Evaluation of the effects of Molten CuCl on Corrosion Resistant Coatings

By

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In the name of Allah, the most beneficent and the most merciful.

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Abstract

The world is facing energy crisis and pollution problems. Clean and renewable energy resources are gaining popularity day by day. Hydrogen is considered as clean energy carrier which is present in on earth in abundance either in the form of water or other chemical. The target is to produce hydrogen by thermo-chemical decomposition of water. Cu-Cl cycle is selected and preferred on other cycles based on its low operating temperature and cost. Plans for the design and construction of a hydrogen production pilot plant using the CuCl thermochemical cycle are being proposed. Currently researchers are facing several challenges to bring this pilot plant in operation. One of the important challenges is to develop materials for the containment vessels and pipes that will encounter the highly corrosive and harsh environment produced by the molten salts at the high temperature of 500°C.

This research is done to evaluate corrosion resistant coatings. Different coating materials were tested in high temperature molten copper chloride environment to evaluate the coating performance. Super hard steel, Diamalloy 4006, YSZ (ZrO2 18TiO2 10Y2O3) and alumina are the candidate materials selected for corrosion test. High Velocity Oxy fuel and Air Plasma Spray are the coating methods used to coat the samples. Series of tests were conducted in the absence of oxygen in a specially designed apparatus. Temperature was selected 500°C, based on Cu-Cl cycle maximum temperature. Tests were conducted for 50 and 100 hours.

Six coating combinations of bond and ceramic coats were tested in this research. Results suggested that, combination of Diamalloy 4006 (Diamalloy, Diamalloy+YSZ, Diamalloy+Al2O3) performed much better than SHS combination (SHS, SHS+YSZ, SHS+Al2O3). All super hard steel coatings fell off completely. Diamalloy 4006 coatings survived for 100 hours on the walls of the sample but the sample tips corroded badly. Corrosion products along with the deposits of pure copper appeared on the samples, in most of the cases. The study showed that alumina and YSZ can prevent diffusion of molten salt if these coatings do not crack. It was concluded that porosity may be the issue of coating failure.

To investigate the issue of porosity, solid samples of coating material (alumina) was tested in CuCl environment. There was no change in shape, size, weight and appearance of these samples after hundred-hour immersion test. It was concluded that the porosity of coating layers has to be minimized to protect the underlying material.
### Glossary

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>APS</td>
<td>Air Plasma Spraying</td>
</tr>
<tr>
<td>Cu-Cl</td>
<td>Copper Chloride</td>
</tr>
<tr>
<td>Cu-Cl₂</td>
<td>Cupric Chloride</td>
</tr>
<tr>
<td>CYSZ</td>
<td>Ceria Yttria Stabilized Zirconia</td>
</tr>
<tr>
<td>EBC</td>
<td>Environmental Barrier Coatings</td>
</tr>
<tr>
<td>EDS</td>
<td>Electron Disperse Spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Electron Disperse X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydro-Chloric Acid</td>
</tr>
<tr>
<td>HVOF</td>
<td>High Velocity Oxygen Fuel</td>
</tr>
<tr>
<td>ITV</td>
<td>Immersion Test Vessel</td>
</tr>
<tr>
<td>OECD</td>
<td>Organization for Economic Cooperation &amp; Development.</td>
</tr>
<tr>
<td>MCS</td>
<td>Medium Carbon Steel</td>
</tr>
<tr>
<td>PPE</td>
<td>Personal Protective Equipment.</td>
</tr>
<tr>
<td>PSZ</td>
<td>Partially Stabilized Zirconia</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>SYSZ</td>
<td>Scandia Yttria Stabilized Zirconia</td>
</tr>
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CHAPTER 1 – INTRODUCTION

1.1 Introduction

The worldwide demand of energy has increased substantially in recent years and is constantly increasing due to the rise in population, advances in technology and rising living standards. Figure 1.1 shows the projected global energy consumption until the year 2040. The increasing trend shows that the global energy consumption is projected to increase by approximately 35% in the next 25 years (EIA, 2016).

Currently, the main source of energy production are the readily available fossil fuels. However, fossil fuel reserves are gradually depleting and pollution from them is one of the major causes of environmental problems. The increase in demand of energy consumption and problems associated with fossil fuels has been the main motivation for researchers to search for sustainable and environmentally benign energy sources. A significant increase in such sources will play an important role in meeting the energy demands of the future.

Wind, solar, hydro and geothermal are the main contributors for a clean energy generation. However, the intermittent nature and seasonal variability of these sources severely limit the usefulness of these clean energy sources. This results in an inconsistency in the production of
energy, therefore there is a need to store the energy produced from clean/renewable sources and nuclear sources. This stored energy can then be utilized effectively during peak hours and/or in the transportation sector. Hydrogen is considered to be environmental friendly if produced using renewable technologies or waste heat from thermal and nuclear plants, therefore, production of hydrogen on a larger scale may address these issues.

1.2 Hydrogen Production Methods
The main advantage of hydrogen is that it can be stored and used whenever or wherever required like fossil fuels. It is also considered a clean fuel since the combustion of hydrogen produces only water. Hydrogen can be produced by dissociation of natural gas, electrolysis of water, coal/biomass gasification and by biological means. Dincer and Acar (2015) reviewed various methods for the production of hydrogen and concluded that hydrogen produced from nuclear waste heat is the cleanest. Renewable and nuclear sources can be applied to thermochemical cycles for hydrogen production. Figure 1.2 illustrates the possible methods of hydrogen production.

Figure 1.2 - Various renewable and nuclear sources based hydrogen production methods (Adapted from Bicer, 2015)

Decomposition of water by thermo-chemical means is an evolving technology for production of hydrogen on large-scale. Thermo-chemical cycle splits water into hydrogen and oxygen utilizing two or more intermediate compounds without polluting the environment (Naterer et al., 2010). More than 200 thermo-chemical cycles have been discovered for production of hydrogen. However, most of the cycles require very high temperature (above 850 °C) and have low conversion efficiencies (McQuillan et al., 2002).
1.2.1 CuCl Cycle

To produce hydrogen on a large scale, an efficient cycle is required. Amongst the various thermo-chemical cycles, CuCl cycle requires less heat input and it works on relatively lower maximum temperature (500°C) (Lewis et al., 2009). The four step Cu-Cl cycle splits water into oxygen and hydrogen by a sequence of reactions in a closed internal loop. The schematic diagram of the Cu-Cl cycle is shown in figure 1.2 and the equation of reactions is given in Table 1.1.

![Figure 1.3 - Schematic of the four step Cu-Cl cycle. (Naterer et al., 2010)](image)

**Table 1.1 – Reaction steps of Cu-Cl cycle**

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 CuCl (aq) + 2HCl (aq) $\rightarrow$ H$_2$ (g) + 2CuCl$_2$ (aq)</td>
<td>&lt;100 (electrolysis)</td>
</tr>
<tr>
<td>2</td>
<td>CuCl$_2$ (aq) $\rightarrow$ CuCl$_2$ (s)</td>
<td>&lt;100</td>
</tr>
<tr>
<td>3</td>
<td>2 CuCl$_2$ (s) + H$_2$O (g)$\rightarrow$CuO*CuCl$_2$ (s) + 2HCl (g)</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>CuO*CuCl$_2$ (s) $\rightarrow$ 2CuCl (l) + $\frac{1}{2}$ O$_2$</td>
<td>500</td>
</tr>
</tbody>
</table>

Source (Naterer et al., 2010)
At first, Cu-Cl reacts with HCl to produce cupric chloride (Cu-Cl₂) and hydrogen gas (H₂) (Magali et., al 2009). The aqueous Cu-Cl₂ is then converted into a solid by drying it. Then it is sent to a fluidized bed reactor where waste heat, input water and solid Cu-Cl₂ is combined together to produce HCl and copper oxychloride (CuO*CuCl₂) (Magali et., al 2009). In a molten salt reactor, CuO*CuCl₂ is decomposed to yield molten cuprous chloride (Cu-Cl) and oxygen. The only inputs in this cycle are water and heat. Other chemicals are recycled and reused, thereby, keeping them in a close internal loop. The highest temperature in a CuCl cycle is at the molten salt reactor i-e 500 °C.

Plans for the design and construction of a hydrogen production pilot plant using the CuCl thermochemical cycle are being proposed. Currently researchers are facing several challenges to bring this pilot plant in operation. One of the important challenges is to develop materials for the containment vessels and pipes that will encounter the highly corrosive and harsh environment produced by the molten salts at the high temperature of 500°C.

1.3 Problem Statement
One of the major obstacle facing the development of hydrogen production pilot plant is to find material for fabricating parts of a pilot plant that can sustain the corrosive environment for prolonged durations. None of the high performance metals are likely to survive. One possible solution is to use special metals coated with metallic or ceramic coatings. After an initial literature search AL6XN and Inconel 625 (Edwin, 2012) were selected as the substrate materials over which bond coatings were applied followed by the application of ceramic coatings. However, neither of the coatings survived. These substrate metals are expensive and there were indications that the coating were failing due reasons not related to adhesion but other factors such as geometry of specimen, integrity of coatings, failure of equipment setup that failed to prevent oxygen from leaking into it, etc. Therefore, it was decided to first evaluate only the coating materials by depositing these on a low cost medium carbon steel as a base metal and the focus will be just to evaluate bond and ceramic coatings. Once a suitable material is found then additional studies will be conducted to evaluate the performance of the adhesion between the bonding layer and the suitable substrate materials such as the ones mentioned earlier. In this study an attempt has been made to discover the best possible corrosion resistant coatings that are able to last for a longer duration in the highly corrosive environment for the propose pilot plant.
1.4 Thesis Objective
The objective of this research is to evaluate the effects of molten CuCl at 500 ºC on a number of corrosion resistant coatings. The coatings have to be exposed to the conditions of molten salt reactors of the CuCl cycle for longer period of time (~initially 100 hours) in the absence of oxygen. The immediate objectives of this research are:

- To improve the equipment setup so that the absence of oxygen in the system during testing can be ensured.
- To design new specimen geometry to avoid lack of the coating integrity on the sharp edge of the sample.
- To conduct immersion tests using the specimen coated with bond coats and bond coats plus ceramic coats for 100 hrs and 50 hrs.
- To evaluate and compare the results of various corrosion resistant coatings after immersion tests using visual observation, weight change studies, SEM and EDX analysis.

1.5 Thesis Organization:
Thesis consist of six chapters namely Introduction, Background, Literature review, Apparatus and Modifications, Experimental Results and discussion, and Conclusions with future work. First three chapters include background, previous work, literature review and some studies of molten salts are presented. Modification in apparatus is presented in chapter 4 of this thesis. Chapters 5 explains the work that has been conducted. The last chapter is the conclusion of overall work along with some useful recommendation for future work.
CHAPTER 2 – BACKGROUND AND LITERATURE REVIEW

The pilot plant proposed to be built for hydrogen production require materials which can withstand highly corrosive environment at 500°C and above. This work proposes the evaluation of coating materials sprayed thermally on metals in order to prolong their life.

2.1 Corrosion

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. It is an electrochemical reaction and generally begins at the surface. It is a serious issue for manufacturers of cars, boats and other metal accessories.

Corrosion is such a destructive phenomenon that it affects almost all kinds of metals. The interaction of material with the environment often changes its physical appearance and may sometimes alter its mechanical properties (e.g. ductility and strength).

The effect of corrosion varies from one material to another. Metals usually corrode to form scales, whereas, ceramics tend to deteriorate at relatively extreme conditions. The mechanisms and consequences for polymers differ from that of metals and ceramics and the term “degradation” is used. Rust is also a type of corrosion reserved specifically for iron (Roberge, 2012).

2.2 Corrosion Electrochemistry

Corrosion is basically a chemical reaction in which the transfer of electrons takes place from one chemical species to another (Callister, 2006). The term “redox” is a better term to use for corrosion as it is a combination of two reactions i.e. oxidation and reduction. Metal atoms lose or give up electrons at anode called oxidation while reduction or gain of electron takes place at cathode.

Reaction at Anode:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(Oxidation)} \]

Reaction at Cathode:

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \text{(gas)} \quad \text{-- (Reduction)} \]

Overall Reaction:

\[ \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \text{(gas)} \]
One important point to note is, all metallic materials do not form oxides with equal ease. When two electrodes of dissimilar metals are combined in an electrochemical cell, the potential differences among them may be thought of as the driving force for an oxidation-reduction reaction. The standard emf series provides the idea that the electrodes in which one will corrode and which one will have deposits on it.

2.3 Corrosion Kinetics

It is very important to understand the concept of corrosion kinetics and the rate of corrosion. Kinetics of corrosion and relevant terminologies that are frequently being used to evaluate the rate of corrosion are discussed briefly.

2.3.1 Polarization

Polarization can be defined as the displacement of electrode potential resulting from a net current. Its magnitude is measured in terms of overvoltage. Overvoltage, $\eta$, is a measure of polarization with respect to the equilibrium potential of an electrode. Consider an electrochemical cell shown in figure 2.1 which is short-circuited. The net oxidation and reduction processes occur at the interface between the electrode and the electrolyte, which results in a change in the potential of electrodes from their equilibrium potential. This deviation from equilibrium potential is called Polarization.

![Figure 2.1 – Schematic of electrochemical cell (Fontana, 1985).](image-url)
2.3.2 Activation Polarization

Electrochemical reactions consist of a series of steps that occur in a particular sequence. Activation polarization refers to electrochemical reactions that are controlled by a slow step in the reaction sequence. This slow step during hydrogen evolution could be the electron transfer step of formation of hydrogen molecules. The relationship between the reaction rate and overvoltage for activation polarization is:

\[ \eta_a = \pm \beta \log \frac{i}{i_0} \]  

(2.1)

This equation is known as Tafel equation where \( \eta_a \) is overvoltage, \( \beta \) is Tafel constant and \( i \) is the rate of oxidation or reduction.

2.3.3 Concentration Polarization:

Consider the hydrogen evolution reaction. At low reduction rates the distribution of hydrogen ions adjacent to the electrode surface is relatively uniform. At very high reduction rates the region adjacent to the electrode surface will become depleted of hydrogen ions. If the reduction rate is increased further, a limiting rate will be reached that is determined by the diffusion rate of hydrogen ions to the electrode surface. This limiting rate is the limiting diffusion current density \( i_L \). The equation for concentration polarization, considering no activation polarization, is:

\[ \eta_c = 2.3 \frac{RT}{nF} \log \left( 1 - \frac{i}{i_L} \right) \]  

(2.2)

Where \( \eta_c \) is concentration polarization, \( R \) is gas constant, \( F \) is faraday’s constant, \( T \) is absolute temperature, \( n \) is no. of electrons transferred.

2.3.4 Combined Polarization:

Both activation and concentration polarization usually occurs at an electrode. At low reaction rates, activation polarization occurs whereas at higher reaction rates, concentration polarization occurs. The total polarization is the sum of concentration and activation polarization.

\[ \eta_T = \eta_a + \eta_c \]  

(2.3)
2.3.5 **Passivity:**

Certain metals and alloys experience loss of chemical reactivity under particular environmental conditions, and act as inert metals such as platinum or gold (Fontana, 1985). This phenomenon is known as passivity and is displayed by chromium, iron, nickel, titanium and various other alloys.

