to:

$$Na_2S + S = Na_2S_2 [79]$$
Reaction 3-7

Then, the coexistence of Na<sub>2</sub>S<sub>2</sub> and sulfur in the electrolyzed salt at E = -1.6 V vs. Ag/Ag<sup>+</sup> assumes the presence of Na<sub>2</sub>S as the electrolysis products, suggesting that the sulfate ions were reduced to sulfide (S<sup>2-</sup>) and sulfur (S) during electrolysis at 700 °C, in agreement with the sulfate reduction reactions (b-c) in Table 3-1 [64,65,70].

## 3.3.3 Influence of Gaseous Atmosphere (O<sub>2</sub>-0.1% SO<sub>2</sub>)

The electrochemical behavior of sulfate ions was examined under the oxidizing, reactive atmosphere (O<sub>2</sub>-0.1% SO<sub>2</sub>) at 700 °C using a platinum WE in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (10 mol%) electrolyte. The equilibrium partial pressure of SO<sub>3</sub>,  $P_{SO_3}$ , was estimated to be  $7 \times 10^{-4}$  atm [39]. Even a small quantity of SO<sub>3</sub>(g) in a gas combustor has been known to cause a substantial increase in corrosion rates of alloys, known as low-temperature type II hot corrosion at 650–750 °C. At 650–750 °C, transition metal oxides (e.g., NiO or CoO) react with SO<sub>3</sub> to form transition metal sulfates e.g.:

$$NiO + SO_3 = NiSO_4$$
 Reaction 3-8

resulting in low-melting temperature sulfate mixtures such as Na<sub>2</sub>SO<sub>4</sub>-NiSO<sub>4</sub> ( $T_{\text{eutectic}} = 670 \,^{\circ}\text{C}$ ) and Na<sub>2</sub>SO<sub>4</sub>-CoSO<sub>4</sub> ( $T_{\text{eutectic}} = 580 \,^{\circ}\text{C}$ ) [37,41,44,80–82]. For this reason, the reduction reactions in molten sulfates under oxidizing atmosphere are often postulated to involve SO<sub>3</sub> and/or O<sub>2</sub>, for example:

$$SO_3 + 2e^- \rightarrow SO_2 + O^{2-}$$
 Reaction 3-9

and 
$$O_2 + 4e^- \rightarrow 2O^{2-}$$
 [69] Reaction 3-10

During the transition from inert argon to oxidizing O<sub>2</sub>-0.1%(SO<sub>2</sub>-SO<sub>3</sub>) atmosphere at 700 °C, a large shift in open circuit potential  $E_{OCP}$  was observed from 0.02 V to 0.65 V vs. Ag/Ag<sup>+</sup> ( $\Delta E_{OCP} = 0.63$  V) in the positive direction [Figure 3-5(a)]. In contrast, the open circuit potentials under inert argon atmosphere remained relatively steady at ~0.14–0.18 V vs. Ag/Ag<sup>+</sup> with a slight shift in the negative direction. Such high open circuit potentials under oxidizing atmosphere may originate from the presence of stronger oxidants such as O<sub>2</sub>, SO<sub>2</sub>, and/or SO<sub>3</sub> in the molten salt electrolyte.



Figure 3-5. (a) Open circuit potentials during the transition from inert argon to oxidizing  $O_2$ -0.1%(SO<sub>2</sub>-SO<sub>3</sub>) atmosphere and (b) cyclic voltammograms using platinum working electrode (WE) in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (10 mol%) at 700 °C under two different gaseous atmospheres.

In efforts to identify reduction reactions in molten sulfates under the oxidizing atmosphere, voltammetric measurements were conducted in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 50 mV/s. As shown in Figure 3-5(b), a single strong reduction wave was observed at potentials below -1.0 V vs. Ag/Ag<sup>+</sup>, similar to that observed under inert argon atmosphere (-1.1 V vs. Ag/Ag<sup>+</sup>). Based upon a similar potential range of this reduction wave to that under inert argon atmosphere, we may conclude that sulfate ions are directly reduced into sulfur and sulfide ions at large negative overpotentials in the oxidizing atmosphere. Hellstrom and Sequeira *et al.* studied sulfate reduction reactions in pure Na<sub>2</sub>SO<sub>4</sub> at 900 °C under oxidizing O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> atmosphere and also obtained a reduction wave at large negative overpotentials [68,83]. They concluded that this reduction wave may come from the reduction of SO<sub>3</sub> according to:

$$SO_3 + 2e^- \rightarrow SO_2 + O^{2-}$$
 Reaction 3-9

 $SO_3 + 8e^- \rightarrow S^{2-} + 3O^{2-}$  Reaction 3-11

reactions (e) in Table 3-1. However, by comparing the voltammograms under two different gaseous atmospheres in this work, this reduction wave is thought to be related to direct sulfate reduction at large overpotentials.

While a large open circuit potential shift in the positive direction suggests the presence of strong oxidants, no relevant reduction waves were observed, possibly due to insufficient concentrations of dissolved  $O_2$  or  $SO_3$  molecules in the electrolyte at 700 °C. Thus, the definite reduction mechanisms involving these oxidants remain inconclusive.

# **3.3.4 Sulfate Reduction Reactions**

Our electrochemical investigation into LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C confirmed that sulfate ions (SO<sub>4</sub><sup>2–</sup>) can be directly reduced at large negative overpotentials (E < -1.1 V vs. Ag/Ag<sup>+</sup>) in both inert argon and oxidizing O<sub>2</sub>-0.1%(SO<sub>2</sub>-SO<sub>3</sub>) atmospheres. Furthermore, the characterization of the electrolysis products at E = -1.6 V vs. Ag/Ag<sup>+</sup> suggests that a direct sulfate ion reduction can result in sulfur (S) and sulfide ion (S<sup>2-</sup>) according to the following reactions of:

$$SO_4^{2-} + 6e^- \rightarrow S + 4O^{2-}$$
 Reaction 3-12

and 
$$SO_4^{2-} + 8e^- \rightarrow S^{2-} + 4O^{2-}$$
 Reaction 3-13

in agreement with reactions (b-c) in Table 3-1. In view of large overpotential requirement for these reactions, Gibbs energies were calculated for the equivalent reduction of  $Na_2SO_4$  at 600 °C, 700 °C, and 800 °C using reference [39]. Table 3-2 shows that these reactions are associated with substantially high positive Gibbs energies, supporting that reduction of  $SO_4^{2-}$  species is an endothermic process requiring large overpotentials.

Table 3-2. Gibbs energies of  $Na_2SO_4$  reduction reactions at three different temperatures calculated from reference [39].

<b>B</b> eaction(s)	Gibbs Energy, ∆ <sub>r</sub> G (kJ/mole)		
Keaction(s)	600 °C	700 °C	800 °C
(a) $Na_2SO_4 \rightarrow Na_2O + S(g) + 3/2O_2(g)$	906.8	870.2	833.9
(b) $Na_2SO_4 \rightarrow Na_2S + 2O_2(g)$	720.0	688.1	656.6

Studies conducted at 550–625 °C by Liu and Johnson *et al.* also suggested that the sulfate ions are reduced to sulfite ions by the reaction of:

$$SO_4^{2-} + 2e^- \rightarrow SO_3^{2-} + O^{2-}$$
 Reaction 3-14

, the reaction (a) in Table 3-1 [64,65]; however, sulfite species were not observed in this work at 700 °C. To examine the possibility of forming sulfite ions at 700 °C, thermal analysis of pure sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) was conducted at the heating rate of 10 °C/min under flowing argon [Figure 3-6(a)]. In the TG-DTA thermmogram of Na<sub>2</sub>SO<sub>3</sub>, a sudden exothermic heat flow was observed during the heating, starting at ~677 °C without mass loss. The reaction associated with this exothermic heat flow was further investigated by heat-treating Na<sub>2</sub>SO<sub>3</sub> powder samples at 600 °C and 700 °C for 6 h under argon, respectively and each sample was characterized by XRD [Figure 3-6(b)].



Figure 3-6. Thermal analysis obtained from ~37 mg of  $Na_2SO_3$  powder at 10 °C/min under 100 ml/min flowing argon and (b) X-ray diffraction pattern of  $Na_2SO_3$  after heat treatment at 700 °C and 600 °C for 6 h, compared to the diffraction patterns of  $Na_2S$ ,  $Na_2SO_4$ , and  $Na_2SO_3$  from crystal structure database [76,78].

A sodium sulfite ( $Na_2SO_3$ ) sample treated at 600 °C maintained its pristine  $Na_2SO_3$  crystalline structure, however, the sample treated at 700 °C was comprised of  $Na_2S$  and  $Na_2SO_4$ , suggesting that sulfite will exothermically decompose into sulfide and sulfate according to:

$$Na_2SO_3 \rightarrow \frac{1}{4}Na_2S + \frac{3}{4}Na_2SO_4$$
 Reaction 3-15

, also supported by thermodynamic estimation ( $\Delta_r G = -38.1 \text{ kJ/mol at 700 °C}$ ) [39]. Considering the thermal instability of sulfite ions above 677 °C, the sulfate reduction reaction into sulfites:

$$SO_4^{2-} + 2e^- \rightarrow SO_3^{2-} + O^{2-}$$
 Reaction 3-14

may not be feasible at temperatures above 700 °C and was not observed in this study.

Several studies suggested that pyrosulfate ions  $(S_2O_7^{2-})$  can be formed under oxidizing atmosphere according to:

$$SO_4^{2-} + SO_3 = S_2O_7^{2-}$$
 Reaction 3-15

and be subjected to the reduction reactions, e.g. :

$$S_2O_7^{2-} + 2e^- \rightarrow SO_4^{2-} + SO_3^{2-}$$
 Reaction 3-16

at 900 °C [69,70]. However, De Vries and Gellings determined that sodium pyrosulfate ( $Na_2S_2O_7$ ) decomposes into  $Na_2SO_4$  and  $SO_3$  at temperatures above 330 °C according to:

$$Na_2S_2O_7 \rightarrow Na_2SO_4 + SO_3$$
 Reaction 3-17

based on thermogravimetric measurements and XRD analysis [84]. Based on the fact that both the pyrosulfate ( $S_2O_7^{2-}$ ) and sulfite ( $SO_3^{2-}$ ) ions are subjected to thermal decomposition reactions at typical temperatures of hot corrosion processes (650–950 °C), the formation of these species is thermodynamically unstable and may not occur in hot corrosion process at 900 °C. It is also to note that the observed reducibility of  $SO_4^{2-}$  in the present work is in contrast with the electrochemical inactivity reported by Burrows and Wrench *et al.* [66,67]. It is believed that due to sluggish reduction kinetics of  $SO_4^{2-}$  species, the amount of reduction products might have remained out of detection limits of their characterization method(s).

In the light of interfacial electrochemical processes in spontaneous hot corrosion of metal alloys, the cathodic (reduction) reactions in the sulfate system will need to be coupled with the anodic (oxidation) reactions of metal alloys [63], e.g.:

$$Ni \rightarrow Ni^{2+} + 2e^{-}$$
 Reaction 3-18

whose redox potential should be more negative than cathodic reactions. Figure 3.7 shows a cyclic voltammogram obtained with pure nickel WE in molten LiCl-KCl-10 mol% Na<sub>2</sub>SO<sub>4</sub> electrolyte under argon environment at 700 °C. An electrochemical potentials,  $E \ge -0.4$  V vs. Ag/Ag<sup>+</sup> is required to oxidize/corrode in sulfate containing environment. In this regard, the observed direct reduction reactions of sulfate ions (SO<sub>4</sub><sup>2–</sup>) may not be coupled with metal oxidation reactions due to their occurrence only at substantially negative overpotentials.



Figure 3-7. Cyclic voltammogram at a scan rate of 100 mV/s obtained with nickel working electrode (WE) in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (10 mol%) electrolyte under argon atmospheres at 700 °C.

In contrast, the shift in open circuit potential by ~0.63 V in the positive direction under oxidizing atmosphere, indicates the presence of strong oxidants such as  $SO_3$  and  $O_2$  in the

electrolyte. Assuming strong oxidants of  $O_2$  and  $SO_3$  are available and can be reduced at more positive potentials than sulfate ions, the reduction reactions of these oxidants are more likely to be coupled with the metal oxidation reactions, leading to spontaneous hot corrosion of metal alloys.

# 3.4. Summary

This study determined that sulfate ions (SO<sub>4</sub><sup>2–</sup>) can be reduced into S and S<sup>2–</sup> at 700 °C at large negative overpotentials:

$$SO_4^{2-} + 6e^- \rightarrow S + 4O^{2-}$$
 Reaction 3-12

and 
$$SO_4^{2-} + 8e^- \rightarrow S^{2-} + 4O^{2-}$$
 Reaction 3-13

At this temperature, sulfite ions  $(SO_3^{2^-})$  were not observed as a reduction product, possibly due to thermal instability of sulfite ions above 677 °C. Under oxidizing O<sub>2</sub>-0.1%(SO<sub>2</sub>-SO<sub>3</sub>) atmosphere, open circuit potentials were shifted in the positive direction, implying the presence of stronger oxidants such as O<sub>2</sub> and SO<sub>3</sub>. The reduction reactions of these oxidants are expected to occur at more positive potentials than sulfate ions (SO<sub>4</sub><sup>2-</sup>) and thus, are more likely to be coupled with the metal oxidation reactions during hot corrosion processes.

This study suggests that the reduction reactions of molten sulfate system are dependent upon (i) the degree of overpotential, (ii) gaseous atmosphere that can provide stronger oxidant in the molten sulfate electrolyte, and (iii) the thermal stability of sulfur-bearing species.

# **Chapter 4**

# Electrochemical Corrosion Behavior of Ni Alloys in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C: The Influence of Oxidizing Atmosphere and the Role of Oxygen-Active Elements (Al and Cr)

## **4.1 Introduction**

The degradation modes of hot corrosion are often classified as high temperature (Type I) hot corrosion (e.g., 900–1000 °C) and low-temperature (Type II) hot corrosion (e.g., 650–750 °C). This classification was made primarily based on the accelerated corrosion rates observed at these two temperature ranges, due to the formation of liquid-state salt deposits [27,37,41,82]. Based on sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) which melts at 884 °C, molten Na<sub>2</sub>SO<sub>4</sub> (Type I, 900–1000 °C) deposits were found to accelerate the degradation of Ni alloys under oxidizing atmospheres, especially in the presence of SO<sub>3</sub> [37,38,41]. At lower temperatures (Type II, 650–750 °C), the degradation reaction could be expected to decrease with solid-state Na<sub>2</sub>SO<sub>4</sub>; however, the degradation rate of Ni was also accelerated in SO<sub>3</sub>-containing atmosphere as NiO reacted with SO<sub>3</sub> molecules to form nickel sulfate (NiSO<sub>4</sub>), resulting in a molten sulfate solution (Na<sub>2</sub>SO<sub>4</sub>-NiSO<sub>4</sub>,  $T_{eutectic} = 670$  °C) [27,41].

A number of studies on sulfate-induced hot corrosion identified a variety of degradation reaction pathways, including sulfidation, formation of transition metal sulfates (NiSO<sub>4</sub> or CoSO<sub>4</sub>), as well as dissolution of metal oxides (e.g., NiO, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>) in the salt deposit (fluxing mechanisms) [59–62], all of which were influenced by gaseous atmosphere (e.g., O<sub>2</sub>, O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub>). In selecting Ni alloys to mitigate hot corrosion reactions, oxygen-active elements (Al and Cr) are critical constituents due to their capability to form protective oxide scales at elevated temperatures [52,47–49].

In both types of hot corrosion processes, the presence of sulfate-containing molten salts is the essential factor in accelerating the degradation reaction of Ni alloys by providing chemically aggressive ionic solutions (electrolytes), suggesting the utility of electrochemical corrosion testing of Ni alloys (electrodes) in understanding and evaluating their degradation behavior in addition to more popular approaches of coupon exposure and burner-rig tests [35]. This work specifically studied the sulfate-induced hot corrosion behavior of three Ni alloys (Ni,  $\beta$ -NiAl at 50-50 mol%, and Ni-Al-Cr at 47.5-47.5-5 mol%), using electrochemical open-circuit potential and potentiodynamic polarization techniques in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C. Due to the importance of gaseous atmosphere in hot corrosion processes [24,27,44,85], the electrochemical corrosion testing was conducted under the control of gaseous atmosphere: from inert argon to pure O<sub>2</sub> and to O<sub>2</sub>-0.1%SO<sub>2</sub> gas mixture.

