

**System for Evaluating Effects of Immersion in Molten Copper Chloride Salts  
on Corrosion Resistant Coatings**

By

**Kaveh Azarbayjani**

In

The Faculty of Engineering and Applied Science

Department of Automotive, Mechanical & Manufacturing Engineering

University of Ontario Institute of Technology

December 2014

© Kaveh Azarbayjani, 2014

All rights of this thesis results and methodology belong to the author.

## ABSTRACT

Hydrogen, as one of the best alternative energy carrier candidates, is easier to sustain than fossil fuel. Hydrogen demand has significantly increased as a clean energy carrier. The Cu-Cl cycle is one of the capable thermochemical cycles which is supposed to develop hydrogen production. Since this cycle has some high temperature stages, a study on these parts is essential to realize the entirety of the cycle.

This research is about designing a system to evaluate candidate coatings following an immersion test in molten CuCl at 500°C for a prolonged time. Medium carbon steel was selected as the base metal. There were six types of combination coatings applied to evaluate the corrosion resistance of the generated coatings during the molten CuCl exposure. A ceramic of Yttria stabilized zirconia with two metallic coatings of Diamalloy 4006, and super hard steel coatings were applied in diverse combinations to the base metal using thermal spray methods.

Previous immersion apparatus was modified and improved to perform an immersion test that has a similar condition at high temperatures with a commercial hydrogen plant. All safety procedures and safety mechanisms were developed and a new geometry was designed for samples. After the immersion test, the materials were evaluated using electrochemical methods in combination with ex-situ surface analysis. The surface condition, including film structure, elemental composition, and resistivity of the materials, was examined and then compared. This examination was performed before and after the mechanism development and then compared. The majority of coatings were intact and did not fall off. New sample geometry may have affected the integrity of the sprayed coating, as there were no deep cracks or corrosions on the coated specimens. If the coating cracked, it could provide a pathway for the corrosive environment to go under the coating layer and react with the base metal. The results suggest that both Diamalloy 4006 and SHS 9172 HVOF coatings seemed to provide better protection to the underlying base metal than YSZ ( $ZrO_2$  18TiO<sub>2</sub> 10Y<sub>2</sub>O<sub>3</sub>).

## ACKNOWLEDGEMENTS

First of all, I would like to thank my best friend for her endless blessings and patience that provided me the chance and power to pursue my studies\_ my wife, Forough.

I would also like to thank my family members (my father, my mother, my sisters, my brother in law and my wife's family) for their support both financially and spiritually throughout my studies.

I would also like to thank Sheikh Ali Karimi, Jung, Louise, Catherine, and all of my UOIT (especially Mohammad Reza), UofT and PUT friends for their spiritual support throughout my studies.

I would like to thank Dr. Zhaolin Wang and the members of CERL for the valuable inputs and discussions to make this thesis possible. I would like to thank Kelvin Seto (Dr. Ikeda's research group) for his help through the project. I would like to thank Edwin Siantar, whose study was on first developing this project

I would like to thank Dr. Brian Ikeda for his valuable support and guidance during this project. I would also like to thank especially Edward Secnik for his valuable knowledge, experience and cooperation while performing my experiments. He was one of my main technical supporters during this project.

I would like to thank Dr. Pershin and Saeid Salavati, a member of his research group at UofT for their support throughout this project.

Last but not least, I would like to express the deepest appreciation to my supervisor, Dr. Ghaus Rizvi, for his support both financially and academically. His knowledge, expertise, patience, and willingness to help have made this thesis completion possible. He enlightened me about most areas of this project.

# TABLE OF CONTENTS

<b>ABSTRACT</b>	<b>I</b>
<b>ACKNOWLEDGEMENTS</b>	<b>II</b>
<b>TABLE OF CONTENTS</b>	<b>III</b>
<b>TABLE OF FIGURES</b>	<b>XI</b>
<b>GLOSSARY</b>	<b>XV</b>
<b>1. INTRODUCTION</b>	<b>1</b>
1.1. Project Introduction	1
1.2. Thesis Objectives	5
1.3. Thesis Organization	6
<b>2. LITERATURE REVIEW</b>	<b>7</b>
2.1. High Temperature Corrosion	7
2.1.1. High-Temperature Corrosion Kinetic Principles	8
2.1.2. The Pilling-Bedworth Relationship	8
2.1.3. Protective Coatings for Corrosion Prevention	9
2.2. Molten Salt Corrosion	10
2.2.1. General Principles	11
2.2.2. Conditions for Corrosion in Molten Salts	14

2.2.3.	Special Properties of Molten Salt Corrosion	16
2.2.3.1.	Thermal Mass Transfer	16
2.2.3.2.	Electrochemical Corrosion of Metals	17
2.2.3.3.	Selective Attack	18
2.2.4.	Molten Chloride Salts	19
<b>2.3.</b>	<b>Passivation</b>	<b>20</b>
2.3.1.	Introduction	20
2.3.2.	Types of Passivation	21
<b>2.4.</b>	<b>The Metallic and Ceramic Coatings</b>	<b>22</b>
2.4.1.	Bond Metallic Coating	24
2.4.2.	Top Ceramic Coating	25
<b>2.5.</b>	<b>EIS Test</b>	<b>26</b>
<b>3.</b>	<b>THEORIES AND BACKGROUND</b>	<b>29</b>
<b>3.1.</b>	<b>Corrosion Background</b>	<b>29</b>
<b>3.2.</b>	<b>Coating Background</b>	<b>33</b>
3.2.1.	Thermal Spray Methods for Applications of Coatings	33
3.2.1.1.	APS	33
3.2.1.2.	HVOF	35
<b>3.3.</b>	<b>EIS Background</b>	<b>37</b>

3.3.1.	Background Theory of EIS	37
3.3.2.	Interpretation of EIS Results	39
<b>4.</b>	<b>EXPERIMENTAL SECTION</b>	<b>41</b>
<b>4.1.</b>	<b>Materials and Supplies</b>	<b>41</b>
4.1.1.	Gas Used and Sources	41
4.1.2.	Chemicals Used and Sources	41
4.1.3.	Coating Materials Used	42
4.1.4.	Metal Samples	43
4.1.5.	Personal Protection Equipment (PPE)	43
4.1.5.1.	Room Temperature Protection Gear	44
4.1.5.2.	High Temperature Protection Gear	44
<b>4.2.</b>	<b>Equipment and Apparatus</b>	<b>45</b>
4.2.1.	EIS Test Equipment	45
4.2.1.1.	EIS Potentiostat	45
4.2.1.2.	EIS Software	46
4.2.1.3.	EIS Test Cell	47
4.2.1.3.1.	EIS Test Cell Description	47
4.2.1.3.2.	EIS Test Apparatus Assembly	48
4.2.2.	Immersion Test Equipment	49

4.2.2.1.	Design of Immersion Test Apparatus	49
4.2.2.1.1.	The Immersion Test Vessel (ITV)	49
4.2.2.1.2.	The Condenser	52
4.2.2.1.3.	The Scrubber	52
4.2.2.1.4.	The Heating System	52
4.2.2.2.	Assembling the Immersion Test Apparatus	53
4.2.2.2.1.	The ITV Subassembly	54
4.2.2.2.2.	The Condenser Subassembly	56
4.2.2.2.3.	The Scrubber Subassembly	56
4.2.2.2.4.	Heating System Subassembly	57
4.2.2.2.5.	Final Assembly	57
4.2.3.	Requirements for Designing New Equipment	58
4.2.3.1.	New Sample Design	63
4.2.3.2.	Vessel Design Improvement	65
4.2.3.2.1.	The Lid Design	65
4.2.3.2.2.	The Lifting Mechanism	65
4.2.3.3.	New Clamps	66
4.2.3.3.1.	New Clamp for Immersion Test	66
4.2.3.3.2.	New Clamp for EIS Test	67

4.2.3.4	New Heating System Design	67
4.2.3.5	Sealing Mechanism	68
4.2.3.5.1	New Sealing Mechanism	68
4.2.3.5.2	Testing the Apparatus Sealing Mechanism	69
<b>4.3.</b>	<b>Immersion Test Apparatus Fault Analysis</b>	<b>73</b>
4.3.1.	Set up Hazard	73
4.3.2.	Pressure Hazard	74
4.3.3.	Temperature Hazard	75
4.3.4.	Toxicity Hazard-Chlorine Gas	76
4.3.5.	Explosion Hazard	78
4.3.6.	Heating System Hazard	78
4.3.7.	Handling Device Hazard	79
<b>4.4.</b>	<b>Experiment Methodology</b>	<b>79</b>
4.4.1.	Initial Raw Sample Preparation	81
4.4.2.	Sample Preparation	81
4.4.3.	Immersion Test	82
4.4.3.1.	Preparation	82
4.4.3.1.1.	Washing the Vessel before Immersion Test	82
4.4.3.1.2.	Preparation before Immersion Test	82

4.4.3.2.	Immersion Experiment	83
4.4.4.	Test Operation Method	84
4.4.4.1.	The Handling Device	84
4.4.4.2.	Pressure Relief Device	85
4.4.4.3.	Thermal Cut-off System	85
4.4.4.4.	Post Experiment Cleaning	86
4.4.5.	Visual Examination	86
4.4.6.	Weight Change Analysis	87
4.4.6.1.	Sample Treatment before Immersion	88
4.4.6.2.	Weight Change Analysis	88
4.4.7.	EIS and SEM/EDX	89
4.4.7.1.	Sample Preparation before SEM/EDX	89
	Cutting and Polishing	89
4.4.7.2.	SEM and EDX Preparation	90
4.4.7.3.	SEM and EDX Experiment	90
<b>5.</b>	<b>RESULTS AND DISCUSSION</b>	<b>92</b>
<b>5.1.</b>	<b>New Geometry Performance</b>	<b>92</b>
<b>5.2.</b>	<b>Sealing Mechanism</b>	<b>93</b>
5.2.1.	Pre-Oxidization Tests	93

5.2.2.	Oxidization Test during the Immersion Test	96
<b>5.3.</b>	<b>Immersion Test Examination</b>	<b>100</b>
5.3.1.	Immersion Tests Results	101
5.3.1.1.	Evaluation of Coating # 1 (YSZ):	101
5.3.1.2.	Evaluation of Coating # 2 (Diamalloy 4006 + YSZ):	103
5.3.1.3.	Evaluation of Coating # 3 (SHS 9172):	106
5.3.1.4.	Evaluation of Coating # 4 (Diamalloy 4006):	110
5.3.1.5.	Evaluation of Coating # 5 (SHS + YSZ):	112
5.3.2.	Effectiveness of the Sealing Mechanism Developed	114
<b>5.4.</b>	<b>Coatings' Performance</b>	<b>114</b>
5.4.1.	Bond Coating Performance	115
5.4.2.	Coatings Corrosion Resistance	115
<b>6.</b>	<b>CONCLUSION</b>	<b>118</b>
<b>7.</b>	<b>RECOMMENDATIONS FOR FUTURE WORKS</b>	<b>120</b>
<b>8.</b>	<b>REFERENCES</b>	<b>121</b>
	<b>APPENDICES:</b>	<b>128</b>
	<b>Appendix 1: CuCl thermodynamic analysis</b>	<b>128</b>
	<b>Appendix 2: EIS Test Experiment Procedure</b>	<b>132</b>
	<b>Appendix 3: Immersion Experiment Procedure</b>	<b>135</b>



## TABLE OF FIGURES

Figure 1-1; The Schematic of Cu-Cl Cycle.....	2
Figure 2-1; An Idealized and Schematic Anodic Polarization Curve of a Passive Metal.....	21
Figure 2-2; In (a) the Bode plot of the EIS experiment; (b) the SEM image of the material cross-section, and (c) the equivalent circuit model to represent the material condition. ....	27
Figure 3-1; APS Spraying Method Apparatus. ....	34
Figure 3-2; The Illustration of HVOF Spraying System.....	35
Figure 3-3; Phase Shift Diagram .....	38
Figure 3-4; Figure (a) is the vector plot of the impedance magnitude and phase angle and (b) is the complex plane plot of $Z''$ vs $Z'$ . ....	40
Figure 4-1; The Setup of EIS Test Apparatus .....	46
Figure 4-2; The Electrochemical Cell for EIS Tests. ....	47
Figure 4-3; The Immersion Test Apparatus Setup Schematic. ....	50
Figure 4-4; The Handling Device (a) Plate and Pillars; (b) Handling Rod, Handling Plate, Clamp ,and Sample.....	54
Figure 4-5; The T-Pipe Joint on ITV.....	55

Figure 4-6; The Complete Assembly of the Immersion Test Apparatus .....	58
Figure 4-7; New designed Samples with Round Edges .....	63
Figure 4-8; New Designed Lid .....	65
Figure 4-9; New Immersion Test Clamp.....	66
Figure 4-10; New EIS Clamp .....	67
Figure 4-11; Schematic of the Blank Test.....	72
Figure 5-1; (a) New Designed Samples and (b) Old Designed Samples .....	92
Figure 5-2; Schematic of Pre-Oxidation Test.....	94
Figure 5-3; Samples (a) Before and (b) After 100 Hours Pre-Oxidization Test....	95
Figure 5-4; Regression Plot of Pre-Oxidization Corrosion Rate.....	95
Figure 5-5; Schematic of the Oxidization Test during the Immersion Test.....	97
Figure 5-6; Sacrificial Metal (a) Before and (b) After the Immersion Test for 48 Hours .....	98
Figure 5-7; Regression Plot of Post-Oxidization Corrosion Rate .....	99
Figure 5-8; Schematic Cross-Sections of Coatings on the Specimen which were Evaluated .....	100
Figure 5-9; Picture of Sample with Coating #1, (a) before, and (b) after Post- Immersion Cleaning .....	101

Figure 5-10; SEM/EDX of Sample with Coating #1 for 5 hours test .....	102
Figure 5-11; Picture of Coating # 2 (a) before and (b) after 48 h Immersion test	103
Figure 5-12; SEM and EDX Results of Coating # 2 after 48 hours Test.....	104
Figure 5-13; Coating # 2 which was immersed for 100 hours .....	105
Figure 5-14; SEM/EDX Results of Coating # 2 which was Immersed for 100 h	106
Figure 5-15; Pictures of Coating # 3 which was Suspended (a) before, and (b) after the Test .....	107
Figure 5-16; SEM/EDX of Suspended Coating # 3 for 48 hours.....	108
Figure 5-17; Pictures of Coating # 3 (a) before and (b) after Immersion Test and (c) after Post-Immersion Test Cleaning.....	109
Figure 5-18; SEM/EDX of the Coating # 3 which was immersed for 48 hours ..	109
Figure 5-19; Coating # 4 Suspended for 100 hours. (a) Before and (b) After the Test .....	110
Figure 5-20; Coating # 4 Immersed in Molten CuCl for 100 hours. (a) Before and (b) After the Test. ....	111
Figure 5-21; SEM and EDX Results of the coating # 4 which was Immersed for 100 hours .....	111
Figure 5-22; Coating # 5 which was Suspended for 100 hours.....	112

Figure 5-23; Coating # 5 which was Immersed in Molten CuCl for 100 hours... 113

Figure 5-24; SEM and EDX Results of Coating # 5 which was Immersed for 100 hours ..... 113

Figure 5-25; Samples Performance which were Coated with YSZ..... 116

Figure 5-26; Intact Bond Coats in Different Tests ..... 117

## **GLOSSARY**

AC: Alternating Current

APS: Air Plasma Spraying

AR: As-received material/sample

CPE: Constant Phase Element

E-cell: Electrochemical cell

EDTA: Ethylenediaminetetraacetic Acid

EDX: Energy Dispersive X-ray Spectroscopy

EIS: Electrochemical Impedance Spectroscopy

Di: Diamalloy 4006 (bond coating)