2.3.6 **Ohmic Drop:**

The ohmic overpotential is the product of resistance and current between the anodic and cathodic sites of a corrosion process. For many corrosion situations these sites are adjacent to each other and the ohmic drop is negligible, particularly, when the environment itself is a good electrolytic conductor such as seawater. However, there are special conditions where the separation of the anodic and cathodic sites can be an important factor in the corrosion progress, for example, galvanic corrosion.

\[ \eta_T = \eta_a + \eta_c + iR \]  

*(Where \( iR \) is ohmic drop.)*

2.4 **Method for Evaluation of Corrosion Rates:**

Corrosion rates have been expressed in a variety of ways in the literature; such as percentage weight loss, milligrams per square centimeter per day and grams per square inch.

2.4.1 **Penetration Method:**

The rate of penetration, or thinning of a structural piece can be used to predict the life of a given component. The expression mm/year is the most desirable way of expressing corrosion rates:

\[ \text{mpy} = \frac{534W}{DAT} \]  

*where,*

\( W \rightarrow \text{Weight loss, mg} \)

\( D \rightarrow \text{density of specimen, g/cm}^3 \)

\( A \rightarrow \text{area of specimen, sq.in} \)

\( T \rightarrow \text{exposure time, hour} \)
For most applications the corrosion penetration rate is less than 20 mpy (0.50 mm/yr) (Vidal et al., 2016; Callister 2006) which is acceptable. In some applications, electric current is also associated with electrochemical corrosion. Corrosion rates can be expressed in terms of current or more specifically as current density.

\[ r = \frac{i}{nF} \]  

(2.6)

\( r = \text{rate of corrosion (mol/m}^2\text{-s)} \)

\( n = \text{No. of electrons associated.} \)

\( F = 95,600 \text{ C/mol.} \)

### 2.4.2 Faraday’s Law:

Faraday’s empirical law of electrolysis relates the current of an electrochemical reaction to the number of moles of the element being reacted and the number of moles of electrons involved. The charge required for such reaction is one electron per molecule, for the corrosion attack of silver.

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag(s)} \]

\[ \text{Ag(s)} \rightarrow \text{Ag}^+ + e^- \]

According to Faraday’s law, 1 mol of silver would require 1 mol of electrons or Avogadro’s number of electrons (6.022 \times 10^{23}). 1 Faraday (F) is equivalent to the charge carried by 1 mol of electrons. The Faraday is related to other electrical units through the electronic charge; the electronic charge is 1.6 \times 10^{-19} coulomb (C). Multiplying the electronic charge by the Avogadro number means that 1 F equals 96,485 C/(mol of electrons). Combining Faraday’s principles with specific electrochemical reactions of known stoichiometry, the following equation is deduced:

\[ Q = F \Delta N \cdot n \]  

(2.7)

where,

\( N \) is the number of moles and \( \Delta N \) the change in that amount.

\( n \) is the number of electrons per molecule of the species being reacted.

The charge Q can be defined in terms of electric current as:

\[ Q = \int_0^t I \cdot dt \]  

(2.8)

where \( I \) is the total current in amperes (A)
**t is the duration of the electrochemical process in seconds (s)**

Table 2.1 - Conversion between Current, Mass loss and Penetration Rates for all Metals.

<table>
<thead>
<tr>
<th>mA cm $^{-2}$</th>
<th>mm y $^{-1}$</th>
<th>mpy</th>
<th>g m $^{-2}$ day$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mA cm $^{-2}$</td>
<td>1</td>
<td>3.28 M/nd</td>
<td>129 M/nd</td>
</tr>
<tr>
<td>mm y $^{-1}$</td>
<td>0.306 nd/M</td>
<td>1</td>
<td>39.4</td>
</tr>
<tr>
<td>Mpy</td>
<td>0.00777 nd/M</td>
<td>0.0254</td>
<td>1</td>
</tr>
<tr>
<td>g m $^{-2}$ day$^{-1}$</td>
<td>0.112 n/M</td>
<td>0.365 /d</td>
<td>14.4 /d</td>
</tr>
</tbody>
</table>

Source: (Roberge, 2012).

where mpy = milli-inch per year

\[
n = \text{number of electrons freed by the corrosion reaction}
\]

\[
M = \text{atomic mass}
\]

\[
d = \text{density}
\]

*Note: the table should be read from left to right, i.e.,

\[
1 \text{ mA cm}^{-2} = (3.28 \text{ M/nd}) \text{ mm y}^{-1} = (129 \text{ M/nd}) \text{ mpy} = (8.95 \text{ M/n}) \text{ g m}^{-2} \text{ day}^{-1}
\]

### 2.5 High temperature corrosion

Almost all metals, alloys and materials undergo corrosion at high temperature. Oxidation is the most common type of high temperature corrosion. This corrosion includes scaling, material loss and a number of changes in physical properties. The nature of corrosion depends on temperature and the condition of environment.

Gaseous attack however is not limited to oxygen only. Corrosive gases with sulphur, carbon oxides, nitrous oxides and halogens all attack materials in a different manner. Furthermore, the corrosive attack is not restricted to gaseous state only. Solid ash and salt deposits also contribute to corrosive attack. Similarly, in a liquid phase, molten salts and metals create challenges to mitigate corrosion attack.

For industries, high temperature corrosion is a big concern. Any metal or alloy exposed to a high temperature in a non-inert environment is potentially at risk. High-temperature corrosion is also
known as dry corrosion or scaling. On the basis of environment and temperature, the following variables widely vary:

- Rate of corrosion
- Nature of the corrosion products
- Mechanism

High-temperature corrosion is a chemical attack from gases, solid or molten salts, or molten metals, typically at temperatures above 750°F (400°C). Different types of high-temperature corrosion have been observed, such as oxidation, sulphidation, carburization, metal dusting, fuel ash, salt deposits and nitridation.

2.5.1 Oxidation

Oxidation is described as the most common type of high temperature corrosion. It results in the formation of an oxide layer on the surface of the oxidizing metal. However, oxidation is not always harmful. Sometimes heat resistant alloys rely on the formation of oxide film to provide resistance to corrosion. Chromium oxide (Cr₂O₃) is the most common of such films. Usually, oxidation does not occur in isolation. The oxidation process is only applicable to uncontaminated air and clean combustion atmospheres. Rate of oxidation increases with increase in temperature.

2.5.2 Sulphidation

It is also a common type of high temperature corrosion. As its name states, sulphidation is due to the presence of sulphur compounds. Sulphidation may occur at low temperatures. Hydrogen sulphide in the presence of hydrogen becomes extremely corrosive between 260 and 288 °C. It is very common in oil industries and cause thinning of piping, pipe fittings, heater tubes and pressure vessels. Sulphidation also effects the engine and gas turbines because of Sulphur presence in fuel.

2.5.3 Carburization

Carburization occurs when metals are exposed to carbon monoxide, carbon dioxide, methane, ethane or any other hydrocarbon at elevated temperatures. It can cause embrittlement and loss of material. Generally, carburization occurs at temperatures higher than 815 °C (Fontana, 1985). In
some applications, materials are intentionally carburized to attain high surface hardness and wear resistance. Metal dusting

Metal dusting is the disintegration of metals and alloys into a dust of metal particles, carbides, oxides and graphite (Grabke, 1995). Metal dusting occurs at a lesser temperature than carburization i.e. between 425 and 815 °C. Maximum rates of metal dusting damage are considered to occur around 650 to 730 °C.

2.5.4 Fuel Ash and Salt deposits

In some cases, the metal surfaces undergo deposits of ash and salts which react with the surface, causing it to corrode. In gas turbines, oxidized sulphur contaminants in fuel and sodium chloride from ingested air tend to react to form sulphates that are subsequently deposited on surfaces (Fontana, 1985).

2.5.5 Nitridation

Nitridation occurs when carbon, low alloy and stainless steel are exposed to an ammonia-bearing environment at elevated temperature (Davis, 1994). The production of ammonia, nitric acid, melamine and nylon generate such conditions. Nitrides are relatively hard and brittle they can produce local or widespread loss of material strength and possible metal wastage.

2.6 Methods of Corrosion Prevention

Several methods for corrosion prevention can be used based on the application. Some of these methods are enlisted below:

- Modification of environment or surroundings.
- Cathodic protection.
- Use of non-corrosive materials (such as alloys)
- Corrosion inhibitors.
- Plating.
- Corrosion resistant coating.
Corrosion prevention via environmental changes cannot take place for CuCl cycle, since the cycle operates at a very high temperature in a closed chamber. Cathodic protection is not suitable as the electric current and electrolyte may disturb the CuCl cycle. Use of non-corrosive materials can be a possible solution and is a part of this study. Paints cannot survive at such high temperatures. Corrosion inhibitors (chemicals) can react with CuCl and may form undesirable compounds. Plating is a lengthy process and has low adhesion to the base metal. Therefore, alteration of surface conditions by applying coatings of different alloys and ceramics can prove to be an effective way for corrosion prevention for molten CuCl. Through the application of coatings, corrosion is prevented by one of the following three main mechanisms or by a combination of two of them:

1. **Barrier effect**, where any contact between the corrosive medium and the metallic material is prevented.
2. **Cathodic protection**, where coated material acts as a sacrificial anode.
3. **Inhibition/ passivation**, where a chemical compound acts as a protective layer.

For CuCl cycle, the barrier effect is the suitable mechanism by which corrosion can be prevented without any interruption.

### 2.6.1 Corrosion Resistant Coatings

Corrosion resistant coatings protect metal against degradation due to moisture, oxidation or exposure to environment. Coatings act as a barrier to inhibit the contact between chemical compound and corrosive environment. Metallic and ceramic coatings can be used for corrosion prevention. In most cases, coating is used to protect unalloyed or low alloyed steel. Metallic coating can be divided into two groups: cathodic coating and anodic coding. In relation to steel, Ag, Ni, Cr and Pb are cathodic while Zn and Cd are anodic in most environments.

### 2.6.2 Coating Methods

Various methods can be used to apply coatings on a substrate. Thermal sprays, ion implantation, physical vapor deposition (PVD), chemical vapor deposition (CVD) and paint application are some of the techniques used to apply coating. Ion implantation, PVD and CVD are very expensive and are not readily available, whereas, paint cannot withstand such high temperatures.
Therefore, thermal spray method is used. Gas turbine blades and boiler tubes are coated using thermal spray method in order to prevent corrosion (Pan et al., 2016). The selection of coating methods depends upon various factors such as, density, porosity, bond strength and coating cost etc.

2.7 Thermal Spraying

Thermal spray is a coating technique in which molten or semi molten material is sprayed onto the substrate at a high temperature and velocity. Coating material is melted using electric arc or combustion of fuel. Metals, ceramics, plastics and alloys are usually used for spraying. The general coating quality is evaluated by its porosity, bond strength, surface roughness and level of oxide. In general, coating quality increases with the increase of particle velocity. Several variations of thermal spraying are used such as:

- Air Plasma Spraying (APS)
- High velocity oxy-fuel coating spraying (HVOF)
- Detonation spraying
- Wire arc spraying
- Flame spraying
- Warm spraying
- Cold spraying

In this study, HVOF and APS, methods are utilized to coat the samples. The HVOF method is used for metallic coatings. Whereas, The APS method is suitable for ceramic coatings since the melting points of ceramics are higher than that of metals.

2.7.1 Air Plasma Spray

The mechanism of air plasma spray is shown in the Figure 2.2. Plasma spray is produced by the ignition of high frequency arc between a tungsten cathode and an anode. The coating powder is injected in front of plasma through a powder port which makes this powder melt and strike with the substrate at a high temperature and velocity. During plasma spray the particles travel at a
velocity of 150-300 m/s. The porosity of ceramic coatings with plasma sprays are 1-2% and the bond strength lies between 21-41 MPa (Vidal et al., 2016). This molten powder sticks and solidifies to form a coating layer on the substrate. The APS method can generate temperature up to 16000K (Metco, 2016).

Figure 2.2 - Air plasma spray gun. (Lagersmit, 2016).

2.7.2 High Velocity Oxy-fuel

HVOF is a thermal spray method which involves melting of a coating powder and spraying it onto the substrate material. High temperature in HVOF is achieved by the combustion of fuel with oxygen. Molten or semi-molten powder gets solidified on the substrate, forming a smooth coated layer with a lamellar structure (Mahesh et al., 2007). The HVOF method is cost effective, flexible and has a superior quality of coating (Stokes and Looney, 2014). This process is being widely used for coating applications in the field of gas turbine, petroleum, paper & pulp, automotive and several chemical industries (Callister 2006). The reason for its popularity is its good wear and corrosion resistant abilities (Bolelli et al., 2008). The porosity for ferrous alloys with HVOF method is less than 2% and its bond strength lies between 48-62 MPa (Vidal et al., 2016).
HVOF spray speed may exceed up to several kilometers per second with temperature ranging in between 4000K to 6000K depending on the fuel used. Having higher particle impact velocity and lower particle temperature, compared to the air plasma spray method, HVOF produce coatings with higher density, bond strength and toughness (Li et al., 2016) with a limited oxide content (Bolelli et al., 2008). Schematic of the HVOF thermal spray gun is shown in figure 2.3.

![Schematic of the HVOF thermal spray gun (High power media, 2016).](image)

2.8 Corrosion Resistant Coating Materials
Several metals are known to possess resistance against corrosion depending upon the environmental conditions and can be used as corrosion preventive material. Alloys with different percentage of composition are also used for the same task. Nickel-chromium and cobalt-chromium alloys produce excellent corrosion resistant coatings. These materials can be deposited with very low porosity levels (less than 1% by volume) to prevent corrosive attack through porous connections (Sidhu et al., 2007). Oxide ceramics are also corrosion resistant material and can be applied to most metal substrates to provide protection against corrosion. Blades of steam and gas turbines usually use thermal barrier coatings of Yttria Stabilized Zirconia (YSZ) (Donachie et al., 2009). The reason why YSZ is preferred as a top coat is because of its low thermal conductivity and high thermal expansion coefficient (Hajizadeh-Oghaz et al., 2015). Moreover, in chemical reactors nickel based corrosion resistant coatings are applied (Li et al., 2009).

Diamalloy 4006 is a nickel based alloy which has a considerable amount of amorphous phases in the sprayed coating. This amorphous or glassy phase is due to the presence of refractory metals like molybdenum, tungsten and metalloids like boron and carbon. It provides excellent resistance to
corrosion in aqueous acidic and alkaline medium. Its oxidation resistance is up to 980 °C while corrosion resistance of up to 875 °C (Oerlikon, 2016). This powder is usually converted to coatings using a high velocity oxy-fuel spray method. It is also known as nickel chromium tungsten molybdenum superalloy powder.

Inconel 625 is nickel–chromium–molybdenum, based superalloy and non-magnetic in nature. The presence of refractory metals, niobium and molybdenum is the reason for its strength (Abioyea et al., 2015). Nickel helps in resisting against non-oxidizing atmospheres, Inconel 625 provides excellent resistance to corrosion against oxidation and corrosive attack (Donachie and Donachie, 2002). This material is used in applications where strength at high temperature and corrosion resistance is required in corrosive medium (Zhong et al., 2010).