Overall, electrochemical corrosion measurements in this work aimed to elucidate the effects of gaseous atmosphere and oxygen-active elements (Al and Cr) in hot corrosion processes, by comparing the stability of oxide scales from each alloy in the molten salt: NiO scale from Ni, Al<sub>2</sub>O<sub>3</sub> scale from  $\beta$ -NiAl, and mixed Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> scale from Ni-Al-Cr. The electrochemical corrosion behavior of Ni alloys was corroborated with the results from immersion tests in the same environment by characterizing the chemistry and microstructure of corrosion scales. The morphologies of the corrosion layers and degradation reactions were discussed within the context of prior hot corrosion studies in the literature under similar environmental conditions.

#### **4.2 Experimental**

#### 4.2.1 Electrochemical Cell Components for Corrosion Testing

*Bulk electrolyte:* Sulfate-containing bulk electrolyte, LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%), was prepared from appropriate weights of lithium chloride (anhydrous, 99.0%, Alfa Aesar, product # 10515), potassium chloride (KCl, 99.0%, Sigma Aldrich, product # 746436), and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, 99.0%, Sigma Aldrich, product # 238597) inside an argon filled glovebox (O<sub>2</sub> and H<sub>2</sub>O < 0.5 ppm) due to the hygroscopic nature of salts. Weighed salts were contained in a plastic

bottle (500 mL) and mixed together by manually shaking the bottle. About 70 g of the bulk electrolyte mixture was poured into an alumina crucible (5.4 cm inner in diameter and 11 cm in height) for electrochemical cell assembly.

*Electrodes:* The alloy working electrodes (WEs) of pure Ni,  $\beta$ -NiAl (50-50 mol%), and Ni-Al-Cr (47.5-47.5-5 mol%) were prepared from pure metals of Ni wire (99.5%, 1 mm in diameter, Alfa Aesar, product # 41361), Al wire (99.0%, 1 mm in diameter, Alfa Aesar, product # 11064), and Cr pieces (99.995%, Alfa Aesar, product # 38494) using an arc-melter (MAM1, Edmund Buhler GmbH). Homogeneous alloys were fabricated in the form of cylindrical rods (0.3 cm in diameter and 3.0 cm in length) by suction casting in a copper mold. The arc-melted alloy rods were annealed at 1100 °C for 24 h under vacuum (< 5 mtorr) to stabilize their microstructures, and the alloy surface was polished using silicon carbide emery papers to remove surface oxides produced during the alloy fabrication. The alloy WEs were electrically connected to stainless steel rods (3.2 mm in diameter, 46 cm in length). Pure Ni WEs were connected to stainless steel rods via stainless steel adapters using 5-40 threads; the brittle  $\beta$ -NiAl and Ni-Al-Cr alloy WEs were directly tied to stainless steel rods using Ni-Cr (78-22 mol%) wire (0.25 mm in diameter), as shown in Figure 4-1(a).







Figure 4-1. Schematic of three-electrode electrochemical cell: (a) approximate electrode geometry for working (WE), reference (RE), and counter (CE) electrodes, and (b) top view of electrode configuration (left) in a test chamber assembly (right).

The Ag/Ag<sup>+</sup> reference electrode (RE) was constructed using a closed one-end mullite tube (6.4 mm in outer diameter, 4.8 mm in inner diameter, and 45.7 cm in length) which contained ~1.0 g of LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> reference electrolyte and Ag wire (1 mm in diameter and 48 cm in length) to establish Ag/Ag<sup>+</sup> half-reaction [Figure 4-1(a)]. The reference electrolyte, LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> (48-33-9-10 mol%), was prepared by adding 10 mol% of Ag<sub>2</sub>SO<sub>4</sub> (99.999%, Sigma Aldrich, product # 204412) into the bulk electrolyte composition. The electrolyte mixture was placed in a quartz crucible (24 mm in inner diameter and 14 cm in length) for premelting in a
stainless steel vacuum chamber. The chamber was loaded in a crucible furnace (Mellen, CC-12), evacuated to less than 5 mtorr, and heated under vacuum at 80 °C for 12 h and at 230 °C for 12 h to remove residual moisture. Then, the chamber was purged with ultra-high purity argon three times, heated at 700 °C for 3 h for premelting, and cooled to room temperature under flowing argon. In an argon-filled glovebox, the dry and homogeneous reference electrolyte was crushed into a fine power, the powder was poured into the mullite tube with Ag wire inserted, and the open-end of the mullite tube was sealed using epoxy.

A graphite rod (0.95 cm in diameter and 1 cm in length) was used as the counter electrode (CE), female threaded at the top and connected to a male threaded steel rod (3.2 mm in diameter, 46 cm in length) via 5-40 threads [Figure 4-1(a)]. The stainless steel rod above the graphite CE was sheathed with a threaded boron nitride (BN) tube (6.35 mm in outer diameter, 3.2 mm in inner diameter, and 1.5 cm in length) in order to minimize its direct exposure to the corrosive bulk electrolyte during the electrochemical measurements.

#### 4.2.2 Electrochemical Cell Assembly and Measurements

*Cell assembly:* Electrochemical corrosion testing of Ni alloys was conducted in a closed one-end alumina test chamber (10.5 cm in inner diameter, 11.4 cm in outer diameter, and 43 cm in length, Coorstek). The chamber was capped with a stainless steel flange (QF100-BF, Kurt J. Lesker) where seven ultra-torr fittings (6.35 mm in inner diameter, Swagelok) were installed to insert electrical leads and a thermocouple (ASTM type K), and was sealed using a silicone O-ring between the test chamber and the flange [Figure 4-1(b)]. The alumina crucible filled with the bulk electrolyte (~70 g) was placed inside the test chamber, on the flat surface established with alumina powder. Two of each WE, RE, and CE were inserted through vacuum fittings of the cap until each electrode touched the bottom of the alumina crucible with the configuration shown in Figure 4-1(b). Electrical leads for WEs and CEs were electrically isolated from stainless steel flange using

quartz tubing (6.35 mm in outer diameter, 4.0 mm in inner diameter, and 15 cm in length) and the top end of the tube was sealed using epoxy. The K-type thermocouple was placed in the electrolyte, but was enclosed by a closed one-end quartz tube (46 cm in length) to avoid the direct contact of the thermocouple sheath (stainless steel) with the corrosive electrolyte at 700 °C.

The assembled test chamber [Figure 4-1(b)] was loaded into a vertical crucible furnace, evacuated to less than 5 mtorr, and heated under vacuum at 80 °C for 12 h and at 230 °C for 12 h to remove moisture from the cell components and the electrolyte mixture. Then, the chamber was purged with ultra-high purity argon three times, heated to 700 °C under flowing argon (~50 mL/min) and the cell temperature was recorded using a thermocouple data acquisition board (NI 9211, National Instruments). Under inert argon, the electrochemical cell was allowed to equilibrate until the cell temperature reached a steady temperature at 700 °C ( $\pm$ 4 °C) and until the potential difference between the two identical REs was less than 5 mV to ensure reliable electrochemical measurements.

*Electrochemical measurements:* Once the cell reached the steady temperature at 700 °C and RE stability within 5 mV difference under inert argon, the electrodes were connected to potentiostat-galvanostat (PGSTAT 302F, Metrohm) for electrochemical measurements using three-electrode cell configuration (graphite CE and Ag/Ag<sup>+</sup> RE). For experiments under oxidizing atmospheres, pure O<sub>2</sub> gas (Praxair) or O<sub>2</sub>-0.1%SO<sub>2</sub> gas mixture (Praxair, OX SD1000C-AS) was introduced into the test chamber at the flow rate of ~50 mL/min, and the open-circuit potentials of the alloy WEs were measured for about 12 h. In the case of experiments under O<sub>2</sub>-0.1%SO<sub>2</sub> atmosphere, a platinum mesh (2.5 cm  $\times$  2.5 cm) was rolled and inserted into the gas inlet tube in order to establish equilibrium partial pressure of SO<sub>3</sub> by facilitating the following reaction:

$$\frac{1}{2}O_2(g) + SO_2(g) = SO_3(g).$$
 Reaction 4-1

The equilibrium partial pressure of SO<sub>3</sub> ( $P_{SO_3}$ ) in O<sub>2</sub>-0.1%SO<sub>2</sub> was estimated at 7 × 10<sup>-4</sup> atm from the above reaction [39].

Following open-circuit potential measurement for 12 h, the alloy WE was subjected to potentiodynamic polarization and the current response was measured in each gaseous atmosphere. The electrode potential of each WE was initially applied at 0.05 V more negative than the open-circuit potential, swept in the anodic (positive) direction at a scan rate of 1 mV/s, and terminated at 0.50 V more positive than the open-circuit potential. Upon completion of electrochemical measurements, the alloy WEs were raised above the bulk electrolyte solution, the cell was cooled to room temperature, and the immersion depth of alloy WEs was measured. Based on the immersion depth (1.6 cm) of the alloy WEs in the electrolyte, the exposed surface area was estimated to be 1.58 cm<sup>2</sup>.

### 4.2.3 Immersion Test and Characterization of Corrosion Layer

In separate experiments using an equivalent set-up in Figure 4-1, the alloys of pure Ni,  $\beta$ -NiAl, and Ni-Al-Cr were immersed in the LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte at 700 °C for 12 h in each gaseous atmosphere. After 12 h immersion, the alloy samples were raised above the electrolyte under argon atmosphere, the test chamber was cooled to room temperature, and the test samples were detached for characterization. Diffraction patterns were obtained from the surface of each alloy sample by X-ray diffractometer (XRD, PANalytical Empryean) over 2 $\theta$  angles of 20–70° with step size of 0.026°, dwell time per step of 100s, and scan rate of 0.033°/s for phase characterization for phase identification. In order to characterize the corrosion layer, the tested alloy samples were cut and mounted using epoxy resin and hardener (Allied High Tech Products) at the ratio of 12:1 for metallographic sample preparation. The samples were ground up to 2000 grit using silicon carbide abrasive papers and polished with diamond powder (6–1 µm) dispersed in ethylene glycol. The polished samples were sputter-coated with gold at ~10 nm thickness and characterized using scanning electron microscopy (SEM, FEI Quanta 200) fitted with energy dispersive spectroscopy (EDS).

## 4.3 Results and Discussion

Electrochemical corrosion behavior of Ni alloys (Ni,  $\beta$ -NiAl, and Ni-Al-Cr) was investigated in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte at 700 °C. Each alloy electrode was subjected to open-circuit potential ( $E_{OCP}$ ) measurements for 12 h, followed by potentiodynamic polarization measurements under three different gaseous atmospheres of inert Ar, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>. The current density (*j*) of each electrode, based on exposed surface area, was obtained as a function of overpotential  $\eta$  (=  $E - E_{OCP}$ ) over  $-0.05 \text{ V} \le \eta \le +0.50 \text{ V}$  at a scan rate of 1 mV/s and the polarization curve (log |*j*| vs.  $\eta$ ) was plotted and compared. The electrochemical response of each alloy in each atmosphere was corroborated from the characterization of corrosion layer obtained from immersion testing for 12 h using SEM-EDS and XRD. These results were compared and analyzed to elucidate the influence of oxidizing atmosphere on the degradation reaction pathways as well as the effect of alloying elements (Al and Cr) in controlling the corrosion resistance of Ni alloys.

# 4.3.1 Electrochemical Behavior and the Corrosion Scale of Pure Ni

Under inert argon, the open-circuit potential ( $E_{OCP}$ ) of pure Ni electrode was initially at about -0.65 V (vs. Ag/Ag<sup>+</sup>) and reached steady-state value at -0.73 V (vs. Ag/Ag<sup>+</sup>) [Figure 4-2(a)]. In contrast, the transition from inert argon to oxidizing atmospheres resulted in a large shift in  $E_{OCP}$ in the opposite direction:  $E_{OCP} = -0.25$  V (vs. Ag/Ag<sup>+</sup>) in pure O<sub>2</sub>, and  $E_{OCP} = -0.29$  V (vs. Ag/Ag<sup>+</sup>) in O<sub>2</sub>-0.1%SO<sub>2</sub> after 12 h. Such a rapid rise in  $E_{OCP}$  could be attributed to the presence of strong oxidants (O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>) in the electrolyte [85], which also resulted in a large increase in currents during anodic polarization [Figure 4-2(b)], indicating accelerated corrosion rate of Ni under oxidizing atmospheres. Compared to the lowest anodic currents obtained under inert argon, the anodic currents increased by 25–45 times in oxidizing atmospheres of both pure O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub>.



Figure 4-2. Electrochemical behavior of pure Ni in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in three different gaseous atmospheres of argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>. (a) Open-circuit potential measurements for 12 h and (b) potentiodynamic polarization curve (log |j| vs.  $\eta$ ) at a scan rate of 1 mV/s over -0.05 V <  $\eta$  < +0.50 V.

Electrochemical behavior of Ni under each gaseous atmosphere was well correlated with the results from immersion testing (Figure 4-3): the formation of uniform NiO scale under inert argon leading to low anodic currents, and non-protective corrosion scales under oxidizing atmospheres leading to increased anodic currents. The corrosion scale thickness drastically changed from 5  $\mu$ m in argon to ~374  $\mu$ m in pure O<sub>2</sub> and ~143  $\mu$ m in O<sub>2</sub>-0.1%SO<sub>2</sub>, indicating a rapid corrosion rate of Ni under oxidizing atmospheres. Under inert argon, phase constituents in the corrosion scale included NiO and Ni<sub>3</sub>S<sub>2</sub>, evidenced by X-ray elemental mapping [Figure 4-3(a)] and XRD [Figure 4-3(d)], suggesting the reaction of Ni metal with the sulfate ions:

$$9Ni + 2SO_4^{2-} = 6NiO + Ni_3S_2 + 2O^{2-}$$
. Reaction 4-2

Under oxidizing atmospheres, diffraction peaks of NiO were evident, but stronger peaks were obtained from the electrolyte phase comprised of KCl, NaCl, and Li<sub>2</sub>SO<sub>4</sub> [Figure 4-3(d)] [76– 78]. Diffraction peaks of Li<sub>2</sub>SO<sub>4</sub> and NaCl, instead of Na<sub>2</sub>SO<sub>4</sub> and LiCl, were observed due to the metathesis reaction in the electrolyte:

$$Na_2SO_4 + 2LiCl = Li_2SO_4 + 2NaCl$$
 ( $\Delta_r G = -32.7 \text{ kJ at } 700 \text{ }^{\circ}C$  [39]). Reaction 4-3

The change from argon to pure  $O_2$  atmosphere destabilized the uniform NiO layer, resulting in the dispersed NiO phase within the electrolyte and the formation of nickel sulfide layer at the metal-scale interface [Figure 4-3(b)]. A similar degradation morphology was also observed by Goebel and Pettit [38] who investigated hot corrosion of Ni coated with Na<sub>2</sub>SO<sub>4</sub> at 1000 °C in air, and identified a porous NiO scale mixed with Na<sub>2</sub>SO<sub>4</sub> as well as nickel sulfide layer at the metaloxide interface. The formation of non-protective oxide scale in air was postulated to occur due to the following reaction:

$$2NiO + \frac{1}{2}O_2(g) + O^{2-} = 2NiO_2^{-}$$
 Reaction 4-4

, resulting in an accelerated dissolution of NiO. The dissolution mechanism of NiO, reaction (4), was rationalized based on the measured solubility of NiO in Na<sub>2</sub>SO<sub>4</sub> as functions of oxygen partial pressure ( $P_{O_2}$ ) and the activity of Na<sub>2</sub>O ( $a_{Na_2O}$ ) at 927 °C by Gupta and Rapp [60].

The accelerated dissolution of NiO under pure  $O_2$  would expose Ni metal surface to the electrolyte, allow the direct reaction of Ni with the sulfate ions, reaction 4-2, and result in a sulfide layer at the metal-scale interface.

The addition of 0.1% SO<sub>2</sub> in O<sub>2</sub> resulted in a complex corrosion scale comprised of several sub-layers [Figure 4-3(c)]: (i) top layer enriched with NiO and nickel sulfides, (ii) electrolyte-rich middle layer which included globular nickel sulfides and dissolved Ni ions, and (iii) nickel sulfide layer at the metal-scale interface. The presence of nickel sulfides in the scale was the most prominent in O<sub>2</sub>-0.1% SO<sub>2</sub>, possibly due to the reaction of Ni with SO<sub>2</sub> or SO<sub>3</sub>:

$7Ni + 2SO_2 = 4NiO + Ni_3S_2$	$(\Delta_{\rm r}G = -201.6 \text{ kJ at } 700 ^{\circ}\text{C})$	Reaction 4-5
$9\mathrm{Ni} + 2\mathrm{SO}_3 = 6\mathrm{NiO} + \mathrm{Ni}_3\mathrm{S}_2.$	$(\Delta_r G = -488.4 \text{ kJ at } 700 ^{\circ}\text{C} \text{ [39]}).$	Reaction 4-6



**(a)** 







Figure 4-3. (a-c) SEM and elemental X-ray mapping images of pure Ni samples after immersion tests for 12 h in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in each gaseous atmosphere of (a) argon, (b) pure O<sub>2</sub>, and (c) O<sub>2</sub>-0.1%SO<sub>2</sub>. (d) XRD patterns from the corroded Ni surface.