FRA: Frequency Response Analyzer

HVOF: High Velocity Oxygen Fuel

ITV: Immersion Test Vessel

OCP: Open Circuit Potential

SEM: Scanning Electron Microscope

SHE: Standard Hydrogen Electrode

SHS: Super Hard Steel 9172 HVOF coating

SS: Stainless steel

TBC: Thermal Barrier Coating

VPS: Vacuum Plasma Spraying

YSZ: Ytria Stabilized Zirconia (YSZ) coating

A: Area of exposure ( $\text{cm}^2$ )

$C_c$ : The coating capacitance (F)

$E_{cell}^\circ$ : The sum of anodic and cathodic reaction standard potential (Volts)

$E_{RMS}^\circ$ : The root mean squared

$E^\circ$ : The reaction standard potential (Volts)

$E_0$ : The amplitudes of applied potential (Volts)

$E(t)$ : The applied potential (Volts)

f: Frequency (Hz)

F: Faraday's constant = 96500 C/mol

$I_{AC}$ : The AC current response (amps)

$I(t)$ : The current response (amps)

$I_0$ : The amplitudes of current response (amps)

$k$ : Solution conductivity (S/cm)

$l$ : Distance between the reference and working electrode (cm)

$n$ : Number of electrons

$Q_{DL}$ : The capacitance double layer (F)

$Q_f$ : The film capacitance (F)

$Q-n$ : A representative of the capacitance non-ideality (F)

$R_c$ : The coating resistance ( $\Omega$ )

$R_f$ : Film resistance ( $\Omega$ )

$R_{f2}$ : The additional resistance to compensate the change after immersion ( $\Omega$ )

$R_p$ : generalized coating resistance of both coating and pores resistance ( $\Omega$ )

$R_s$ : The solution resistance ( $\Omega$ )

$t$ : Coating thickness (cm)

$V_{AC}$ : The applied AC potential (Volts)

$\omega$ : Radial frequency (rad/sec)

$Z$ : Impedance ( $\Omega$ )

$Z''$ : Impedance Imaginary Value ( $\Omega$ )

$Z'$ : Impedance Real Value ( $\Omega$ )

$|Z|$ : Impedance Magnitude ( $\Omega$ )

$\Phi$ : Phase shift between the potential and current wave

$\epsilon$ : The relative electrical permittivity

$\epsilon_0$ : The electrical permittivity constant (F/m)

%ED1: Percentage error day 1

%ED2: Percentage error day 2

%ED3: Percentage error day 3

$\Delta G$ : Change in Gibbs Free Energy

# 1. INTRODUCTION

## 1.1. Project Introduction

Hydrogen is considered to be one of the best alternative energy carrier candidates and is easier to sustain than fossil fuel. Since hydrogen is a copious chemical element, there are no concerns about running out of it. Hydrogen production demand has arisen in many major industries such as petroleum, gas, agriculture and transportation. [2] Particularly, hydrogen is supposed to be the most promising candidate for the future clean energy in the transportation industry. [3]

An abundant and easily available source of hydrogen is water. Therefore, research is underway to develop efficient methods for thermochemical decomposition of water for hydrogen production by using heat and chemical compounds. Some of these methods propose to utilize waste heat from other industrial processes to improve efficiency. For instance, the waste heat from a nuclear power plant can be recycled in a close internal loop [2].

Some methods for hydrogen production cycles being studied have better efficiency and can possibly be practical for commercial use [3]. These methods are based on using catalysts in a thermo chemical cycle to dissociate hydrogen from water. The majority of hydrogen productions cycles being considered, involve processes require temperature over 800°C [3]. The high operating temperature will bring other challenging problems including plant design and material selection [3]. The method based on using CuCl as the catalyst, which is called Cu-Cl cycle, has several advantages compared to the other cycles being investigated, including a lower operating temperature [3]. The highest operating temperature in the Cu-Cl cycle is around 530°C, which is much lower than highest temperature for other cycles [2, 3].

The lower operating temperature means fewer problems associated with plant design, energy efficiency, environmental impact, material selection, and cost.

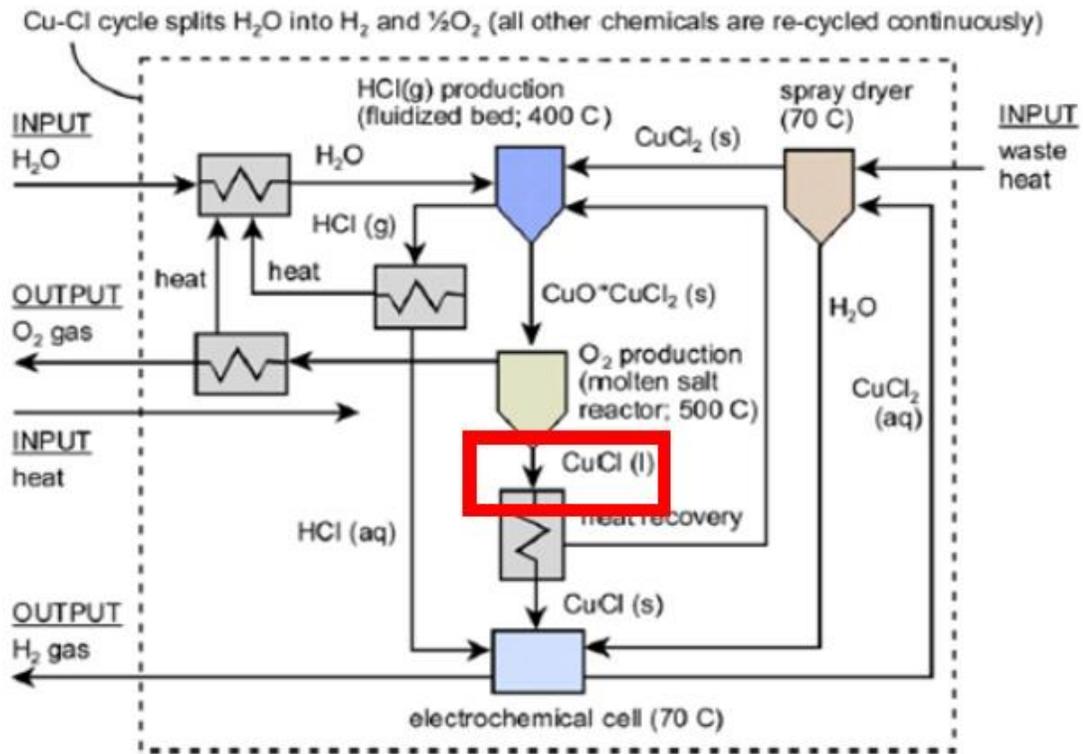


Figure 1-1; The Schematic of Cu-Cl Cycle

(The figure was adopted from Naterer et al. [3].)

The Cu-Cl cycle uses a combination of chemical and electrochemical reactions of copper chloride compounds to separate water into hydrogen and oxygen [2, 3]. The process schematic and reactions of the Cu-Cl cycle are given in **Figure 1-1** and **Table 1-1**. First, the hydrogen gas and aqueous CuCl<sub>2</sub> are generated by the reaction between aqueous HCl and aqueous CuCl [3]. The aqueous CuCl<sub>2</sub> is then dried to produce solid CuCl<sub>2</sub> which is transferred to a fluidized bed reactor [3]. Using the heat that is recovered from the waste heat of the cycle, the reaction between input water and solid CuCl<sub>2</sub> will produce HCl gas and CuO·CuCl<sub>2</sub>, also known as copper

oxychloride [3]. The copper oxychloride is then transferred to a molten salt reactor to produce aqueous or molten CuCl and oxygen [3]. The Cu-Cl cycle is kept closed so that the chemicals and waste heat are recycled and reused during the hydrogen production process.

One of the most important parameters to economically design a commercial thermochemical Cu-Cl hydrogen plant is the lifetime of all of materials used for molten CuCl vessels and transport system. Molten CuCl at 500°C is highly corrosive and under such conditions none of the known materials can resist chemical attacks for long period. A possible solution is to use metals which are highly resistant to corrosion as a substrate materials and apply some metallic and ceramic coating layers which will further help improve corrosion resistance.

This project focuses on the materials required for the execution of step 1.4 of the Cu-Cl cycle reactions of **Table 1-1** which is within the red rectangle of **Figure 1-1** which represent molten copper chloride and oxygen produced by solid “copper oxychloride” at an elevated temperature (around 500°C). As molten CuCl is an aggressive compound in this environment, developing special materials to resist corrosion failure is important. This study was undertaken to identify potential materials that can be used in a pilot plant for this cycle.

**Table 1-1, Steps and reactions of the Cu-Cl cycle step**

Step #	Reaction	Temperature	Description
1.1	$2\text{CuCl}_{(aq)} + 2\text{HCl}_{(aq)} \rightarrow \text{H}_2(g) + 2\text{CuCl}_2(aq)$	< 100 °C	Q input
1.2	$\text{CuCl}_2(aq) \rightarrow \text{CuCl}_2(s)$	< 100 °C	Q input
1.3	$2\text{CuCl}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{CuO} \cdot \text{CuCl}_2(s) + 2\text{HCl}(g)$	400 °C	Q input
1.4	$\text{CuO} \cdot \text{CuCl}_2(s) \rightarrow 2\text{CuCl}_{(l)} + \frac{1}{2}\text{O}_{(aq)}$	500 °C	Q input

The table was adopted from Naterer et al. [3].

After an initial literature search, many possible candidate coating materials were identified for this purpose, but due to a lack of confirmed data or a proper study on the corrosion caused by the molten CuCl, more research is required in this area. A number of potential substrate materials were also identified during the initial literature survey. In order to improve the corrosion resistance and survivability of the selected alloy, a ceramic coating can be applied to act as an insulator and protector of the underlying metal. The selected ceramic coatings should have a high corrosion resistance which will prevent the molten CuCl from corroding the underlying material. The adhesion between the selected ceramic coating and the substrate material should be very strong, so that it does not delaminate during operation. Not all materials form strong bonds and if the selected materials are not very compatible, the coating will not have the required adhesion strength. In such cases, a metallic bond coating can be applied to the substrate alloy in order to improve the adhesion between the ceramic top coatings and the substrate metals. High Velocity Oxygen Fuel (HVOF) and Air Plasma Spraying (APS) are the two common methods identified for applying the bond coat and ceramic top coating on the substrate metals.

Siantar [1] designed and developed a system to carry out coating evaluations; however, none of the coatings tested by him survived the immersion test in which these were exposed to molten CuCl at 500°C. After studying Siantar's research and his conclusions [1], it was decided to re-evaluate the entire experimental process and the specimen geometry. A bullet shape was chosen as the sample geometry to avoid lack of coating integrity on the sharp edges. The apparatus was also modified to accommodate the new geometry and to remove the sources of errors.

In this thesis, the performance of the metallic and ceramic coatings on the base metal which is exposed to molten CuCl at 500°C will be investigated. In order to only evaluate the coating materials without focusing on the substrate materials, it was decided to carry out the initial tests on medium carbon steel as a substrate material. Medium carbon steel is not expensive and also its corrosion deposit color would be easier to recognise after performing the immersion tests. An immersion apparatus that was used to perform exposure tests could provide similar environmental conditions as may exist in the proposed hydrogen plant. The performance of the candidate materials and coatings will be evaluated using visual observation, SEM images and EDX results and an electrochemical method (Electrochemical Impedance Spectroscopy (EIS)).

## 1.2. Thesis Objectives

This study develops the earlier work of Edwin Siantar [1]. The main objective of this project is re-evaluation of the molten CuCl immersion system and the evaluation of the selected coating candidates by exposure to molten CuCl at 500°C for a prolonged period (around 100 hours), so that the performance of the coating and integrity of adhesion with base materials can be studied. The objectives of this thesis are to:

1. Design new specimen geometry to avoid lack of coating integrity on the sharp edges of the sample to improve corrosion resistance during immersion tests.
2. Improve the apparatus assembly, mechanism and system performance to minimize oxygen leakage into the ITV contains the molten CuCl at 500°C during prolonged testing.
3. Monitor and evaluate the selected coating candidates after exposure to molten CuCl at 500°C for prolonged period.

### **1.3. Thesis Organization**

In Chapter 2 of this thesis, the background of the corrosion process, coating methods, and all tests that had been done during this project are discussed briefly to better clarify the project. Literature review of the previous studies on corrosion of the selected materials, high temperature corrosion, molten copper chloride behaviour, appropriate coating, and EIS test are provided in Chapter 3. Within Chapter 4, EIS, SEM/EDX, immersion test apparatus and experimental procedures and setup are described. In Chapter 5, all the results are reported and discussed. Chapter 6 contains the conclusion and finally in Chapter 7 recommendations for future work are given.

## 2. LITERATURE REVIEW

### 2.1. High Temperature Corrosion

The terms ‘high-temperature corrosion’ or ‘hot corrosion’ are normally taken to apply to the reactions taking place between metals and gases at temperatures above 100°C. During the hot corrosion, the presence of a liquid electrolyte does not require. This type of damage is called *dry corrosion* or *scaling*. [48] It is obviously in contrast with cases of wet corrosion at temperatures above 100°C, i.e. in pressurised boilers. Practically, some specific metals and alloys used at temperatures above normal do not suffer too much measurable attack in the atmosphere till the temperature is considerably above 100°C. Some kind of metals such as iron and low-alloy steels form only the thinnest of interference oxide films at around 200°C. Copper usually shows the first sign of tarnishing at around 180°C, and while aluminium forms a thin oxide film at room temperature, the growth rate is extremely slow even around its melting point.