Super Hard Steel (SHS) 9172 is an iron based steel alloy which exhibits resistance to corrosion, erosion, abrasion and high temperature oxidation (NSC, 2016). It has good bond strength for substrate materials including aluminum, copper and stainless steel. At elevated temperatures, it prevents sulfidation attack and is widely used for corrosion protection. It has excellent damage tolerance even in harsh environments. Because of its fine microstructure it has good ductility, toughness and fatigue resistance.

Alumina, also known as aluminum oxide (Al₂O₃), can be produced with additives such as silicon dioxide, magnesium oxide calcium oxide to induce certain properties. Physically it looks like white powder similar to table salt. It is resistant to corrosion, has good thermal stability, hardness and wear resistance.

2.9 Molten Salts

Molten salts are one of the high temperature liquids ranging from low melting point of 120°C to high temperature melting points of 1400°C. When a temperature gradient exists in a system containing metal in contact with molten salt, thermal potential is setup, causing removal of metal at high temperature points and deposition of metal at low temperature points (Smith et al., 1957, Las and Simon, 1954). Corrosion of ceramics in molten salts involves dissolution and invasive penetration, where diffusion, grain boundary and stress corrosion may all be present.
2.9.1 Corrosion resistance by ceramics in molten salts

Jagadesh et al. (2011) studied the effects of molten LiCl-KCl salt on high density graphite and partial zirconia coated high density graphite at 600 °C for 150, 1000 and 2000 hours in the absence of oxygen. They found a loss in weight in high density graphite while there was gain in weight of PSZ. No degradation was observed on the surface of PSZ, after 2000 hours, while few microcracks were found on the bond coat interface. PSZ showed excellent resistance to corrosion in LiCl-KCl molten salt at high temperature.

Hajizadeh-Oghaz et al. (2015) also investigated corrosion resistant coatings that were coated with air plasma spray. Molten salts were Na₂SO₄ and V₂O₅, with 45-55&w% by volume, and tests were conducted at different intervals of 6 hours to 300 hours at 1000 °C. It was determined that the nanostructured of CYSZ is better than the conventional YSZ in terms of resistance to corrosion. The two reasons reported were the high content of a stabilizer in comparison with YSZ and the diffusional resistance in nano-porous CYSZ microstructures.

Xu and Li (2014) investigated the environmental barrier coatings (EBC) that has a higher temperature capability. They exposed coatings to a combustion atmosphere temperature and molten salts at 950 °C. They mixed both the coating compounds in different ratios, say 40-60%, and evaluated the results. In molten salts at 950°C, Lu₂SiO₅ show excellent corrosion resistance and chemical stability.

Gomez-Vidal and Morton (2016) used cast able cements to protect the base metal. The cement used was Aremco 645-N and boron nitride coating was layered to fill up the pores. The idea was to block the direct contact of molten salt with the base metal. The baseline they selected for stainless steel corrosion rate was 7.72 ±0.32 mm/year in NaCl – 65.5 wt% LiCl at 650 °C. The results after applying Aremco 645-N and Boron Nitride coat was 9E-04 mm/year.

Hirata et al. (2002) investigated hot corrosion of alumina in V₂O₅– Na₂SO₄ molten salt. Impurities like SiO₂, MgO and CaO were added to alumina to observe the influence on the corrosion rates. It was found that the thickness of the damaged region in alumina ceramics with high purity was linearly related to the duration of its immersion in the molten salt. Additionally, the thickness of the damaged region in alumina ceramics with low impurity depended on the square root of the immersion time in molten salt. Corrosion rates are effected more by the impurities of silicon oxide rather than the impurities of magnesium oxide or calcium oxide. It was
also found that silicon oxide influenced the diffusion rate through grain boundaries of the element.

Wang et al. (2015) studied zirconium and silicon carbide ceramics corrosion in molten FLiNaK salts (LiF–NaF–KF: 46.5/11.5/42mol%) at 850°C, his study led to a conclusion that the ZrC-SiC based ceramic was more resistant to corrosion than ZrC ceramic. This carbide was better at withstanding molten fluorides than ZrC. The study shows that corrosion characteristics of ZrC-SiC were impacted by oxygen content. Oxygen or its ions were major contributors in corrosion of ceramic. The reason shows C\(^4\) ion from ceramics getting oxidized to C by impurities, which causes corrosion of carbide ceramics. Therefore, to hinder corrosion of molten salts, C is added which further results in enhancing corrosion resistance of carbide ceramics.

2.9.2 Corrosion resistance by metals and alloys in molten salts

Sidhu et al. (2016) studied HVOF coatings on nickel based super alloys in a molten salt environment. The coating materials used was Cr\(_3\)C\(_2\)-NiCr, NiCrBSi, Stellite-6 and Ni-20Cr while the base metal was nickel based super alloy. Samples were tested by immersing it in molten salt at 900 °C under cyclic conditions. Their results show that Ni-20Cr performed the best among the tested materials while stellite-6 indicated the minimum resistance to hot corrosion. Molten salt used in this study was Na\(_2\)SO\(_4\)-60% V\(_2\)O\(_5\) and they tested on 50 cycles. Each cycle was of 1 hour followed by 20 minutes of cooling at room temperature. The samples were tested with and without coating for comparison. The coated samples indicated a higher resistance to corrosion in comparison to uncoated samples. The weight change in the samples observed was higher in the beginning of cycles which became gradual in later cycles.

Morales-Hernandez et al. (2016) tested MCrAlY and Diamalloy 4006 coatings for geothermal fluids. This fluid is currently being used in steam turbines for power generation. To make coating materials stick properly to substrate, sand blasting was done (Al\(_2\)O\(_3\) grade G-20) with a pressure and distance of 4 bar and 0.4 m. The roughness of 5-10 \(\mu\)m was achieved for strong adhesion using the method of HVOF. The samples were heat treated to 780°C for three hours in atmospheric conditions to reduce interconnected porosity. Test were conducted in autoclave at 170°C at different intervals of time. Failure by pitting, crevice corrosion and corrosion by fatigue got reduce due to presence of Cr\(_2\)O\(_3\) in Diamalloy and AlCo in MCrAlY.

Gomez-Vidal and Tirawat (2016) studied the corrosion effects of solar thermal salts. They used 34.42 wt% NaCl and 65.58 wt% LiCl at 650-700 °C in nitrogen environment. The temperature
was increased in 50 °C intervals and they found that stainless steel 310 and Incoloy 800H corrosion rate doubles after every interval of temperature. Inconel performed best in their case. The rate of corrosion of Inconel with the said conditions was 2.80±0.38 mm/year.

Dorcheh et al (2016) conducted a study on corrosion by molten nitrates at 600°C by immersing Inconel 626 and different steels for 5000 hours. They used ferric steels P91 and X20CrMoV11-1 and austenitic steels SS316 and SS347H. The molten salt consisted of 40% KNO₃ and 60% NaNO₃. The corrosion behavior was determined by weight change and SEM analysis. They found that ferric steels (P91 and X20CrMoV11-1) could not offer long term resistance to corrosion and the stainless steel formed protective oxide layer on its surface. Inconel 625 showed linear graph of loss in weight. The results revealed the formation of multiphase oxide layers on SS347H. Inconel 625 performed better than ferric and austenitic steel.

Mills and Nuttall (2013) coated NiCr, IN625 and super hard steel 9172 using HVOF technique and were investigated in the NaCl-KCl-Na2SO4 salt. The effect of these coatings on the high temperature corrosion were investigated. The results showed that most of the coating provided suitable protection to the base material.

2.9.3 Corrosion resistance by metals and ceramics in molten salts

Lee and Baik (2009) investigated the ceramic oxide coatings in molten LiCl-Li₂O in oxidizing environment. They used air plasma spray to coat the Al₂O₃ and YSZ on to nickel based alloy. The corrosion was evaluated at 650°C by reduction of coating thickness method. YSZ coating thickness did not change with time while alumina showed linear trend of losing thickness. Aluminum oxide reacted with molten salt and produced some porous compounds like LaAl, Li₅AlO₄ and LiAl₅O₈. YSZ showed superior resistance to corrosion than Al₂O₃.

Loghman et al. (2016) tested corrosion resistant coatings in the presence of molten V₂O₅ at 910 °C. Thermal barrier coating of NiCrAlY with a top coat of YSZ and SYSZ were coated on Inconel 728 super alloy. They found that the mechanism of corrosion of YSZ and SYSZ was dissimilar. The SYSZ layer degraded due to the formation of cracks and the YSZ deformed due to developed stresses in the coat layer. High surface roughness and porosity issues cause fast degradation of the coating and thus a faster corrosion rate. The samples were coated with air plasma spray.

Shankar et al (2013) conducted a study taking into account 2.25Cr-1 Mo steel, 9Cr-1 Mo steel and Ni-based alloys which were coated with partially stabilized zirconia (PSZ) and then tested for
corrosion resistance with LiCl-KCl eutectic salt at 873K in a controlled argon atmosphere across various time lines. It was found that PSZ coated materials outperformed others, where 2.25Cr-1 Mo steel performed worst. However, PSZ coating should be performed carefully as oxygen interaction can lead to underperforming coating, as analyzed under electron microscopy scan and grazing incidence x-ray diffraction.

2.10 Evaluation of coating:
The selection of coating materials is based on the study conducted by Edwin (2012). The literature review resulted in selection of materials such as superhard steel, Diamalloy 4006 and Inconel 625 for bond coat. It was suggested that the ceramic coat of YSZ and alumina can be used for secondary top layer. Edwin (2012) worked on two alloys, one with high nickel content and another one was ferrous alloy. Combinations of metallic and ceramic coatings were tested to enhance resistivity against corrosion. Thermal sprays were used to apply coating on a coin shaped sample. The base metals used by Edwin (2012) were:

- Ni based superalloy (Inconel 625)
- Super Austenitic stainless steel (AL6XN)

Four sets of coatings with eleven combinations were used which are as follow:

1. Metal only
2. Metal coated with ceramic coating
3. Metal coated with bond coat
4. Metal coated with bond coat & ceramic coating

The cross sectional views of aforementioned sets and subsequent combinations are shown in Figure 2.4.

Figure 2.4 - Schematic of coating combinations tested by Edwin (2012).
The purpose of a ceramic coating is to shelter the base metal from molten Cu-Cl, whereas, Diamalloy 4006 protects the base metal from corroding and provide better adhesive strength to the ceramic coating. Table 2.1 provides the list of coating combinations tested by Edwin (2012).

Table 2.2 - The coating combinations tested by Edwin (2012).

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Samples</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bare (Uncoated) Inconel 625</td>
<td>In625</td>
</tr>
<tr>
<td>2</td>
<td>Bare (Uncoated) Stainless steel AL6XN</td>
<td>SS</td>
</tr>
<tr>
<td>3</td>
<td>Inconel 625 coated with Diamalloy 4006 coating</td>
<td>InDi</td>
</tr>
<tr>
<td>4</td>
<td>Stainless Steel AL6XN coated with Diamalloy 4006 coating</td>
<td>SSDi</td>
</tr>
<tr>
<td>5</td>
<td>Inconel 625 coated with Diamalloy 4006 and YSZ coatings</td>
<td>InDiYS</td>
</tr>
<tr>
<td>6</td>
<td>Inconel 625 coated with Diamalloy 4006 and Alumina coatings</td>
<td>InDiAl</td>
</tr>
<tr>
<td>7</td>
<td>Stainless Steel AL6XN coated with Diamalloy 4006 and YSZ coatings</td>
<td>SSDiYS</td>
</tr>
<tr>
<td>8</td>
<td>Stainless Steel AL6XN coated with Diamalloy 4006 and Alumina coatings</td>
<td>SSDiAl</td>
</tr>
<tr>
<td>9</td>
<td>Inconel 625 coated with Diamalloy 4006 and YSZ coatings</td>
<td>InYS</td>
</tr>
<tr>
<td>10</td>
<td>Stainless Steel AL6XN coated with Diamalloy 4006 and YSZ coatings</td>
<td>SSYS</td>
</tr>
<tr>
<td>11</td>
<td>Stainless Steel AL6XN coated with Diamalloy 4006 and Alumina coatings</td>
<td>SSAI</td>
</tr>
</tbody>
</table>

The high nickel content base metal was supposed to provide excellent corrosion resistance. The coating layers were uniform throughout the surface of samples but not at the edges. The sharp edges had improper coating layer due to the limitations of thermal spray method. Non-uniform or relatively weak layer on the edges could cause coating to crack. Consequently, this cracking of coating may lead into cracking of whole protected surface. Figure 2.5 represents the geometry of samples used by Edwin.
It was found that most of the coatings fell off during the immersion test. Samples, with combination of both ceramic and Diamalloy 4006, couldn’t survive in molten Cu-Cl at high temperature. It was identified that a nickel based super alloy, Inconel 625, performed better than austenitic stainless steel AL6XN. Observations disclose the information that Diamalloy 4006 and YSZ coating provided a better protection than alumina (Al$_2$O$_3$ 3TiO$_2$) to the base metal (Edwin, 2012).

Kaveh et al. (2016a) replaced the base metal with cost effective metal such as medium carbon steel. It was decided to investigate the performance of corrosion resistant coatings only in order to find out the most suitable coating material before investigating the performance of the base metals. Six coating combinations were tested for immersion test. Kaveh et al. (2016b) studied and tested YSZ and Diamalloy+YSZ coatings in molten copper chloride. Diamalloy 4006 and superhard steel 9172 were applied on base metals as a bond coat whereas YSZ top coat was applied as a secondary coat. They tested the YSZ coating for 5 hours and found coating to be stripped off as well as corrosion on the base metal. The reason mentioned was lack of integrity between base metal and the YSZ coating. Moreover, thickness of coating was not enough to bear CuCl attack. Diamalloy + YSZ was tested for 48 hours which showed more resistance to corrosion. The top layer of YSZ delaminated from some portions and got dissolved. However, the Diamalloy coating remained intact for 48 hours. The schematic of coating combinations tested by Kaveh are shown in Figure 2.6:
Kaveh (2014) reported that coatings of Diamalloy 4006 and super hard steel 9172 performed much better than ceramics coat of YSZ. The coatings and combinations used by Kaveh (2014) are given in Table 2.3 which is as follow:

Table 2.3 - The coating combinations tested by Kaveh (2014).

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Bare (uncoated) medium carbon steel – 1045</td>
<td>Mild</td>
</tr>
<tr>
<td>1</td>
<td>Medium carbon steel (1045) coated with YSZ coating</td>
<td>YSZ</td>
</tr>
<tr>
<td>2</td>
<td>Medium carbon steel (1045) coated with Diamalloy 4006 and YSZ coating</td>
<td>Dia + YSZ</td>
</tr>
<tr>
<td>3</td>
<td>Medium carbon steel (1045) coated with SHS 9172 coating</td>
<td>SHS</td>
</tr>
<tr>
<td>4</td>
<td>Medium carbon steel (1045) coated with Diamalloy 4006</td>
<td>Dia</td>
</tr>
<tr>
<td>5</td>
<td>Medium carbon steel (1045) coated with SHS 9172 and YSZ coatings</td>
<td>SHS + YSZ</td>
</tr>
</tbody>
</table>

Kaveh (2014) improved the geometry by introducing bullet shape samples for testing. The bullet shape samples were provided with a threaded hole which helped in holding and hanging of sample during thermal spray processes. Sharp edges were eliminated with round edges to overcome non-uniform coating sprays. Now it was easier to hold the samples during thermal spray processes as well as during immersion test. The improved bullet shape geometry of samples is shown in Figure 2.7.