Furthermore, the SO<sub>3</sub> molecules in O<sub>2</sub>-0.1%SO<sub>2</sub> ( $P_{SO_3} = 7 \times 10^{-4}$  atm) are well known to

accelerate the dissolution of NiO into the bulk electrolyte [27]:

$$NiO + SO_3 = Ni^{2+} + SO_4^{2-}$$
 Reaction 4-7

, evidenced by X-ray mapping of Ni in the electrolyte-rich middle layer [Figure 4-3(c)]. While the presence of nickel sulfides was evident from SEM-EDS analysis, the diffraction peaks related to nickel sulfides (e.g., Ni<sub>3</sub>S<sub>2</sub>) were not detected [Figure 4-3(d)], possibly due to the formation of complex, off-stoichiometric nickel sulfides. The globular shape of nickel sulfides in the middle layer suggests that nickel sulfides could be in the liquid state at 700 °C. Based on the eutectic temperature (637 °C) and composition (~34 mol% S) from the binary Ni-S phase diagram

[86], the formation of liquid-state nickel sulfides at 700  $^{\circ}$ C is reasonable and supports the possibility of forming off-stoichiometric nickel sulfides away from the Ni<sub>3</sub>S<sub>2</sub> phase.

Overall, the corrosion behavior of Ni in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> was highly dependent upon the gaseous atmosphere which drastically affected the stability of NiO scale through the dissolution and/or formation of nickel oxides, sulfides, and sulfates. In the case of the uniform NiO layer in inert argon, the anodic currents during polarization could be related to the following anodic half-reactions:

$$Ni \rightarrow Ni^{2+} + 2e^-$$
 or Reaction 4-8

$$NiO + O^{2-} \rightarrow NiO_{2-} + e^{-}$$
 Reaction 4-9

; however, in oxidizing atmospheres, far more complex anodic half-reactions are expected due to the presence of additional degradation reaction pathways involving nickel sulfides and sulfates.

# 4.3.2 Electrochemical Behavior and the Corrosion Scale of β-NiAl Alloy

The electrochemical corrosion behavior of oxidation-resistant  $\beta$ -NiAl alloy was conducted in the same electrolyte (Figure 4-4) utilizing its excellent capability to form a protective alumina (Al<sub>2</sub>O<sub>3</sub>) scale as well as the lower solubility of Al<sub>2</sub>O<sub>3</sub> than that of NiO in pure Na<sub>2</sub>SO<sub>4</sub> [59–61]. Similar to the trend observed in Ni, the open-circuit potential ( $E_{OCP}$ ) was shifted in the negative direction under argon, and in the positive direction under both oxidizing atmospheres [Figure 4-4(a)]. However,  $\beta$ -NiAl electrodes under both oxidizing atmospheres exhibited a frequent but aperiodic drop in open-circuit potential, followed by gradual recovery towards steady-state values. A sudden drop and gradual recovery of open-circuit potential clearly indicates an instability of alumina scale in the electrolyte under oxidizing atmospheres, possibly in the form of localized damage (or transient pitting) in the alumina scale followed by repassivation [87]. Interestingly, the recovery time was about 10–20 min under pure O<sub>2</sub>, but was longer (20–180 min) under O<sub>2</sub>-0.1%SO<sub>2</sub>, implying a more sluggish recovery (or passivation) of the oxide scale in O<sub>2</sub>-0.1%SO<sub>2</sub>.



Figure 4-4. Electrochemical behavior of  $\beta$ -NiAl alloys in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in three different gaseous atmospheres of argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>. (a) Open-circuit potential measurements for 12 h and (b) potentiodynamic polarization curve (log |*j*| vs.  $\eta$ ) at a scan rate of 1 mV/s over -0.05 V <  $\eta$  < +0.50 V.

The subsequent polarization measurements of the  $\beta$ -NiAl alloy clearly differentiated the electrochemical corrosion behavior in each gaseous atmosphere [Figure 4-4(b)]. Compared to the lowest anodic currents in inert argon, the anodic currents increased by about three times under pure O<sub>2</sub>, and increased further by more than an order of magnitude under O<sub>2</sub>-0.1%SO<sub>2</sub>. Interestingly, the anodic currents under pure O<sub>2</sub> increased rapidly at large overpotentials above 0.40 V, suggesting a transpassive dissolution of alumina scale. In general, the anodic currents of  $\beta$ -NiAl electrode were lower than those of Ni, indicating better corrosion performance of  $\beta$ -NiAl with alumina scale. However, the stability of alumina scale in the electrolyte was questionable, in particular under oxidizing atmospheres, indicated by the instability in open-circuit potentials, transpassive dissolution at large overpotentials (pure O<sub>2</sub>), and high anodic currents (O<sub>2</sub>-0.1%SO<sub>2</sub>).

Under both inert argon and oxidizing atmospheres, the formation of alumina scale was confirmed by SEM-EDS and XRD (Figure 4-5). The alumina scale thickness after a 12 h immersion test was measured to be 5–13 µm under argon, 10–14 µm under pure O<sub>2</sub>, and 23–29 µm under O<sub>2</sub>-0.1%SO<sub>2</sub>. Notably, the alumina scale grown under O<sub>2</sub>-0.1%SO<sub>2</sub> was comprised of an intact inner layer and a defective outer layer with micro-cracks and increased sulfur content [Figure 4-5(c)]. The formation of the defective outer layer in O<sub>2</sub>-0.1%SO<sub>2</sub> could be attributed to the reaction of aluminum oxide with SO<sub>3</sub> molecules into solid aluminum sulfates, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ( $T_m = 770$  °C):

$$Al_2O_3 + 3SO_3 \rightarrow Al_2(SO_4)_3$$
 ( $\Delta_r G = -35.61 \text{ kJ at } 700 \text{ °C } [39]$ ) Reaction 4-10

, causing micro-cracks in the outer oxide layer and thus, the highest anodic currents [Figure 4-4(b)].



**(b)** 









Figure 4-5. (a-c) SEM and elemental X-ray mapping images of  $\beta$ -NiAl alloys after immersion tests for 12 h in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in each gaseous atmosphere of (a) argon, (b) pure O<sub>2</sub>, and (c) O<sub>2</sub>-0.1%SO<sub>2</sub>. (d) XRD patterns from the corroded  $\beta$ -NiAl surface.

Since the formation of alumina scale accompanies the selective consumption (or depletion) of Al from the  $\beta$ -NiAl substrate, a phase change occurred beneath the oxide scale: from a dense single-phase  $\beta$ -NiAl to microporous two-phase [ $\beta$ -NiAl +  $\gamma'$ -Ni<sub>3</sub>Al] microstructures (Figure 4-5). Similar two-phase porous microstructures were reported from oxidation studies of  $\beta$ -NiAl under oxidizing atmosphere ( $P_{0_2} = 0.13$  atm) at 900–1200 °C by Brumm and Grabke [88,89], where the formation of micropores was ascribed to outward diffusion of Al and inward diffusion of Ni from the chemical potential gradient of each element. Figure 4-6 shows the depth profiling on the cross sections of corroded alloys using optical microscope. It is to note that due to uneven oxide scale surfaces, depth profiling on metallic regions exhibited erroneous behavior; therefore, only metallic regions were analyzed. It was observed that regions far from the oxide scale exhibited plane surface indicated by red/orange colors. However, the regions closer to the oxide scale showed several nonplanar spots with large depth indicated by blue color. The presence of deeper sites in alloy crosssection indicate the pore formation during the hot corrosion.



(a)





Figure 4-6. Depth profile images of  $\beta$ -NiAl alloy after immersion tests in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution for 12 h at 700 °C under the gaseous atmospheres of (a) argon, (b) pure O<sub>2</sub>(g), and (c) O<sub>2</sub>-0.1%(SO<sub>2</sub> + SO<sub>3</sub>).

Compared to Ni, the formation of alumina scale from  $\beta$ -NiAl under pure O<sub>2</sub> enhanced corrosion resistance against the sulfate-containing electrolyte by blocking severe degradation reactions of Ni and NiO. Weight gain measurements were also performed with Ni and  $\beta$ -NiAl specimens coated with Na<sub>2</sub>SO<sub>4</sub> thin layer (~ 35 mg/cm<sup>2</sup>). At constant temperature of 700 °C, both, Ni and  $\beta$ -NiAl showed increased corrosion under the influence of SO<sub>2</sub>-SO<sub>3</sub> gases [Figure B-1, Appendix B]. A comparison between Ni and  $\beta$ -NiAl showed a lesser weight gain with  $\beta$ -NiAl confirming the superior corrosion resistance of Al<sub>2</sub>O<sub>3</sub> as compared to that of NiO. The instability of alumina scale was evident from electrochemical corrosion behavior. Moreover, the stability of alumina scale was severely deteriorated in O<sub>2</sub>-0.1%SO<sub>2</sub>, leading to high anodic currents comparable to those of pure Ni. Open circuit potential measurements were also performed with pre-oxidized  $\beta$ -NiAl specimen [Figure B-2, Appendix B]. Under SO<sub>2</sub>-SO<sub>3</sub> containing environment a sudden rise in OCP was noticed in contrast to the constant OCP for approximately 1.5 h under pure O<sub>2</sub>, suggesting that alumina scale is vulnerable to sulfur oxide gases.

### 4.3.3 Electrochemical Behavior and the Corrosion Scale of Ni-Al-Cr Alloy

The addition of 5 mol% Cr into  $\beta$ -NiAl (Ni-Al-Cr, 47.5-47.5-5 mol%) resulted in a much less frequent drop in open-circuit potential compared to  $\beta$ -NiAl, indicating enhanced stability of the oxide layer in both oxidizing atmospheres of pure O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub> [Figure 4-7(a)]. In contrast to  $\beta$ -NiAl which exhibited increased anodic currents from pure O<sub>2</sub> to O<sub>2</sub>-0.1%SO<sub>2</sub> by an order of magnitude [Figure 4-4(b)], the Ni-Al-Cr alloys could maintain low anodic currents under both oxidizing atmospheres [Figure 4-7(b)], indicating the beneficial effect of Cr against hot corrosion, especially under O<sub>2</sub>-0.1%SO<sub>2</sub>.



Figure 4-7. Electrochemical behavior of Ni-Al-Cr (47.5-47.5-5 mol%) alloys in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in oxidizing atmospheres of pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>. (a) Open-circuit potential measurements for 12 h and (b) potentiodynamic polarization curve (log |j| vs.  $\eta$ ) at a scan rate of 1 mV/s over -0.05 V <  $\eta$  < +0.50 V.

The cross-section analyses of the corrosion layer from the Ni-Al-Cr sample in each oxidizing atmosphere are displayed in Figure 4-8. Under both atmospheres of pure O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub>, intact oxide scales with 5–10 µm thickness were observed. Interestingly, the oxide scale was comprised of both Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>; however, Cr<sub>2</sub>O<sub>3</sub> was enriched in the outer layer and was depleted in the inner layer, suggesting a bilayer structure of the oxide scale. The composition of Cr by EDS was about 9–14 mol% in the outer layer, but was less than 0.8 mol% in the inner layer. While the diffraction peaks from Al<sub>2</sub>O<sub>3</sub> were identified by XRD [Figure 4-8(c)], the crystalline Cr<sub>2</sub>O<sub>3</sub> phase was not evident in the oxide scale, possibly due to the formation of a solid solution (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>). Due to the formation of a mixed oxide (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>) scale, the depletion of Al and Cr in the substrate also resulted in a phase change from [ $\beta$ -NiAl + Cr] to [ $\beta$ -NiAl +  $\gamma'$ -Ni<sub>3</sub>Al] beneath the oxide scale [Figure 4-8(c)].

SEM	Pure O <sub>2</sub> atmosphere
<u>10 µ</u> m	<ul> <li>Outer oxide scale</li> <li>Inner alumina scale</li> <li>Al/Cr depletion region</li> <li>(β-NiAl + γ'-Ni<sub>3</sub>Al)</li> <li>Ni-Al-Cr substrate</li> </ul>
Ni	Al
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Figure 4-8. (a-b) SEM and elemental X-ray mapping images of Ni-Al-Cr (47.5-47.5-5 mol%) alloys after immersion tests for 12 h in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in each gaseous atmosphere of (a) pure O<sub>2</sub> and (b) O<sub>2</sub>-0.1%SO<sub>2</sub>. (c) XRD patterns from the corroded Ni-Al-Cr surface.

Similar to the subsurface behavior observed with  $\beta$ -NiAl alloy, NiAl-5Cr also demonstrated the formation of micro-pores during the hot corrosion. Shida [90] reported the relative diffusivity of Cr in Ni stating the higher diffusion of Cr towards the alloy surface. As a result, NiAl-5Cr also developed micropores in the subsurface region due to opposite diffusion of Ni with respect to oxide scale formers (Al, Cr). Figure 4-9 shows the depth profiling on the cross-sections of corroded NiAl-5Cr alloys after degradation in sulfate electrolyte under pure oxygen and O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> environments.

The enhanced electrochemical corrosion behavior of Ni-Al-Cr alloy under oxidizing atmospheres (Figure 4-7) could be attributed to the  $Cr_2O_3$ -rich outer layer at the scale-electrolyte interface. The addition of Cr in Ni-Al alloys has been well known to enhance hot corrosion resistance in molten sulfates [23,52,25]. The beneficial effects of Cr (and Al) were postulated to occur due to the minimal solubility of  $Cr_2O_3$  and  $Al_2O_3$  under typical oxidizing atmospheres found in gas turbines ( $O_2$ -SO<sub>2</sub>-SO<sub>3</sub>) as well as the positive gradient of oxide solubility in the salt film (fluxing mechanisms) [59,62]. A number of oxidation studies of ternary Ni-Al-Cr alloys also identified a simulaneous formation of both oxides ( $Cr_2O_3$ -Al\_2O\_3) in thermally grown oxide scales, and that the various types of oxide scales with complex structures can be formed depending upon alloy composition, oxidation temperature, and gaseous atmosphere [52,47,91]. The formation of mixed-oxide scale ( $Cr_2O_3$ -Al\_2O\_3) in this work could be explained based on the gaseous oxidation mechanisms; however, the detailed mechanism in sulfate-containing molten salts could be more complicated due to the continuous dissolution of oxides at 700 °C.



**(b)** 



Figure 4-9. Depth profile images obtained from the cross-sections of corroded Ni-Al-Cr (47.5-47.5-5 mol%) alloy after immersion tests in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution for 12 h at 700 °C under the gaseous atmospheres of (a) pure  $O_2(g)$ , and (b)  $O_2$ -0.1% (SO<sub>2</sub> + SO<sub>3</sub>).

### 4.3.4 Effect of Al and Cr in Hot Corrosion Resistance of Ni Alloys

In each gaseous atmosphere, polarization curves of three Ni alloys were compared and further analyzed to contrast the effects of Al and Cr addition (Figure 4-10). Based on the stable anodic currents observed at an overpotential range of 0.10–0.30 V (log | j| vs.  $\eta$ ) in each curve, corrosion current density ( $j_{corr}$ ) was evaluated by extrapolation into corrosion potential ( $E_{corr}$ ), similar to an approach used for Tafel extrapolation under active dissolution of corroding metal [40,92]. Unlike typical passivation characteristics in an aqueous system near room temperature, the anodic currents continued to increase in sulfate-containing molten salts at 700 °C. The analyzed results are summarized in Table 4-1, including the estimated anodic slope ( $d \log |j| / d\eta$ ) as well as the corrosion scale thickness obtained from immersion tests by SEM.





Figure 4-10. Potentiodynamic polarization curves (log |j| vs.  $\eta$ ) of Ni alloys in (a) argon, (b) pure O<sub>2</sub>, and (c) O<sub>2</sub>-0.1%SO<sub>2</sub>, at a scan rate of 1 mV/s at 700 °C after 12 h immersion in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte.

Table 4-1. Open circuit potential ( $E_{corr}$ ), corrosion current density ( $j_{corr}$ ), and the slope (  $d \log |j| / d\eta$ ), estimated from polarization curve of Ni alloys over 0.10 V <  $\eta$  < 0.30 V in each gaseous atmosphere, as well as corrosion scale thickness. Measured after immersion for 12 h at 700 °C in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte.