A few of these cases occur in which wet corrosion and hot-corrosion are interdependent. The wet corrosion occurred if the condensation of liquids generated during a period at elevated temperatures. Such cases are properly considered as aqueous corrosion. [48]

For the most significant practical hot-corrosion phenomena, reactions are controlled by the kinetics of the proceeding, rather than by the thermodynamic stability of the reactants or products involved. It is considerable that reaction occurred under simplified laboratory conditions are inappropriate for the more complicated conditions in practice. [53]

### 2.1.1. High-Temperature Corrosion Kinetic Principles

The main and first step of high-temperature oxidation is the oxygen adsorption on the metal surface, followed by oxide nucleation and the development of the oxide nuclei into a non-stop oxide film which covers the metal substrate area. Defects, such as porosity, microcracks and macrocracks can develop through the film as it thickens. [48] These kind of defects tend to render an oxide film nonprotective, so that oxygen can simply reach the metal substrate to cause more oxidation. The term *oxidation* is ambivalent because it can either mean the formation of oxides or refer to the mechanism of oxidation of a metal (i.e., its change to a higher oxidation number than the metallic state). [49]

### 2.1.2. The Pilling-Bedworth Relationship

The volume of the oxide produced, relative to the volume of the metal consumed, is a key parameter in predicting the degree of protection estimated by the oxide scale, theoretically. If the oxide volume is relatively low, tensile stresses could crack the oxide film. Oxides, basically representing brittle ceramics, are mostly prone to fracture and cracking under such tensile stresses. If the oxide volume is very high, stresses will be set up that can suppose to a break in the adhesion between the metal and oxide. For a high level of protection, it can therefore be mentioned that the volume of the oxide formed should be comparable to that of the metal consumed. This argument is the basis for the Pilling-Bedworth ratio:

$$PB = \frac{\text{volume of oxide produced}}{\text{volume of metal consumed}} = \frac{Wd}{nDw}$$

Where  $W$  = molecular weight of oxide (u)

$D$  = density of the oxide ( $\text{kg/m}^3$ )

$n$  = number of metal atoms in the oxide molecule

$d$  = density of the metal ( $\text{u}$ )

$w$  = atomic weight of the metal ( $\text{kg/m}^3$ )

P-B ratios slightly more than 1 (less than 2) could be anticipated to designate “optimal” protection, with uncertain compressive stresses generated in the oxide layer. It has been found that PB ratios are generally poor estimation of the actual and practical protective properties of scales. Some of the causes advanced for deviations from the P-B rule include;

- There are some oxides in fact grow at the oxide-air interface, opposite to the metal-oxide interface.
- Component and Specimen geometries can have a serious effect on the stress distribution in the oxide films.
- Continuous oxide films are observed even if  $PB < 1$ .
- Cracks and crevices in the oxide layers can be “self-healing” as oxidation progresses.
- Porosity through the oxide is not precisely anticipated by the P-B parameter. [4]

### **2.1.3. Protective Coatings for Corrosion Prevention**

Coatings are applied like a layer on the surface of an object which is called “substrate” to protect, cover or make it lux. For protection purpose, this layer could protect substrate material for longer time in a specific corrosive environment. One of main purpose of applying coating is to keep the integrity of the material if we

consider the high cost of the maintaining or replacing the base material. There are lots of parameters to choose an appropriate coating for a specific substrate material and environment (corrosion environment, stress, heat resistance, adhesion and et al.). Coatings are categorized in four different classes which are “organic, inorganic, conversion and metallic”. [5] Any mistake in coating material selection can cause a serious hazard to the environment due to let a corrosive substance reacts or escapes when the material loses its integrity. Usually a material with high corrosion resistance and nobility has to be selected as a coat which is adapted to the desired process environment. Generating and selecting a noble metal to prevent corrosion may be impractical due to the high cost involved. Sometimes applying coating could be the solution of the problems.

Protective coatings are perhaps the most extensively used products for corrosion control. They are used to provide a long-term protection under a wide range of corrosive environments, extending from atmospheric exposure to the most severe chemical processing conditions. Coatings provide little or no structural strength, yet they protect other materials to keep their strength and integrity. The main purpose of a protective coating is to isolate structural reactive elements from environmental corrosives. The point that coatings occupy only a very small portion of the total volume of a system is reasonably telling of the heavy requirements imposed on these materials. A coating has to provide a non-stop barrier to a substrate, and any defectiveness can become the principal point for corrosion and degradation of the substrate.

## 2.2. Molten Salt Corrosion

A widespread variety of molten salts is used in industries and there exists a similarly widespread range of possible chemical reactions with metallic portions being heated

in the baths. Molten salts involve mostly of mixtures of carbonates, nitrates or alkaline metals or halides of the alkaline-earth and these commonly have a prepared solubility for oxides of the other metals. Therefore, the molten salts can be adequately oxidising to react with other alloys in order to produce oxide. This oxide production does not have a protective effect and is consequently taken into solution of the molten salts and then the attack steadily progresses. In some cases adsorption of components of the salt mixture into the alloy can take place, with either beneficial or deleterious results. [54, 53]

Attentions in the performance of molten salts in processes are constantly growing. The modification is enhanced by the enhancing demand for the novel refractory metals \_often formed by processes containing molten salts\_ and by the innovative chemical engineering techniques also that have been established in all the energy industry, as well. Such difficulties have inspired the study of corrosion in the molten salts and have directed this project to a fairly high degree of accepting of corrosion reactions.

Furthermore, the material is strictly related to high-temperature corrosion that is usually caused by a layer of molten salts such as chlorides and sulphates. Considerations have been concentrated on the relevant thermodynamic data and the electrochemistry of this type of corrosion.

### 2.2.1. General Principles

In electrochemical view, the system molten salt is slightly like the system aqueous solution, although there are some more important differences, rising largely from differences in electrical conductivity and temperature. Molten salts are mostly ionic, but contain a proportion of molecular parts, while pure water is mostly molecular;

they are holding very low activities of hydrogen ions. Since the aqueous system has been comprehensively studied, it is helpful to indicate some equivalents in molten-salt systems.

The exchanging reaction of a metal,  $M$ , and a molten salt,  $AB$ , that produce metal corrosion product,  $MB$ , and moved metal,  $A$ , can be written:



For which there is equilibrium constant;

$$K = \frac{a_{MB}a_A}{a_M a_{AB}} \quad (2.2)$$

That the metal  $M$  is noble and the cation  $A$  of the salt is base, the constant of equilibrium (3.2) has a small value, thus the activities of displaced metal  $A$  and corrosion product  $MB$  stay small. The metal  $M$  and the salt  $AB$ , being pure substances, have an activity, however the corrosion product  $MB$  and the exchanged metal  $A$  will in the most cases be in solution upper than the melting point at an activity of less than one. Only if there are no other factors present which could combine with  $MB$  or  $A$  or remove them, the system will extent to equilibrium after a small amount of reaction during the corrosion has occurred and the system will then be “immune” against further corrosion. [64, 4, 53]

Putting away for the instant effects due to passivity phenomenon, a metal can be corroded (oxidised) only if it is in exchange with a material that is reduced; in an aqueous electrolyte, either some other solute (regularly dissolved oxygen) is reduced, or hydrogen ions are moved to form hydrogen gas; in a molten salt, either one of the metal cations (analogous to hydrogen ions in the aqueous solution) is

moved to produce metal, or some molecular types or an ion is reduced. In aqueous electrolytes, consequently, metals that are so noble to transfer hydrogen corrode only if dissolved oxygen or some other reducible substance is present, and when the reducible material has been consumed, corrosion stops; the metal has become 'immune', i.e. has reached electrochemical equilibrium with the environment. The condition is like molten salt corrosion, and the relative nobilities of the molten salts and the metal are important. A noble metal in exchange with a pure melt of a base metal cation can react individual to a very restricted amount delivered the anion is not reducible; for instance, nickel cannot move sodium from a sodium chloride melt to any considerable amount and therefore in molten sodium chloride, nickel will not corrode except if reducible impurity presents. [64, 4, 48]

Usually a sufficiently noble metal container is selected for molten salts to neglect the displacement reaction (3.1). The most important features of corrosion in aqueous solutions are those which include reducible impurities, although in a molten salt there is another possibility of a reducible anion. General aspects can be defined for monitoring the "oxidising power" of the molten salt, which can be explained in terms of a "redox potential" in aqueous solutions. The redox potential is expressed by relationships of the form

$$E = E^0 + \frac{RT}{zF} \ln \frac{a_{ox}}{a_{red}} \quad (2.3)$$

For instance, the redox potential of a system holding oxide ions and oxygen might be determined as:

$$E = E^0_{O_2/O^{2-}} + \frac{RT}{2F} \ln \frac{a_{O_2}^{1/2}}{a^{2-}} \quad (2.4)$$

Similar equations can be expressed for other equilibria, e.g.  $\text{Na}^+/\text{Na}$ ,  $\text{NO}_3^-/\text{NO}_2^-$ , etc.

The redox potential of a melt is a scale of its aggressiveness to the metals, and a metal in exchange with the melt will react with it until its potential becomes the same as the redox potential of the melt. The potential of the metal usually depends on the activity of its ions in solution in the melt

$$E = E_M^0 + \frac{RT}{ZF} \ln a_{M^{z+}} \quad (2.5)$$

Hence the oxidising power (higher the redox potential) of the melt, the metal will be more oxidised (corrode) —providing  $M^{z+}$  ions —before reaching to the equilibrium. (Oxidation of the metal will also cause reduction of the oxidising kinds present in the melt, which under certain conditions can cause the redox potential of the melt to drop during the sequence of the reaction, in which circumstance equilibrium will occur at a potential slightly lower than the initial redox potential of the melt.) [64]

### 2.2.2. Conditions for Corrosion in Molten Salts

Corrosion will be determined by environments under which metals are exposed to molten-salts in three conditions:

1. Environments under which equilibrium between metal and salt melt can be established and continued.
2. Environments under which passivity is possible.
3. Environments under which equilibrium cannot be reached. [4]

In molten/metal systems, similar to aqueous systems, one imaginable way of ensuring adequate corrosion resistance is to select conditions so that the metal is passive, which involves that it have to become covered with an insoluble, compact

film or deposit, adherent, preventing direct connection of the metal with its environment. Any molten salts which reacts with a metal to give a corrosion product insoluble in the melt is in principle accomplished of passivizing the metal, e.g. passivity can be estimated to occur in oxidizing salts in which metal oxides are cautiously soluble. Therefore, iron is highly resistant to molten alkali nitrates since it develops passive, and passivity has also been experiential by electrode potential measurements of an iron electrode in chloride molten containing nitrates, while in this specific condition the oxide corrosion product is not principally protective. Generally, molten salts are acceptable solvents for inorganic compounds therefore passivity is not possible to be a commonly encountered phenomenon. [48]

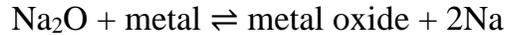
If passivity is not possible, corrosion can be prevented if the metal can reach to the equilibrium with its molten salt (case 1). The system usually undertakes some corrosion firstly, when small amount of oxidising impurities are reduced and the redox potential of the molten salt falls. At last, after a definite amount of corrosion has happened, the metal becomes “immune” and corrosion stops. The primary reaction can be supposed to:



And for all metals at all temperature, equilibrium was reached at some characteristic pressure.

The reaction can be withdrawn by applying a hydrogen pressure at the start of the reaction, or alternatively can be driven to the right by releasing the hydrogen formed, e.g. by removing with a gas stream.

Secondary reactions for example;



This reaction can be driven to accomplishment by frequently removing some of the reaction products, in this situation by distillation of sodium metal. Equilibration was delayed once the molten chloride were in contact with any glass containers which are not inactive and inert at such a high temperature.

Under some conditions (case 2), it will be impossible for the metal and the molten salt to reach at to equilibrium and continuously corrosion will occur; this case happens often when metals are in exchange with molten salts practically. There are two main factors: first one, the redox potential of the molten salt may be prohibited from falling, because either it is in exchange with an outer oxidizing environment (like an air atmosphere) or the conditions could cause the products of its reduction to be removed continually (for instance condensation of a colder part of the system and distillation of metallic sodium); second one, the electrode potential of the metal may be prohibited from rising (e.g. if the products of the metal corrosion is volatile). Furthermore, reaching to the equilibrium may not be achievable when there is a temperature gradient in the system or when alloys are involved in the reaction, but these cases should be considered in detail, separately. Rates of corrosion under these conditions where reaching to the equilibrium is not possible are controlled by interphase mass transfer and diffusion of oxidizing materials and/or corrosion products; geometry of the system will be a critical factor.

### **2.2.3. Special Properties of Molten Salt Corrosion**

#### ***2.2.3.1. Thermal Mass Transfer***

Whenever a temperature gradient exists in some reactions included metal in exchange with molten salt, thermal potentials are assembled, causing removal of

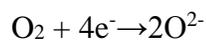
metal at high-temperature and metal deposition at cooler places. This mass transfer is basically unlike in nature from that happened in aqueous corrosion, which is only a temperature-solubility effect. In molten salts, both the corrosion and deposition reactions are electrolytic, and it has been presented that an electrical path is necessary between the hot and cold areas of the metal. Edeleanu and Gibson [63] recommend that this kind of mass transfer be called '*Faradaic mass transfer*' to show that it requires an electrolytic current.

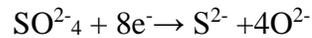
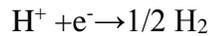
Mass-transfer deposits can direct to obstructions in non-isothermal circulating systems, if it is liquid-metal corrosion. In molten salts, the effect can be reduced by keeping pollution and contaminations of the molten by metal ions to a minimum; e.g. by keeping reducing conditions over the molten part or by removing oxidising impurities. [64]

### ***2.2.3.2. Electrochemical Corrosion of Metals***

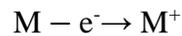
Since the aggressiveness of molten salt is directed by redox equilibria, and is usually controlled by composition of the outer atmosphere, in aqueous systems effects equivalent to 'electrochemical' or 'oxygen-concentration' corrosion can occur in molten salt.

Tomashov and Tugarinov [62] determined cathodic polarisation curves in molten chlorides and concluded that the cathodic reactions of impurities could be indicated as:





The anodic reaction was:



Because metals are known as electrical conductors, the anodic and cathodic reactions will not necessarily occur at the same position, and ‘anodic’ and ‘cathodic’ areas can progress as in aqueous solutions. For instance, ‘wash-line’ attack is usually a property of corrosion by molten salts in exchange with air. [64, 4, 48, 54]

#### ***2.2.3.3. Selective Attack***

High temperatures corrosion of alloys is more complicated by effects due to diffusion, especially where the alloy components have different similarities for the environment, and corrosion of an alloy in a molten salt at high temperature usually shows properties related to those of internal oxidation. When Inconel (high-nickel alloy) is exposed to molten sodium hydroxide, a two-phase corrosion-product layer could be formed, resulting from evolution of the reaction product (a mixture of oxysalts and oxides). “Selective removal of the less noble components happen, and as it is called diffuses outwards (Kirkendall effect). Voids tend to form at the grain boundaries and specimens often have the appearance of having undergone ordinary

intercrystalline corrosion, as diffusion rates are faster at grain boundaries than in the grains.” [8] More careful analysis has shown, however, that in the case of Fe-19Cr-8Ni corroding in a fused 50-50 NaCl/KCl molten salt at 800°C in the existence of air, the occurrence is not unceasing at the boundaries of grains, and the voids formed are not in exchange with each other. In high-nickel alloys, a greater amount of voids are formed within the grains and the presence of intercrystalline attack is less marked. [64]

#### **2.2.4. Molten Chloride Salts**

Copper Chloride (CuCl) is one of the compounds that are regularly used as a desulfuring agent in the petroleum and gas industries. There are limited references and publications available on molten CuCl corrosion; however, there are several researches on other molten chloride salts that can be related to molten CuCl corrosion because the chloride ions (Cl<sup>-</sup>) is the main reason of corrosion of molten CuCl which is usually cause the corrosion reaction. One of the most common applications of molten chloride salts are metal reduction for recycling [20] and pyrochemical fuel reprocessing [21] and generally the nuclear industries. Molten chloride salts could be found as a waste in furnace plants products too.

During the corrosion reaction, the aqueous electrolyte provides an easier environment for ion transport. However, the mechanism of corrosion in aqueous corrosion is similar to the molten salts behaviour. The lower operating temperature and less ionic conductivity in any molten salt solution would decrease the corrosion rate compared to corrosion in an aqueous solution [23, 24].

Based on the condition and environment of the reaction, the corrosion product of a molten salt reaction can appear in diverse forms. The most common corrosion forms

in molten chloride are selective leaching, pitting, metal oxidation, and uniform corrosion [21]. The corrosion products are usually in the form of a thin layer of salty deposit on the sample surface. The thin layer that is deposited on the surface can accelerate metal and alloy oxidation, decrease the rate or keep it constant based on the environment. Sidhu *et al.* [25] explained a failure that could happen by the protective oxide layer corrosion where was permitted the molten chloride to have more access to the substrate at high temperature. The molten chloride would react and remained on the substrate could increase the corrosion effects.