Figure 2.7 - Bullet shape sample geometry with one end round by Kaveh (2014).
In current study, the base metal chosen is medium carbon steel. Some of the combinations are repeated to validate the previous works done by Kaveh (2014) and Edwin (2012). The schematic of coating combinations tested in current study are shown in Figure 2.8:

Figure 2.8 - The coating combinations tested in current study.

Furthermore, aluminum oxide is now added in the coating combinations whereas, previously only YSZ was used as secondary layer of ceramic. A total of six combinations of alloys and ceramics are used in this study which are listed in Table 2.4:

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Combination details</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Medium Cabon Steel (1045) – (Uncoated)</td>
<td>MCS</td>
</tr>
<tr>
<td>1</td>
<td>Medium Cabon Steel (1045) coated with Diamalloy 4006 - bond (YSZ top)</td>
<td>MCSYS</td>
</tr>
<tr>
<td>2</td>
<td>Medium Cabon Steel (1045) coated with SHS - bond (Al₂O₃ top)</td>
<td>MCSHSAI</td>
</tr>
<tr>
<td>3</td>
<td>Medium Cabon Steel (1045) coated with Diamalloy 4006</td>
<td>MCSDi</td>
</tr>
<tr>
<td>4</td>
<td>Medium Cabon Steel (1045) coated with SHS - bond coat (YSZ top)</td>
<td>MCSHSYS</td>
</tr>
<tr>
<td>5</td>
<td>Medium Cabon Steel (1045) coated with Bond Diamalloy 4006 (top Al₂O₃)</td>
<td>MCSDiAl</td>
</tr>
<tr>
<td>6</td>
<td>Medium Carbon Steel (1045) coated with SHS-9172</td>
<td>MCSHS</td>
</tr>
</tbody>
</table>

Kaveh’s modification in sample geometry improved the integrity of coating layers. Further modification could be done by making both ends of the sample round in shape. This would help in more uniform thermal spray coatings. The flat end could be the reason of improper coating. It was assumed if the coatings cracks from the flat end, it would provide a pathway for corrosive environment to get through the coating layer and react with the base metal. The modified design is shown in Figure 2.4
2.11 Gaps in Literature
This project investigates the use of ceramic and metallic coatings over corrosion resistant materials. Based on the above literature review, it was found that there are very few studies available for molten CuCl corrosion. The use of nickel and chromium based alloys with coating method of HVOF in high temperature molten salts is very common. It is found that for ceramics, YSZ is a common candidate for corrosion resistance. SYSZ, CYSZ and PYZ are some other candidates of ceramics that are widely been used in molten salts to enhance the life of metallic accessories in different applications. Alumina also serves as a good candidate for this purpose. Diamalloy and stainless steel with the HVOF coating method is widely being used for corrosion applications due to its lower porosity and higher bond strength, compared to other methods.
CHAPTER 3 – APPARATUS AND MODIFICATIONS

3.1 Apparatus
According to the ASTM G31 standard, the apparatus should consist of a heating mantle, an Immersion Test Vessel (ITV), a condenser, a scrubber, a flowmeter for controlling oxygen and a test specimen support (NACE, 2012). The lid of an ITV should have multiple inlets/outlets for thermocouples and connecting pipes (Kaveh et al., 2016). Fume hood is used in conducting experimental work for safe operation. Personal Protective Equipment (PPE) are a must to wear during immersion tests. ITV, condenser, scrubber and connecting tube are made of glass and therefore not corrosive. J & K type thermocouples, temperature controllers and gas flowmeters are monitoring devices are installed in the setup. Hanging and lifting mechanism is designed to immerse and lift samples in molten CuCl during experiment.

3.1.1 Overall setup:

Figure 3.1 shows the picture of a running experiment. A controller, an ITV, a condenser and a scrubber can be seen interconnected with each other inside the fume hood. A gas flowmeter is installed to control the flowrate of inert gas inside the ITV. This system is made air tight to avoid infiltration of oxygen gas which is why the pressure inside vessel is kept above atmospheric pressure to prevent entering oxygen. A tripod stand holds the vertical pipe through which inert gas enters the vessel. This same pipe is used for supporting the lifting mechanism of the system.

Figure 3.1 - Overall experimental setup.
3.1.2 Fume hood:

Fume hood is a ventilation device that is used to conduct experiments with toxic and hazardous gases. Molten CuCl fumes are hazardous and should be exhausted through fume hood. Also CuCl may react with coating or base metal to produce other gases. Continuous supply of argon gas eliminates gases that are present in test vessel. Therefore, it is mandatory to conduct experiments inside a fume hood to meet safety requirements.

3.1.3 Heating Mantle

Due to the high temperatures needed to heat up a test vessel (upto 500°C) this is the purpose of using a heating mantle. It was purchased from Glas-col mantle. It is 1300 W with a maximum temperature of 650 °C. During experiments, its heating coil was burnt off which was replaced with two heating tapes each 650 W. It has no built in temperature controller or any temperature monitoring device which is why external controller is required to maintain the temperature. It has good insulation and its outer surface remains at room temperature during experiments. Its interior is strengthened with a layer of aluminum. An image of the heating mantle used in the experiment is shown in Figure 3.2:

![Figure 3.2 - 1000 W Glas-Col heating mantle.](image)

3.1.4 Temperature Controller:

Two temperature controllers are added in an apparatus to maintain and monitor the temperature inside an immersion test vessel. One thermocouple is inserted inside the test vessel through an ITV while the second one is inserted in the heating mantle to note the temperature of heating tape. Two controllers are installed in parallel combination to maintain the required temperature. Omron has a K type thermocouple while a Glas-col utilizes a J type thermocouple. Wiring was done manually to condense electrical setup which previously had a lot of wires, extension cables
and three pin connectors. For the immersion test, the Glas-col temperature is set to 550 °C while the second one is set to 500 °C. During start-ups, the temperature is set to 50°C and it cuts off the power supply after achieving this temperature, the set point is moved to 100°C and continues this cycle at 50°C increments. It is good practice to increase the temperature in intervals. Setting the temperature directly to 500 °C at startup may damage the heating mantle. The process takes approximately one hour to achieve 500°C inside the ITV. Figure 3.3 shows the temperature controllers used in the apparatus.

![Figure 3.3 - Glas-Col and Omron temperature controllers.](image)

### 3.1.5 Immersion Test Vessel (ITV):

ITV is made of quartz glass which can be used for operations at a higher temperature of up to 1050 °C (AVT, 2016). Glass is the only material used for this purpose as no other material was able to withstand at such high temperature and a CuCl environment. This vessel has the leading role in experimental work. Samples, CuCl, crucibles, lifting and hanging mechanism stays inside the ITV during experimental work. The ITV itself stays in heating mantle and remains at a high temperature during the immersion test. The top lid of the ITV consists of three openings. One of the opening has a place to insert a thermocouple for temperature monitoring. The second opening is used to operate the lifting mechanism and serves as the inlet path for argon gas. The third opening is used to vent gas from the vessel. Figure 3.4 shows the image of the immersion test vessel.
3.1.6 Connecting Tube:

The connecting tube is also made of quartz glass and serves as a passage for transferring inert gas along with CuCl fumes into a condenser. It is a very critical part of the apparatus and without the connecting tube, gases cannot be sent to the condenser. Its temperature noted during the experiment was around 100°C. Special care should be given to the connecting tube as it is light in weight and made of glass. Mishandling it may break this tube and it is not readily available in market. Figure 3.5 shows the schematic of connecting tube.

3.1.7 Condenser:

The condenser is also made of quartz glass. Its purpose is to condense gases which enters in from the immersion test vessel. It is also provided with a top lid with three openings. The first opening is to receive gases from the ITV. The second opening is used for the exiting those gases to the next section of the apparatus. The third opening is provided with a pressure gauge to monitor the
inside pressure of the system. Like an ITV, a condenser has a separate top lid and is pasted with a condenser with adhesive glue. The temperature of the condenser noted during the experiment, was found to be slightly above room temperature and is cool to the touch. Figure 3.6 shows the photo of condenser used in the experimental setup.

![Condenser photo](image)

Figure 3.6 - Condenser photo used in the experiments.

### 3.1.8 Scrubber:

The scrubber is made of quartz glass as well and has SS 316 lid with two openings. The gas from the condenser enters through one opening and exits through the other. Its function is to neutralize gases before releasing to the fume hood. The solution inside the scrubber is a mixture of 4.5 liters of water and 390g sodium hydrogen carbonate (NAHCO₃). The scrubber is also provided with plastic beads to reduce the formation of bubbles in the liquid.

### 3.1.9 Hanging and lifting Mechanism

A specially designed mechanism is used for hanging samples in the test vessel. This mechanism consists of two horizontal plates made of stainless steel with three long screws to hold the plates. Nuts in the screws are used to set the height of the horizontal plates. The upper plate has a long vertical rod used to lift the upper plate during experimental work. The reason for lifting and dropping the upper plate is to dip samples in Cu-Cl after it melts and to lift samples up before solidification of Cu-Cl. The samples are provided with threaded holes which are used to hang them with the upper plate via screws of appropriate length. This mechanism stays inside the ITV during immersion test. Lifting the plate via a vertical rod should be done using high temperature
gloves, as high temperatures are used during experiments. Lifting is done before turning the heaters off after the completion of experiment. Figure 3.7 shows the photo of hanging & lifting mechanism.

![Figure 3.7 – Hanging and lifting mechanism.](image)

### 3.1.10 SEM/EDX Equipment

SEM and EDX analysis was performed in University of Toronto, at Center of Advanced Coating Technology (CACT). TM-3000 Hitachi with wide magnification range of 15X – 30,000X was used for scanning electron microscopy. Electron dispersion x-ray spectroscopy was performed on variable pressure scanning electron microscope (Hitachi SU1510) with EDX spectrometer (Bruker QUANTAX 100). Samples were cut with the cutting machine AbrasiMet™ 250 while for polishing of samples Buehler Ecomet 300 was utilized.

### 3.1.11 Personal Protective Equipment (PPEs)

Toxic and poisonous hazards can easily be avoided by using a fume hood. It is always a good practice to keep the apparatus inside the fume hood. A high temperature protection set should be worn during the immersion test which consists of a respirator, safety goggles, fiber glass high temperature gloves, a face shield and latex gloves.

During the immersion test, the condenser, the connecting tube and the scrubber are cool to the touch. Since the heating mantle has good insulation around it, it doesn’t get hot enough to cause any hazard. It is better to keep away from the mantle during experiment because the top lid has no insulation. If the steel lid is in operation, it will be at the same temperature indicated by the heat controller. The top lid shouldn’t be touched in any case unless wearing high temperature gloves.
While handling the lifting mechanism use high temperature gloves and a respirator. During operation there will be argon gas and CuCl fumes releasing from the top of the exit pipe.

Personal protective equipment must be worn during an experimental work. While dealing with chemicals the use of surgical gloves, lab coat, a fume hood and a safety mask are highly recommended for safe operation. Most of the experimental work in this research requires use of personal protective equipment even though some of the work carried out is at high temperatures and some at room temperature. The main task, in which the use of PPEs are mandatory, are mentioned below:

- Scrubber solution preparation.
- Sealing the scrubber.
- Sealing of ITV and condenser.
- Filling of powder CuCl in crucibles.
- Opening of ITV lid after experiment.
- Filling of reference electrodes.
- Cleaning of crucibles by concentrated HCl
- EDTA solution preparation.

When dealing with high temperatures, it is not recommended to touch the apparatus unless high temperature gloves and a coat is used. Also it’s better to use a wind shield with a mask while opening the ITV lid and recommended to place a note on the fume hood while running the experiment to indicate to anyone working in the lab.

Drying the samples post immersion, cleaning requires temperature of 800°C. High temperature gloves are mandatory to lift and insert the samples in to the furnace. Similarly, EDTA solution works at 80 °C and gloves are also mandatory. Samples will produce colored compounds in EDTA solution which might be harmful for human skin and must be handled with care.

Washing the apparatus, like ITV, condenser, scrubber etc always use surgical gloves. CuCl sticks on hands and could go into your lungs through respiration. It is a harmful compound and special care should be taken while dealing with new and used CuCl.
3.2 Modification in Apparatus

A series of experiments were conducted to examine the performance of the apparatus. Some modifications in the design were made to improve the quality of the experiments. The apparatus used occupied a big space and had a lot of wires and switch board connections. The electrical circuit was redesigned into a compact size box by eliminating un-necessary switch boards. The heating mantle was repaired with some modifications and gasket material was changed to make it re-usable. Addition of higher order gas flowmeter enhanced the capacity to monitor higher gas flowrates during purging or operation. The oxygen content was always a problem therefore an oxygen analyzer was affixed to eliminate this problem.

3.2.1 Heating mantle modification:

The heating mantle that was previously used was home made. A steel pot was used with heating tape and insulation as a heating mantle. The readymade heater was burnt off. The heating mantle was repaired and modified with higher power wattage and the heating tape was replaced with two heating tapes that were 627 Watts each. The specifications of the heating tapes that were inserted in heating mantle, are presented in Table 3.1. The power rating of the heating mantle is now enhanced from 1000 watts to 1254 watts. Images of the heating mantle during repair are shown in Figure 3.8:

![Figure 3.8 – (a) Burnt heating mantle (b) Heating mantle with new heating tape during modification.](image)

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>627</td>
<td>Watts</td>
</tr>
<tr>
<td>Voltage</td>
<td>120</td>
<td>Volts</td>
</tr>
<tr>
<td>Current</td>
<td>5.23</td>
<td>Ampere</td>
</tr>
<tr>
<td>Type</td>
<td>SAM HTG TP</td>
<td>-</td>
</tr>
</tbody>
</table>
3.2.2 *Introduction of oxygen analyzer*

One of the requirement to conduct these experiments is to run them in the absence of oxygen. The method used earlier to check the presence of oxygen was by heating the dummy samples for couple of hours and measuring their weight change. If there is no change taking place in weight and physical appearance, then the apparatus was considered free of oxygen. Repeated tests show that sample appearance and weight is changing. It was not concluded if oxygen was present in ITV or not. To validate the presence of oxygen, an oxygen analyzer was introduced to the apparatus. Figure 3.9 shows oxygen analyzer that was installed. It was purchased from omega and its specifications are given in Table 3.2:

Table 3.2 - Oxygen Analyzer Specifications.

<table>
<thead>
<tr>
<th>Description</th>
<th>Oxygen</th>
<th>Relative Humidity</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement Range</td>
<td>0.0 to 30.0%</td>
<td>-10 to 60°C (14 to 140°F)</td>
<td>0.1 to 99% RH</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.1%</td>
<td>1°C (77°F)</td>
<td>-</td>
</tr>
<tr>
<td>Accuracy</td>
<td>±1%</td>
<td>±0.6°C (0.9°F)</td>
<td>±3% RH [at 25°C (77°F), from 10 to 90% RH], ±5% RH above and below</td>
</tr>
</tbody>
</table>

Source: (Omega, 2016)
Oxygen analyzer shows the oxygen percentage, relative humidity and temperature of the environment. It has some limitations too; its working temperature is between -40 to 70°C therefore it cannot be inserted directly into the ITV. The condenser in the apparatus has a lower temperature of just above the environments temperature, so it was installed on the condenser lids. (one port for sample intake and second for sample exhaust). Figure 3.10 shows the connection of the analyzer on the condenser.