Gaseous atmosphere	Alloy	$E_{ m corr}$ vs. Ag/Ag <sup>+</sup> (V)	j <sub>corr</sub> (mA/cm²)	d log j /dη (dec/V)	Scale thickness (µm)
Ar	Ni	-0.75	0.26	3.56 (±0.01)	5.0 (±1.5)
	β-NiAl	-0.76	0.25	2.16 (±0.02)	15 (±2)
O <sub>2</sub>	Ni	-0.25	11.97	2.90 (±0.02)	374 (±20)
	β-NiAl	-0.20	0.78	2.18 (±0.02)	12 (±2)
	Ni-Al-Cr	-0.10	0.55	2.47 (±0.03)	8 (±1.2)
O2-0.1%SO2	Ni	-0.30	7.03	3.42 (±0.01)	143 (±12)
	β-NiAl	-0.40	8.86	1.19 (±0.01)	26 (±3)
	Ni-Al-Cr	+0.05	0.09	2.71 (±0.02)	7.5 (±1.5)

In inert argon, comparable corrosion current densities ( $0.25-0.26 \text{ mA/cm}^2$ ) were obtained for both Ni/NiO and  $\beta$ -NiAl/Al<sub>2</sub>O<sub>3</sub> electrodes; however, the lower slope ( $d \log j / d\eta$ ) for  $\beta$ -NiAl/ Al<sub>2</sub>O<sub>3</sub> than Ni/NiO indicates a better stability of Al<sub>2</sub>O<sub>3</sub> than NiO during anodic polarization [Figure 4-10(a)]. In pure O<sub>2</sub>, the corrosion current density of Ni substantially increased to 11.97 mA/cm<sup>2</sup>, compared to 0.78 mA/cm<sup>2</sup> for  $\beta$ -NiAl and 0.55 mA/cm<sup>2</sup> for Ni-Al-Cr alloys, indicating enhanced hot corrosion resistance of Al<sub>2</sub>O<sub>3</sub> and/or Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> scales [Figure 4-10(b)]. However, the addition of 0.1%SO<sub>2</sub> resulted in an increased corrosion current density of  $\beta$ -NiAl at 8.86 mA/cm<sup>2</sup> [Figure 4-10(c)], compared to 0.78 mA/cm<sup>2</sup> in pure O<sub>2</sub>, due to the defective oxide scale [Figure 4-5(c)]. In contrast, the corrosion current densities of Ni-Al-Cr were the lowest among the tested Ni alloys at 0.09 mA/cm<sup>2</sup> in O<sub>2</sub>-0.1%SO<sub>2</sub> and 0.55 mA/cm<sup>2</sup> in pure O<sub>2</sub>. In other words, hot corrosion performance of Ni-Al-Cr alloys was enhanced by forming an oxide scale that incorporates both  $Al_2O_3$  and  $Cr_2O_3$  under oxidizing atmospheres, evidenced by the lowest corrosion current density as well as intact oxide scale.

# 4.4 Summary

Electrochemical corrosion properties of Ni alloys (Ni,  $\beta$ -NiAl, and Ni-Al-Cr) were determined in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte under three different gaseous atmospheres (inert argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>) at 700 °C. Pure Ni developed a uniform NiO layer only in the inert argon atmosphere, and rapidly degraded in oxidizing atmospheres due to the formation of non-protective corrosion scales comprised of NiO, nickel sulfides, and nickel sulfate. The  $\beta$ -NiAl alloys developed alumina scales under oxidizing atmospheres with an indication of local breakdown of the oxide film during open-circuit potential measurements. Moreover, the  $\beta$ -NiAl alloy performed poorly in O<sub>2</sub>-0.1%SO<sub>2</sub>, indicated by a high corrosion current density and non-protective oxide scale with micro-cracks. The addition of 5 mol% Cr in  $\beta$ -NiAl (Ni-Al-Cr alloy) enhanced corrosion resistance both under pure O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub>: the lowest corrosion current density among the tested alloys and the formation of thin, intact oxide scales comprised of both Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. Overall, hot corrosion resistance of Ni alloys in the sulfate-containing molten salt was affected by gaseous atmosphere and alloying elements (Al and Cr), both of which controlled the formation of oxide scales as well as their stability.

# Chapter 5

# Electrochemical Corrosion Behavior of Ni-Al-Cr Alloys in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C: The effect of Cr Content

# 5.1 Introduction

High temperature components are constructed using nickel based superalloys which are surface enriched with aluminum to nucleate  $\beta$ -NiAl phase and counter hot corrosion [23,24]. The stability of nickel-based alloys in hot corrosive environments relies on passive protection from an alumina scale which results from the oxidation of aluminum on the alloy surface. However, the alumina passive layer undergoes localized damages resulting in internal metal oxidation and reduced corrosion resistance in sulfate containing environment [43,48,49]. Usually, passivity is lost at few local sites, exposing the metal surface to corrosive species [SO<sub>4</sub><sup>2-</sup>, O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>].

In order to improve the integrity of the alumina scale and corrosion resistance of nickel alloys, the addition of secondary elements such as platinum, iridium, palladium, ruthenium, hafnium, and chromium in  $\beta$ -NiAl has been studied [25,47–49]. Leyens *et. al.* reported that Cr addition in  $\beta$ -NiAl imparts the most beneficial effect in obtaining improved corrosion resistance against molten Na<sub>2</sub>SO<sub>4</sub> [25]. Task *et. al.* stated that Cr addition supports the rapid formation of the Al<sub>2</sub>O<sub>3</sub> scale on  $\beta$ -NiAl at the beginning of hot corrosion as well as in the event of localized damage, improving the corrosion resistance drastically [48,49]. Thus, the addition of Cr in  $\beta$ -NiAl is necessary to obtain higher corrosion resistance in a hot corrosive environment. Though the beneficial effects of Cr in  $\beta$ -NiAl are established, studies reporting the dependence of corrosion resistance on the chromium content in ( $\beta$ )NiAl-Cr alloys are sparse in the literature [25].

During hot corrosion, dissociation of molten  $Na_2SO_4$  into  $Na^+$  and  $SO_4^{2-}$  ions suggests the utility of electrochemical measurements in assessing corrosion properties, in addition to the popular

methodologies – burner-rig test and exposure test [35]. Specifically, this study aims to elucidate the corrosion behavior of Ni-Al-Cr alloys with varying chromium content ( $0 \le Cr \le 10.0$  at%) [Table 5-1] in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte solution at a constant temperature of 700 °C. Electrochemical measurements including open circuit potential (OCP) and potentiodynamic polarizations were conducted on Ni-Al-Cr alloys under the controlled gaseous environment of pure O<sub>2</sub> and O<sub>2</sub>–0.1%(SO<sub>2</sub> + SO<sub>3</sub>). In parallel, immersion tests were performed with Ni-Al-Cr alloys in similar experimental environments to corroborate electrochemical measurements with the microstructural and phase analyses on corroded alloy specimens. Briefly, corrosion properties of Ni-Al-Cr alloys such as corrosion rate, corrosion potential, and thickness of oxide scale (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>) were measured under each of pure O<sub>2</sub> and O<sub>2</sub>–0.1%(SO<sub>2</sub> + SO<sub>3</sub>) environments. Further, these corrosion properties were compared to distinguish the role of the sulfur oxide species on the corrosion behavior of each alloy composition.

Alloy	Elemental Composition				
·	Ni (at%)	Al (at%)	Cr (at%)		
β-NiAl	50.0	50.0	0		
NiAl-1Cr	49.5	49.5	1.0		
NiAl-2.5Cr	48.75	48.75	2.5		
NiAl-5Cr	47.5	47.5	5.0		
NiAl-7.5Cr	46.25	46.25	7.5		
NiAl-10Cr	45.0	45.0	10.0		

Table 5-1. Elemental composition of Ni-Al-Cr alloys considered in the present study

# **5.2 Experimental**

# 5.2.1 Synthesis of Ni-Al-Cr Alloys and Ternary Phase Diagram

Weights of pure nickel (Ni, 99.5%), aluminum (Al, 99.0%), and chromium (Cr, 99.995%) were calculated to synthesize Ni-Al-Cr alloys. These alloys were prepared in rod shape (3.0 mm diameter, 3.0 cm height) using an arc-melter (MAM1, Edmund Buhler GmbH). In order to remove

any metastable phase during the cooling in the arc-melter, alloy specimens were annealed at 1100 °C for 24 h under vacuum (< 5 mtorr). Annealed specimens were further polished using silicon carbide (SiC) abrasive papers up to 600 grit and ultrasonically cleaned in isopropanol twice for 10 min each. Thermodynamic calculations were performed to understand the microstructural behavior of Ni-Al-Cr alloys. Utilizing the elemental databases reported by Dupin *et al.* [93], Thermo-Calc software [94] was used to calculate the Ni-Al-Cr ternary phase diagram at 700 °C.

# 5.2.2 Electrochemical Measurements and Immersion test

Experimental procedure to perform the electrochemical measurements was similar as described in Chapter 4. Briefly, electrochemical assembly consisting of two instances of Ni-Al-Cr working electrodes (WEs), and Ag/Ag<sup>+</sup> reference electrodes (REs) with one graphite counter electrode (CE) was developed as shown in Figure 5.1, following the electrode preparation steps, as described in Section 4.2.1. After achieving temperature equilibrium (700 ± 4 °C) and verifying the stability of reference electrodes, open circuit potentials and potentiodynamic polarization measurements were performed with Ni-Al-Cr alloy WEs in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte (53.3-36.7-10 mol%) under different environments of pure O<sub>2</sub> and O<sub>2</sub>-0.1% (SO<sub>2</sub>-SO<sub>3</sub>) at a flow rate of ~50 mL/min, with the similar steps as described in Section 4.2.2. Further, to validate the reproducibility of electrochemical measurements, potentiodynamic polarization measurements were repeated with few selected compositions of Ni-Al-Cr alloys. As shown and discussed in Appendix C, a reproducible current densities were observed over applied overpotentials (-0.05  $\leq \eta \leq$  +0.50 V) during these measurements [Figure C-1 and C-2, Appendix C].

Additionally, corrosion studies on Ni-Al-Cr alloys included electrochemical impedance spectroscopy. An electrochemical potential with 10 mV AC amplitude was applied on NiAl-5Cr WE within the frequency range of 0.1Hz – 100kHz. The obtained impedance response was used to draw Nyquist plots and understand the growth behavior of the passive layer (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>) under different gaseous environments of pure  $O_2$  or  $O_2$ -SO<sub>2</sub>-SO<sub>3</sub>. Corrosion behavior of Ni-Al-Cr alloys was also studied by performing immersion tests with annealed alloy specimens, following the experimental procedures described in Section 4.2.3.



Figure 5-1. Schematic of electrochemical cell depicting the configuration of Ni-Al-Cr working electrode (WE), graphite counter electrode (CE), Ag/Ag+ reference electrode (RE), and thermocouple in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte at 700 °C.

# 5.3 Results and Discussion

# 5.3.1 Microstructural Analysis of Ni-Al-Cr Alloys

Annealed Ni-Al-Cr alloys were analyzed using X-ray diffraction and energy dispersive spectroscopy. Based on the diffraction patterns, the alloys were found to be composed of two distinct phases – (i)  $\beta$ -NiAl (BCC) and (ii) elemental Cr (BCC) as shown in Figure 5-2(a). It is believed that elemental Cr settles along the grain boundaries in polycrystalline  $\beta$ -NiAl as well as develop separate regions. As shown in Figure 5-2(b), elemental distribution of Cr in Ni-Al-Cr alloys shows the distinct regions of pure Cr phase. It was also observed that Cr regions grew in size with increasing content of Cr in Ni-Al-Cr alloys, which ultimately leads to interconnected Cr regions in NiAl-10Cr alloy.

In order to understand the growth of Cr regions in Ni-Al-Cr alloys, solubility of Cr in  $\beta$ -NiAl was evaluated utilizing thermodynamic and mobility databases [93,94] at 700 °C and 1 atmosphere pressure. A complete ternary phase diagram depicting the phase behavior of Ni-Al-Cr alloys at 700 °C is shown in Figure 5-2(c). Based on the calculated phase equilibria, Ni-Al with 1:1 stoichiometry ( $\beta$  phase) has a negligible affinity for Cr addition, supporting our XRD results that Ni-Al-Cr alloys with an equal fraction of nickel and aluminum are composed of  $\beta$ -NiAl (BCC) and Cr (BCC) phases.



**(a)** 







Figure 5-2. Microstructural analysis of Ni-Al-Cr alloys by (a) X-ray diffraction patterns, (b) X-ray EDS elemental maps for Cr distribution on annealed alloys over  $0.01 \le Cr \le 0.10$ , and (c) calculated ternary phase diagram using thermodynamic and mobility database [93,94] at 700 °C at 1 atmosphere pressure (Courtesy: Bi-Cheng Zhou<sup>1</sup>).

# 5.3.2 Corrosion Behavior of Ni-Al-Cr Alloys under Pure O2

Initially, electrochemical hot corrosion of Ni-Al-Cr alloys was assessed by measuring open

circuit potentials of freely corroding alloy working electrodes. After obtaining thermal equilibrium

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in the electrochemical cell, the inert argon atmosphere was replaced with pure  $O_2$  at a flow rate of ~50 mL/min. During the transition,  $\beta$ -NiAl and Ni-Al-Cr alloys demonstrated a sudden rise in the open circuit potential [Figure 5-3(a)] possibly arising due to the stronger oxidizing ability of  $O_2$  gas. Within a few minutes, quasi-stable potentials of Ni-Al-Cr alloys were observed. Notably,  $\beta$ -NiAl WE showed frequent drops in the open circuit potentials and subsequent recovery. A drop in OCP suggests exposure of the alloy surface to the electrolyte and gaseous species, due to the localized damage in the passive scale of alumina. However, subsequent diffusion of aluminum toward the  $\beta$ -NiAl surface heals these damaged sites through fresh growth of alumina, leading to the recovery of the electrochemical potentials. Interestingly, alloy specimens with Cr showed reduced instability in the OCP measurements, suggesting that Ni-Al-Cr alloys develop a more stable passive scale [Figure 5-3(a)]. Moreover, Ni-Al-Cr alloys showed a similar potential trend and achieved similar magnitudes after 12 h long measurements as indicated by NiAl-1Cr, and NiAl-10Cr alloys in Figure 5-3(a), implying that a small amount of Cr is sufficient to improve the integrity of alumina scale on  $\beta$ -NiAl.

Corrosion behavior of Ni-Al-Cr alloys was further evaluated by performing immersion tests in molten sulfate solutions for 12 h under pure O<sub>2</sub>. Surface morphologies of corroded alloy specimens are shown in Figure 5-3(b). After the immersion tests, Ni-Al-Cr alloys developed a bilayer passive scale composed of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> phases with Cr<sub>2</sub>O<sub>3</sub> present on the edge of the oxide scale. Elemental maps representing the distribution of nickel, aluminum, chromium, oxygen, and sulfur are given in Figure C-3 of Appendix C. The relative presence of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> phases in the passive scale is in agreement with the reported oxidation behavior of Ni-Al-Cr alloys at 1000 – 1200 °C under oxygen ( $P_{O_2}$ = 0.1 atm) by Giggins and Pettit [52]. During corrosion, both Al and Cr diffuse toward the alloy surface; however, the relative diffusivity of Cr is faster due to its presence along grain boundaries and in separate phase regions [Figure 5-2(b)], causing preferential formation of Cr<sub>2</sub>O<sub>3</sub>. On continued chromium oxide growth, the partial pressure of oxygen below

the chromia layer decrease to sufficiently inhibit the growth of  $Cr_2O_3$ . Due to lower oxygen requirement for the formation of Al<sub>2</sub>O<sub>3</sub> than that for  $Cr_2O_3$  (~10<sup>-51</sup> atm and ~10<sup>-32</sup> atm, respectively, [39]), alumina growth takes place in the reduced oxygen environment below the chromia layer.

All the composition of Ni-Al-Cr alloys showed similar corrosion behavior, having an Al<sub>2</sub>O<sub>3</sub> layer on the alloy surface and Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> solid solution on the outer edge of the passive scale, agreeing with the corrosion behavior of Ni-Al-Cr (59-36-5.0 at%) alloy at 700 °C reported by Task *et. al.* [48]. Notably, Cr<sub>2</sub>O<sub>3</sub> was detected as a minor phase in the passive layer on alloys with Cr  $\leq$  2.5 at%. On further addition of Cr, the presence of Cr<sub>2</sub>O<sub>3</sub> became stronger. Based on the enhanced growth of Cr<sub>2</sub>O<sub>3</sub>, the overall thickness of the passive layer on Ni-Al-Cr alloys increased with increasing Cr content [Figure 5-3(b)]. It is also noteworthy that after corrosion, alloy specimens developed Al and Cr depleted phases in the subsurface region [beneath the passive scale] which also exhibited the presence of micro-size pores. Similar pore formation was observed by Brumm and Grabke [88,89] during the oxidation studies of  $\beta$ -NiAl under oxidizing atmosphere ( $P_{O_2} = 0.13$  atm) at 900–1200 °C. It was suggested that diffusion. Due to relatively higher diffusivity of nickel ( $D_{Ni}$ ) with respect to aluminum ( $D_{Al}$ ), the subsurface region develops lattice vacancies. After coalescing, these lattice vacancies produced micro-pores which could also result in the poor adherence of the passive scale as observed for NiAl-10Cr in Figure 5-3(b).