Metal chlorides can be produced as a result of a redox reaction, once an active metal and the molten chloride react [22]. The metal chloride is one of the usual products that can be formed in the presence of molten chloride. Some recent studies [20, 25, 26] presented variety patterns of phenomenon which could happen during the immersion. In terms of thermodynamic view, the Gibbs free energies for the metal chloride formation can represent if the metal chloride could be produced. A positive value of Gibbs free energy proves a weak driving force for the formation reaction of metal chloride. [1]

## **2.3. Passivation**

### **2.3.1. Introduction**

Most of metals and alloys have a thin layer protective corrosion film on the outer surface resulting from reaction with the environment solution. However, it is considerable that gold and platinum are exceptions. Some of passive layers on some kind of alloys and metals, not all of alloys and metals, have exceptional qualities which assist them to arrange for greater corrosion resistant surfaces. The passivity is for what is mentioned protective "passive" films. [48, 54]

### 2.3.2. Types of Passivation

There are two types of passivity [48]:

Type 1: "Passivity is when a metal significantly resists corrosion in an identified environment producing from marked anodic polarization" (noble potential, low corrosion rate). [48]

Type 2: "Passivity is when a metal significantly resists corrosion in an identified environment even though a marked thermodynamic tendency to react". (Low corrosion rate, active potential) [53]

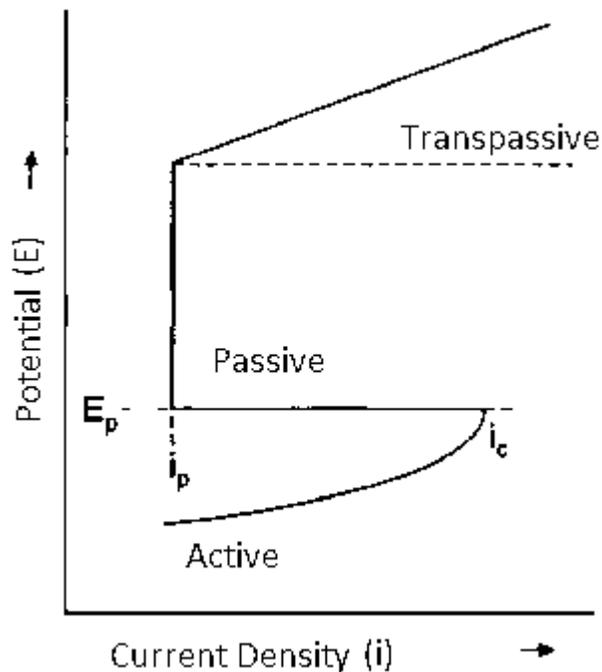


Figure 2-1; An Idealized and Schematic Anodic Polarization Curve of a Passive Metal

Adapted from Uhlig, Herbert Henry, and R. Winston Revie. Uhlig's Corrosion Handbook. 51 Vol. John Wiley & Sons, 2011. [48]

On this figure, three different areas are defined; the transpassive, the passive, and the active. Once the current density reaches to the critical current density for passivation ( $i_c$ ) at the specific passivation potential ( $E_p$ ), any potential more than  $E_p$  descends to the low passive current density ( $i_p$ ). [48]

This type covers just Type 1 passivity. Titanium, Chromium, Iron and Nickel in oxidizing environments, stainless steels and several others are in Type 1. Iron in an inhibited pickling acid are in Type 2. [48]

In polarization curve of **Figure 2-1**, Type 1 passive system is shown.

A helpful definition of passivity has been provided by ASTM (G15-83); “passive: the state of a metal surface characterized by low corrosion rates in a potential region that is strongly oxidizing for the metal” [53, 48].

#### 2.4. The Metallic and Ceramic Coatings

- a) There are numerous metal alloys that have good performance when exposed to a molten chloride salt environment [9]. Nevertheless, it is improbable that any alloy can resist hot corrosion attack (especially in the existence of an aggressive agent such as molten chloride) for a long exposure time. A high temperature or thermal barrier coating can be used to protect the underlying surface so that the portion can last longer in the high temperature corrosive environment. The need for a protective coating to keep the underlying surface is developing because higher temperature applications have similarly increased significantly in industry.
- b) A coating is applied for numerous reasons such as, providing a thermal barrier for high temperature environment, and improving the hot corrosion

resistance. There are dissimilar types of coating methods that can be characterized based on how the coating is deposited. One of the most conjoint coating methods used in industry are electrochemical deposition (electroplating, sol-gel, and anodizing), physical vapour deposition (electron beam, sputtering, ion plating, and cathodic arc), and thermal spray [10]. Each of these coating methods has some specific advantages and disadvantages. Compared to the other coating methods, thermal spraying has been widely used in the industry and has a higher deposition rate [10, 11]. The thermal spray method also allows the material to hold free during spraying process, which is suitable for coating large construction and structural materials.

Nowadays, there are several different thermal spraying methods practical in the industry, such as vacuum plasma spraying (VPS), HVOF, and APS. The different methods are categorized based on the source of heat and the fuel (gas) used to spray the coating powder. The coating materials (can be in the form of metal rod or refined powder) are placed in a feeder storage tank and heated. The molten material is then converted into elements using high velocity stream of compressed air, plasma or gases and then sprayed onto the specimen to be coated [10, 11]. APS and HVOF are normally selected because of the capability of both methods to produce a coating with acceptable quality and low porosity [10, 13].

The strength and quality of the sprayed coating is determined by its composition and adhesiveness, microstructure, porosity, and hardness [10, 12]. The presence of micro-cracks and pores can provide some pathways for corrosive substances to penetrate into the protected substrate. The quality of the coating can be changed by the other spraying process parameters as well, such as, the powder spraying distance,

spraying feed rate, the type of fuel used, the spraying temperature, and the particle size distribution [10].

#### **2.4.1. Bond Metallic Coating**

Usually a bond coat is applied in order to provide an uneven surface to improve the mechanical bonding during top-layer coating application. The bond coat also assists the top coating purpose which is keeping the underlying alloy substrate from corrosion and high temperature oxidation. In addition, the bond coat can minimize any effects of different coefficients of thermal expansion between top coat material and the substrate in order to prevent thermal shock. These differences will create problems during the heating and cooling process, as the coating might be damaged or crack.

Uusitalo *et al.* [14] recommended that HVOF coating has better coating density than arc spray coating. The better coating density presents that an HVOF coating will demonstrate better corrosion resistance because it has fewer oxide, voids, and splat boundaries that are often prone to attack. The molten chloride salt has an affinity to attack surface defects. Typically both micro-crack splat boundaries and porosity form an interconnected network through the coating. These defects are possible reasons to attack as the molten chloride could penetrate the coating, and then form the corrosion product underneath the coating. This is one of the reasons to allow attack of the underlying surface and decrease the bonding strength.

Porosity is one of the important parameters to determine some properties of thermal barrier coatings, e.g., thermal shock and thermal cycling resistance. HVOF has the quality of improving the corrosion and erosion resistance of any amount used in plants when high temperature and a corrosion environment are presented, it is also

known for its low porosity. Ni-based alloys (e.g. Diamalloy) are usually used as popular material for HVOF bond coating system because Ni-alloy has an acceptable corrosion resistance [10, 13]. Diamalloy 4006 is a nickel based amorphous alloy (Ni-20Cr-10W-9Mo-4Cu-1C-1B-1Fe) and as-sprayed coating is crystalline.

Super Hard Steel (SHS) 9172 HVOF is an iron based steel alloy which was used for this project.

#### **2.4.2. Top Ceramic Coating**

The APS coating method is another method that is used in order to apply coatings with a wide range of thickness and acceptable mechanical properties [15]. However, some problems that could be raised are poor porosity and adhesion, particularly when it is used for joining two different types of materials, such as metals and ceramics. However, the use of a bonding coat or a smaller particle size powder will improve the quality and adhesion of the top ceramic coating.

Yttria Stabilized Zirconia (YSZ) which is used for an insulating top coat strictly matches the majority of high nickel content alloys [17]. Matching the coefficients of thermal expansion values for the underlying metal and the YSZ coating decreases any chance of damaging the coating during heating and cooling process. Shankar *et al.* [15, 18] studied on molten LiCl-KCl that samples coated with thermal plasma. Sprayed YSZ performed well, which is shown by minimal damage experienced by the underlying metal and coating. The visual observations showed that there was no accelerated corrosion on the APS coated metal after some immersion periods [15]. On the other hand, the uncoated sample showed damage on the surface of the sample that was worse as the exposure time was enhanced [15].

## 2.5. EIS Test

EIS can provide an indication that materials were actually damaged or corroded. In the EIS method, a circuit model is used to fit the EIS data and represent the surface condition. There are many electric circuit models that can fit the EIS data, but this does not mean that each of those circuit models is the correct representation of the surface. *Ex-situ* surface analytical methods, such as SEM and EDX are required to validate the analysis gathered from the EIS test. Zhong and Desai [16] correlated EIS results (**Figure 2-2a**) and cross-section SEM images (**Figure 2-2c**) of the sample: the equivalent circuit (**Figure 2-2b**) was selected to represent the surface condition of the tested material. The cross-section SEM image showed the microstructure and the many different layers on the sample.

A suitable circuit representation for the EIS spectra is approximated. The Bode plot given in **Figure 2-2** suggested that there were three time constants in the system. Each of these time constants ( $\tau=RC$ ) was represented by a combination of a resistor and capacitor electric circuit element (R-C network). This equivalent circuit used has been described in the established literature [16]. The pores and defects in the coating are represented by a capacitor ( $C_p$ ) and a resistor ( $R_p$ ) in parallel, as can be seen in **Figure 2-2b** [16]. The equivalent circuit that represents the sample consists of a resistor in series with a node for a network of a capacitor in parallel with resistor. The resistor in the node is in series with another node also consisting of an R-C parallel circuit. Another R-C parallel node is connected in series with the node as shown in (**Figure 2-2b**).

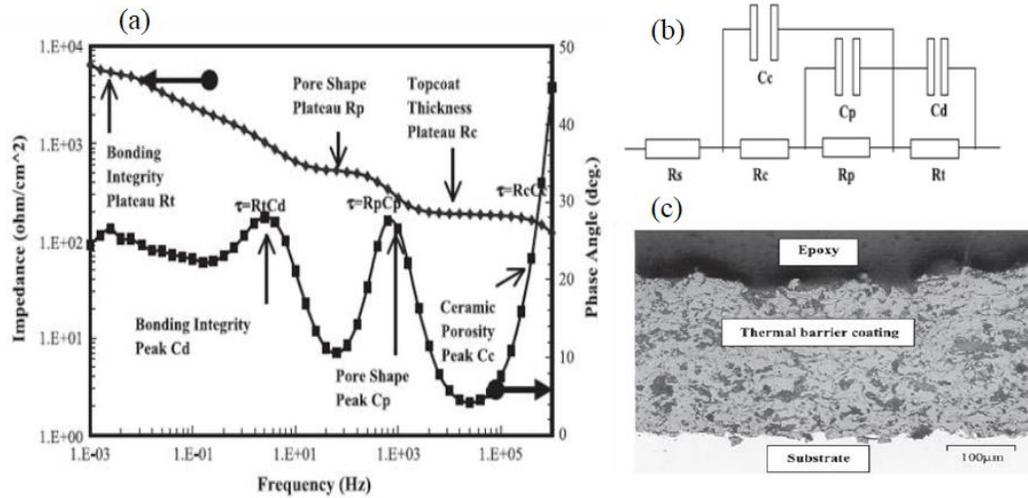


Figure 2-2; In (a) the Bode plot of the EIS experiment; (b) the SEM image of the material cross-section, and (c) the equivalent circuit model to represent the material condition.

All figures were taken from Zhong and Desai [16].

The equivalent circuit could be correlated with the Bode plot by looking at the peaks of the plot. The first peak was interpreted as the coating capacitance (the arrow on the right) occurring at high frequency [12]. The second peak was interpreted as the pore capacitance of the materials (occurring at mid-range frequency). The last peak was the electrode double layer capacitance. Each of these capacitors in parallel with a resistor are consistent with the resistance plateaus seen in the Bode plot (**Figure 2-2a**). The horizontal line at the lower frequency represents the solution resistance. The  $R_c$ - $C_c$  node (**Figure 2-2b**) represents the top coating matrix and the  $R_p$ - $C_p$  node represents the porous surface of the coating [15]. The  $R_t$ - $C_d$  node (**Figure 2-2b**) was attributed to the interface between the materials and the electrolyte. The  $R_s$  represented the solution resistance. Each of the elements were associated with an actual physical condition of the material and the values used to indicate surface changes or damage to the tested material [15]. Each of the R-C networks was a representation of a surface in the sample. Zhong and Desai [15] used both EIS and

SEM results to support each result and determined the actual surface condition of the tested material.

### 3. THEORIES AND BACKGROUND

#### 3.1. Corrosion Background

One of the definitions of corrosion is the degradation of a material due to a reaction with its environment. Degradation indicates deterioration of physical properties of the corroded material. This weakening can occur due to a loss of cross-sectional area, the metal shattering from hydrogen embrittlement, or the breaking up of a polymeric material due to UV sunlight.

The corrosion process is an electrochemical reaction that involves one pair of half reactions namely oxidation and reduction reactions. It means one of the substances increases its oxidation number and receive  $H^+$ , or donate electron(s), and the other substance donates  $H^+$ , or receives electron(s), therefore its oxidation number is reduced. As an example of the electrochemical reaction, if carbon steel is placed in an acidic solution, it elevates in oxidation number and is oxidized at the “anode”, and acid cation ( $H^+$ ) is reduced or gains electrons at the “cathode”. This “redox” reaction is considered as the corrosion of steel.

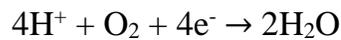
When metal is placed into an acidic electrolyte, it acts as an anode and its oxidation number is elevated from zero to positive value and forms  $M^{m+}$ . The acidic solution/electrolyte (the cathodic electrode) is reduced at the cathode and accepts electron  $xe^-$ .

Generally metals are elements that tend to release electrons or **oxidized** when they have reaction and nonmetals are those elements that tend to gain electrons or **reduced**.

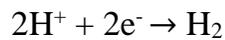
A common oxidation reaction in corrosion is the oxidation of metal atoms to positively charged metal ions:



The lost electrons from a metal usually go to a non-metallic atom forming a negatively charged non-metallic ion. The atom which has gained the electron(s) is said to have been **reduced** or the oxidation number is reduced.



Or,



The amount of oxygen in an environment, and its ability to absorb electrons, is an important factor in determining the affinity to corrode for that metal. [50]

Generally, there are two aspects of corrosion process; thermodynamics and kinetics. The thermodynamic aspects cover the energy changes in the corrosion process to determine if the reaction may occur or not. The thermodynamic view also discusses the stability of the reaction and the corrosion reaction products but it does not consider the corrosion rate. The corrosion rate can be determined by studying the kinetics of corrosion.

From a thermodynamic prospective, change of the Gibbs energy,  $\Delta G$ , is the main factor which is related to the electrochemical potential between the two redox reactions, and determines the possibility of a reaction occurring [4, 5]. The Gibbs energy equation based on the corresponding potential can be described as:

$$\Delta G = -nFE_{cell}^{\circ} \quad (3.1)$$

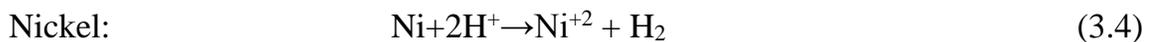
Where,  $n$  is the number of electrons being exchanged during the corrosion reaction,  $F$  is the Faraday's constant (which is 96,500 C/mol), and  $E_{cell}^{\circ}$  is the corresponding potential or the sum of the anodic and cathodic reaction standard potential.