Figure 3.10 - Possible location for oxygen analyzer installation on the condenser.

For actual experiments, it is not a good idea to install this analyzer on the condenser because it will be taking samples that contain fumes of CuCl. The fumes will corrode the analyzer during an immersion test. To solve this problem, it was installed after the scrubber where the CuCl fumes exit after passing through a scrubber solution. Operating conditions of the oxygen analyzer are shown in Table 3.3.

Table 3.3 - Operating conditions of an oxygen analyzer.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure Range</td>
<td>30 to 110</td>
<td>kPa</td>
</tr>
<tr>
<td>Memory capacity</td>
<td>32,000</td>
<td>Readings</td>
</tr>
<tr>
<td>Storage Temperature</td>
<td>-40 to 70</td>
<td>°C</td>
</tr>
<tr>
<td>Response Time</td>
<td>@ 2 minute to 100 %</td>
<td>-</td>
</tr>
</tbody>
</table>

Source: (Omega, 2016).
The data logger chart in Figure 3.11 is representing oxygen (yellow line), temperature (green line) and relative humidity (red line). The red vertical line in the center is the cursor, which can be moved horizontally to check the values at any time. At the beginning, the yellow line drops with a steep curve, showing the purging of inert gas. As it continues, some yellow peaks can be seen. These peaks were formed when the flowrate was dropped below a certain value or was stopped and increased as the flowrate did. The green line is continuously increasing, representing a continuous rise in temperature, which is due to the furnace temperature rising. Relative humidity was higher in the beginning but decreased after inert gas was purged into the system.

![Data logger chart](image)

Figure 3.11 - Graph taken by Oxygen analyzer.

### 3.2.3 Gas flowmeter:

When the oxygen content issue was resolved, the need to upgrade the flowmeter rose. Previously, it was assumed that the flowrate should be set to a minimum possible rate to save inert gas. After installing the oxygen analyzer, it was realized that the flowrate required to keep the oxygen content to zero percent, was higher than the measurement range of the flowmeter. A new flowmeter was purchased from Dwyer which has a capacity of 30-240 cc/min as shown in Figure 3.12. While the previous one had a measurement capacity of 0-100 cc/min, the new one could not measure flowrates below 30 cc/min. Both meters were installed in series which gave us the advantage to validate the performance of both flowmeters.
3.2.4 Sealants

High temperature sealants are a critical part of this experimental work, without sealants these experiments could not be performed. High temperature stove and furnace cements were used which can work at 1000 to 1500 °C. Kwik seal was used for sealing the joints and it works at room temperature. The sealants used in these experiments are shown in Figure 3.13:

3.2.5 Gasket Material:

A hypalon gasket is made of rubber containing chlorosulphonated polyethylene and was used previously to provide the seal between the ITV and the lid. After every test, it had to be removed and changed as it couldn’t survive at such high temperatures. After every 8-hour test, the gasket becomes brittle and cracked. Investigations showed its operating temperature is between -35°C to + 125°C (Hennig, 2016)

Glass fiber gaskets were introduced in place of the hypalon gasket. It is a low cost material that can survive temperatures of up to 1000 °C. It was tested in place of the hypalon gasket and performed well, maintained its original shape and gesture after a high temperature test. Sealants
are the cause of damage to gaskets. When a sealant applied to a gasket, it cannot be removed as it is made of fiber glass. It gets stuck on the lid from the top and on the ITV from the bottom. On opening of lid, it breaks into two halves from the center therefore, a fresh gasket needs to be installed. Figure 3.14 shows the gaskets used in experiments.

Figure 3.14 - (a) New glass fiber gasket (b) Used fiber glass gasket (c) Used hypalon gasket.
CHAPTER 4 – EXPERIMENTS, RESULTS AND DISCUSSION

4.1 Pre-Immersion Tests
Before conducting immersion tests with coated samples few pre-immersion tests are performed. Tests were conducted to check the performance of the apparatus and also to counter issues related to the presence of oxygen. Electrical conductivity of molten CuCl was determined and the changes in colour of the ITV glass lid was monitored during the test. Molten CuCl images were taken at high temperature to notice the physical appearance of liquid CuCl. Thermal expansion of solid CuCl is observed with experiments. A thermal cycling test of coated samples was also performed to evaluate whether the coatings can sustain their integrity at repeated thermal cycles.

4.1.1 Purging optimization

The immersion test vessel has to be purged with argon gas before starting the experiment. Oxygen analyzer ensures the absence of oxygen while purging. Argon gas flowrate and purging time were calculated based on the volume of the immersion test vessel:

Diameter of ITV = 150 mm
Height of ITV = 160 mm

Volume of ITV = \( \frac{\pi}{4} \times (150)^2 \times (160) = 2628000 \text{ mm}^3 \)

Volume of ITV = 2628 cm³

If set flowrate is 80 cc/min then,

\[
\text{Time} = \frac{2628 \text{ cc}}{80 \text{ cc/min}} = 35.32 \text{ min}
\]

According to purging principles, the purging volume should be between 1.5 to 2.5 times the volume of the vessel (AGA, 2011). Based on the above calculations, at 100 cc/min with 1.5 times volume, the purging time should be approximately 42 mins. Argon gas is 1.4 times denser than the air (Fire, 2009) therefore, it should replace oxygen easily due to its higher weight.
4.1.2 Oxygen test

An oxygen analyzer was installed to double check the presence of oxygen. The apparatus was sealed properly and purged with argon gas. The oxygen analyzer was installed at the condenser as it cannot withstand high temperatures from the furnace. It takes samples from the condenser and sends it back to condenser. As the ITV, the condenser and the scrubber are connected in a series sample for oxygen testing can be taken from any of these components. Figure 4.1 shows temperature, humidity and oxygen percentages with green, red and yellow curves respectively, taken from the oxygen analyzer. The yellow line declines with a steep curve at the beginning of the graph and represents the trend of oxygen elimination from the apparatus.

![Figure 4.1 - Graph taken by the Oxygen analyzer during the oxygen test.](image)

The oxygen presence can be seen intermittently. This happens when we try to reduce the purge gas flowrate. The presence of O₂ indicate that due to low flowrate O₂ is able to get inside the ITV and flow needs to be increased. There is a slight increase in temperature which shows the condenser is always cool to touch during operation. Its temperature is around 22 °C. Humidity also decreases initially and then attains a constant level throughout the experiment.
4.1.3 Determining Corrosion Rates

Three uncoated samples as shown in Figure 4.2a of MCS were tested for corrosion. One of the samples was immersed in CuCl, the second one was hung on CuCl fumes and the third one was left inside the vessel in a high temperature CuCl environment.

![Figure 4.2 - MCS samples (a) before and (b) after immersion test](image)

The lifting mechanism, samples and glass lid turned black during experiment. Black deposits were found on the samples after an eight-hour test. The images of samples after the corrosion test are shown in Figure 4.2b. Corrosion appeared on all the samples. The corrosion rates were calculated based on measured data. The three sample’s corrosion rates are given in Table 4.1. The immersed sample in CuCl has the highest corrosion rate while the hanged sample has less. The third sample, which was put aside in the ITV, has the least corrosion rate. Calculated corrosion rates are much higher than the standard corrosion penetration rate. For most applications the corrosion penetration rate is less than 20 mpy (0.50 mm/yr) which is acceptable (Roberge, 2012).

![Table 4.1 - Calculated corrosion rates of uncoated medium carbon steel samples.](image)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Status</th>
<th>Weight before test (gram)</th>
<th>Weight after test (gram)</th>
<th>Time (hour)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-</td>
<td>Immersed</td>
<td>64.8602</td>
<td>63.7344</td>
<td>8</td>
<td>5802</td>
</tr>
<tr>
<td>2-</td>
<td>Hanging in air</td>
<td>64.4152</td>
<td>63.8830</td>
<td>8</td>
<td>2743</td>
</tr>
<tr>
<td>3-</td>
<td>ITV floor</td>
<td>64.8229</td>
<td>64.5991</td>
<td>8</td>
<td>1153</td>
</tr>
</tbody>
</table>

Corrosion rates are calculated using an equation 2.5. The exposure time is 8 hours and the density measured for each sample was around 7.85 g/cm³. The surface area for each sample measured was 2.2 sq.in
Stainless steel 304 uncoated samples were immersed in molten CuCl for 100 hours. The images taken before and after the immersion test are shown in Figure 4.3. Corrosion was found on the samples after cleaning with the EDTA solution. The weight of the samples decreased during the 50-hour immersion test. The loss in weight indicates that the SS-304 has corroded away.

The change in the weight along with the corrosion rates calculated are presented in the Table 4.2. The density of SS-304 is taken 8.03 g/cm³. The results showed that Medium carbon steel corroded faster than stainless steel 304.

Table 4.2 - Corrosion Rate of uncoated stainless steel 304.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Weight before test (grams)</th>
<th>Weight after test (grams)</th>
<th>Change in weight (grams)</th>
<th>Time (hours)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130.46</td>
<td>120.4712</td>
<td>9.9888</td>
<td>50</td>
<td>3163</td>
</tr>
<tr>
<td>2</td>
<td>130.258</td>
<td>120.7277</td>
<td>9.5303</td>
<td>50</td>
<td>3018</td>
</tr>
</tbody>
</table>

4.1.4 Thermal Cycling Test

A thermal cycling test was performed to investigate whether the coatings can maintain its shape due to repeated thermal expansion and contraction. Coated samples were heated and kept at 500 °C for two hours and then were cooled to room temperature in the furnace. This cycle was repeated five times in two days and each time the samples were inspected physically for cracks in the coating. The vessel was not sealed in this experiment and no purging was done with argon gas. It was carried out at atmospheric conditions. Figure 4.4 shows the samples before the testing.
All six coating combinations were tested together in the same furnace. No CuCl was used. No cracks were formed in any of the coating combinations and no significant change was observed in the weight of the samples. The spots on the samples after the test are due to the presence of leftover particles of CuCl in the test vessel. Larger differences in coefficient of thermal expansion of base metal and coatings leads to cracks if the coating is brittle. The coefficient of thermal expansion for YSZ is \( \approx 7.8 \times 10^{-6} \text{ K}^{-1} @ 800\text{K} \) (Hayashia et al., 2005). The photo of samples after the expansion test is given in Figure 4.5.

### 4.1.5 Physical behavior of CuCl

Cupric chloride (CuCl) is a white solid which turns light green due to the presence of oxidized impurities and copper (II) chloride. Its melting point is of 426 °C and is sparingly soluble in water. It is highly corrosive to almost all metals. Once it is melted, it turns dark green on
solidification. While in a molten state its appearance is dark black. Molten CuCl was photographed in the lab at 500°C. A beaker containing solidified CuCl, was melted in a heating mantle. While the temperature was being raised in furnace, the beaker cracked due to thermal expansion of CuCl. Images of the beaker before and after thermal expansion are shown in Figure 4.6a and 4.6c. The ITV lid was removed at 500 °C to take images of the molten CuCl. A respirator, a wind shield, high temperature gloves and a coat are mandatory to wear during this exercise. Figure 4.6b shows the ITV with the molten CuCl.

![Figure 4.6 - (a) Crucible before test, (b) ITV with molten CuCl, (c) Cracked crucible after test.](image)

### 4.2 Immersion Tests

The coatings were evaluated by visual inspection, SEM, EDX and weight change analysis after immersing them in molten CuCl. A series of tests were conducted for 50 and 100 hours in the absence of oxygen and the temperature was set at a constant (500 °C) for all the experiments. Medium carbon steel was used as base metal for all samples. A set of six coating combinations (see table 2.6) was investigated for corrosion. Super hard steel and diamalloy 4006 are the bond coats used to provide better adhesion between base metal and the ceramics coatings. YSZ and alumina are the ceramics coatings applied on the bond coats. The ceramic coatings were applied using the APS method while the HVOF method was utilized for the bond coat. All coatings were applied at CACT university of Toronto courtesy be Dr. Javad Mostaghimi.

#### 4.2.1 Methodology for Immersion test

The methodology for immersion test was developed based on ASTM-G-31-72 standards. The designed samples were coated first with the HVOF and the APS method. Before immersion test, samples were weighed properly. The ITV and top glass lid were washed with the distilled water.
Hang the samples in lifting mechanism with crucibles containing 25g of CuCl below the samples. Seal the ITV lid properly and then purge with argon gas to ensure complete absence of oxygen. Turn on the heating mantle and raise the temperature in 50°C intervals until 500 °C is achieved. On achieving 500 °C, immerse the samples in molten CuCl using lifting mechanism rod. Before completion of immersion test, lift the samples up, so that molten CuCl deposits can drip off. Once the apparatus cools down, open the top lid cover and measure weight of the samples. Then clean the samples with the EDTA solution at 80°C. Weight the samples again and inspect visually. For SEM/EDX analysis, put the samples in epoxy containing fixture for eight hours. Upon solidification of epoxy, cut the samples to observed the desire cross-section. Polish the samples with grit papers followed by ultrasonic cleaning. Analyze the samples with SEM and EDX machine. The detailed methodology is attached in Appendix A.

4.2.2 **SHS-9172 – 100-hour test**

SHS-9172 coating was tested for 100 hours in the absence of oxygen. The flowrate of argon gas in the apparatus was set at 110 cc/min to make the system free from oxygen. Figure 4.7 shows the sample before and after the immersion test. White powder deposits as well as solid black deposits appeared on the sample after the immersion test. These are CuCl deposits which were cleaned by an EDTA solution. Upon cleaning the samples with EDTA, it was found that the layer of SHS-9172 has fallen off.

![Figure 4.7 - SHS-9172 sample (a) Before immersion test (b) after immersion test (c) after cleaning with EDTA solution.](image)

After the immersion test, it seemed that there was no coating left on the sample. Corrosion was observed on the top part of the sample while just a few deposits of the coating layer were left near the screw. To confirm if there is still a coating layer left on the sample, a SEM analysis was performed. The SEM image of the sample is presented in Figure 4.8. It is clear from the SEM
image that there is no coating left on the sample. SHS-9172 failed to bear the corrosive attack of CuCl at high temperature. The reason could be the high content of iron in SHS -9172. The high content of iron may have corroded and caused the coating layer to lose adhesion with the base metal.

![SEM image](image)

**Figure 4.8 - SEM images of the sample after immersion.**

### 4.2.3 **SHS-9172 + Al₂O₃ – 100-hour test**

The bond coat of SHS-9172 with the ceramic coat of Al₂O₃ was tested for 100 hours in the absence of oxygen. The experiment ran at purging gas flowrate of 110 cc/min. New hypalon gasket was inserted between the ITV lid and the vessel for sealing. The visual inspection after hundred-hour test indicated that most the coatings fell off from the sample. Black deposits of CuCl were found on the sample after the immersion test as shown in Figure 4.9. The addition of an alumina layer could not resist the effects of corrosion. The severe attack of CuCl delaminated both of the coating layers from the sample. Very few deposits of SHS-9172 coatings were left on the sample as shown in Figure 4.9c

![Sample images](image)

**Figure 4.9 - SHS 9172 + Al₂O₃ sample (a) before the immersion test (b) after the immersion test (c) after cleaning with the EDTA solution.**

After cleaning with the EDTA solution, the sample looked clear without the coating layers. SEM image (see Figure 4.10) confirmed the complete absence of coating layers. Ideally, there should
be two visible coating layers, one of SHS-9172 and the second one of Al₂O₃, however, the addition of Al₂O₃ made no positive results. The reason for this could be the severity of CuCl attack or the porosity of the ceramic layer. The pore size might be big enough to allow molten salt to get through and react with the base metal to cause corrosion. Another possibility could be the difference of the thermal expansion coefficients of the base metal and the coatings layers which is causing the ceramic coating to crack. The samples had already gone through thermal cycling test and therefore this possibility is ruled out.