To evaluate the corrosion resistance of the grown passive scale on these alloys, potentiodynamic polarization measurements were performed at a scan rate of 1 mV/s within the overpotential range of  $-0.050 \text{ V} \le \eta \le 0.50 \text{ V}$ . Figure 5-3(c) shows the electrochemical current response plotted on a logarithmic scale as a function of applied overpotentials. Due to interest in corrosion behavior of these alloys, oxidation current response at positive overpotentials ( $\eta > 0 \text{ V}$ ) has been considered to compare the corrosion resistance. It was noticed that anodic currents of

these alloys decreased with increasing Cr, implying the beneficial effect of chromium in acquiring higher corrosion resistance.

Utilizing the extrapolation of linear regions ( $\eta = 100-300 \text{ mV}$ ) in polarization plots (*i.e.*  $log | j| vs. \eta$ ), corrosion current densities (at  $\eta = 0$ ) and slopes of linear region ( $dlog | j / / d\eta$ ) have been calculated and are presented in Table 5-2 along with corrosion potentials and thickness of passive layer (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>). Considering the corrosion potential of  $\beta$ -NiAl at  $-0.202 \text{ V} vs. \text{ Ag/Ag}^+$  and Ni-Al-Cr alloys between -0.143 V and  $-0.080 \text{ V} vs. \text{ Ag/Ag}^+$ , it is believed that Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> scale growth on Ni-Al-Cr alloys imparts a similar passive surface under pure O<sub>2</sub>. Therefore, the decreasing corrosion current densities may arise due to reduced ionic diffusion through thicker passive scales. In summary, open circuit potentials, corrosion morphology, and polarization measurements on Ni-Al-Cr alloys demonstrated that chromium addition in  $\beta$ -NiAl provides higher corrosion resistance in molten sulfate under pure O<sub>2</sub> environment.








Figure 5-3. (a) Open circuit potentials measured for ~12 h, (b) corrosion morphologies of Ni-Al-Cr ( $0 \le Cr \le 0.10$ ) alloys, (c) potentiodynamic polarization plots ( $\log |j| \text{ vs. } \eta$ ) at a scan rate of 1 mV/s over -0.05 V <  $\eta$  < +0.50 V after immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C for 12 h under pure O<sub>2</sub> gas.

Alloy	E <sub>corr</sub> vs. Ag/Ag <sup>+</sup> (V)	$j_{\text{corr}} (\eta = 0)$ (mA/cm <sup>2</sup> )	d log  j  /dη (dec/V)	Scale thickness (µm)
β–NiAl	-0.202	0.78	2.18 (±0.02)	12 (±2)
NiAl-1Cr	-0.109	0.66	2.34 (±0.03)	2.3 (±0.8)
NiAl-2.5Cr	-0.080	0.76	2.14 (±0.02)	8.7 (±0.97)
NiAl-5Cr	-0.096	0.55	2.47 (±0.03)	8 (±1.2)
NiAl-7.5Cr	-0.143	0.43	2.36 (±0.02)	10.3 (±2.3)
NiAl-10Cr	-0.123	0.30	2.58 (±0.02)	43.6 (±2.9)

Table 5-2. Corrosion potential ( $E_{corr}$ ), corrosion current density ( $j_{corr}$ ), and the slope ( $dlog|j|/d\eta$ ), estimated from polarization plots of Ni-Al-Cr alloys over 0.10 V <  $\eta$  < 0.30 V, as well as corrosion scale thickness measured after immersion in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte for 12 h at 700 °C under pure O<sub>2</sub>

#### 5.3.3 Corrosion Behavior of Ni-Al-Cr Alloys under O<sub>2</sub>-0.1% (SO<sub>2</sub>+SO<sub>3</sub>) Environment

Petroleum feed within the combustor of gas turbines is known to carry sulfur contamination, which results in the formation of sulfur oxide gases, e.g. SO<sub>2</sub> and SO<sub>3</sub>. Jose *et. al.* [61] and Zhang [62] reported the solubility behavior of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> phases, respectively, at 927 °C. Even a slight increase in the activity of SO<sub>3</sub> ( $a_{SO_3}$ ) was found to significantly increase the solubility Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> phases in molten Na<sub>2</sub>SO<sub>4</sub>. In order to understand the corrosion behavior of Ni-Al-Cr alloys in SO<sub>2</sub> and SO<sub>3</sub> containing gaseous environment, open circuit potentials, immersion tests, and potentiodynamic polarizations measurements were performed in O<sub>2</sub>-0.1%(SO<sub>2</sub>-SO<sub>3</sub>) environment, analogous to that under pure O<sub>2</sub> gas.

During the transition from inert argon to  $O_2$ -SO<sub>2</sub>-SO<sub>3</sub> atmosphere, OCP measurements with  $\beta$ -NiAl and Ni-Al-Cr working electrodes showed an increasing trend [Figure 5-4(a)], which was similar to the behavior under pure  $O_2$  gas [Figure 5-3(a)]. However, the OCP of these alloys showed different magnitudes after 12 h immersion in sulfate electrolyte;  $\beta$ -NiAl had the smallest potential and NiAl-5Cr had the highest. The different magnitudes of OCPs of Ni-Al-Cr alloys under SO<sub>2</sub>-SO<sub>3</sub> containing environment might have arisen due to the following degradation reactions on Ni-Al-Cr alloys:

Al<sub>2</sub>O<sub>3</sub> + 3SO<sub>3</sub> → Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (
$$\Delta_r G = -35.61$$
 kJ at 700 °C [39]) Reaction 5-1  
Cr<sub>2</sub>O<sub>3</sub> + 3SO<sub>3</sub> → Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ( $\Delta_r G = -33.22$  kJ at 700 °C [39]) Reaction 5-2

Further,  $\beta$ -NiAl alloy in O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> atmosphere undergoes localized damages requiring ~20–180 min to repassivate the surface. Interestingly, the repassivation time was reduced with increasing Cr addition as shown in Figure 5-4(a). It is also evident that the frequency of localized damages was dependent on the Cr content. Increased Cr content was required to reduce passive scale damages under O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> atmosphere, in contrast to the need of small Cr addition under pure O<sub>2</sub>.

Immersion tests with  $\beta$ –NiAl alloy in sulfate solution under O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> environment demonstrated several cracks in the corrosion layer [Figure 5-4(b)], which are believed to be due to the formation of solid Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ( $T_m = 770$  °C) during the corrosion. Interestingly, all the composition of Ni-Al-Cr alloys under SO<sub>2</sub>-SO<sub>3</sub> containing atmosphere did not show such cracks, implying the improved stability of passive layer. In general, corrosion layer on Ni-Al-Cr alloys showed similar growth of the passive scale as observed under pure O<sub>2</sub>: bi-layer oxide scale consisting of inner layer of Al<sub>2</sub>O<sub>3</sub> layer and outer layer of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> solid solution. Moreover, the overall thickness of oxide scale increased with increasing Cr content in Ni-Al-Cr alloys. The elemental maps corresponding to the surface of Ni-Al-Cr alloys after corrosion in O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> environment are given in Figure C-4 of Appendix C.

# **(a)**







**(c)** 

Figure 5-4. (a) Open circuit potentials measured for ~12 h, (b) corrosion morphologies of Ni-Al-Cr ( $0.0 \le Cr \le 0.10$ ) alloys, and (c) potentiodynamic polarization plots ( $\log |j| \text{ vs. } \eta$ ) at a scan rate of 1 mV/s over  $-0.05 \text{ V} < \eta < +0.50 \text{ V}$  after immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C for 12 h under O<sub>2</sub>-0.1% (SO<sub>2</sub>+SO<sub>3</sub>) gas.

Subsequently, polarizations measurements were evaluated to understand the corrosion resistance of Ni-Al-Cr alloys under O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> gas. Figure 5-4(c) shows that  $\beta$ -NiAl alloy has the highest magnitude of electrochemical current densities among all the studied alloys. Interestingly, NiAl-1Cr alloy exhibited current densities ~6 time smaller in comparison to that with  $\beta$ -NiAl, suggesting the beneficial effect of Cr in improving the corrosion resistance. Notably, NiAl-5Cr showed the lowest current densities in all the Ni-Al-Cr alloys; higher addition of Cr increased the magnitude of electrochemical currents. By extrapolating the linear region of current densities into

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corrosion potentials, the calculated slope  $(dlog/j//d\eta)$ , corrosion current density, along with corrosion potential and passive layer thickness are given in Table 5-3. From Table 5-3, it is evident that the addition of Cr up to 5 at% shows increasing corrosion potentials. Further addition of Cr commences a decreasing trend. In agreement to the maximum stability of NiAl-5Cr alloy predicted by corrosion potential, corrosion current densities were lowest for NiAl-5Cr alloy, which were approximately two orders of magnitudes smaller in comparison to that with  $\beta$ -NiAl alloy.

Table 5-3 Corrosion potential ( $E_{corr}$ ), corrosion current density ( $j_{corr}$ ), and the slope ( $dlog|j//d\eta$ ), estimated from polarization plots of Ni-Al-Cr alloys over 0.10 V <  $\eta$  < 0.30 V, as well as corrosion scale thickness measured after immersion test in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte for 12 h at 700 °C under O<sub>2</sub>-0.1% (SO<sub>2</sub>+SO<sub>3</sub>).

Alloy	E <sub>corr</sub> vs. Ag/Ag <sup>+</sup> (V)	$j_{\text{corr}} (\eta = 0)$ (mA/cm <sup>2</sup> )	d log  j  /dη (dec/V)	Scale thickness (µm)
β–NiAl	-0.402	8.86	1.19 (±0.01)	26 (±3)
NiAl-1Cr	-0.208	1.43	2.51 (±0.01)	4.0 (±1.0)
NiAl-2.5Cr	-0.091	0.90	2.54 (±0.04)	3.1 (±0.6)
NiAl-5Cr	+0.050	0.09	2.71 (±0.02)	7.5 (±1.5)
NiAl-7.5Cr	-0.148	2.26	2.10 (±0.02)	8.4 (±1.7)
NiAl-10Cr	-0.157	2.38	2.19 (±0.02)	29.3 (±3.2)

#### 5.3.4 Role of Sulfur Oxides (SO<sub>2</sub>, SO<sub>3</sub>) in Hot Corrosion on Ni-Al-Cr Alloys

Corrosion properties of each composition of Ni-Al-Cr alloys under pure O<sub>2</sub> [Table 5-2] and O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> [Table 5-3] environments were compared to elucidate the effect of SO<sub>2</sub>, SO<sub>3</sub> species on different Cr additions in  $\beta$ -NiAl. Figure 5-5(a) shows the trend of passive scale thicknesses as a function of Cr content in Ni-Al-Cr alloys. Under both of the gaseous environments, a similar trend and magnitudes of corrosion layer thicknesses were observed for each composition of Ni-Al-Cr alloys. Briefly, 1at% Cr addition in  $\beta$ -NiAl alloy reduced the thickness of corrosion layer which slightly increases for 1at%  $\leq$  Cr  $\leq$  7.5at% and abruptly increases for the addition of 10at% Cr. It is

believed that the presence of  $Al_2O_3$ - $Cr_2O_3$  solid solution on the outer edge of passive layer acts as a strong barrier against the diffusion of corrosion species [SO<sub>4</sub><sup>2–</sup>, O<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>] and oxide scale formers (Al<sup>3+</sup> and Cr<sup>3+</sup>) across the passive layer. However, particular to NiAl-10Cr alloy, interconnected Cr regions within the bulk alloy might have provided shorter diffusion paths for accelerated diffusion and oxidation of Cr at the outer edge of passive scale, leading to abrupt increase in the thickness.

Comparison of corrosion potentials measured after 12 h long immersion in sulfate electrolyte shows that addition of 1at% Cr in  $\beta$ -NiAl increased the corrosion potentials under both of the gaseous environments. However, magnitudes of corrosion potentials under pure O2 environment remained within the range of -0.143 V to -0.080 V vs. Ag/Ag<sup>+</sup> for alloys with 1at%  $\leq$  Cr  $\leq$  10.0 at%, implying a somewhat invariant nature of corrosion potential on Cr content [Figure 5-5(b)]. Conversely, corrosion potentials under O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> increased linearly as a function of Cr content up until a higher than 5at% which led to decreased corrosion potentials. It is also evident from Figure 5-5(b) that NiAl-1Cr and NiAl-10Cr exhibit lower magnitudes of corrosion potentials under the influence of SO<sub>2</sub>-SO<sub>3</sub> species; whereas, the corrosion potentials of NiAl-2.5Cr and NiAl-7.5Cr did not change on switching the gaseous environment. Interestingly, NiAl-5Cr exhibited higher corrosion potential in  $SO_2$ - $SO_3$  containing environment compared to that under pure  $O_2$ . Subsequently, corrosion current densities were compared to understand the impact of sulfur oxides on the corrosion rate of Ni-Al-Cr alloys. Figure 5-5(c) shows a trend of slightly decreasing magnitudes of corrosion current densities under pure O<sub>2</sub>. In contrast, corrosion current densities decreased drastically under O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> for alloy with increasing Cr content up to 5at%; further addition of Cr demonstrated an increasing current densities. While other alloy compositions showed higher corrosion currents under the influence of SO<sub>2</sub>-SO<sub>3</sub> species, NiAl-5Cr alloy showed a lower current density in SO<sub>2</sub>-SO<sub>3</sub> containing environment, agreeing with the increased stability predicted based on the corrosion potential measurements [Figure 5-5(b)].





**(a)** 



Figure 5-5. Influence of sulfur oxide species (SO<sub>2</sub>, SO<sub>3</sub>) on Ni-Al-Cr alloys corrosion: comparison of (a) oxide scale thickness ( $\Delta$ w), (b) corrosion potential ( $E_{corr}$ ) vs. Ag/Ag<sup>+</sup>, and (c) corrosion current density (*j*) over  $0.0 \le Cr \le 0.10$  after immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C for 12 h under different atmospheres of pure O<sub>2</sub> and O<sub>2</sub>-0.1%(SO<sub>2</sub>+SO<sub>3</sub>) gas.

6

Cr content, x (at%)

8

4

0

2

To understand the effect of  $SO_2$  and  $SO_3$  species on the growth of passive scale (*i.e.* Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>), electrochemical impedance measurements were performed under pure O<sub>2</sub> and O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> environments. Typically, non-corroding metals such as platinum in contact with sulfate species have substantially high polarization resistance making them inert in hot corrosive reaction. Due to the wide gap in oxidation and reduction potentials of inert metal and sulfate ions, respectively, the charge transfer across metal surface becomes a rate limiting step. However, in the case of corroding alloys like Ni-Al-Cr, corrosion reactions are influenced by additional factors such as diffusion of

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charged species across the passive layer, transport through the electrolyte, passive layer porosity, and/or localized damaged in the passive scale [95].

NiAl-5Cr alloy after immersion in the sulfate electrolyte was subject to polarizations with a 10 mV AC potential over a frequency range of 0.1Hz-100kHz. Impedance measurements were performed at t = 3, 6, 9, 12, and 18 h to elucidate the growth of the passive scale by comparing polarization resistance over time in each gaseous atmosphere. Nyquist plots representing the impedance of corrosion scale on NiAl-5Cr alloy in both gaseous environments are shown in Figure 5-6. Interestingly, NiAl-5Cr alloy showed similar Nyquist plots over a period of 18 h [Figure 5-6(a)]. The semicircular trend in high frequency regime, which is indicator of a polarization resistance, might be due to the charge transfer resistance at the NiAl-5Cr alloy vs. sulfate electrolyte interface [71,95]. Linear behavior in the low frequency regime indicates diffusion resistance (Warburg impedance,  $(Z_w)$ ] [1,92] which could be due to transport of gaseous molecules (O<sub>2</sub>) from electrolyte vs.  $O_2$  gas interface to passive scale vs. electrolyte interface as suggested by Zeng and Li, based on the corrosion behavior of nickel-based superalloy M38G [71]. Therefore, it is concluded that the growth of passive layer on NiAl-5Cr alloy is controlled by the diffusion of  $O_2$ molecule through the electrolyte phase, instead of diffusion of charged species across the passive layer [71]. An equivalent circuit for this observed behavior is given in the inset of Figure 5-6(a), where  $R_s$ ,  $R_{ct}$ ,  $C_{dl}$ , and  $Z_w$  represent the electrolyte resistance, double-layer resistance, double layer capacitance, and Warburg impedance, respectively.