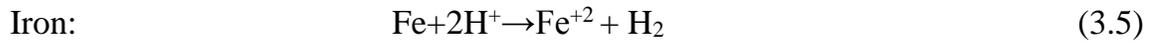
Each of the cathodic or anodic reactions has their specific standard potential value, known as  $E^{\circ}$ . The electrons that are involved in corrosion reaction tend to flow from the anode to the cathode. In order to measure the standard potential of the two reactions, a reference value or standard electrode is required. The standard hydrogen electrode (SHE) potential is usually used as the reference for potential measurements since the SHE equilibrium potential is defined as zero at any temperature [4].

For instance, two metals (nickel and iron) are placed in two separate containers filled with HCl solution. By comparing the Gibbs free energy change ( $\Delta G$ ) values of the two reactions, the reaction which is more thermodynamically favorable can be determined. These reactions for nickel and iron in HCl solution are:



Both nickel and iron when placed in HCl solution will produce metal chloride (iron chloride or nickel chloride) and hydrogen gas. Both reactions can be simplified into ionic reactions:





Each of these ionic reactions can be separated into individual anodic and cathodic reactions. The redox reactions for nickel and iron in HCl solution and the standard reduction potential value of each reaction [6] are:



By comparing the  $E_{cell}^\circ$  value of each redox reaction of nickel and iron, the more favourable reaction is determined using.

$$E_{cell}^\circ = E_c^\circ - E_a^\circ \quad (3.9)$$

Where  $E_a^\circ$  is standard potential of anodic reaction and  $E_c^\circ$  is standard potential for cathodic reaction. The  $E_{cell}^\circ$  values of nickel and iron in HCl solution are:

Nickel: 
$$E_{cell}^\circ = 0 \text{ V} - (-0.25 \text{ V}) = 0.25 \text{ V}$$

Iron: 
$$E_{cell}^\circ = 0 \text{ V} - (-0.44 \text{ V}) = 0.44 \text{ V}$$

The reaction between iron and HCl solution is more thermodynamically possible since  $E_{cell}^\circ$  value is greater positive value. The  $E_{cell}^\circ$  value is directly proportional to the greater  $E_{cell}^\circ$  value, the larger negative value of  $\Delta G$  is for iron-HCl reaction. The larger negative value of  $\Delta G$ , the more thermodynamically favourable the reaction is due to the larger driving force of the reaction.

## 3.2. Coating Background

Coatings are different type of materials which are applied like a layer on the surface of an object which is called “substrate” to protect, cover or make it lux. For protection purpose, this layer could protect substrate material in a corrosive environment. There are a number of parameters to be considered for choosing an appropriate coating for a specific substrate material and environment such as corrosion environment, stress, heat resistance, adhesion, etc. Usually a material with high corrosion resistance and nobility has to be selected as a coat and it should be compatible with the desired process environment. Making an entire product from a noble metal to prevent corrosion may be impractical due to the high cost involved. Applying an appropriate coating could be the solution of the problems.

### 3.2.1. Thermal Spray Methods for Applications of Coatings

#### 3.2.1.1. APS

For this project, coating were applied by Air Plasma Spraying (APS) and High Velocity Oxyfuel (HVOF) methods. In APS method, an electric arc is used as the heat source to generate a high-temperature plasma jet by an inner high-velocity gas to apply the coating on the substrate. However, as oxygen enters into the plasma injector from the air, some oxide layers or compounds are typically formed on the coating. APS coating are known for the higher bond strength, higher density and better surface roughness and are less expensive than other spraying methods [8, 54].

Briefly, APS process involves heating the plasma that is fed into the furnace or chamber; (**Figure 3-1**) in order to increase the ionization process. It also expands the plasma gas to create a plasma stream [7]. Therefore, this stream will carry the powdered material to coat the substrate metal. In this method, both the plasma

stream velocity and temperature depend on the generated arc current in the chamber. In order to increase the size of the arc, a high AC current can be used in APS method. This also accelerates expansion of the plasma gas, so that increases the velocity of the plasma stream. The plasma stream temperature can generate up to 1370°C and velocities up to 800 m/s, which is enough for melting a large amount of coating material powders [7].

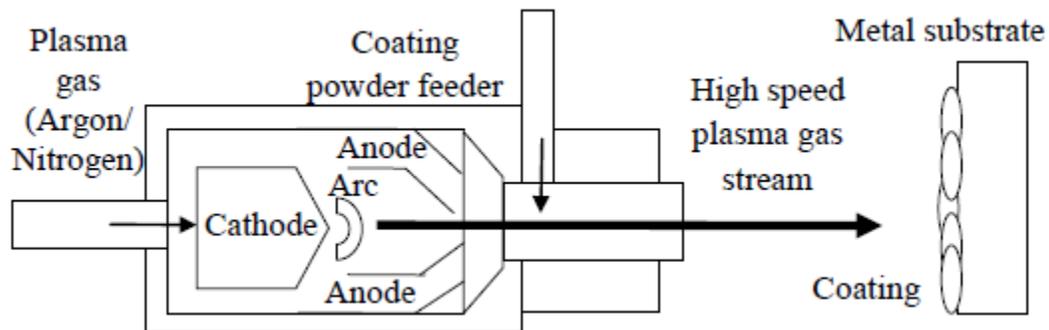


Figure 3-1; APS Spraying Method Apparatus.

The figure was adopted from Siantar [1].

*(The coating powder is sprayed on to the metal substrate through the gun nozzle by the plasma stream which is generated from the passing of electric current of the arc to the gas. The powder is distributed from the powder feeder.)*

For high temperature applications, ceramic coatings are usually applied by thermal barrier coatings (TBC) since they have high melting points. Ceramics behave like an insulating layer to the underlying metal. APS high spraying temperature can provide a better homogeneity of the ceramic particles applied on underlying substrate which has a big effect on improving the coating quality [10]. There are some technical methods to avoid the APS disadvantages by other spraying parameters that could be helpful for the APS method quality. For instance, one method could be the higher speed of the sprayed particle which would increase the

bond strength and affect the porosity of the applied layer [10]. In order to have a better coating quality, the spraying could happen in a vacuum chamber that will remove all the unwanted gaseous elements, furthermore, this method could provide a better control of the residual stress and bond strength and integrity for the coating [10]. Obviously, the lack of oxygen always could eliminate the oxidation problem during the spraying process at an elevated temperature. Although, once a vacuum chamber is used, the size of the sample could make some limitations because the sample has to be fitted with the chamber cell.

### 3.2.1.2. *HVOF*

HVOF (High velocity oxy-fuel spraying) is a usual thermal spraying method that uses Kerosene as fuel gas combustion and mix it with oxygen to create a high velocity impact which is used to apply the coating material onto the substrate [4,7]. This combustion occurs inside a chamber which is connected to a nozzle at the outlet to exit the high velocity gas stream which is carrying the coating powder from the feeder to the purposed substrate (**Figure 3-2**).

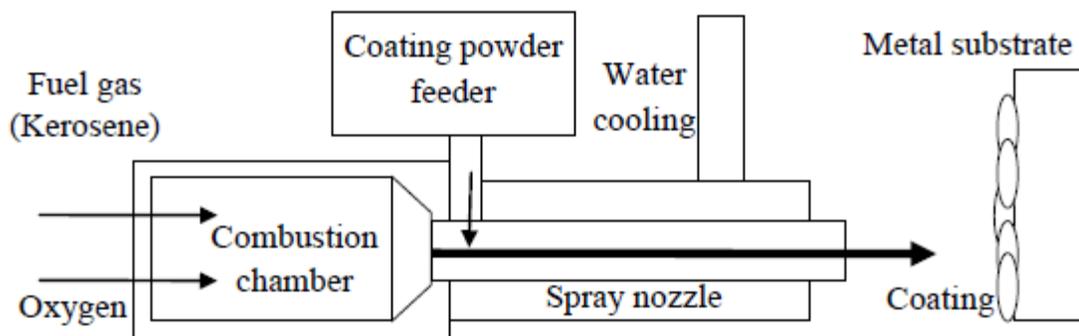


Figure 3-2; The Illustration of HVOF Spraying System.

The figure was adopted from Siantar [1].

The generated coating powder is distributed from the powder feeder into the path of the high velocity gas stream. The coating powder is sprayed onto the metal substrate through the spray nozzle by energy created by the ignition of fuel and oxygen.

An advantage of the HVOF technique is that this method works at a relatively low temperature and creates the high velocity of the sprayed powder particles in comparison with other methods. This technique improves coating quality compared to other coating thermal spray processes [8]. HVOF method is also known as it has a good adhesive strength, reliability, and long lifetime [9].

As shown in **Figures 3-1** and **Figure 3-2**, in both of APS and HVOF methods, spray nozzles could coat materials of various sizes and hold samples by holder during the spraying process. However, this could be a disadvantage as well as an advantage. When the sample geometry has sharp edges, the problem would be appeared. It is difficult to coat the specimen uniformly when it is held by holder. The coating can be applied in several more layers around the edges of the sample to compensate the edge effect although this could not produce a uniform coating layer with appropriate integration on a flat surface. Any poor quality coating could cause crack and damage on the edges and let a corrosive environment penetrate the coating. Then, by penetrating and cracking the coating from the underneath surface it could crack whole of the protected surface. Therefore, the best way to prevent these defects is replacing sharp edges with rounded edge samples.

### 3.3. EIS Background

#### 3.3.1. Background Theory of EIS

The base of the EIS technique is electrical impedance. Since actual electrochemical process is complicated, electrical impedance would be more preferred to use than a resistor element. In the other word, the ohmic electrical resistance ( $R = V/I$ ) is too simple [12, 13]. Impedance analysis ( $Z$ ) is used instead of resistance analysis ( $R$ ), so that capacitive and resistive elements are consisted in the circuit assessment. The total impedance ( $Z = V_{ac}/I_{ac}$ ) explains how well the circuit resists the AC (Alternating Current) current flow that can be related to the features of the coating or film [13, 14].

By applying an AC potential to the electrochemical cell and calculating the current response, the impedance of an EIS test could be estimated. Both the applied AC potential and the calculated current are like a sinusoidal wave (**Figure 3-3**). The current and applied AC voltage response can be determined by using following equations [14]:

$$E(t) = E_0 \sin (\omega t)$$

$$I(t) = I_0 \sin (\omega t + \phi)$$

where,  $I(t)$  and  $E(t)$  are the current response and applied potential, with respect to the time, respectively,  $I_0$  and  $E_0$  are the amplitudes of the applied current and potential responses,  $f$  is the frequency,  $\omega$  is the radial frequency ( $2\pi f$ ), and  $\phi$  is the phase shift or angle between the current wave and potential. Impedance also represents the ability of a system to impede a current flow and can be expressed as:

$$Z = \frac{E}{I} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)}$$

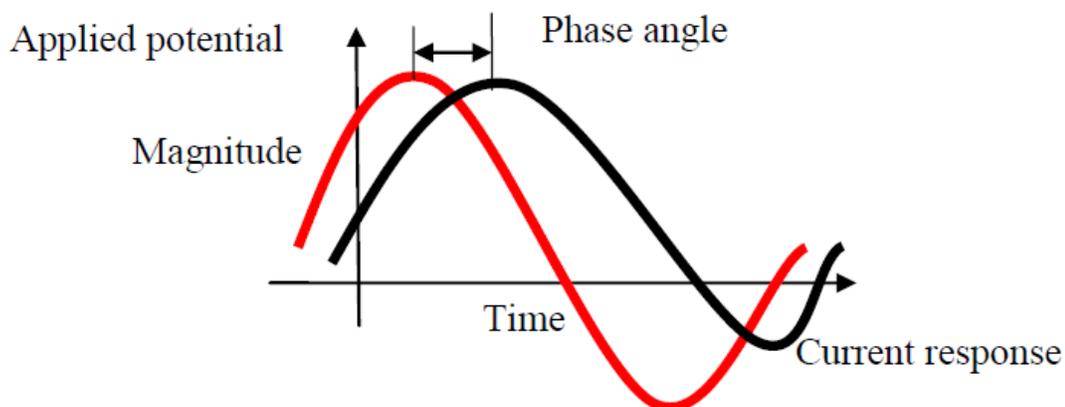


Figure 3-3; Phase Shift Diagram

The current response displayed with the black line and the applied voltage with the red line. The phase angle stands for shift or the lag between the two signals.

The three basic elements are capacitors, inductors, and resistors that used in an electric circuit. Each provides different current responses. The current response will have different phase shifts or angles in its sinusoidal wave based on the characteristics of the element when the potential is applied to an electric circuit with these circuit elements. A resistor is inclined to resist or avoid the electric current flow. The phase shift is  $0^\circ$  when an AC current is passing through a resistor because the current response stays on the same phase as the applied voltage. A resistor is usually related to the conductivity of the electrolyte, the film resistance, or the charge transfer of a corrosion reaction [15]. A capacitor is a circuit element that can keep and include the electron charge or delay a current. We will have a lag of  $-90^\circ$  in the resulting current when a current is passing through a capacitor [15]. A capacitor is regularly related to the double layer capacitance on the border between

the electrolyte and working electrode or the film capacitance of a coating interface [15]. An inductor is a circuit element that advances current and is frequently related to absorption effects within the film [15]. The resulting current will have a phase shift (advance) of 90° when a current is passing through an inductor [15]. The total impedance of the system can be determined with combining the phase angle and the magnitude of the applied potential and current response.

### 3.3.2. Interpretation of EIS Results

Impedance ( $Z$ ) is composed of two components, the magnitude ( $|Z|$ ) and the phase shift ( $\phi$ ), values of which are plotted into a vector plot (**Figure 3-4a**) [14]. A vector graph is a suitable way to represent the applied potential and current response with regard to the  $Z$  magnitude and the phase angle [16]. The imaginary value of the impedance ( $Z''$ ) is plotted versus the real value of the impedance ( $Z'$ ) and  $Z$  can be plotted as well as in a complex plane (**Figure 3-4b**). The complex number demonstration is used hence it can mathematically express the phase angle relationship between electric circuit components [16]. The relationship between the phase angle,  $|Z|$ ,  $Z''$ , and  $Z'$  can be explained as:

$$\phi = \tan^{-1} \frac{Z''}{Z'}$$

$$\boxed{Z^2 = Z'^2 + Z''^2}$$

The  $Z''$  versus  $Z'$  plot is called a Nyquist plot which is a frequency dependent graph of all the AC impedance values concluded [14]. The frequency dependent plot allows the researcher to analyze the data concluded over a frequency range. There are two additional Bode plots, Bode  $|Z|$  and Bode phase angle, which are plotted versus frequency. The number of time constants and the electric circuit elements

required to model or represent the system can be approached, by analysing these two plots.

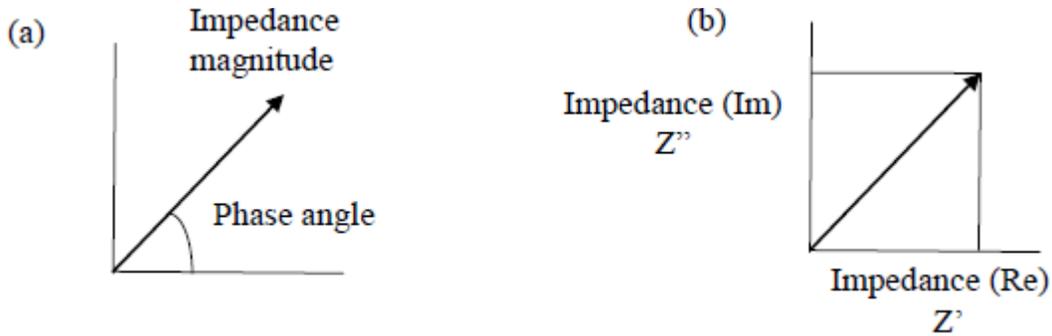


Figure 33-4; Figure (a) is the vector plot of the impedance magnitude and phase angle and (b) is the complex plane plot of  $Z''$  vs  $Z'$ .