Figure 4.10 - SEM images of sample after immersion.

4.2.4  

**SHS-9172 + YSZ – 100-hour test**

MCS + SHS-9172 with a ceramic coat of YSZ was tested for 100 hours. The argon gas flowrate in this experiment was set to 85 cc/min to ensure complete absence of oxygen in the apparatus. Several reaction products appeared on the sample after the immersion test. There were some CuCl deposits as well shiny copper particles observed on the exposed area of ceramic coating. The results indicated that the copper is reducing while iron is dissolving in molten salt to produce iron chloride. The condition of the sample after the immersion test was so rough, that it seemed that the sample layers have burst off and CuCl has penetrated into the base metal. After cleaning the sample with the EDTA solution, a brown smooth layer of copper was found on the sample. It seems that the copper is reduced like an electroplating process. This layer was not on the whole sample, the upper round section of the sample had no layer of copper. The bond coats of SHS-9172 and YSZ had fallen off completely. Figures 4.11a and 4.11b shows the sample before and after the immersion test. Figure 4.11c shows the sample after cleaning it with the EDTA solution.
The SEM images were taken at the magnification of 100 and 300 are shown in Figure 4.12. A layer of copper is clearly visible on the base metal. There were no coatings of SHS-9172 and YSZ left on the sample. The YSZ layer could not withstand in a CuCl environment. The reason could be the porosity in this ceramic layer. This coating was sprayed with the APS method which has porosity of 1-2\% by volume (Vidal et al., 2016). The molten salt may have penetrated through the pores and reacted with the base metal. Copper is reduced on the base metal and iron chloride along with other compounds formed during the immersion test.

All the three combinations of SHS-9172 failed to survive against the molten CuCl environment even with the secondary coat of ceramics. One possible reason for the coatings failing could be the high content of iron in SHS-9172 coating which corrodes faster in CuCl environment. The three combinations of SHS-9172 were then tested for 50 hours to observe if they can survive during this interval.
4.2.5 **Super Hard Steel Combinations (50 hours)**

The three combinations of super hard steel;
- Super Hard Steel – (SHS-9172)
- Super Hard Steel + Al$_2$O$_3$
- Super Hard Steel + YSZ

Most of the coating fell off even after the 50-hours test and base metal was found corroded with some of coating deposits. The high content of iron seems to be the main reason for the corrosion. In short SHS-9172 coatings failed to survive even for the 50-hours test.

4.2.6 **Diamalloy 4006 – (100-hour test)**

The base metal with the bond coat of Diamalloy 4006 was immersed in molten CuCl. The hundred-hour test was conducted with similar operating conditions with the argon gas flowrate of 200 cc/min. Interestingly no large deposits were found on the sample after the immersion test. Even the digit written by marker on the sample remain un-effected after the immersion test as shown in Figure 4.13b. Its tip had a few solid deposits on it and cleaning with EDTA didn’t cause it to fall off. Neither the deposits fell off nor dissolved in the EDTA solution. The solution turned very light green in colour and the coating looked intact at this stage. However, without SEM or EDX analysis, it was not sure. Figure 4.13a and 4.13b shows the sample before and after the immersion test. The reduction of copper occurred and its particles were visible at the tip section of the sample.

![Figure 4.13 - Diamalloy 4006 sample (a) before test (b) after immersion test (c) after cleaning with EDTA.](image)

The SEM images were taken by cutting the sample from the center as indicated by the black line in Figure 4.13b. The SEM image (Figure 4.14) showed very good results i.e. the coating layer was found intact on the sample. No abnormality was observed on the coating layer. Everything
looks fine throughout the cross-section, but the problem was to analyze the sample from its tip which was found with metallic deposits.

Figures 4.15b to 4.15k are SEM images taken throughout the longitudinal periphery of the sample. On the tip section, pure copper deposits can be seen clearly. Figures 4.15f and 4.15j show the complete absence of the Diamalloy coating layer. Figure 4.15g and 4.15k represent that there is copper penetrating at the tip in between the base metal and the ceramic layer causing the coating layer to be damaged. Figure 4.15e and 4.15i shows that the coating layer is delaminated from the base metal due to the penetration of pure copper.

As we move away from the tip, the cross section shows that the layer of copper gets thinner and the coating layer is getting thicker. On the tip section, there is just pure copper and no coating layer. The copper has reduced and no deposits of CuCl observed on the sample. To validate the presence of pure copper on the tip and to identify the elements present on coating layer, an EDX analysis was performed on the cross-section of the sample.
4.2.7 Diamalloy 4006 + Al₂O₃ (100 hours):

Diamalloy 4006 with an aluminum oxide ceramic coat was tested for 100 hours in the absence of oxygen. The argon gas flowrate was set to 110 cc/min while the gasket of fiber glass was inserted in between the top lid cover and the glass vessel. The image of the sample before the test is shown in Figure 4.16.

Figure 4.16 - Sample before 100 hours’ immersion test.
After the 100-hour immersion test, the sample turned black in colour with some green shading on it (see Figure 4.17a and 4.17c). The coating at the tip was found to be cracked as shown in Figure 4.17b. No large deposits of CuCl were observed on the sample. The overall appearance of the sample was good but its tip was found cracked. It was not determined if the cracks were on coating or if these were the deposits of CuCl.

![Figure 4.17 - (a) Sample after immersion test (b) Sample tip after the immersion test (c) The sample with green shades after the immersion test.](image)

Cleaning the sample with the EDTA solution turned the solution colour to greenish blue. The change in weight before and after the immersion test are given below:

Weight before immersion test : 64.6726g
Weight after immersion test : 65.9147g
Increase in weight observed : 1.2421g

Once again, the tip was more important to analyze as there were cracks formed. So the sample was cut into two halves and the SEM images were taken throughout its cross section. The set of SEM images taken throughout the tip cross section are shown in the Figure 4.18. It shows that the primary layer of aluminum oxide was damaged badly by the CuCl attack. Figure 4.18a is the image of the sample tip. The bottom right part of this image shows that there is no coating at all, also, there are some gaps between the base metal and the coating layer. Images on right hand side shows the presence of both the coating layers with some deposits and gaps between them. Therefore, the higher the elevation from tip, the better the coating layer is.

The difference in the coefficient of thermal expansion of the base metal and coating layers could be the issue but it should have cracked from the walls of the sample as well. This sample has already passed through a thermal cycling test, so this possibility is ruled out. The porosity of the YSZ layer could be the issue as it is coated by the APS method. The pores are allowing molten
CuCl to get through and this molten salt separates the layers of coatings. Upon cooling, the CuCl shrinks, leaving some gaps in between coating layers.

![Figure 4.18 - SEM images of cross section through the tip.](image)

The EDX analysis was performed on the sample tip to identify the elements left after the immersion test. Figure 4.19 shows the distribution of elements present on the selected region of the tip section. Particles of chlorine are present at the lowest part of the tip while copper can’t be seen. The presence of the Nickel, Chromium, Tungsten, Molybdenum and Silicon in the same region shows that some of the particles of diamalloy 4006 are still there. Alumina is completely absent at the tip section.
At some elevation on the sample periphery, a region is selected for a diffusion analysis. Figure 4.20 represents the selected section in which three layers are visible on the base metal. Starting from the left, which is the base metal, the first white layer is the diamalloy 4006 layer. The region between 800 to 1200 µm is the layer which is formed due to the reaction of CuCl with the coating components. Some of the copper has reduced and formed corrosion products with the coating elements. The layer of diamalloy 4006 has lost its thickness and looks thinner than 100 µm.
There were supposed to be two layers one on top of the other. The new layer in the center is the formation of unwanted reactions.

Between 1200 µm to 1400 µm there is a layer of aluminum oxide as indicated in Figure 4.20c. There is no diffusion of copper and chlorine in this alumina layer. This ceramic layer looks intact and smooth with no cracks. On top of the alumina layer, there are some deposits of CuCl. The layer of alumina maintained its shape and thickness of 200 µm.

From 1200 µm to 800 µm, the graph of copper (see Figure 4.20b) is declining and there is a peak just at the surface of the diamalloy 4006 layer. CuCl entered between the layers from the crack formation at the tip section. The peak at the surface of the diamalloy layer indicates blockage to copper diffusion be the bond coat.

Figure 4.20 - (a) Left to right; base metal, Diamalloy 4006 layer, mixture of CuCl, Alumina layer, CuCl deposits (b) Graph representing diffusion of Copper (c) Graph of alumina coating.
4.2.8 Diamalloy 4006 + YSZ

Diamalloy 4006 bond coat with a ceramic layer of YSZ is tested for hundred-hours in the absence of oxygen. The images of the sample before and after the immersion test are shown in Figure 4.21. A black layer of CuCl was observed on the sample and the particles of pure copper can easily be seen near the tip section of the sample. The reduction of copper took place and the coating fell off from the tip (see Figure 4.21c)

![Image of sample before and after immersion test](image)

Figure 4.21 - (a) Sample before the immersion test (b) Sample after the immersion test (c) Sample tip after the immersion test.

The sample was then cut from the center as indicated by a black horizontal line in Figure 4.21b. The SEM images were taken to observe the coating condition (see Figure 4.22). There were some gaps observed in between the coating layers and the base metal. The diffusion of copper and CuCl particles observed through the coating layers. The YSZ layer seems separated from the bond coat. The possible reason for this could be the porosity of the YSZ layer. It didn’t provide enough blockage to CuCl to get through its layer. Penetration of CuCl through the layer and then expansion in between the layers, may cause the ceramic coating to separate from the bond coat. Same thing happened at the tip of the sample as it was immersed in molten CuCl completely for hundred hours.

![SEM image of sample cross](image)

Figure 4.22 - SEM images of sample cross.
An EDX analysis was performed to confirm the presence of the coating elements. Nickel, chromium, Tungsten Molybdenum, Zirconia, Chlorine, Copper, Iron, calcium, Oxygen and silicon were all present. Nickel and chromium are the main constituents of the diamalloy 4006 which were found attached to the base metal. Zirconia was present after the layer of diamalloy 4006 but its particles were diffused in the bond coat. Copper and chlorine were also present in the YSZ coating with very little diffusion of copper in the diamalloy 4006 layer.

The tip of the sample was analyzed with the SEM images to check if the coating has actually fallen off. Figure 4.23 shows the images taken near the tip section of the sample. It can be seen in Figure 4.23a that the coating layer is thinner near the tip while it is thicker at the upper level. Not only the ceramic layer but also the layer of diamalloy 4006 is thinner near the tip. In Figure 4.23a, a bond coat and a ceramic layer are separated from each other and the gap is clearly visible.

Figure 4.23 - SEM images of the sample near the tip section.

Figure 4.24 is the SEM image of the tip. There is no coating layer left of either of diamalloy 4006 nor the ceramic layer. Severe CuCl attack could not allow both the layers to survive at such a high temperature environment. In this case, the YSZ layer seemed weaker in bond strength and like in the other cases, there were no deposits of copper. Diffused CuCl took away the layers of coating from the tip section. The same thing could happen to the sides of the samples if the sample was left in immersion for a longer duration than hundred hours.
Some EDX images were taken at some distance from the tip to analyze the diffusion of copper and chlorine in the coating layers. Figure 4.25 shows the selected section in which base metal is on the left hand side of the picture. As we move horizontally along the green line to the right, a gap and then two layers of coatings are visible. The right most layer is the YSZ layer and its confirmation can be seen in Figure 4.25d and Figure 4.25e. The YSZ layer is in between 780 and 820 µm as shown by the high peaks of yttrium and zirconia. Figure 4.25b shows that YSZ layer has blocked both copper and chlorine diffusion into its layer. Copper and chlorine peaks are high exactly at 820 µm which is the surface of YSZ layer. Then below 780µm there is another peak of both the elements. It shows that the copper and chlorine could not diffuse through YSZ layer. The peak at 780µm is due to the penetration of CuCl from the tip section where there was no coating left or through other possible cracks.

Diamalloy 4006 layer is in between 600 and 760 µm which can be seen in Figure 4.25f with high weight percentage of Nickel. The bond coat also showed good blockage to diffusion of copper and chlorine in it. The main tip got damage badly by CuCl attack and effected the samples as CuCl penetrated in between coating layers through the crack formed at the tip. In 400 to 600 µm there is a gap in bond coat and the base metal. Chlorine percentage is higher approximately 4-6 wt% which is due to the presence of epoxy content. The epoxy was used to keep the coating layers intact during cutting and polishing of the sample.
Figure 4.25 - (a) The SEM image of the sample (left side is the base metal). (b) Graph of copper diffusion. (c) Graph of chlorine diffusion (d) Graph of Zirconia diffusion (e) Graph of Yttrium diffusion (f) Graph of Nickel diffusion.
4.2.9 Diamalloy 4006 coating combinations (50-hour test)

The Diamalloy 4006 coating combinations were tested for fifty hours in the absence of oxygen. After an unsatisfactory performance in the hundred-hour test, an immersion test was performed to find out if the coatings could survive for fifty hours. The results concluded that the performance was better than the hundred-hour test. Still in this short duration test, some of the coatings fell off from the samples. The tested combinations are as follows:

- Diamalloy 4006
- Diamalloy 4006 + YSZ
- Diamalloy 4006 + Alumina

Figure 4.26 shows the sample after the immersion test. Deposits of CuCl appeared on the samples but during the fifty-hour test, the deposits were less than the hundred-hour test. The crucible containing CuCl had more CuCl left at its bottom. This means, in the fifty-hour test, CuCl did not get enough chance to adhere the coatings. In conclusion, all three samples appear to be in better condition during the fifty-hour test compared to the hundred-hour immersion test. Coating layer looks intact on all the three samples except at the bottom tip.

![Figure 4.26- Diamalloy 4006+ YSZ, Diamalloy 4006 + Alumina , Diamalloy 4006 samples (left to right) after the immersion test.](image)

The SEM image of the Diamalloy 4006 sample near the tip is shown in Figure 4.27. The layer of Diamalloy 4006 looks intact with the base metal but the outer surface is not as smooth as it should be. Molten CuCl did some damage on the coating surface and some of the bond coat particles have fallen away. The diffusion of copper can be observed from Figure 4.27b. The wt% of copper is around 90% at the surface of coating which has been reduced to 70% at the base metal. It shows that copper has passed through the layer of diamalloy 4006. This indicates that the molten metal instead of diffusing has seeped through cracks or voids in the coating material.
Diamalloy 4006 + Al₂O₃ cracked at the tip in the way in the hundred-hour test. Copper and chlorine seep in between the coating layers. SEM image of this coating combination along with the diffusion of copper and chlorine are shown in Figure 4.28. From 200 µm to 500 µm, the concentration of copper in the alumina coating layer is depleting (see Figure 4.28b) and from 500 to 800 µm the same trend is observed in the diamalloy 4006 layer.
Figure 4.28 – (a) Diamalloy 4006 + Alumina SEM image the immersion test (b) Graph of copper diffusion in coating layers.