In contrast to the constant impedance behavior under pure  $O_2$ , NiAl-5Cr alloy showed a growth of additional semicircular trend in the low frequency regime over time, which overshadowed the diffusion resistance (*i.e.* linear region) [Figure 5-6(b)]. Notably, SO<sub>2</sub> and SO<sub>3</sub> are more soluble than  $O_2$  in the sulfate electrolyte. In that case, the diffusion of sulfur oxides through the electrolyte might not be a limiting step. Growth of an additional semicircle in Nyquist plot indicates a new capacitive and resistive component in the electrochemical circuit [1,92]. The observation of two semi-circular loops in Nyquist plot is similar to the behavior of FeAl in  $(Li,K)_2CO_3$  electrolyte at 650°C, reported by Zeng *et. al.* [95]. In the early phase of corrosion, FeAl showed a semicircle and a linear trend. However, after an exposure of 20 h, two semicircular loops were observed. The formation of second loop (in low frequency regime) was suggested due to the protective behavior of external LiFeO<sub>2</sub> layer and inner Al<sub>2</sub>O<sub>3</sub> layer. Considering the behavior of NiAl-5Cr alloy in SO<sub>2</sub>-SO<sub>3</sub> containing environment, which also includes a semicircle and a linear trend, it is believed that the initial growth of passive layer (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>) was predominantly controlled by the diffusion of gaseous species [O<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>]. However, on extended exposure to the sulfate electrolyte solution, the passive scale becomes protective and shows a semicircular behavior. An equivalent electrochemical circuit, as suggested by Zeng *et. al.* [95], is given in the inset of Figure 5-6(b), where R<sub>ox</sub> and C<sub>ox</sub> are the resistance and capacitance of passive oxide layer (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>).



**(a)** 



Figure 5-6. Electrochemical impedance measurements (Nyquist plots) obtained with ( $\beta$ )NiAl-5at% Cr alloy in the frequency range of 0.1Hz–100 kHz with 10 mV AC potential at different immersion times (3 h  $\leq t \leq$  18 h) in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C under atmosphere of (a) pure O<sub>2</sub> and (b) O<sub>2</sub>–0.1%(SO<sub>2</sub>+SO<sub>3</sub>) gas.

In summary, NiAl-5Cr alloy in molten sulfate environment containing pure  $O_2$  gas undergoes corrosion reactions which are limited by the diffusion of  $O_2$  molecules across the electrolyte solution. In contrast, addition of  $SO_2$ -SO<sub>3</sub> species in the surrounding gas provides an additional circular loop in the Nyquist plot, suggesting an increased protectiveness by the passive layer. The beneficial effect of Cr addition under  $SO_2$ -SO<sub>3</sub> environment is found to be in agreement with the conclusions from OCP and potentiodynamic polarization measurements.

#### 5.4 Summary

Hot corrosion behavior of Ni-Al-Cr alloys with varying Cr content was obtained by performing electrochemical measurements in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C. Under the controlled gaseous atmospheres of pure O<sub>2</sub> and O<sub>2</sub>-0.1%(SO<sub>2</sub>-SO<sub>3</sub>), open circuit potentials, potentiodynamic polarizations, and electrochemical impedance measurements were performed to elucidate the role of Cr content in obtaining higher corrosion resistance. OCP measurements showed that Ni-Al-Cr alloys under pure O<sub>2</sub> exhibit similar potentials on varying Cr content, implying a comparable stability of Ni-Al-Cr alloys under Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> scale. In general,  $\beta$ -NiAl based alloys undergo localized damage in alumina scale. Addition of Cr in  $\beta$ -NiAl improves the repassivation ability of alloy surface in the event of scale damage. Based on the OCP and potentidynamic polarization measurements in 0.1% SO<sub>2</sub>-SO<sub>3</sub> environment, NiAl-5Cr alloy exhibited the best corrosion properties among the studied compositions.

#### **Chapter 6**

#### **Conclusions and Recommendations for Future Work**

High temperature processes in oil refinery plants, coal gasification systems, and gas turbines necessitate construction alloys that exhibit high creep resistance, thermal stability, and corrosion resistance. Nickel-based alloys are well known for their attractive high temperature properties and therefore, are often used in the construction of high temperature components as well as surface coatings. During operation, these components are exposed to an aggressive chemical and thermal environment containing molten sulfates (e.g. Na<sub>2</sub>SO<sub>4</sub>), resulting from the combustion of sulfur containing fuel in NaCl-containing polluted or marine air. As a consequence, molten salts are deposited on metallic components and accelerate degradation reactions, also known as hot corrosion.

In the context of coating applications for nickel alloys in hot corrosive environments, this dissertation attempts to establish a fundamental electrochemical understanding of the corrosion properties of nickel alloys. On exposure to molten sulfates, nickel alloys undergo oxidation reactions ( $M \rightarrow M^{n+} + ne^-$ ) which are coupled with the reduction of SO<sub>4</sub><sup>2-</sup> ions and/or gaseous species such as O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>. In order to elucidate the corrosion behavior of nickel alloys and the reduction mechanism of SO<sub>4</sub><sup>2-</sup> ions, electrochemical measurements were performed with several metals and alloys in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10) solution at 700 °C, and under differing atmospheres of argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1% (SO<sub>2</sub>+SO<sub>3</sub>). Thermodynamic measurements and immersion tests in similar experimental conditions were also performed to corroborate electrochemical observations.

Electrochemical studies on the behavior of  $SO_4^{2-}$  ions showed that the reduction of sulfate ions requires a large negative overpotential (< -1.1 V vs. Ag/Ag<sup>+</sup>). On a platinum working

$$SO_4^{2-} + 6e^- \rightarrow S + 4O^{2-}$$
 Reaction 6-1

and 
$$SO_4^{2-} + 8e^- \rightarrow S^{2-} + 4O^{2-}$$
 Reaction 6-2

Sulfate ions are known to accelerate alloy degradation; however, the present study revealed that the deleterious effect of sulfate ions may not occur in inert gaseous environments, instead requiring stronger oxidants such as O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub> to participate in hot corrosion reactions.

Hot corrosion studies with pure Ni and  $\beta$ -NiAl (1:1) alloys in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte under argon environment exhibited negative corrosion potentials (< -0.75 *vs.* Ag/Ag<sup>+</sup>) and low corrosion rates (~0.25 mA/cm<sup>2</sup>). Moreover, cross-sectional analyses on corroded Ni and  $\beta$ -NiAl specimens revealed an adherent and protective layer of NiO and Al<sub>2</sub>O<sub>3</sub>, respectively. Nickel alloys exposed to sulfate electrolyte under oxidizing gaseous species such as O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>, showed a sudden rise in open circuit potential, which implies stronger oxidizing activities of these gaseous species. It is believed that the accelerated degradation of nickel alloys is governed by the cumulative reduction of SO<sub>4</sub><sup>2-</sup> and gaseous molecules (O<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub>). In oxidizing environments, Ni rapidly degraded due to the instability of NiO, and  $\beta$ -NiAl demonstrated localized damage in a alumina passive layer. Particularly, alumina scale developed cracks under a O<sub>2</sub>--0.1%(SO<sub>2</sub>+SO<sub>3</sub>) environment, which increased the corrosion rate of  $\beta$ -NiAl by ~11 times in comparison to that under pure O<sub>2</sub>. This behavior is attributed to sulfur-bearing gaseous species reacting with the alumina layer, and forming aluminum sulfate according to

$$Al_2O_3 + 3SO_3 \rightarrow Al_2(SO_4)_3$$
 ( $\Delta_r G = -35.61 \text{ kJ at } 700 \text{ }^\circ\text{C} \text{ [39]}$ ) Reaction 6-3

In order to further enhance corrosion resistance, chromium (Cr) addition in  $\beta$ -NiAl was observed to produce a solid solution of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> on the outer edge of the passive scale, which in turn reduced corrosion rates and recovery time required to re-passivate the damaged sites on the Ni-Al-Cr alloy surface. Upon varying Cr content in Ni-Al-Cr alloys, it was observed that a small quantity of Cr is sufficient to improve the integrity of passive layer under pure O<sub>2</sub>. With increased Cr content ( $0.01 \le Cr \le 0.1$ ) in  $\beta$ -NiAl, the corrosion rate linearly decreased from 0.78 mA/cm<sup>2</sup> to 0.30 cm<sup>2</sup>. In contrast, with the increased addition of Cr in  $\beta$ -NiAl in SO<sub>2</sub>-SO<sub>3</sub> containing atmosphere, re-passivation time for damaged sites was reduced. Interestingly, open circuit potential and potentiodynamic polarization measurements revealed that 5 at% Cr addition in  $\beta$ -NiAl provides excellent corrosion properties among the studied Ni-Al-Cr alloys ( $0.01 \le Cr \le 0.1$ ).

#### **6.1 Recommendations for Future Work**

During the course of this dissertation, the primary focus remained on the stability and corrosion resistance of passive scales (NiO, Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>) grown on the alloy surface. As described in Chapter 2, the oxide layer on the alloy surface develops interfacial stresses due to different lattice parameters. Over an extended period of corrosion, the passive layer may spall off the alloy surface; therefore, further efforts are needed to strengthen the integrity of passive layer.

#### 6.1.1 The Effect of Other Alloying Elements for Enhanced Environmental Resistance

During the growth of oxide scales, metal ions diffuse toward the alloy surface by movement along grain boundaries and lattice defects. On the other hand, corrosive species such as  $O^{2-}$  move in the opposite direction through the oxide scale. It has been reported in the literature that reactive elements such as hafnium, zirconium, silicon, and yttrium, when added in small fractions (< 1 at%), tend to segregate at the interface. [55,57,96]. This way, the outward motion of metal ions is inhibited. Moreover, the grown passive layer develops inwardly oriented pegs which significantly strengthen the alloy *vs*. the metal-oxide interface. An exemplary view of the reactive element effect is shown in Figure 6-1, which depicts the effect of Hf in FeAl alloy [96].



Figure 6-1. Growth of oxide scale on Fe-10Al-1Hf alloy exhibiting inwardly growing pegs under the influence of Hf addition, making the alloy vs. alumina interface stronger [96].

Electrochemical studies focused on the effect of reactive element(s) in nickel alloys are sparse in the literature. Therefore, it is recommended that an initial framework on reactive element effects be understood by performing electrochemical measurements with Zr, and/or Hf additions in  $\beta$ -NiAl alloys. Microstructural characterizations of the corroded specimens can be used to complement electrochemical findings. After establishing a generic framework with  $\beta$ -NiAl binary alloys, ternary, and quaternary alloys can be studied.

Besides the electrochemical methodologies described in this dissertation, additional experimental methods, such as current-noise tests, can be accommodated in the course of future studies. Additionally, the effect of the surrounding temperature on the degradation profile of these alloy compositions requires further understanding.

#### 6.1.2 Estimation of Aluminum Activities in Nickel and Cobalt Alloys

The corrosion resistance of nickel alloys in corrosive environments has been found to be dependent on the growth of the passive oxide scale. Movement of oxide scale forming elements (Al, Cr) from the alloy matrix to the surface can be understood in terms of a gain in thermodynamic stability after oxidation [Section 2.2, Chapter 2]. In other words, elements such as aluminum and chromium have high thermodynamic activity in nickel when exposed to oxidizing environments. Therefore, they tend to diffuse toward the alloy surface, and oxidize to achieve lower activity. A fundamental thermodynamic study on the behavior of nickel alloys can be developed by performing electromotive force (emf) measurements. There are few reports available in the literature informing the thermodynamic activity of aluminum in the temperature range corresponding to type I corrosion regime [97] and a temperature range (547-647 °C) below the type II corrosion regime [98,99]. Bonnet *et. al.* performed thermodynamic studies in the temperature range of 577-1027 °C [100]. However, the focus was primarily on aluminum rich ( $0.84 < x_{AI} < 1$ ) nickel compositions.

An electrochemical study focused on aluminum activity, particularly in the  $\beta$ -NiAl composition range and type II corrosion temperature regime can be performed to elucidate the thermodynamic activity of aluminum in nickel matrix. An electrochemical cell design and calculations of thermodynamic parameters can be performed in the following way.

An electrochemical cell having an Al(s)|Electrolyte (l)|Al(in Ni) arrangement can be developed; where, an electrolyte (e.g. LiCl-KCl-AlX<sub>3</sub>,  $X = Cl^-$ ,  $F^-$ ) capable of ionic conduction, and with a low melting point (< 400 °C), should be selected.

Afterwards, the emf measurements can be performed with pure Al as the reference electrode (RE) and various compositions of  $\beta$ -NiAl as the working electrodes (WEs). During the measurements, the following half-cell reactions will be established.

**RE:** 
$$Al(s) + 3X^- = AlX_3(s) + 3e^-$$
Equation 6-1**WE:**  $AlX_3 + 3e^- = Al(in Ni) + 3X^-$ Equation 6-2

Which leads to the overall cell reaction:

$$Al(s) = Al(in Ni)$$
 Equation 6-3

Therefore, the change in partial molar Gibbs energy of Al is given by

$$\Delta \overline{G}_{Al} = \overline{G}_{Al \text{ (in Ni)}} - \overline{G}_{Al}$$
 Equation 6-4

Subsequently, the partial molar Gibbs energy can be related to aluminum activity by:

$$\overline{G}_{Al (in Ni)} = \overline{G}_{Al (in Ni)}^{o} + RT \ln a_{Al(in Ni)}$$
Equation 6-5
$$\overline{G}_{Al} = \overline{G}_{Al}^{o} + RT \ln a_{Al(s)}$$
Equation 6-6

Where *a* denotes the activity,  $\overline{G}^{\circ}$  the standard partial molar Gibbs free energy, *R* the gas constant, and *T* the temperature.

Applying the Nernst equation ( $\Delta G = -nFE_{cell}$ ) and  $a_{Al(s)} = 1$ , the following relation can be obtained relating  $E_{cell}$  and  $a_{Al(in Ni)}$ .

$$E_{cell} = -\frac{\Delta \overline{G}_{Al}}{nF} = -\left(\frac{RT}{nF}\right) lna_{Al (in Ni)}$$
Equation 6-7

Where *n* is number of electrons exchanged and *F* is Faraday's constant.

Using equation 6-7, activity values of Al in nickel can be directly calculated. Also, the activity of Ni can be estimated using the Gibbs-Duhem equation. Subsequently, thermodynamic properties such as partial molar entropy and enthalpy can also be obtained.

Similar to nickel based alloys, cobalt (Co) based compositions are also observed to have good mechanical and corrosion resistant properties suitable for gas turbine applications [23,24]. Therefore, thermodynamic activity estimation for Al in Co will also provide a perspective on the oxidation/corrosion properties of cobalt alloys.

#### Appendix A

#### Solution Resistance and Cyclic Voltammetry in Different Sulfate Solutions

Prior to electrchemical measurements with platinum/tunsgten/glassy carbon electrodes in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte to elucidate sulfate reduction reactions, solution resistance of molten electrolyte was calculated by electrochemical impedance spectroscopy. Figure A-1 shows the Nyquist plot obtained with platinum working electrode in LiCl-KCl-10 mol%Na<sub>2</sub>SO<sub>4</sub> electrolyte at 700 °C. The inset shows the zoomed view of high frequency regime depicting the intersection with Z' axis at ~0.3  $\Omega$ . This value was utilized in correcting cyclic voltammograms in Figure 3-2 [Chapter 3] for IR losses.



Figure A-1. Nyquist plot obtained with platinum WE in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte, with an AC input signal of 10 mV amplitude and frequency range of 10 Hz -100 kHz at 700 °C.

In addition to the sulfate reduction studies with LiCl-KCl-10mol% Na<sub>2</sub>SO<sub>4</sub> electrolyte, the reduction behavior of SO<sub>4</sub><sup>2-</sup> species was also understood with different electrolytes containing molten SO<sub>4</sub><sup>2-</sup> species. Exemplary cyclic voltammograms obtained with glassy carbon working electrode in Li<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub> and NaCl-Na<sub>2</sub>SO<sub>4</sub> electrolytes at 700 °C are shown in Figure A-2. A comparison of these voltammograms with that obtained in LiCl-KCl-10mol% Na<sub>2</sub>SO<sub>4</sub> indicates that reduction potential of SO<sub>4</sub><sup>2-</sup> ions remained invariant on changing the electrolyte solutions.