Resistors and capacitors are the circuit factors that are regularly used to demonstrate the film condition of an uncovered metal or a coating. The resistor has only one real impedance value and no imaginary impedance value [14]. The resistance value does not modify with the frequency so the Nyquist graph of a resistance is a single point. The resistance in the Bode plot will be plotted as a horizontal line throughout the range of frequency for this experiment, since it is only one constant value. On the other hand, the capacitance in the Nyquist graph has only imaginary impedance values [14]. Absolute capacitance impedance will lie on the  $Z''$  axis of a Nyquist plot and the impedance will reduce as the frequency rises. The capacitance should be plotted as a straight line with a slope equal to -1, in the Bode plot.

## 4. EXPERIMENTAL SECTION

### 4.1. Materials and Supplies

The materials and chemicals used during the experiments are described below;

#### 4.1.1. Gas Used and Sources

Nitrogen (ultra high purity~99.99%, oxygen content less than 3 ppm) gas was used for deaerating the electrolyte during the running of immersion test. Argon (ultra high purity~99.99%, oxygen content less than 3 ppm) gas was used for deaerating the electrolyte before running EIS experiment. Both gases were purchased from Praxair.

#### 4.1.2. Chemicals Used and Sources

CuCl (Cuprous-copper chloride) powder was used to provide an environment with similar conditions that will exist in the proposed CuCl cycle that the coated samples will be exposed to. CuCl (Reagent Plus®, purity,  $\geq 99.0\%$ ), a green-grey powder, was purchased from Fisher Scientific. The CuCl powder was stored in the oven at 80°C for 4 hours prior to immersion test to remove the moisture from the powder (drying purposes).

NaHCO<sub>3</sub> (Sodium Bicarbonate) fine ACS grade powder, purchased from Sigma Aldrich, was used as the scrubber solution. The solution was made by dissolving 390 g sodium bicarbonate in 4.5 L distilled water. The purpose of this solution is to neutralize the gaseous waste of the immersion test apparatus before releasing it to the fume hood for safety and preventing environment issues.

EDTA (Ethylenediamine tetraacetic acid) was used as a cleaning solution to dissolve the residual CuCl left on the sample surface, after the immersion test. EDTA is a

chelating agent purchased from Fisher Scientific. To dissolve the solidified Copper chloride faster from the surface of the sample, the EDTA was dissolved in water at 80°C and the solution stirred at 75 rpm. Each two gram of EDTA was dissolved in one Liter of water in 1.5 L beaker.

NaCl (Sodium Chloride) 99% purity powder was used to make up the electrolyte for the EIS test to evaluate coating before and after immersion test. The concentration that was used was 3.55 w/V%. The 3.55 w/V% was made by dissolving 17.750 ( $\pm$  0.001) g of NaCl in 500 ml distilled water (in volumetric flask). The ACS reagent grade NaCl powder ( $\geq$  99.0%) was purchased from Fisher Scientific.

HCl (Concentrated Hydrochloric acid) was used as a cleaning agent to dissolve the solidified CuCl that remained in the crucible and immersion vessel. The concentrated HCl (Reagent, 32 wt %) was purchased from Fisher Scientific.

KCl (Potassium chloride) was used as a filling solution in the reference electrode. The saturated KCl filling solution was purchased from Princeton Applied Research to refill the AgCl reference electrode.

#### **4.1.3. Coating Materials Used**

All coating materials were purchased and used by Centre for Advanced Coating Technologies (CACT) at University of Toronto (UofT). As a bond coat, Diamalloy 4006 and SHS 9172 were used. YSZ powder was sprayed on the samples as a ceramic coating.

Diamalloy 4006 is a nickel based amorphous alloy (Ni-20Cr-10W-9Mo-4Cu-1C-1B-1Fe) and as-sprayed coating is crystalline.

Super Hard Steel (SHS) 9172 HVOF is an iron based steel alloy which properties special resistance to erosion, corrosion, abrasion, impact and high temperature oxidation. SHS 9172 HVOF coatings feature brilliant resistance to abrasion and a major ability to survive corrosion and high temperature oxidation. SHS 9172 is a glass-forming steel alloy that is generated with high concentrations of transition metals which voluntarily dissolve in the glass structure. Furthermore, the SHS 9172 enormously fine microstructure improves ductility, fatigue resistance and toughness. SHS 9172 is used as top coating.

Yttria Stabilized Zirconia (YSZ) which is used for an insulating top coat because of its high thermal expansion coefficient and low thermal conductivity, which strictly matches the majority of high nickel content alloys [17]. YSZ, known as Metco 143 ( $ZrO_2-18TiO_2-10Y_2O_3$ ) as well.

#### **4.1.4. Metal Samples**

The substrate metal for the coated specimen in this phase of the project was medium carbon steel (1045). This metal was chosen since it is not expensive and it is easy to machine. Furthermore, corrosion deposits are visually easy to distinguish on this material.

#### **4.1.5. Personal Protection Equipment (PPE)**

During the experiment especially during the immersion test which is the high-risk experiment, appropriate personal protective equipment must be worn while handling the equipment and chemicals. The personal protection equipment could be categorized into “room temperature” and “high temperature” protection gear.

#### ***4.1.5.1. Room Temperature Protection Gear***

Room temperature protection equipment was worn during the EIS test and the immersion test. The room temperature protection set include; Latex gloves, laboratory coat, and chemical safety glasses. The operations that require room temperature protection set include; cleaning all of the crucibles and the ITV by using concentrated HCl solution, making the scrubber's solution and handling the cooled equipment after running of the immersion test, and refilling the reference electrode solution (saturated KCl) and making the 3.55 w/V% NaCl during the EIS test. At this temperature, the most dangerous part is chemical solutions or vapor contact with skin; therefore covering body and using fume hood is the best solution to avoid any risk. Except for making the 3.5 w/V% NaCl solution, all the operation was done in the fume hood.

#### ***4.1.5.2. High Temperature Protection Gear***

With regard to the toxic hazard of experiments, the majority of the operations for the immersion test were done inside the fume hood to avoid poisoning. High temperature protection must be worn during the operations that involve a high temperature exposure, such as, working with heater and hot equipment, filling crucibles with CuCl powder, handling materials and equipment during the immersion test, and during the post-immersion cleaning process. The high temperature protection set consists of safety goggles, fiberglass high temperature gloves (from Fisher Scientific), latex gloves, laboratory coat, face shield, and respirator.

The operation stages in which high temperature PPE should be used; first, during the immersion test preparation, the operator requires to fill crucibles with CuCl

powder that was stored in an oven at 80°C. Second, during the handling of any parts of the immersion test apparatus (e.g. the use of handling device) the operating temperature of the apparatus is around 500°C. Third one, the post-immersion cleaning step which includes dissolving the deposited CuCl on the equipment and samples using saturated EDTA solution at 80°C.

## 4.2. Equipment and Apparatus

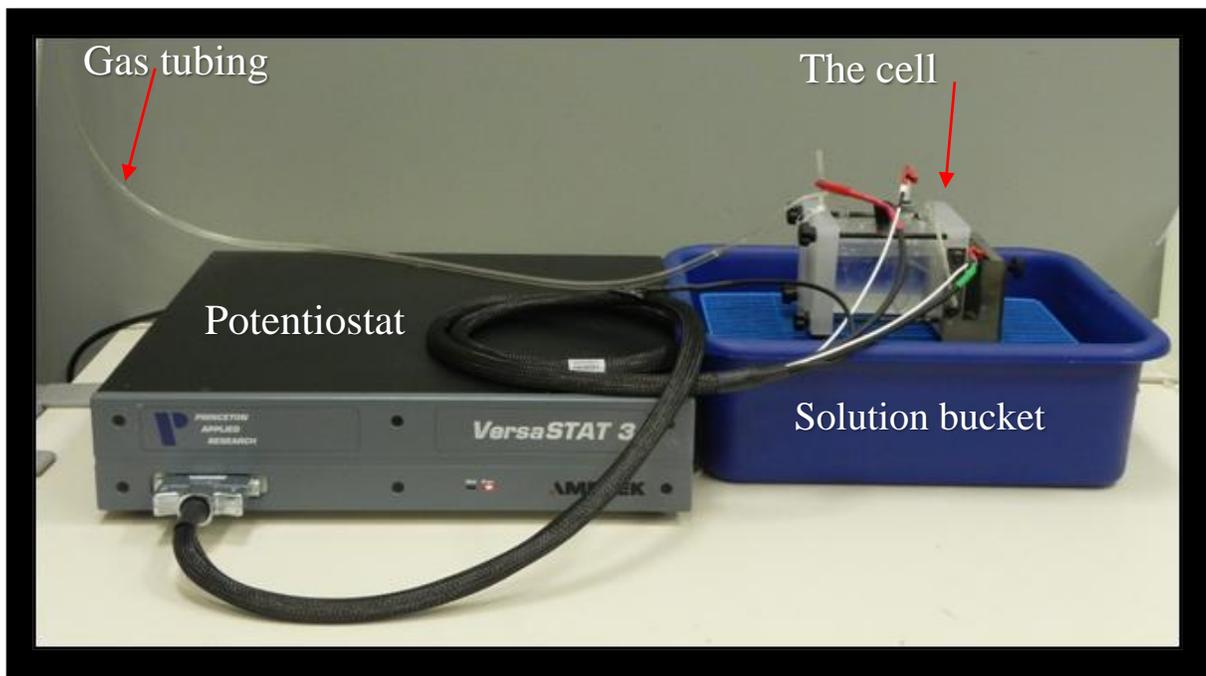
The equipment and apparatus includes the EIS and the immersion test equipment. A potentiostat is used to control the potential during the EIS experiment.

In this section, Siantar's apparatuses are initially described, however some parts were modified based on recent requirements which are represented in **Section 4.3.4**.

### 4.2.1. EIS Test Equipment

#### 4.2.1.1. EIS Potentiostat

The potentiostat was used for EIS testing was the VersaSTAT 3 (Figure 4-1) that is purchased from Princeton Applied Research. The VersaSTAT 3 has a built in FRA (Frequency Response Analyzer) capable of measuring the impedance in the frequency range of 10  $\mu$ Hz to 1 MHz. The wide range of frequency signals which are also generated by the FRA via potentiostat, allowed different phenomena to be observed. The voltage compliance of the VersaSTAT 3 is  $\pm 10$  V, and the current range is 1A to 200 nA. The accuracy of applied potential is  $\pm 0.2\%$  reading,  $\pm 2$  mV. Potentiostat resolution is 16 bits so DAC ("Bias" Digital/Analog Converters) resolution is  $1/2^{16} = 1.526 \times 10^{-5}$ . More detailed specification is given in Appendix 2. Laptop or computer could connect to the potentiostat by USB interface to analyse the EIS results in any type of software.



**Figure 4-1; The Setup of EIS Test Apparatus**

*(The EIS equipment consists of potentiostat (the left side of Figure 4-1) connected to the electrochemical cell by the instrument cables and fixed by alligator clip. The gas tubing used for purging the Argon (as an inert gas) is connected to the inlet tube of the cell, and the solution bucket is to contain the electrolyte spill if we have any leakage.)*

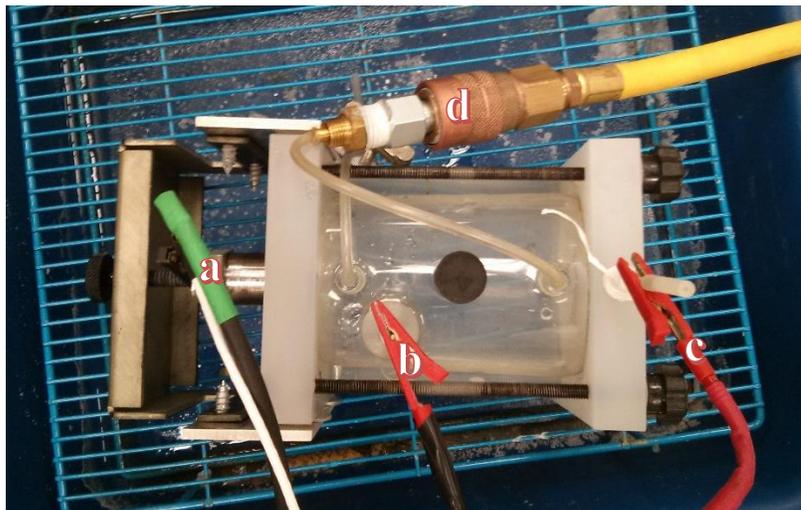
#### **4.2.1.2. EIS Software**

For the EIS experiment controller, VersaStudio 3 from Princeton Applied Research was using. The EIS data generated is analyzed using fitting software packages, Zview 3.1c and ZPlot (Scribner Associate Inc.).

### 4.2.1.3. EIS Test Cell

#### 4.2.1.3.1. EIS Test Cell Description

An electrochemical cell (e-cell) was used for the EIS experiments. The e-cell was a Flat cell K0235 purchased from Princeton Applied Research. For e-cell three standard electrodes used that are a counter (Figure 4-2a), reference (Figure 4-2b), and working (Figure 4-2c) electrodes. The reference electrode is an Ag/AgCl (that is maintained in the saturated KCl solution) standard reference electrode (0.22 V vs SHE) used as a reference point for the potential measurement. All potentials quoted in this report are based on Ag/AgCl (in saturated KCl solution). The working electrode is connected to the sample. The counter electrode (platinum mesh) is needed to ensure that the current can flow through the system and complete the circuit.



**Figure 4-2; The Electrochemical Cell for EIS Tests.**

*(The cell setup is included of (a) working electrode (sample material), (b) counter electrode, (c) reference electrode, and (d) inlet gas for aeration purposes.)*

The cell has an inlet tube (Figure 4-2d) to allow the cell interior to be purged with inert gas, Argon (ultra high purity~99.99%) during the EIS test. The electrolyte used for the EIS tests is 3.5 w/V% NaCl. The cell opening or exposure area of the working electrode is 1 cm<sup>2</sup>. The sample was bullet shape with 2 cm<sup>2</sup> diameter so it is greater than the exposed area allowing the elbowed portion which was completely under the electrolyte exposer. The surface area of the counter electrode was 6 cm<sup>2</sup>. The distance of the working to counter electrode was mentioned 80 cm in manual. The cell could contain up to 250 mL of the electrolyte solution. The luggin well for the reference electrode could contain up to 5 mL electrolyte solution.

#### 4.2.1.3.2. EIS Test Apparatus Assembly

The Flat cell K0235 was designed to work with any flat samples. However, as our samples geometry changed to the bullet shape after first series of experiments (which was flat samples), the E-cell clamp was modified to hold bullet shape samples. The working electrode or sample was regularly suspended while being exposed to electrolyte. The samples which were tested in this project, was improved since they did not have any sharp edges and holes for suspending. Holes are undesirable for maintaining the integrity of the coatings applied to the surface of the metal. Therefore, the Flat cell K0235 was chosen as it allowed the EIS test to be performed without having to be suspended. The cell had an opening (Figure 4-2) at one end for the sample and electrolyte connection. During the EIS test, only round portion of the sample was exposed to the electrolyte. The sample was hold by tightening the designed clamp holder. The reference electrode was placed in the luggin well and the counter electrode was placed at the other end of the cell.