Figure 4.29a shows the tip of the YSZ coated sample and it shows that the layer of a ceramic has fallen off. The SEM image taken at the periphery to inspect if the coatings is intact on the wall of the sample. Figure 4.29b is the SEM image of Diamalloy+YSZ coating which shows that both of the coating layers are set but there is a gap in between the bond coat and the ceramic coat. The diffusion of CuCl is not visible and the ceramic layer seems to be in good condition without any cracks. This gap could have been caused by the cutting process during sample preparation for SEM.

![Image of Diamalloy 4006 + Alumina SEM image the immersion test and Graph of copper diffusion in coating layers.]

Figure 4.29- (a) Tip of the sample after immersion test (b) The SEM image after the immersion test.

4.2.10 Diffusion Analysis:

In molten salt environment, the salt wets the surface of oxide and penetrates through the pores and cracks by capillary action. In molten salts, the diffusion is much faster than the solid state diffusion (Porcayo et al., 2014). These salts permeate through porous connections and wide range of oxidizing and reducing reactions may occur. To observe the trend of diffusion of CuCl in coating layers, EDX analysis was performed. The graphs were extracted for copper diffusion in the layers.
of diamalloy 4006, alumina and YSZ. The rate of diffusion can be estimated using this analysis for various intervals.

The diffusion coefficient of copper in Diamalloy 4006 are calculated using Fick’s second law. The coating thickness in this study ranged from 100-300 µm for bond coats as well as for ceramic secondary layer. The samples are immersed in molten CuCl having 64% of copper by weight while there is 4% of copper by weight present in Diamalloy 4006 composition. Parameters used to calculate diffusion coefficients are shown in Table 4.3. Coefficients are calculated based on 50 and 100-hour immersion test durations and are presented in table 4.4. The values of concentration of copper are taken from EDX graphs and are shown with dotted lines. The values are calculated using equation 4.1

\[
\frac{C_x - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)
\]  

(4.1)

where,

\(C_x\) \(\rightarrow\) Concentration at point \(x\), %

\(C_s\) \(\rightarrow\) Concentration at the surface, %

\(C_0\) \(\rightarrow\) Concentration in the material, %

\(erf\) \(\rightarrow\) error function

\(x\) \(\rightarrow\) distance

\(D\) \(\rightarrow\) Diffusion coefficient, \(m^2/s\)

\(t\) \(\rightarrow\) time, sec

Table 4.3 – Data for calculation of diffusion coefficient of copper in diamalloy 4006

<table>
<thead>
<tr>
<th>Description</th>
<th>Diamalloy 4006</th>
<th>Diamalloy 4006 + Alumina (50hrs)</th>
<th>Diamalloy 4006 + Alumina (100hrs)</th>
<th>Diamalloy 4006 + YSZ</th>
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</thead>
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<tr>
<td>Cx</td>
<td>8%</td>
<td>4%</td>
<td>9%</td>
<td>7%</td>
</tr>
<tr>
<td>Cs</td>
<td>4%</td>
<td>4%</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>Cs</td>
<td>92%</td>
<td>68%</td>
<td>88%</td>
<td>90%</td>
</tr>
<tr>
<td>X</td>
<td>50 µm</td>
<td>40 µm</td>
<td>20 µm</td>
<td>70 µm</td>
</tr>
<tr>
<td>T</td>
<td>50 hours</td>
<td>50 hours</td>
<td>100 hours</td>
<td>100 hours</td>
</tr>
</tbody>
</table>
Table 4.4 – Diffusion Coefficients of Copper in Diamalloy 4006.

<table>
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<tr>
<th>Sample</th>
<th>Duration</th>
<th>Diffusion Coefficients.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamalloy 4006</td>
<td>50 hours</td>
<td>$1.73 \times 10^{-15} \text{ m}^2/\text{s}$</td>
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<tr>
<td>Diamalloy 4006 + Alumina</td>
<td>50 hours</td>
<td>$1.77 \times 10^{-16} \text{ m}^2/\text{s}$</td>
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<tr>
<td>Diamalloy 4006 + Alumina</td>
<td>100 hours</td>
<td>$1.52 \times 10^{-15} \text{ m}^2/\text{s}$</td>
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<tr>
<td>Diamalloy 4006 + YSZ</td>
<td>100 hours</td>
<td>$1.56 \times 10^{-16} \text{ m}^2/\text{s}$</td>
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</table>

4.2.11 Sapphire and Alumina:

The failure of coatings leads to think, what should be the next step as we have been trying the best available corrosion resistant materials. Metallic, ceramics and their combinations have failed to survive in a molten CuCl environment. The point to be noted here was the performance of crucibles which were being used to keep the molten CuCl during the immersion test. No physical damage occurred to the crucibles in any of the tests except its colour changed every time. Therefore, one possible solution was to try a glass coating. A coating of glass is challenging as its viscosity is very high in a molten state. It was difficult to coat the sample using the thermal spray methods but we concluded, if glass can survive these conditions, then alumina should have performed well as their properties are similar.

The one significant issue with coatings identified was the porosity. The coatings we have been using were porous. Although the porosity levels were very low (less than 1% by volume) but still this factor can’t be ignored. Glass crucibles are solid with no porosity and they are not damaged by CuCl. Therefore, it was decided to test pure alumina for 100 hours in molten CuCl. A sapphire ball and an aluminum oxide hollow cylinder were tested for hundred hours in the same operating conditions. Sapphire is a kind of aluminum oxide which is coloured in nature. The sapphire ball used in this experiment had grey colour and the colour of aluminum oxide is white. The specification of the samples is given in Table 4.5.
Sapphire is aluminum oxide with the formula $\alpha$-Al$_2$O$_3$. In nature, it is found mostly in blue colour and is used in jewelry. It can have blue, yellow, purple, orange, and green colours and is also known as fancy Sapphire. It possesses excellent optical, and mechanical properties with good corrosion resistance (Shi et al., 2015). Images of both the samples before the immersion test are shown in Figure 4.30

![Sapphire ball](image1) ![Alumina hollow cylinder](image2)

Figure 4.30 - (a) The Sapphire ball before the immersion test. (b) Alumina hollow cylinder before the immersion test.

Hundred-hour test was conducted with proper seals and sealants in the absence of oxygen. A Hypalon gasket was used while the flowrate of argon gas was kept at 180 cc/min. The sample were found with colourful deposits surrounding the samples. Green, brown, orange and red mix deposits are observed on the sample. The clip was used for holding the sample corroded badly. The deposits were hard like metal, and couldn’t be removed chemically. The EDTA solution tuned greyish in colour and some of the deposits were dissolved in solution while most of them

<table>
<thead>
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<th>Parameter</th>
<th>Description / Value</th>
<th>Parameter</th>
<th>Description / Value</th>
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<tr>
<td>Weight</td>
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<td>Weight</td>
<td>1.5786g</td>
</tr>
<tr>
<td>Diameter</td>
<td>11.13 mm</td>
<td>Inner/Outer Dia</td>
<td>5.52mm/7.32mm</td>
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<tr>
<td>Colour</td>
<td>Grey</td>
<td>Length</td>
<td>24.90 mm</td>
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<tr>
<td>Remarks</td>
<td>Sample has four flat spots on it.</td>
<td>Colour</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 4.5 – The specifications of Sapphire and Alumina samples before test.
were not. The sample was pulled out mechanically from the deposits. The Alumina tube had solid deposits in it and it was not possible to thoroughly clean the inner section of the cylinder. Images of the sapphire ball before and after the immersion test are shown in Figure 4.31.

![Figure 4.31 - Sapphire ball before and after immersion test.](image1)

Images of both the samples before and after the immersion test are shown in Figure 4.32. No significant change or damages were observed after the test. No cracks, corrosion or degradation were found in any of the sample and the physical appearance remained unaffected. Even the colour of samples remained unchanged. The change in weight of the samples are given in Table 4.6.

![Figure 4.32 - The sapphire ball and alumina cylinder (a) before (b) after immersion test in CuCl.](image2)
There was a slight increase in weight to the alumina cylinder after the immersion test and no change to the sapphire ball. The weight gain by alumina cylinder is due to the left overs of CuCl deposits on the hollow cylinder. They could be removed mechanically but it was too risky as alumina is brittle and might be damaged. Moreover, the amount of deposits inside the tube were too difficult to remove and of insignificant quantity.

This experiment was a clear indication that the issue is not with the coating material but either the porosity or the structure of the sample coating. The coatings of alumina on the metal substrate has to be densified or the problem related to the structure has to be identified.

### 4.3 High Temperature Paints:

#### 4.3.1 High Temperature refractory coatings:

To overcome the issue of porosity, a special kind of high temperature refractory coating (a kind of paint), are applied onto coated samples. These refractory coatings were purchased from Aremco Products. There are several kinds of refractory coatings available but the selection was made based on the corrosion application. The selected coating is:

- **Pyro Paint 634-BN**

Pyro Paint 634-BN is actually a highly filled boron solution which is extremely inert and lubricious (Aremco, 2012a). They remain un-wet by molten salts, glasses, plastics and most of the metals including aluminum and magnesium. These paints are used in high temperature
applications and are capable to survive against corrosion. The selection of this specific model number is due to its application to a molten salt environment. It is also a type of sealer or adhesive used with porous ceramics and refractories of a temperature of up to 1500 °F (816 °C). The properties of the 634-BN refractory coatings are given in Table 4.7.

Table 4.7 - Pyro Paint 634-BN properties (Aremco, 2012a).

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Major constituent</td>
<td>Boron Nitride</td>
</tr>
<tr>
<td>2</td>
<td>Colour</td>
<td>White</td>
</tr>
<tr>
<td>3</td>
<td>Temperature limit</td>
<td>850 °C</td>
</tr>
<tr>
<td>4</td>
<td>Viscosity</td>
<td>500-1500 cP</td>
</tr>
<tr>
<td>5</td>
<td>Specific gravity</td>
<td>1.34 g/cc</td>
</tr>
<tr>
<td>6</td>
<td>Application Temperature</td>
<td>50-90 °C</td>
</tr>
<tr>
<td>7</td>
<td>Thinner</td>
<td>634 BN-T</td>
</tr>
<tr>
<td>8</td>
<td>Coating pH</td>
<td>11-12</td>
</tr>
<tr>
<td>9</td>
<td>Weight/Gallon</td>
<td>9.5 lbs</td>
</tr>
<tr>
<td>10</td>
<td>Storage Temperature</td>
<td>40-90 °F</td>
</tr>
</tbody>
</table>

This paint coat was applied without any thermal spray process. It is recommended to abrade and clean the surface of the sample for the best result. Mix the paint content thoroughly before use, and apply a 2-3 mm wet film by brushing, dipping or spray gun. Thin as required with up to 10% 634 BN-t thinner by weight. Air dry at room temperature for 2 hours then, a final cure is needed at 200 °F (i.e 93 °C) for 2 hours before placing in operation.

To apply a uniform coating, the dipping method was selected. The samples were immersed by hanging them with screws into a paint filled beaker for a few minutes. The paints were well shaken before pouring them into the beaker, otherwise it will appear too transparent. After dipping the samples were left to soaks for two hours in open air. They were then put in the furnace for 2 hours at 176 °C. As the samples were already coated, it was not possible to make its surface rough. The problem with adhesion is expected to appear and there is no point to make the coated surface rough again.

The image of the coated samples after paint during soaking are shown in Figure 4.33. The three coating combinations painted with the pyro paint are:
- MCS uncoated sample.
- MCS + SHS
- MCS + SHS + Al₂O₃

Figure 4.33 - Samples are left for soaking after immersing in Pyro Paint.

After every dip in the paint, some bubbles appear on the samples, and when the sample start to dry, the bubbles leave their spots on the surface. A Secondary coat of paint was then applied to the sample to make the paint layer thicker. The results after two hours of soaking were still not good enough. The paint layer started to crack even before two hours. Some of the paints layer survived after soaking but after the heat treatment in furnace the paint coat cracked. There was no point of testing these samples in CuCl environment after formation of cracks. Sand blasting, etching or oxidation could provide better adhesion to the samples.

Pyro paint-634 BN could be a good option to test the samples in a CuCl environment, but its adhesive strength was too low. Etching, and sand blasting was not possible on the already coated samples. The paint did not stick onto the uncoated MCS sample even though the surface was rough. Therefore, these samples were not tested in a CuCl environment. Images of sample before and after soaking are shown in Figure 4.34.

Figure 4.34 - Samples before and after soaking of 634 BN pyro Paints.
### 4.3.2 High temperature coating for ceramics, glass & quartz:

The second type of paint coat used was a high temperature coat that can be applied to ceramics, glass & quartz. This type of coat is good for the alumina and ceramics samples. The selected coat is:

- Aremco seal 617

It is a glass filled adhesive (Aremco, 2012b) and has good adhesive properties as a sealer. It is specially designed for ceramics and refractories. Its curing temperature is 816 °C. Fifty-hours CuCl immersion test was conducted after applying the layer of paint. The samples tested were:

- MCS + SHS
- MCS + SHS + Al$_2$O$_3$

The results were almost the same as in the previous CuCl immersion tests and no improvement was observed. Figure 4.35a and 4.35b are the images taken before and after the CuCl immersion test. Some copper particles were observed on the sample of SHS. CuCl deposits were found on both the samples as usual, however no improvement in the end results was seen on any of the sample.

![Sample Images](image1.png)

Figure 4.35 - Samples (a) after soaking of Aremco seal (b) after immersion test in CuCl.

Almost all the coatings fell off from the sample. The Aremco seal couldn’t resolve the issue of porosity. The CuCl attack was very severe and the adhesiveness of the Aremco seal was not strong enough to provide protection to the coating layers. Images after cleaning of sample with the EDTA solution are shown in Figure 4.36.
Figure 4.36 - Samples (a) after CuCl immersion test (b) after cleaning with the EDTA solution.
CHAPTER 5 – CONCLUSIONS AND FUTURE RECOMMENDATIONS

5.1 Conclusions

In this research, corrosion resistant coatings were evaluated by immersing them in molten CuCl. Bullet shaped samples with round ends were designed and coated using thermal spray process. The base metal selected for the samples is medium carbon steel. A bond coat of Diamalloy 4006 and Super hard steel 9172 was applied on the samples to protect the base metal and improve its adhesion with ceramics. It can also reduce the effects of thermal expansion during the heating and the cooling. The selection of bond coat materials was based on their excellent corrosion resistant properties. The ceramic coatings of alumina and YSZ were applied onto the bond coat to enhance the resistance to corrosion.

To conduct the required experiments, apparatus was modified. The issue of oxygen gas presence in the apparatus was resolved by the addition of oxygen analyzer. The flowrates for gas purging were optimized to ensure complete elimination of oxygen. Gasket material was replaced with the fiberglass to keep the apparatus leak proof during the operation. Controlling devices like temperature controller and gas flowmeters were upgraded for better monitoring.