Figure A-2. Cyclic voltammograms obtained with glassy carbon working electrode (WE) in different solutions of  $Li_2SO_4$ - $K_2SO_4$ , LiCl-KCl-Na\_2SO\_4 (53.3-36.7-10 mol%), and NaCl-Na\_2SO\_4 at a scan rate of 100 mV/s under inert argon environment at 700 °C.

#### **Appendix B**

#### Influence of SO<sub>2</sub> and SO<sub>3</sub> Species on the Corrosion Rate of Ni and β-NiAl

Chapter 4 in this dissertation focused on the effect of Al and Cr addition in nickel. Based on electrochemical potentiodynamic measurements, a qualitative understanding on the corrosion resistance of Ni alloys was established in molten sulafte environment at 700 °C. Efforts were also made to obtain the weight/loss behavior of nickel alloys during corrosion.

Weight gain measurements were performed to obtain an understanding on the corrosion rate of nickel alloys in sulfur oxide containing environment. Specifically, alloy specimens coated with Na<sub>2</sub>SO<sub>4</sub> salt layer (~ 35 mg/cm<sup>2</sup>) were isothermally heated at 700 °C for 12 h under different environments of O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub> (flow rate = 40 mL/min) gases to contrast the effect of the SO<sub>2</sub>-SO<sub>3</sub> species on the oxidation rate of Ni alloys. It is also to note that, due to sensitive design of thermogravimetric analyzer, it was difficult to place platinum catalyst at the inlet of O<sub>2</sub>-0.1%SO<sub>2</sub> gas mixture. However, in the absence of catalytic conversion, ~0.1% SO<sub>2</sub> is transformed to SO<sub>3</sub>, establishing  $P_{SO_3} \approx 1 \times 10^{-6}$  atm in the gaseous atmosphere at 700 °C [101].

Weight gain measurements with pure nickel, as shown in Figure B-1(a), demonstrated the effect of  $SO_2$ -SO<sub>3</sub> species on nickel hot corrosion. In contrast to immersion test where a clear influence of  $SO_2$ -SO<sub>3</sub> on the amount of NiO and NiS<sub>x</sub> was difficult to observe due to continuous nickel dissolution in molten phase [Figure 4-3(b,c)], thermogravimetric measurements showed that  $SO_2$ -SO<sub>3</sub> species severely increased nickel corrosion. In a period of 12 h, Ni specimen showed a weight gain of ~0.8 and ~2.6 mg/cm<sup>2</sup> under O<sub>2</sub> and O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> gases, respectively. This enhanced corrosion is in agreement with the reported studies by Gheno & Gleeson [37], where nickel exposure test under sulfur oxide gases at 700 °C showed increased thickness of NiO and NiS<sub>x</sub> scale.

Similar measurements with  $\beta$ -NiAl alloy showed a weight gain of ~0.15 and 1.0 mg/cm<sup>2</sup> under O<sub>2</sub> and O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub> environments, respectively [Figure B-1(b)], implying substantially

increased corrosion under SO<sub>2</sub>-SO<sub>3</sub> atmosphere, which agrees with weaker corrosion resistance observed in potentiodynamic measurements under sulfur oxide gases.



Figure B-1. Weight change measurements with nickel alloys covered with thin layer of Na<sub>2</sub>SO<sub>4</sub> (~ 35 mg/cm<sup>2</sup>) during isothermal oxidation at 700 °C: (a) pure Ni, and (b)  $\beta$ -NiAl, under pure O<sub>2</sub> and O<sub>2</sub>-0.1% (SO<sub>2</sub>+SO<sub>3</sub>) gases with flow rate of 40 ml/min.

In order to obtain a fundamental outlook on reaction tendency between alumina and SO<sub>2</sub>-SO<sub>3</sub> species,  $\beta$ -NiAl rod was preoxidized at 1100 °C under air for 24 h which resulted in the growth of ~3 µm thick alumina scale on  $\beta$ -NiAl surface. OCP measurements were performed with preoxidized  $\beta$ -NiAl WE in LiCl-KCl-10mol%Na<sub>2</sub>SO<sub>4</sub> electrolyte under different gaseous atmospheres. It was found that OCP under O<sub>2</sub> remained unchanged for ~1.5 h indicating that corrosive species were unable to reach  $\beta$ -NiAl surface due to alumina scale barrier. However, a sudden rise in OCP was noticed under SO<sub>2</sub>-SO<sub>3</sub> containing gas, suggesting that alumina scale promptly reacted with SO<sub>2</sub> and/or SO<sub>3</sub> species [Figure B-2].



Figure B-2. Open circuit potentials ( $E_{OCP}$ ) measured with preoxidized  $\beta$ -NiAl WE immersed in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte under different gaseous environments of argon, pure O<sub>2</sub> (g), and O<sub>2</sub>-0.1% (SO<sub>2</sub>+SO<sub>3</sub>) with flow rate of ~50 ml/min at 700 °C.

#### Appendix C

# Reproducibility of Potentiodynamic Polarization Measurements and Elemental Maps corresponding to Corroded Ni-Al-Cr Alloys

Prior to the potentiodynamic polarization measurements with Ni-Al-Cr alloys under different gaseous atmospheres, the effect of potential sweep rate was estimated by performing measurements with  $\beta$ -NiAl working electrode in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte solution under inert argon atmosphere. Figure C-1 shows the electrochemical current response within the overpotential of -0.050  $\leq \eta \leq$  +0.500 V at scan rate of 1 mV/s and 0.1 mV/s. It was observed that the electrochemical current densities show very similar magnitudes on applied overpotentials.



Figure C-1. Potentiodynamic polarization plots obtained with  $\beta$ -NiAl working electrode within the overpotential of  $-0.050V \le \eta \le +0.500$  V at a scan rate of 1 mV/s after 12 h long immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte under argon environment at 700 °C.

Further, to validate the reproducibility of potentiodynamic polarization plots, experiments were repeated with few selected compositions of Ni-Al-Cr alloys under pure  $O_2$  and  $O_2$ -0.1% (SO<sub>2</sub> + SO<sub>3</sub>) gaseous environments. Figure C-2 shows the comparison of NiAl-10Cr alloys under pure  $O_2$ , and NiAl-1Cr and NiAl-7.5Cr alloys under  $O_2$ -0.1% (SO<sub>2</sub> + SO<sub>3</sub>) environments. It was noticed, that electrochemical current densities were similar on repeated experiments.





Figure C-2. Comparison of potentiodynamic polarization plots on repetitive experiments with (a) NiAl-10Cr alloys under pure O<sub>2</sub>, (b) NiAl-1Cr alloy, and (c) NiAl-7.5Cr alloy under O<sub>2</sub>-0.1% (SO<sub>2</sub> + SO<sub>3</sub>) within the overpotential of  $-0.050V \le \eta \le +0.500$  V at a scan rate of 1 mV/s after 12 h long immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte at 700 °C.

Corresponding to the corrosion layers on Ni-Al-Cr alloys  $(0.01 \le Cr \le 0.10)$  after immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte under pure O<sub>2</sub> and O<sub>2</sub>-0.1%(SO<sub>2</sub> + SO<sub>3</sub>) [Figure 5-3(b) and Figure 5-4(b), Chapter 5] at 700 °C, the elemental maps for aluminum, chromium, oxygen, and sulfur are given below.



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(c) NiAl-5Cr



# (d) NiAl-7.5Cr



25µm

25µm

25µm

## (e) NiAl-10Cr



Figure C-3. X-ray elemental maps corresponding to aluminum, chromium, oxygen, and sulfur distribution obtained from the surface of corroded Ni-Al-Cr alloys with (a) Cr = 1 at%, (b) Cr = 2.5at%, (c) Cr = 5.0 at%, (d) Cr = 7.5 at%, and (e) Cr = 10 at%, after 12 h long immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte under pure O<sub>2</sub> gas at 700 °C.

(a) NiAl-1Cr



(b) NiAl-2.5Cr



# (c) NiAl-5Cr



(d) NiAl-7.5Cr







Figure C-4. X-ray elemental maps corresponding to aluminum, chromium, oxygen, and sulfur distribution obtained from the surface of corroded Ni-Al-Cr alloys with (a) Cr = 1 at%, (b) Cr = 2.5 at%, (c) Cr = 5.0 at%, (d) Cr = 7.5 at%, and (e) Cr = 10 at%, after 12 h long immersion in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) electrolyte under O<sub>2</sub>-0.1% (SO<sub>2</sub> + SO<sub>3</sub>) gas at 700 °C.

### References

- [1] E. Mccafferty, Introduction to Corrosion Science, Springer, 2009. doi:10.1007/978-1-4419-04553.
- [2] V.S. Sastri, Green Corrosion Inhibitors, Wiley, 2011.
- [3] M. Schütze, The Past, the Present and the Future of High Temperature Corrosion Research an EFC View, (2008). http://efcweb.org/ppf.html (accessed December 14, 2017).
- [4] I. Langmuir, Chemical reactions at very low pressures. II. The chemical clean-up of nitrogen in a tungsten lamp, J. Am. Chem. Soc. 35 (1913) 931–945. doi:10.1021/ja02197a002.
- [5] G. Tammann, Die Anlauffarben von Metallen, J. Inorg. Gen. Chem. 111 (1920) 78.
- [6] N.B. Pilling, R.E. Bedworth, The Oxidation of Metals at High Temperatures, J. Inst. Met. 29 (1923) 529.
- [7] J.S. Dunn, The High Temperature Oxidation of Metals, R. Soc. 111 (1926) 203–209.
- [8] J.S. Dunn, The Low Temperature Oxidation of Copper, R. Soc. 111 (1926) 210–219.
- [9] C. Wagner, Beitrag zur Theorie des Anlaufvorgangs, Z. Phys. Chemie. 21 (1933) 25.
- [10] C. Wagner, Theoretical Analysis of the Diffusion Processes Determining the Oxidation Rate of Alloys, J. Electrochem. Soc. 99 (1952) 369–380. doi:10.1149/1.2779605.
- [11] C. Wagner, Reaktionstypen bei der Oxydation von Legierungen, Zeitschrift Fuer Elektrochemie. 63 (1959) 772–782. doi:10.1002/bbpc.19590630713.
- [12] N.S. Bornstein, W.P. Allen, The Chemistry of Sulfidation Corrosion-Revisited, Mater.
   Sci. Forum. 251–254 (1997) 127–134. doi:10.4028/www.scientific.net/MSF.251-254.127.
- [13] N. Eliaz, G. Shemesh, R.M. Latanision, Hot corrosion in gas turbine components, Eng. Fail. Anal. 9 (2002) 31–43. doi:10.1016/S1350-6307(00)00035-2.
- [14] W.T. Reid, R.C. Corey, B.J. Cross, -, Trans. Amer. Soc. Mech. Eng. 67 (1945) 279.
- [15] L.H. Satz, General Electric Report DF 50SL305, n.d.
- [16] C. Sykes, H.T. Shirley, Special Report No. 43, 1952.
- [17] B.O. Buckland, C.M. Gardiner, D.G. Sanders, Paper A-52-161, Annu. Meet. Am. Soc. Mech. Eng. (n.d.).
- [18] E.L. Simons, G. V. Browning, H.A. Liebhafsky, Sodium Sulfate in Gas Turbines, Corrosion. 11 (1955) 17–26.
- [19] S. Hradecky, Incident: TAP A332 at Lisbon on Jul 12th 2014, engine shut down in flight, (n.d.). http://avherald.com/h?article=47732041 (accessed February 7, 2018).
- [20] GPIAA, GPIAA SAFETY REPORT, Incident Occurence Investigation (18/INCID/2014), 2016. http://www.skyscanner.net/airline/airline-tap-portugal-tp.html.
- [21] The Guardian, Engine failures on 787 Dreamliners prompt ANA to overhaul entire fleet, (n.d.). https://www.theguardian.com/business/2016/sep/01/engine-failures-on-787-dreamliners-prompt-ana-to-refit-entire-fleet (accessed February 7, 2018).
- [22] S. Metals, INCONEL® Alloy 600, SMC-027. (n.d.). http://www.specialmetals.com/assets/smc/documents/alloys/inconel/inconel-alloy-600.pdf.
- [23] J.R. Nicholls, Designing Oxidation-Resistant Coatings, JOM. 52 (2000) 28–35. https://doi.org/10.1007/s11837-000-0112-2.
- [24] B. Gleeson, High-Temperature Corrosion of Metallic Alloys and Coatings, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2008. doi:10.1002/9783527619306.ch14.
- [25] C. Leyens, B.A. Pint, I.G. Wright, Effect of composition on the oxidation and hot corrosion resistance of NiAl doped with precious metals, Surf. Coatings Technol. 133–134 (2000) 15–22. doi:10.1016/S0257-8972(00)00878-1.

- [26] F.T. Talboom, R.C. Elam, L.W. Wilson, Report CR7813: Evaluation of Advanced Superalloy Protection Systems, Houston, TX, 1970.
- [27] K.L. Luthra, O.H. LeBlanc, Low Temperature Hot Corrosion of Co-Cr-Al Alloys\*, Mater. Sci. Eng. 87 (1987) 329–335. doi:10.1149/1.2114105.
- [28] K.L. Luthra, Low Temperature Hot Corrosion of Cobalt-Base Alloys: Part II. Reaction Mechanism, Metall. Trans. 13A (1982) 1853–1864. doi:10.1007/BF02647841.
- [29] J. Stringer, Hot Corrosion of High-Temperature Alloys, Annu. Rev. Mater. Sci. 7 (1977) 477–509.
- [30] K.L. Luthra, Kinetics of the Low Temperature Hot Corrosion of Co-Cr-Al Alloys, J. Electrochem. Soc. Electrochem. Sci. Technol. 132 (1985) 1293–1298. doi:10.1149/1.2114105.
- [31] K. Zhang, M.M. Liu, S.L. Liu, C. Sun, F.H. Wang, Hot corrosion behaviour of a cobaltbase super-alloy K40S with and without NiCrAlYSi coating, Corros. Sci. 53 (2011) 1990– 1998. doi:10.1016/j.corsci.2011.02.022.
- [32] K.L. Luthra, J.H. Wood, High chromium cobalt-base coatings for low temperature hot corrosion, Thin Solid Films. 119 (1984) 271–280. doi:10.1016/0040-6090(84)90011-7.
- [33] F.S. Pettit, G.H. Meier, Oxidation and Hot Corrosion of Superalloys, Miner. Met. Mater. Soc. Superalloys (Fifth Int. Symp. 1984) 651–687. doi:10.7449/1984/Superalloys\_1984\_651\_687.
- [34] P. Crook, Corrosion- Resistant Nickel Alloys Part 1, Adv. Mater. Process. (2007) 37–39.
- [35] D.A. Shores, Use of Anodic Polarization in Fused Na<sub>2</sub>SO<sub>4</sub> for Estimating Hot Corrosion Rates, CORROSION. 31 (1975) 434–440.
- [36] M.N. Task, Assessment of the Factors Affecting Protective Alumina Formation Under Hot Corrosion Conditions, 2012.
- [37] T. Gheno, B. Gleeson, On the Hot Corrosion of Nickel at 700 °C, Oxid. Met. 84 (2015) 567–584. doi:10.1007/s11085-015-9588-6.
- [38] J.A. Goebel, F.S. Pettit, Na<sub>2</sub>SO<sub>4</sub>-Induced Accelerated Oxidation (Hot Corrosion) of Nickel, Metall. Trans. 1 (1970) 1943–1954.
- [39] A. Roine, HSC Chemistry 5.0, (2002).
- [40] E. McCafferty, Introduction to Corrosion Science, Springer, New York, 2010. doi:10.1007/978-1-4419-04553.
- [41] K.P. Lillerud, P. Kofstad, Sulfate-Induced Hot Corrosion of Nickel, Oxid. Met. 21 (1984) 233–270. doi:10.1007/BF00656835.
- [42] J.R. Nicholls, S.R.J. Saunders, High Temperature Materials for Power Engineering, (1990) 865–875.
- [43] J.R. Nicholls, N.J. Simms, W.Y. Chan, H.E. Evans, Smart overlay coatings concept and practice, Surf. Coatings Technol. 149 (2002) 236–244. doi:10.1016/S0257-8972(01)01499-2.
- [44] G.W. Goward, Low-Temperature Hot Corrosion in Gas Turbines: A Review of Causes and Coatings Therefor, J. Eng. Gas Turbines Power. 108 (1986) 421–425. doi:10.1115/1.3239921.
- [45] H. Okamoto, Binary alloy phase diagrams, J. Phase Equilibria. 14 (1993) 257–259.
- [46] R.L. McCarron, N.R. Lindblad, D. Chatterji, Environmental Resistance of Pure and Alloyed  $\gamma'$ Ni<sub>3</sub>Al and  $\beta$ -NiAl, Corrosion. 32 (1976) 476–481.
- [47] T. Gheno, M. Zahiri Azar, A.H. Heuer, B. Gleeson, Reaction morphologies developed by nickel aluminides in type II hot corrosion conditions: The effect of chromium, Corros. Sci. 101 (2015) 32–46. doi:10.1016/j.corsci.2015.08.029.
- [48] M.N. Task, B. Gleeson, F.S. Pettit, G.H. Meier, Compositional effects on the Type I hot corrosion of β-NiAl alloys, Surf. Coatings Technol. 206 (2011) 1552–1557.

doi:10.1016/j.surfcoat.2011.06.025.