## 4.2.2. Immersion Test Equipment

The corrosion testing apparatus was designed to evaluate the material performance in an environment similar to the proposed Copper Chloride (Cu-Cl) cycle hydrogen production. A practical method to simulate an environment for candidate materials was immersing samples in molten CuCl at an elevated temperature (500°C) for a prolonged period of time (more than 100 hours) to evaluate the effects of exposure to molten CuCl. This section explains the design requirements and material selections for an immersion apparatus. It goes on to describe the design, assembly, and operation of the immersion apparatus. [1]

### 4.2.2.1. Design of Immersion Test Apparatus

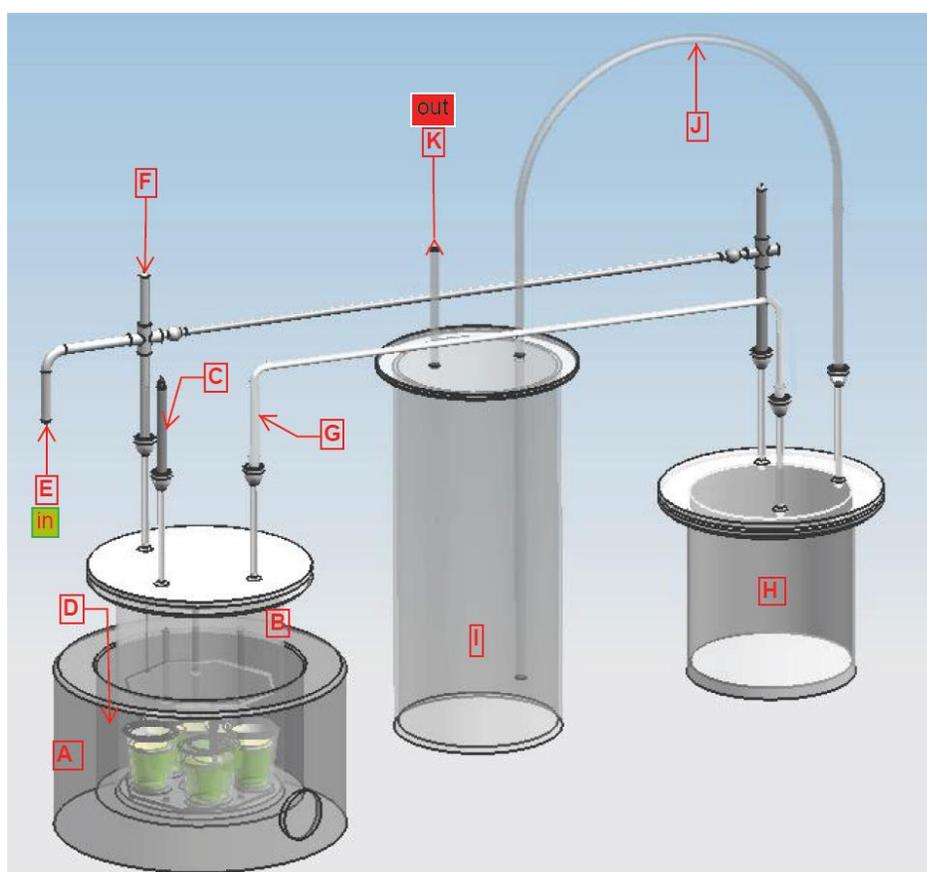
The immersion test system consisted of the Immersion Test Vessel (ITV) (Figure 4-3 B), the Condenser Vessel (Figure 4-3 H), the Scrubber Vessel (Figure 4-3 I), and heating and controlling systems. The heating and controlling systems included a heating mantle (Figure 4-3 A), a temperature controller (Figure 4-3 D), and a thermal cut-off system (Figure 4-3 C).

Each of the three vessels had a different function. The ITV (**B**) was used for corrosion testing of the coated candidates by immersing the specimen in molten CuCl. It was heated directly by the heating mantle (**A**). The condenser (**H**) cooled the hot gas and then the scrubber (**I**) neutralized the gaseous waste before releasing it to the fume hood.

#### 4.2.2.1.1. The Immersion Test Vessel (ITV)

The immersion test vessel design was based on ASTM G31 for immersion testing [37]. The ITV consists of two main parts, the body and the lid that were made of

fused quartz. The ITV lid had three insertion stems which were used for different functions: first stem was used for a K-Type thermocouple (Figure 4-3 C) to monitor the working temperature inside the ITV which was connected to the cut-off system to keep the system safe; another stem was used for exhausting the hot gases through the connecting pipe to the condenser and the scrubber (Figure 4-3 G); and third stem was for deaerating the atmospheric air by injecting inert gas ( $N_2$ ) through it before and during operation. The pressure relief valve and handling device were also connected to the third stem (Figure 4-3 E).



**Figure 4-3; The Immersion Test Apparatus Setup Schematic.**

*(The immersion test apparatus consists of (A) heating mantle , (B) ITV, (C) thermocouple for cut-off system, (D) thermocouple for heating controller, (E) inlet for gas and pressure relief, (F)*

*handling device, (G) joint tubing, (H) condenser, (I) scrubber, (J) tubing for the gas exhaust to the scrubber and (K) scrubber gas outlet tubing.)*

In the ITV, three safety components were made to solve three of main possible hazards during the operation. A thermocouple installed in one of the stems which was connected to the cut-off system to ensure that the test was running at the proper temperature and to shut it off in case the temperature exceeded 550°C. Second stem was for the pressure relief valve which was installed to keep the immersion tests under a safe pressure. A handling device was designed to immerse the sample in molten CuCl and to help in removing the sample during the post-immersion cleaning process by lifting the sample from copper chloride solution crucible. Maintaining and cleaning the sample surface condition from CuCl deposits was necessary to improve the analysis. If the sample was not lifted out from the molten CuCl, before cooling process, it will be stuck in the solidified CuCl after it was cooled. Chemical methods (Strong acids such as concentrated HCl) as well as mechanical methods were not acceptable since they might cause the damage to the sample surface. Once drip drying was completed, the best method to dissolve the remained solidified CuCl was immersing the sample in a saturated chelating agent (like EDTA solution at around 80°C).

For safety, a pressure relief device was installed on the ITV to let hot gas exhaust from the main vessel through the connecting pipes to the condenser and then to the scrubber, to avoid the pressure build-up in the system. The pressure relief valve should be installed to allow the excess pressure to escape and preventing having pressure build-up during immersion test.

#### 4.2.2.1.2. The Condenser

The condenser function was used to cool the exhaust gas of the ITV before exhausting it to the scrubber and then releasing to the environment by fume hood. The condenser consisted of two parts, the lid and the body, which were made of fused quartz. The condenser lid had three insertion stems for: the joint tube which was connecting pipe of exhaust gas from ITV (Figure 4-3 G); the tubing that was connected to the pressure relief system of ITV (Figure 4-3 E) and the connecting pipe of the hot gaseous exhausting to the scrubber (Figure 4-3 J). [1]

#### 4.2.2.1.3. The Scrubber

The scrubber function was neutralizing the exhaust gas before releasing it to the fume hood. The scrubber consisted of two main parts, the lid and the body. The scrubber lid was made of SS 316 and the body was made of quartz glass. The solution inside the scrubber was mixed of water (4.5L) and saturated sodium bicarbonate ( $\text{NaHCO}_3$ ) (390g). Scrubber should be filled with some plastic beads into the solution in order to reduce the size of bubbles formed by exhausting cooled gas of the condenser. [1]

#### 4.2.2.1.4. The Heating System

Based on high temperature that was needed to produce molten  $\text{CuCl}$  in this project, the heating system was installed. This system was consisted of: a heating mantle for heating the ITV; a heater controller in order to control the heating mantle (and a J-type thermocouple to control the heating mantle temperature by a controller); and a thermal cut-off system to prevent excessive heating for safe operation. The thermal cut-off system was installed to prevent increasing the maximum temperature (i.e.

560°C) which might crack the ITV body or the crucibles containing the molten CuCl. This thermal cut-off system was included of a K-type thermocouple (Omega) to monitor and check the inside temperature of ITV. [1]

A heating mantle purchased from Glas-Col could heat up to 650°C, which was more than required temperature of 500°C. The heater had soft fabric fibreglass in the heating interior to minimize any thermal shock and damage to the heated vessel. The heater had a controller with a “J type” thermocouple (1/8” Dia, X 12”long sheath, 72” leads/ subminiature plug) that was located inside the heating mantle to control the working temperature of the heater. The controller which was used for the heating management, had only one feedback (the temperature of the heating mantle) from the thermocouple placed inside the heating mantle. When the temperature inside the mantle reached to the set temperature (e.g., 500°C), the controller stopped continuous heating and maintains the temperature steady. If The ITV outside temperature also reached to the set temperature of thermal cut-off system (e.g., 550°C) the system also would be shut off to prevent any danger.

#### ***4.2.2.2. Assembling the Immersion Test Apparatus***

In order to assemble the immersion system there were four subassemblies (ITV, condenser, scrubber and heating system) that properly connected together. All of these immersion test assemblies should be inside the fume hood. The ITV is connected to condenser with fused quartz connecting pipe and a polyethylene hose. The condenser and scrubber were connected through the polyethylene hose. Details of each part (ITV, condenser, scrubber, and heating system) sub-assemblies are provided in following.

#### 4.2.2.2.1. The ITV Subassembly

The ITV assembly involved putting together parts that included the handling device, ITV vessel, the pressure relief device, the inlet gas hose and connections, and the thermocouples which were attached by joints and clamps.



Figure 4-4; The Handling Device (a) Plate and Pillars; (b) Handling Rod, Handling Plate, Clamp ,and Sample

The handling device consisted of five separate parts; the lifting rod, the plate which was used for hanging the sample, three threaded rod for pillars, and the nuts for the stopper. (**Figure 4-4**)

When the handling device was assembled properly, the plate with the samples which were attached to it, should be carefully placed on the pillars.

The ITV subassembly had three main parts; the ITV body, the gasket, and the lid that was clamped by C-clamps to the body. The ITV lid had three quartz stems that ended with a socket for coupling with the other joints (two quartz-metal joints (thermocouple and pressure relief device) and one quartz-quartz). The metal ball joint had a smaller diameter so it could easily fit into the fused quartz socket. An O-

ring was placed around the top of the ball joint to create a gas-tight seal when the joint was clamped. Teflon tape was also wrapped around the ball joint to ensure about sealing mechanism.

ITV was connected to a thermocouple which had a compression fitting installed to create a complete gas tight seal. The compression fitting was coupled with the metal tube of the ball joint that was clamped with the quartz socket through the first insertion. The second stem used for the connection tube that was connected to the condenser for exhausting the gas. The handling device rod, gas inlet, and the pressure relief device all were arranged together to be coupled and placed through the third stem. To accommodate the three components in the first insertion (Figure 4-3) there were two T-connectors that were connected to each other; these were installed where one input was connected to the nitrogen (inert) gas cylinder, another was connected to a pressure relief device, and the last one was for the handling device rod.

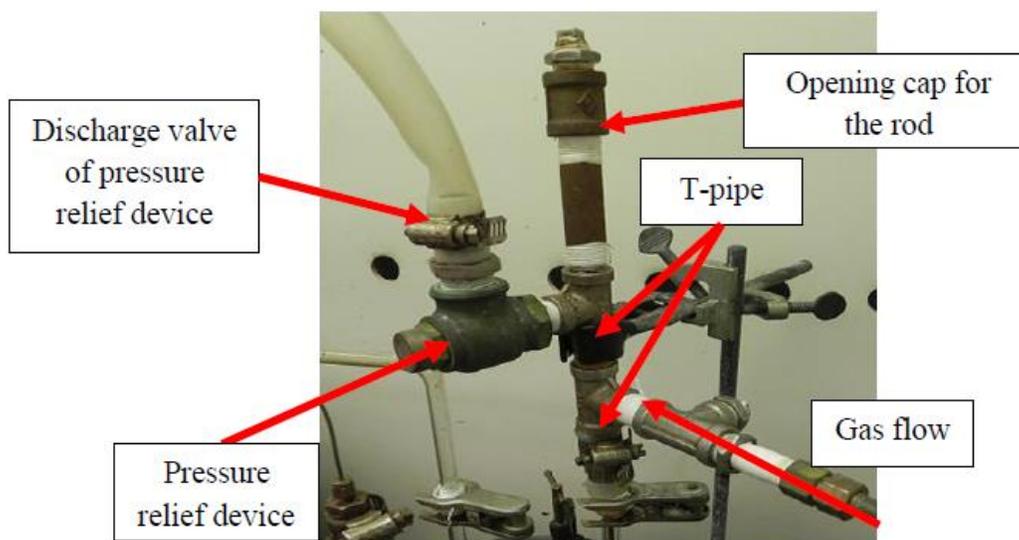


Figure 4-5; The T-Pipe Joint on ITV

The handling rod was used to lift the sample during or after the immersion tests. This rod was attached to the plate of the handling device. There was a cap coupled with the T-connection that had to be opened when the operator needed to lift the samples by using the rod. Figure 4-5 shows the arrangement of the joint of three devices which includes two T-connectors and a hose which was attached to the pressure relief device and then connected to the condenser to discharge the gas from the condenser into the scrubber.

#### 4.2.2.2. The Condenser Subassembly

The condenser had three parts in assembly. The body (Figure 4-3 H), the gasket, and the lid that were clamped together by using C-clamps. The procedure for the condenser assembly was same as the ITV (using ball and socket joints). The condenser lid had three stems which were used for connecting the pipes which were coupled to the hoses from the pressure relief device (Figure 4-3 E), the exhaust gas from the ITV (Figure 4-3 G), and the hose for exhausting the cooled exhaust gas to the scrubber (Figure 4-3 J).

#### 4.2.2.3. The Scrubber Subassembly

The scrubber (Figure 4-3 I) had two separate parts, the lid and body with a gasket in between. The scrubber lid was made of stainless steel which had a long metal tube that was welded in order to allow the exhaust gas to enter the scrubber body below the solution level and be bubbled through the scrubber solution. On the end of this inlet tube, a metallic mesh was also installed to help create smaller bubbles of exhaust gas. Some plastic beads were also placed in the solution above the end of the tubing to further refine the bubble size. The scrubber body, gasket, and lid all were clamped together by using C-clamps.

#### 4.2.2.2.4. Heating System Subassembly

The heating system included five main parts which were; the heating mantle (Figure 4-3 A), the heater controller, the thermal cut-off system, and two thermocouples (one was directly attached to the heater controller and the other one was connected to the thermal cut-off system). The ITV was placed inside the heating mantle which was connected to the heater controller by a thermocouple (this thermocouple was placed inside the heating mantle in order to provide the feedback signal to the controller). The thermal cut-off system was operated by the second thermocouple to limit the maximum operating temperature of the ITV.

#### 4.2.2.2.5. Final Assembly

The assembled immersion test apparatus is shown in the Figure 4-6. The scrubber subassembly was placed in the fume hood first, followed by the scrubber, the condenser, and the heating system subassembly.



**Figure 4-6; The Complete Assembly of the Immersion Test Apparatus**

Placing the CuCl powder in the ITV must be the last step before starting the experiment to reduce the chance of contaminating CuCl powder during the assembly process. Each of the samples was immersed in each individual crucible that contained molten CuCl (this is to eliminate the chance of having cross contamination from another sample during immersion test period.)