High velocity oxy-fuel method was utilized to apply the bond coat onto the substrate. For ceramics coat, the method of Air plasma spray was used. There were six coating combinations used in this research; Uncoated base metal, the base metal coated with bond coat of SHS or Diamalloy 4006, the base metal coated bond coat and ceramic layer of alumina or YSZ. The samples after immersion test were inspected visually and by SEM to observe the surface and the coating cross section. EDX analysis was carried out to identify the elemental composition across the coating cross section.

Super hard steel coating combinations (SHS, SHS+YSZ, SHS+Al2O3) were evaluated after hundred-hour immersion test. All of the coatings fell off from the substrate. Deposits of CuCl, corrosion products and particles of pure copper were observed on the samples after every immersion test. Reduction of copper appeared as the corrosion product in most of the samples. The coatings of SHS+YSZ sample fell off and the base metal was found with uniform layer of pure copper after the immersion test. The possible reason for failure of coatings could be the high percentage of iron in super hard steel which corrodes at a faster rate.
These SHS coating combinations (SHS, SHS+YSZ, SHS+Al₂O₃) were also tested for fifty-hours. Results were almost the same as in 100-hour test. Most of the coatings fell off from the substrate. Very few particles of coatings remained on the samples. A possible reason could be the porosity in ceramics layers is allowing molten CuCl to penetrate through the pores and react with the bond coat. Due to these reactions, the bond coat lost its adhesive strength onto the substrate. Both YSZ and alumina could not provide protection to the underlying SHS bond coat as well as the base metal.

The coating combinations of Diamalloy 4006 (Diamalloy, Diamalloy+YSZ, Diamalloy+Al₂O₃) performed much better than super hard steel coating combinations. Diamalloy 4006 bond coat showed good resistance to corrosion in 100-hours test. Coating remained intact throughout the sample walls but the tip was damaged. Formation of cracks at the tip of the sample probably lead molten CuCl to penetrate in between the bond coat and the base metal. The coating delaminated from the tip section leaving some deposits of copper at the base metal. Diamalloy 4006 + Al₂O₃ was tested for 100 hours in which coating cracked from the tip section of the sample. Molten CuCl penetrated in between the coating layers causing the coating to fall off. Diamalloy 4006 + YSZ was tested for 50 and 100 hours. In both the cases, the coating layer of YSZ fell off from the tip while its coating remained intact on the walls of the sample. The study showed that alumina and YSZ can possibly prevent diffusion of molten salt if these coatings do not crack.

Most of the coatings fell off during immersion test and the possible reason could be the porosity of coating methods. To investigate the issue of porosity, solid samples of alumina were tested in CuCl environment. Alumina hollow cylinder and the solid sapphire ball was immersed in molten CuCl for 100 hours. These samples were then inspected visually. There were no obvious effects of corrosion on any of these samples. There was no change in weight, shape, size or appearance of the samples. The results suggested that the porosity of alumina coating has to be minimized to provide better protection to the underlying metal.

In short, the bond coat of Diamalloy 4006 performed much better than the bond coat of super hard steel 9172. The ceramic coat of alumina seemed to perform better than YSZ as indicated by the SEM and EDX results. The results also suggested that the method of HVOF and APS are not suitable for molten CuCl corrosion application because of high porosity.
5.2 Contributions

The major contributions of this thesis are:

- Modified sample geometry.
- Developed method to prevent oxygen infiltration in the apparatus.
- Purging gas flowrates were optimized.
- Tested new materials; SHS-9172, Alumina and SS304.
- Studied and calculated diffusion coefficient of copper in Diamalloy 4006.

5.3 Recommendations for future work:

Some of the recommendations are mentioned below:

1- The main recommendation is to make the coating layer denser. The porosity as quoted in literature with the APS method is 5% by volume while with the HVOF is 1% by volume. The method which can reduce the porosity below 1% should be tried.

2- Physical Vapor deposition (PVD) method, to coat the samples could be tried as this method makes the coating layer denser. Solid alumina remained unaffected by CuCl attack. The coating of alumina should be applied on the samples using physical vapor deposition method.

3- More test needs to be conducted with Diamalloy 4006 bond coat with the denser layer of other ceramics. The possible ceramic candidates could be CYSZ, SYSZ and PSZ.
References


Appendices

Appendix A: Methodology

ASTM standards were adopted for the development of methodology for immersion test. Generally, the whole experiment consists of coating the samples, immersion test, post immersion cleaning, immersion in epoxy, sample cutting, sample polishing by grit papers, SEM and EDX analysis. Overall it’s a lengthy process and takes couple of months to conduct test of one sample. Step by step detailed method is given below:

1- Samples were prepared in accordance with ASTM standards while sample geometry was modified to bullet shape geometry with both sides round.

2- Thermal spray coating is being used in this research. Air Plasma Spray (APS) and High velocity oxy fuel (HVOF) methods were used to coat the samples. Usually coated quality is evaluated based on porosity, bond strength, oxide content and surface roughness.

3- Preparation for immersion test consists of cleaning and washing of the apparatus including ITV, lifting mechanism and other accessories with distilled water. It is highly recommended to clean ITV with wet tissue paper to clean out all the deposits that were left in the previous experiment. Lifting mechanism should be cleaned with a scraper. Scraper is better option to clean out all the dust and deposits of previously conducted test. Take sample weights and pictures before inserting the sample into the immersion test vessel.

Take 25g CuCl in crucible and immerse sample as shown in figure. New screw should be used every time as it is not possible to open up the screw after the test due to corrosion. The sample should be immersed in molten CuCl properly, at least 50%. If crucibles are not available, then small beakers can be used for the same purpose.

4- Screw should be hanged from lifting mechanism with the support of another screw as shown in figure. Unscrewing is not possible as it makes coating to crack after the test. That is why hanging mechanism was preferred for the test. The second screw is just to

Figure A1 - Crucible containing CuCl powder and sample.

Figure A3 - Lifting mechanism screws.
make sure that original sample screw can remain at their original position. A maximum of three samples can be hanged together at once for the test.

5- Figure is shown to give the idea how the samples can be hanged with lifting mechanism. The two platforms of lifting mechanism contain layers of aluminum and the purpose for those layers are to provide better support to the mechanism. After hanging properly, insert this whole mechanism in the ITV.

6- Sealing is the next step, which is very important for making the internal environment inert. Apply WD-40 spray on vessel before application of sealant to ensure it will detach easily after immersion test. Paste high temperature sealant on ITV flange using plastic scrapper. Surgical gloves must be worn while pasting the sealant. Calking gun can be used to spill sealant uniformly on the vessel flange. Once a layer of sealant if spilled on flange then put hypalon gasket over it. Again put another layer of sealant and then close the top lid cover with lifting rod passing through the lid’s hole. Then take some more sealant, fill in the gaps of gasket and flange shown in figure. Make sure there should be no hole visible throughout. Otherwise it will leak and there will be no bubble formation in the scrubber. Then clamp with paper clips as shown in figure.

Figure A5 – (a) ITV top view. (b) Sealed ITV
7- Insert thermocouples in place. The one from Omron controller should be placed inside ITV from top lid hole while the second one will remain in contact with heating tape just outside of the glass vessel. Fix connecting tube, argon gas pipe and seal all the joints with kwik seal. Then leave the system for 30 to 50 mins for soaking.

8- Once the sealants get fix, start purging argon gas slowly and keep an eye on the scrubber. There should be formation of bubbles. If not, then the seal is not proper and gas is leaking somewhere. Check the system again for possible leaks. Identify, repair and then try again.

9- For oxygen analyzer, there are two possible locations to fit in the system. The first one is to install it in condenser opening as shown in figure. Analyzer will keep taking samples in regular intervals and will keep returning the sample back into condenser. The temperature in condenser noted was not more than 30 ℃. With respect to temperature it was safe to operate analyzer in condenser. But the point is, CuCl fumes may corrode analyzer. That is why, purge the apparatus with argon while monitoring oxygen level and then dismantle oxygen analyzer before starting the heating mantle.

The second option is to install analyzer at the exit of scrubber. This point is safe to operate for analyzer as it is low temperature zone and CuCl fumes has already been condensed and neutralized. Leave analyzer on recording mode with appropriate sample rate, based on the length of experiment.

10- Purging with argon gas takes around 30 mins. Set flowrate to a point where bubble formation in the scrubber starts to form. If the seal is very good, then flowrate will be lower around 50-80
cc/min otherwise between 100 to 180 cc/min. Or if it is exceeding 200 plus then the seal is very poor. Keep an eye on the oxygen analyzer. Oxygen percentage should start to decrease. Less than 5% oxygen level, will turn the analyzer alarm on. Once you reach the minimum level of oxygen, then proceed with the next step.

11- Start heating mantle. Set Glas-col and omron controller’s temperature to 100 °C. When Glas-col mantle achieves that temperature, its red light “Load” will turn off. Then increase temperature to 150 °C by turning the knob to the right. Keep increasing the temperature with 50°C intervals unless the internal vessel temperature touches 100 °C. Omron will cut off power supply when it reaches the set point. Increase its set point to 200 °C and keep increasing Glas-col temperature with 50 °C interval. Keep repeating the cycle unless you reach 500 °C internal temperature. The maximum temperature recommended for glas-col is 580 °C. Leave it at 580 °C and omron at 500 °C.

12- Place a tag/note on the fumehood, in front of the apparatus, that the experiment is running at high temperature with continuous supply of argon gas. Put emergency contact details and safety measures to take in case of any abnormality. The first thing to do, is the cut off the power supply and then turn off the argon gas supply.

13- Do not touch the apparatus, specifically, the heating mantle during experiment. Use gloves, safety mask and lab coat while handling the apparatus and CuCl.

14- Keep an eye on apparatus during experiment. It is not possible to stay with apparatus for 100 hours, but keep visiting your station and make sure bubbles are forming in the scrubber. If not, then adjust flowrate again. Also check the set temperature by adjusting the omron knob below 500 °C. It should cut off power supply below set temperature.
15- Lift the samples up, by pulling lifting mechanism rod, at least 4 hours before turning off the heating mantle. It is necessary to drip off of all liquid CuCl from sample otherwise it will make a solid CuCl block.

16- Shut off power supply after 100 hours and leave the apparatus to cool down. It takes 2 to 3 hours to get back to room temperature.

17- When it cools down, open the top lid and take out the lifting mechanism. Note down the observations and take pictures.

18- After every test, there will be deposits of CuCl left on the sample. To clean those deposits chemically, prepare EDTA solution. Take 1 liter of water in a beaker and add 2.0 g of EDTA. Heat the solution to 80 °C and keep stirring at 75 rpm. Use magnetic stirrer and do not insert sample unless reaches at 80 °C. The solution color will change. Prepare another solution and immerse sample in it. Keep preparing solution unless there is no change in color or the sample becomes clean. Do not put the sample closer to stirrer platform. Immerse it from top.

19- Dry the sample by putting in furnace at 80 °C for 20 mins. Store the samples on Ziploc bag or plastic container to keep it safe from corrosion due to atmosphere.

20- The next step is the cutting of samples to observe its cross-section. But cutting a sample damages its coating layer. To avoid damage of coating layer, it is first set an epoxy hardener. Preparation of epoxy with hardener take a few minutes. Combine epoxy and hardener in a ratio of 1:5 by weight and mix them thoroughly. Apply release agent in plastic mold and then pour epoxy in it.
21- Dip the samples in the mould and leave it for at least 8 hours. Check the status after soaking time. If it has become solid block, then pull this out by opening its bottom lid and by applying light hammer. If still it is soft, then leave it for more hours till it gets hard. The blocks should look like as the way shown in figure.

![Figure A9](image1.png)  
(a) Epoxy preparation (b) Release agent (c) Samples dipped in epoxy.

22- Cutting the sample becomes easy when it is equipped with epoxy. Set feed rate of 1.5 mm/min and fit the sample in cutting machine as shown in the figure. It takes around 30 mins to cut a single sample. Supply of water jet on the sample should be applied throughout the cutting process to keep the cutter and sample at room temperature.

![Figure A10](image2.png)  
Samples after solidification of epoxy.
23- Polishing is the next and important step. It also takes around 30 mins as the sand paper has to be replaced with finer grit after certain intervals. It helps in improving the visibility of microstructure through SEM. Start polishing with lower grit then refine it higher grit. Sand papers used in series are as follows:

- Grit 240/P280
- Grit 320
- Grit 600/P1200
- Grit 1200/P2500
24- The samples should look shiny after polishing as shown in the photos. Clean then with compressed air to make them dry. Then, immediately wrap in tissue paper and try to put them in closed container. It starts to corrode instantly, if left in open environment. Now the samples are ready for next step i-e SEM.

![Polished samples](image1.png)

Figure A14 - Polished samples.

25- Scanning Electron Microscopy was done on TM-3000 Hitachi machine in university of Toronto. It has its own software with options to zoom in, focus and to change the orientation of the sample. It operates in the air. It is equipped with a suction pump to eliminate all the air present in the chamber. Software shows the live picture of the sample with coating conditions. Photo of SEM machine is shown below. Some of the SEM images taken from this machine are shown below.

![SEM machine](image2.png)

Figure A15 - SEM machine.

![SEM images](image3.png)

Figure A16 - SEM images.
26- Initially samples were cut into two halves from the center as indicated by the black line in picture. Some of the results showed total absence of coating layer. It was not necessary to do any further step on those samples as nothing was left on the base metal. But for the case where coating layer was observed on the base metal needs to be analyzed further. The next step is to find that the coating which is visible in SEM images is actually the coating layer or the deposits of CuCl or corrosion.

27- One more step is the find the coating condition at the tip of sample. For that reason, it was needed to cut the sample tip into two halves as shown in the figure. Tip is the deepest submerged part in molten salt, so it is the best option to focus on the tip coating. Cut the sample tip and polish it again. No need to dip this sample in epoxy as it is already in epoxy.

28- Electron Dispersion X-ray spectroscopy detects the elements present in the sample. It shows mapping of elements and also the percentage weight values of the elements present in the sample. If the elements or percentage weight of elements are similar to the coating material, then it’s the confirmation of intact coating. The figure below is the electron image with the colored images of elements present in this image.
Appendix B – Chemical Compositions of alloys and ceramics used in this work.

**Inconel 625**

Table B1 - Percentage wise composition of Inconel 625.

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<tr>
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<tr>
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</table>

Source: (Abioyea et al., 2015).

**Super Hard Steel (SHS 9172)**

Table B2 - Percentage Composition of SHS 9172.

<table>
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<tr>
<td>Fe</td>
<td>28</td>
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</tbody>
</table>

**Yttria Stabilized Zirconia:**

YSZ also known as METCO 143, its composition is $\text{ZrO}_2$-$18\text{TiO}_2$-$10\text{Y}_2\text{O}_3$.

(METCO 143)

**Diamalloy 4006:**

Table B3 – Percentwise composition of Diamalloy 4006.

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</table>

**Alumina**

In experimental work, 98% pure alumina is used with formula is $\text{Al}_2\text{O}_3$. 
Medium carbon steel (1045)

MCS is composed of 97.81-99.11% Fe with 0.29-0.52%C and 0.60-1.65% of Mn.

**AL6XN**

Table B4 - Percentwise composition of AL6XN.

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Source: (RA, 2011).
Appendix C - New Sample Geometry (SS-304)