- [49] M.N. Task, B. Gleeson, F.S. Pettit, G.H. Meier, Compositional Factors Affecting Protective Alumina Formation Under Type II Hot Corrosion Conditions, Oxid. Met. 80 (2013) 541–552. doi:10.1007/s11085-013-9410-2.
- [50] M. GmbH, Sapphire (Al<sub>2</sub>O<sub>3</sub>), (n.d.). http://www.mtberlin.com/frames\_cryst/descriptions/sapphire.htm (accessed February 9, 2018).
- [51] A. Taylor, N.J. Doyle, Further studies on the nickel–aluminium system. I. β-NiAl and δ-Ni<sub>2</sub>Al<sub>3</sub> phase fields, J. Appl. Crystallogr. 5 (1972) 201–209. doi:10.1107/S0021889872009203.
- [52] C.S. Giggins, F.S. Pettit, Oxidation of Ni-Cr-Al Alloys Between 1000° and 1200°C, J. Electrochem. Soc. 118 (1971) 1782–1790. doi:10.1149/1.2407837.
- [53] M. Malik, Morbioli, P. Huber, High Temperature Alloys for Gas Turbines, (1982) 87–98.
- [54] R.C. Novak, Coating Development and Use: Case Studies, Presentation to the Committee on Coatings for High-Temperature Structural Materials, National Materials Advisory Board, National Research Council, (n.d.).
- [55] B.A. Pint, Optimization of Reactive-Element Additions to Improve Oxidation Performance of Alumina-Forming Alloys, J. Am. Ceram. Soc. 86 (2003) 686–95. doi:10.1111/j.1151-2916.2003.tb03358.x.
- [56] D. Naumenko, B. Gleeson, E. Wessel, L. Singheiser, W.J. Quadakkers, Correlation between the microstructure, growth mechanism, and growth kinetics of alumina scales on a FeCrAlY alloy, Metall. Mater. Trans. A. 38 (2007) 2974–2983. doi:10.1007/s11661-007-9342-z.
- [57] J. Stringer, The Reactive Element Effect in High-temperature Corrosion\*, Mater. Sci. Eng. A. A120 (1989) 129–137. doi:10.1016/0921-5093(89)90730-2.
- [58] H. Hindam, D.P. Whittle, Microstructure, adhesion and growth kinetics of protective scales on metals and alloys, Oxid. Met. 18 (1982) 245–284. doi:10.1007/BF00656571.
- [59] R.A. Rapp, Hot corrosion of materials: A fluxing mechanism?, Corros. Sci. 44 (2002) 209–221. doi:10.1016/S0010-938X(01)00057-9.
- [60] D.K. Gupta, R.A. Rapp, The Solubilities of NiO, Co<sub>3</sub>O<sub>4</sub>, and Ternary Oxides in Fused Na<sub>2</sub>SO<sub>4</sub> at 1200°K, J. Electrochem. Soc. SOLID-STATE Sci. Technol. 127 (1980) 2194– 2202. doi:10.1149/1.2129374.
- [61] P.D. Jose, D.K. Gupta, R.A. Rapp, Solubility of α-Al<sub>2</sub>O<sub>3</sub> in Fused Na<sub>2</sub>SO<sub>4</sub> at 1200 K, J. Electrochem. Soc. SOLID-STATE Sci. Technol. 132 (1985) 735–737.
- [62] Y.S. Zhang, Solubilities of Cr<sub>2</sub>O<sub>3</sub> in Fused Na<sub>2</sub>SO<sub>4</sub> at 1200 K, J. Electrochem. Soc. SOLID-STATE Sci. Technol. 133 (1986) 655–657.
- [63] A. Nishikata, H. Numata, T. Tsuru, Electrochemistry of Molten Salt Corrosion, Mater. Sci. Eng. A. 146 (1991) 15–31. doi:10.1016/0921-5093(91)90265-O.
- [64] C.H. Liu, Electrode Potentials in Molten Lithium Sulfate-Potassium Sulfate Eutectic, J. Phys. Chem. 66 (1962) 164–166.
- [65] K.E. Johnson, H.A. Laitinen, Electrochemistry and Reactions in Molten Li<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>, J. Electrochem. Soc. 110 (1963) 314–318.
- [66] B.W. Burrows, G.J. Hills, Electrochemical Studies of Molten Alkali Sulphates, Electrochim. Acta. 15 (1970) 445–458. doi:10.1016/0013-4686(70)87004-9.
- [67] D.M. Wrench, D. Inman, A Chronopotentiometric Investigation of the Dissociation of Sulphate Ions in Molten Equimolar NaCl-KCl at 750 °C, Electrochim. Acta. 12 (1967) 1601–1608.
- [68] C.A.C. Sequeira, M.G. Hocking, Polarization Measurements on Solid Platinum-Molten Sodium Sulphate-Sodium Chloride Interfaces, Electrochim. Acta. 23 (1978) 381–388.
- [69] D.A. Shores, W.C. Fang, Transport of Oxidant in Molten Na<sub>2</sub>SO<sub>4</sub> in O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub>

Environments, J. Electrochem. Soc. 128 (1981) 346-348.

- [70] C.O. Park, R.A. Rapp, Electrochemical Reactions in Molten Na<sub>2</sub>SO<sub>4</sub> at 900°C, 5 (1986) 1636–1641.
- [71] C.L. Zeng, J. Li, Electrochemical impedance studies of molten (0.9Na,0.1K)<sub>2</sub>SO<sub>4</sub>-induced hot corrosion of the Ni-based superalloy M38G at 900 C in air, Electrochim. Acta. 50 (2005) 5533–5538. doi:10.1016/j.electacta.2005.03.034.
- [72] C.L. Zeng, T. Zhang, Electrochemical impedance study of corrosion of B-1900 alloy in the presence of a solid Na<sub>2</sub>SO<sub>4</sub> and a liquid 25 wt.% NaCl-75 wt.% Na<sub>2</sub>SO<sub>4</sub> film at 800 °C in air, Electrochim. Acta. 49 (2004) 1429–1433. doi:10.1016/j.electacta.2003.10.029.
- [73] G. Gao, F.H. Stott, J.L. Dawson, D.M. Farreil, Electrochemical Monitoring of High-Temperature Molten-Salt Corrosion, Oxid. Met. 33 (1990) 79–94.
- [74] C. Cuevas-Arteaga, Corrosion study of HK-40m alloy exposed to molten sulfate/vanadate mixtures using the electrochemical noise technique, Corros. Sci. 50 (2008) 650–663. doi:10.1016/j.corsci.2007.11.011.
- [75] K. Shirvani, M. Saremi, A. Nishikata, T. Tsuru, Electrochemical study on hot corrosion of Si-modified aluminide coated In-738LC in Na<sub>2</sub>SO<sub>4</sub>-20 wt.% NaCl melt at 750 °C, Corros. Sci. 45 (2003) 1011–1021. doi:10.1016/S0010-938X(02)00127-0.
- [76] PDF-4+, International Centre for Diffraction data, (2016).
- [77] FIZ Karlsruhe, Inorganic Crystal Structure Database (ICSD), (2016).
- [78] R.T. Downs, M. Hall-Wallace, The American Mineralogist Crystal Structure Database, Am. Mineral. 88 (2003) 247–250.
- [79] O. El Jaroudi, E. Picquenard, N. Gobeltz, A. Demortier, J. Corset, Raman Spectroscopy Study of the Reaction between Sodium Sulfide or Disulfide and Sulfur: Identity of the Species Formed in Solid and Liquid Phases, Inorg. Chem. 38 (1999) 2917–2923. doi:10.1021/ic9900096.
- [80] F. Pettit, Hot Corrosion of Metals and Alloys, Oxid. Met. 76 (2011) 1–21. doi:10.1007/s11085-011-9254-6.
- [81] C.B. Alcock, M.G. Hocking, S. Zador, The Corrosion of Ni in O<sub>2</sub>+SO<sub>2</sub> Atmospheres in the Temperature Range 500–750 °C, Corros. Sci. 9 (1969) 111–122. doi:10.1016/S0010-938X(69)80047-8.
- [82] K.L. Luthra, D.A. Shores, Mechanism of Na<sub>2</sub>SO<sub>4</sub> Induced Corrosion at 600°-900°C, J. Electrochem. Soc. 127 (1980) 2202–2210. doi:10.1149/1.2129375.
- [83] E.E. Hellstrom, A Preliminary Study of the Redox Behavior of Tungstate and Molybdate Ions in Na<sub>2</sub>SO<sub>4</sub> at 1203 K, Corros. Sci. 23 (1983) 709–715.
- [84] K.J.D. Vries, P.J. Gellings, The Thermal Decomposition of Potassium and Sodium-Pyrosulfate, J. Inorg. Nucl. Chem. 31 (1969) 1307–1313.
- [85] K. Kumar, N. Smith, T. Lichtenstein, H. Kim, Electrochemical Studies of Molten Sulfates in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C, Corros. Sci. 113 (2018) 17-24. doi:https://doi.org/10.1016/j.corsci.2017.12.022.
- [86] R.C. Sharma, Y.A. Chang, Thermodynamics and Phase Relationships of Transition Metal-Sulfur Systems: IV. Thermodynamic Properties of the Ni-S Liquid Phase and the Calculation of the Ni-S Phase Diagram, Metall. Trans. B. 11 (1980) 139–146. doi:10.1007/BF02657183.
- [87] G. Berthomé, B. Malki, B. Baroux, Pitting transients analysis of stainless steels at the open circuit potential, Corros. Sci. 48 (2006) 2432–2441. doi:10.1016/j.corsci.2005.09.012.
- [88] M.W. Brumm, H.J. Grabke, Oxidation behaviour of NiAl—II. Cavity formation beneath the oxide scale on NiAl of different stoichiometries, Corros. Sci. 34 (1993) 547–561. doi:10.1016/0010-938X(93)90271-H.

- [89] H.J. Grabke, Oxidation of NiAl and FeAl, Intermetallics. 7 (1999) 1153–1158. doi:10.1016/S0966-9795(99)00037-0.
- [90] Y. Shida, G.C. Wood, F.H. Stott, D.P. Whittle, B.D. Bastow, Intergranular Oxidation and Internal Void Formation in Ni-40% Cr Alloys, Corros. Sci. 21 (1981) 581–597. doi:10.1016/0010-938X(81)90010-X.
- [91] D. Wu, S. Jiang, Q. Fan, J. Gong, C. Sun, Hot Corrosion Behavior of a Cr-Modified Aluminide Coating on a Ni-Based Superalloy, Acta Metall. Sin. (English Lett.) 27 (2014) 627–634. doi:10.1007/s40195-014-0108-5.
- [92] A.J. Bard, L.R. Faulkner, ELECTROCHEMICAL METHODS Fundamentals and Applications, Second, JOHN WILEY & SONS, INC., 2000.
- [93] N. Dupin, I. Ansara, B. Sundman, Thermodynamic re-assessment of the ternary system Al-Cr-Ni, Calphad Comput. Coupling Phase Diagrams Thermochem. 25 (2001) 279–298. doi:10.1016/S0364-5916(01)00049-9.
- [94] T.-C. Software, Thermodynamic and Mobility Databases Overview, (2017).
- [95] C.L. Zeng, W. Wang, W.T. Wu, Electrochemical impedance models for molten salt corrosion, Corros. Sci. 43 (2001) 787–801. doi:10.1016/S0010-938X(00)00108-6.
- [96] H.M. Hindam, W.W. Smeltzer, Growth and Microstructure of α-Al<sub>2</sub>O<sub>3</sub> on Ni-Al Alloys: Internal Precipitation and Transition to External Scale, J. Electrochem. Soc. SOLID-STATE Sci. Technol. 127 (1980) 1622–1630.
- [97] J. Wang, Investigation of the thermodynamic properties of Ni-Al intermetallic compounds by an EMF method.pdf, Steel Res. 63 (1992) 320–323.
- [98] G. Róg, G. Borchardt, M. Wellen, W. Löser, Determination of the activities in the (Ni + Al) alloys in the temperature range 870 K to 920 K by a solid-state galvanic cell using a CaF<sub>2</sub> electrolyte, J. Chem. Thermodyn. 35 (2003) 261–268. doi:10.1016/S0021-9614(02)00361-0.
- [99] G. Róg, A. Kozlowska-Róg, G. Borchardt, L. Dörrer, W. Löser, Determination of the standard Gibbs free energy of the intermetallic compound Ni<sub>3</sub>Al in the temperature range (820 to 920) K by a solid-state galvanic cell method, J. Chem. Thermodyn. 37 (2005) 97– 100. doi:10.1016/j.jct.2004.07.033.
- [100] M. Bonnet, J. Rogez, R. Castanet, EMF INVESTIGATIONS OF Al-Si, Al-Fe-Si AND Al-Ni-Si LIQUID ALLOYS, Thermochim. Acta. 155 (1989) 39–56.
- [101] L.P. Belo, L.K. Elliott, R.J. Stanger, R. Spörl, K. V. Shah, J. Maier, T.F. Wall, High-Temperature Conversion of SO<sub>2</sub> to SO<sub>3</sub>: Homogeneous Experiments and Catalytic Effect of Fly Ash from Air and Oxy-fuel Firing, Energy and Fuels. 28 (2014) 7243–7251. doi:10.1021/ef5020346.
## VITA

Kuldeep Kumar was born in a small village, Talabpur, located in the northern state -Uttarakhand of India, to Umesh Kumar and Asha Rani. Kuldeep shared his childhood with his younger brothers - Sandeep Kumar and Dalip Kumar. In August 2006, he started his undergraduate education at the Indian Institute of Technology (BHU), Varanasi, India, and graduated in May, 2011 with B. Tech and M. Tech degrees. For his academic excellence, Kuldeep became a gold medalist from the Department of Ceramic Engineering at IIT-BHU for securing first rank in the graduating class of 2011. During his masters, Kuldeep pursued his thesis under the tutelage of Prof. Om Parkash who also instilled in him a zeal to pursue higher studies in the field of science and technology. In fall 2014, Kuldeep joined Prof. Hojong Kim at the Penn State University in the pursuit of his doctoral degree in Materials Science and Engineering.

## List of publications

1) <u>Kumar, K.,</u> Smith, N. D., Lichtenstein, T., Kim, H., Electrochemical studies of molten sulfates in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C, Corrosion Science, 2018, 133, 17

2) <u>Kumar, K.</u>, Gesualdi, J., Smith, N. D, Kim, H., Influence of Gaseous atmosphere on Electrochemical Behavior of Nickel Alloys in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C, (*submitted*).

3) Mondschein, J., <u>Kumar, K.</u>, Holder, C., Seth, K., Kim, H., Schaak, R., Intermetallic Ni<sub>2</sub>Ta Electrocatalyst for the Oxygen Evolution Reaction in Highly Acidic Electrolytes, (*submitted*)

4) Nigl, T. P., Smith, N. D., Lichtenstein, T., Gesualdi, J., <u>Kumar, K</u>., Kim, H. Determination of Thermodynamic Properties of Alkaline Earth-liquid Metal Alloys Using the Electromotive Force Technique. J. Vis. Exp. (129), e56718, doi:10.3791/56718 (2017)

5) Lichtenstein, T., Smith, N., Gesualdi, J., <u>Kumar, K.</u>, Kim, H., Thermodynamic Properties of Barium-Bismuth Alloys Determined by EMF, *Electrochimica Acta*, 2016, 228, 628

6) Smith, N., Lichtenstein, T., Gesualdi, J., <u>Kumar, K.</u>, Kim, H., "Thermodynamic Properties of Strontium-Bismuth Alloys Determined by Electromotive Force Measurements", *Electrochimica Acta*, 2017, 225, 584

7) Kim, H., Smith, N., <u>Kumar, K.</u>, Lichtenstein, T., Electrochemical Separation of Barium into Liquid Bismuth by Controlling Deposition Potentials, *Electrochimica Acta*, 2016, 220, 237

8) <u>Kumar, K.,</u> Lichtenstein, T., Gesualdi, J., Zhou, B. C., Kim, H., Effect of Cr Content on the Electrochemical Corrosion Behavior of Ni-Al-Cr Alloys in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C, (*manuscript in preparation*).