#### **4.2.3. Requirements for Designing New Equipment**

A good and safe apparatus is required which remains unaffected at elevated temperature such as 500°C, for long and uninterrupted times that should be performed even without any supervision. The exposure conditions also must be assumed as another limiting factor of the design process so the immersion test should not be stopped or failed due to equipment breakdown. The apparatus must be properly designed in order to prevent any hazard to the operator, the laboratory, or

nearby people. ASTM G31-72 standard [37] is used for a typical laboratory setup for immersion testing (including exposure conditions) as a main guideline for this designed apparatus.

During any kind of experiment (such as the immersion test), the operating requirements and restrictions are associated. The operating requirements are all the conditions that are needed to be met to ensure an immersion test could achieve the whole project objectives and restrictions are intended to make sure the experiment can be conducted safely. Both operating requirements and restrictions could have some intersections during design process. Therefore, an apparatus had to be designed in a way that both factors could be met.

For a safe and reliable operation, the immersion test apparatus requirements are listed below;

1. The test vessel had to contain the molten CuCl test solution. The materials of vessel or any other container that were in contact with the molten CuCl should be chemically inert, and they should not react with the molten CuCl and CuCl salt, and should have an operating temperature higher than 550°C.
2. The immersion test vessel needed to be sealed completely in order to prevent any leakage and other gaseous impurities from entering the vessel. Main parts that required more attentions during the designing were the joints between the tubing and pipe connection, and the joint between lid and body of the vessel. Eliminating unwanted gas presence was one of the most important factors. Unwanted gas could interfere with the reaction during the sample exposure, which could affect the corrosion reaction. For instance, if oxygen was inside the vessel due to a leak, it could react with the surface of the

material being tested. The reaction between oxygen and a metallic surface at high temperature could create an oxide layer as well as from water vapour. The surface condition of these samples would be different compared to the condition of the sample that do not have oxygen in the system during the test.

3. The lid of the immersion vessel must have several insertions for outlet and inlet pipes, a thermocouple, and connecting pipes. The pipes includes; an inert gas inlet and outlet. In order to have a uniform condition to compare samples with fewer errors for all of the experiments, it was important to maintain the same flow and atmospheric condition. In all tests, another factor that should be kept consistent was temperature (550°C). A thermocouple was added to measure and monitor the temperature inside the immersion vessel.
4. After the immersion test, the sample condition should be preserved so that further corrosion should not occur during storage and before ex-situ surface analysis. When the exposure period is reached, the apparatus is cooled down before removing the tested material out. When the vessel is cooled down, the molten CuCl will be solidified and remained on the surface of tested material. The solid CuCl could not be removed mechanically since it could damage the tested material surface. Opening the immersion vessel to remove the sample from the molten CuCl during the experiment running could cause several serious safety problems. It would be dangerous for the operator to handle or breathe waste vapours or CuCl vapour during the immersion test (especially at 500°C). Contacting with room temperature by opening the lid during experiment could have accelerated the cooling process. A sudden temperature drop could cause a thermal shock and change the material properties and it might cause creating some cracks on the coating. To address

these problems, the apparatus should have a mechanism that allows the operator to elevate the sample while the CuCl is still molten and let the liquid to drip-off into the crucible and not stick to the surface of the material. The mechanism should help the operator to remove the sample outside the immersion vessel without opening the ITV lid or any interfere with the progressing experiment.

5. Samples should be immersed in the molten CuCl, only at round end. In order to have a better coating evaluation by EIS test which is explained on section 4.5.4., the other side (flat end) of sample was in contact with the clamps to hold the sample in ITV.
6. The heating system should have the ability to heat the outer side of the vessel to more than 500°C, so it could compensate for the thermal gradients and heat lost during the heating process and maintain the inner temperature at 500°C. The immersion vessel should have an insulation system in order to minimize heat loss. A heating controller was also used to control and monitor the inside temperature of immersion vessel.

Generally all the design requirements were intended to ensure that the test could achieve the project objectives and could be performed according to the desired conditions with as few as possible mistakes or technical and logical problems, in a safe manner without creating any hazards. Design restrictions are included:

1. The experiment vessels required a material that can withstand 550°C and thermal shocks during the heating or cooling process. Any cracks in the molten CuCl container (vessel or crucibles) and immersion vessel could

cause the molten chemical or the waste gases escaped to the fume hood and laboratory.

2. With regard to operate the system without supervision for long time at an elevated temperature (around 500°C); the heating system should have an electrical safety device that would ensure the heater runs in a safe manner. The heating system was used to heat the immersion vessel continuously for a prolong period of time (e.g. 100 h). Hence, if any heating malfunction occurred, the apparatus should not being overheated and cracked the vessel, which can cause a disaster for personnel of lab and the environment.
3. The inert gas used in the system could cause over-pressure. The system has a pressure relief device. The pressure could develop in an unexpected situation, such as clog in one of the pipes or joints, and pressurize the immersion system. It is important to have the pressure relief, in order to bleed the purged gas through a relief valve before a high pressure build-up.
4. The condenser was used in the system to cool the exhaust gases. This prevented hot gases waste to be directly purged into the water-based scrubber. The condenser prevented that the hot gas to be fed into water and raise its temperature and produce steam in to the system.
5. The immersion test should be run inside a fume hood to release the waste gases of the system into the hood. However, a scrubber was also designed to neutralize most of the system hazardous gases waste and all chemicals transported by the purge gas.

It should be emphasised that safety is the first priority. Neglecting safety will harm the operator, laboratory personnel and environment.

#### *4.2.3.1. New Sample Design*

Based on Siantar's results [1], sharp edges were probably the most susceptible to corrosion because they are difficult to coat uniformly by thermal spray application methods (APS and HVOF). Thus, these edges are more prone to crack, and corrosion. Bulky round surface samples can generally be more uniformly coated and hence should be less prone to damage.



**Figure 4-7; New designed Samples with Round Edges**

Therefore, new samples were designed to avoid the possible problem pointed out by Siantar's experiment. Round edges of the samples were supposed to be more resistant to corrosion while the samples were immersed inside the molten CuCl. Newly designed clamps for the new sample had to be designed in order to hold the sample. These samples also needed new clamps for the EIS test, the immersion test, and coating application. As this area had to be tightened by the clamp, it would have been out of the immersed area but under clamp stress. One of the most important

requirements was that the samples' surfaces should be coated uniformly and those should also have enough area to uniformly distribute the clamp pressure.

In order to satisfy these requirements, some different choices were available. Full spherical samples, which mean the samples would be completely rounded, were the first option. However, this choice was not satisfactory due to the difficulty of holding the samples' clamps during coating applications, EIS, and immersion tests. Hemispherical samples were the second choice. They would be designed with a complete flat surface on one side and also a round end. Due to limitations in holding the samples during the coating application and in the immersion test, this option was not acceptable. Another option was bullet shape samples with a complete flat surface on one side and a round tip on the other end of a cylindrical part. This option was more acceptable since it covers all requirements. As a bulky round surface was designed, this sample could be more uniformly coated and withstand the immersion test. The flat side was supposed to be more resistant under clamp pressure and stress. Another advantage of the new designed sample was the cylindrical part. This part (because of its height) was designed to hold the sample by a clamp and immersing the sample inside a crucible.

Based on the requirements and the considered options, the best design to work on was the bullet shape sample. This sample could be held by a clamp during coating applications, EIS tests, and immersion tests by new designed mechanism and equipment. A treated hole was drilled on the flat side of the sample. This hole was designed to hold the sample by a stainless steel wire and a clamp during the immersion test and hold also by coating application machine holder.

## 4.2.3.2 Vessel Design Improvement

### 4.2.3.2.1 The Lid Design

Two new lids were designed in order to manage the experiment risks and any consequences. One lid was made from fused quartz similar to the lid of the previous project that Siantar's used. Another lid was made of stainless steel to have a metallic lid in case high pressure test performed. Two lids were also ordered from each type to have an alternative in case of any accident. The main difference between the new designed lid and previous one was that the new one had three stems and one of the stems was shorter than the other two. It could cause the exact adjustment happen between the lid stem and handling rod equipment. The old designed lid was without third stem (it was a hole instead of the steam) and it caused leakage during the immersion test.

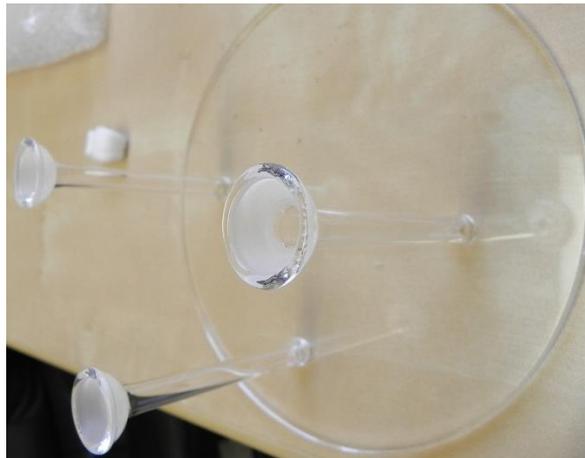


Figure 4-8; New Designed Lid

### 4.2.3.2.2 The Lifting Mechanism

The lifting mechanism was changed through when the mechanism changed. New handling mechanism, was easy to access, and clamps were easy to attach. Clamps

were stainless steel clips and they were easy to hang on the crucibles. New mechanism was made of stainless steel. (**Figure 4-4**)

The main differences of the newly designed mechanism was that the handling rod was fixed and welded on the stainless steel plate, and three hole were made on the plate to let the wire hold the plate. This mechanism helped the operator to manage and access the samples easier.

#### **4.2.3.3 New Clamps**

After choosing new geometry for the samples, normally new clamps should be chosen and designed for holding them in further tests.

##### **4.2.3.3.1 New Clamp for Immersion Test**

In order to hang on the samples in the immersion test vessel, typical stainless steel clips were used as the clamp. The stainless steel clamps has the resistance at high temperature on top of the molten CuCl container. The sample and clamp were connected as on **Figure 4-4** represented.



**Figure 4-9; New Immersion Test Clamp**

#### 4.2.3.3.2 New Clamp for EIS Test

In order to run the EIS test, new clamps were designed to hold the bullet shape sample. This clamp was designed by changing the height of the previous clamp.



Figure 4-10; New EIS Clamp

#### 4.2.3.4 New Heating System Design

A new heating mechanism was designed for running the immersion tests. This mechanism included a new cutting-off system and a new designed heater. Most steps of this experiment which happen during the immersion test, were inside the heating mantle. The heating system should be safe and also run in a desired condition. In order to run the experiment in a safe condition, a controller was designed. If it is necessary to guarantee that the controller works in a reliable condition, a thermal cutting-off mechanism should be designed. This was explained in detail in section 4.2.2.2.4.

A new heater was designed which consisted of a simple pot, two heating tapes and thermal insulation. In order to design a heater, it is important to cover all the requirements. The main requirements for the new designed heater were that heat should be distributed uniformly to the ITV. An appropriate size should be chosen to

have easy access to the vessel, and easy lifting and handling of the vessel because typical heating mantels cannot burden the ITV weight, which causes some damage to the tapes and elements. The heating mantle should resist temperature fluctuation. It should be capable of sustaining in wide range of temperature from room temperature up to 600°C. Appropriately isolating the mechanism and also keeping the heating tapes and heating elements undamaged could help improve the heating mantle. Two heating tapes could maintain the desired temperature. These two could cover the input current which is required for controllers.

#### **4.2.3.5 *Sealing Mechanism***

##### **4.2.3.5.1 *New Sealing Mechanism***

To design a proper sealing mechanism, all the vessels, pipes and connections should be separately evaluated. The sealing of each of the vessels and pipes should be connected to a flow meter to measure inlet pressure and compare it with an outlet flow meter in order to ensure that the condition of the body, lid and pipes is good. Outlet pressure drop should be negligible. Tubes, hoses, connection pipes and vessels are tested and could be guaranteed by this mechanism.

The most difficult part of the evaluating sealing was when the ITV and connection pipes were assembled together. The handling system and inert gas connections should be connected to a stem of the ITV, and the thermocouple should be sealed and connected to the other stem. The last ITV stem was connected to an outlet connection pipe (which was connected to the condenser). The lid connection to the ITV body which was sealed by a Hypalon gasket and two layers of high temperature sealant, is a different feature of this new method. A number of configurations were examined before identifying this setup. Inlet pressure should not increase, since pressure build up could cause some holes and penetration in the sealant causing

problems. Once the inert gas has entered the handling pipe and ITV cell, leakage should be checked by using soapy water. The outlet stem should also be checked by the flow meter to ensure that the pressure drops in the comparison of inlet stream. When sealed perfectly, condenser and scrubber should also be checked by the flow meter. It is proved experimentally, once the bubbles inside the scrubber are observable, there is no leakage through the system. This phenomenon is due to the bubble production occurred from pressure build-up inside the vessel. This happens only if there is no leakage from the vessel.

For this method, one layer sealant should be applied to the lid edges then the gasket would be placed on top. Another layer of sealant should be applied but all of the sealing steps should be re-applied for each following test. It should be noted, that sealing starts to work at around 200°C after 30 minutes.

#### 4.2.3.5.2 Testing the Apparatus Sealing Mechanism

Once initial results were obtained, there were some points that indicated corrosion was more severe than what it had to be. Modifying the apparatus and operating mechanism was the first step to improve the mechanism. Although, equipment and devices assembly in following to the sealing mechanism were the main possibilities that caused more severe corrosion on the new samples.

The results of this part were categorised in two section; first was analysis of set-up and operations before the immersion test in order to ensure about mechanism, assembly and operation development if it was performed correctly, second was analysing the mechanism performance during the immersion test at elevated temperature.

#### *4.2.3.5.2.1 Evaluation of the Sealing Mechanism without Materials*

A new method was used to evaluate the sealing mechanism. Initially, the apparatus was analysed part by part. The entire system was then analysed by an oxidization test.

##### *Functional Tests*

In order to have a safe and reliable mechanism and process, some functional tests should be run prior to the main experiments. The main purpose of these tests is to check the sealing system and objectives which are explained in the section 4.3.4.

##### *Pressure Tests*

As it has been already noted, the pressure relief valve should be installed for the inert gas inlet pipe to prevent pressure build-up through the system and vessels. In order to test the pressure relief valve separately, it is possible to connect the pipe directly to the inert gas hose and the pressure flow meter to check if the pressure relief valve performs when it exceeds set pressure (10 psi) is passed how works. It shows if clog or blockage happen through the valve.

##### *Temperature Tests*

Based on the temperature test of system, two thermocouples are set through the test; one is inside the heating mantel and out of ITV. This thermocouple sets on 550°C. The other one is inside the ITV and sets on 500°C.

### *Overall System Tests*

Once all the system equipment works separately at room temperature, sealing of the system should be checked at high temperature while nitrogen enters the system at a specific flow rate. Two methods were designed to test the system: A “blank test”, which was a dry test without testing any samples and an “oxidation test”, which was performed to evaluate the sealing mechanism by calculating the weight loss of the uncoated samples (mild steel specimen).

### *Blank Tests*

The “Blank test” was designed to evaluate effectiveness of the sealing mechanism during the operation in prevailing leakage of oxygen through the gasket, sealant, and Teflon tapes, which were resistant to high temperature. This test was performed in the absence of any experimental metal in the ITV.

This test should be repeated at different temperatures and for different durations of time. High temperature sealants and gaskets were the main parts that must be evaluated for performance. As it was not possible to connect the flow meter at high temperature to the vessel outlet, sealing performance should be evaluated if any bubbles released in the scrubber as well as soapy water bubbles could be created when they were sprayed on the connections and gaskets.

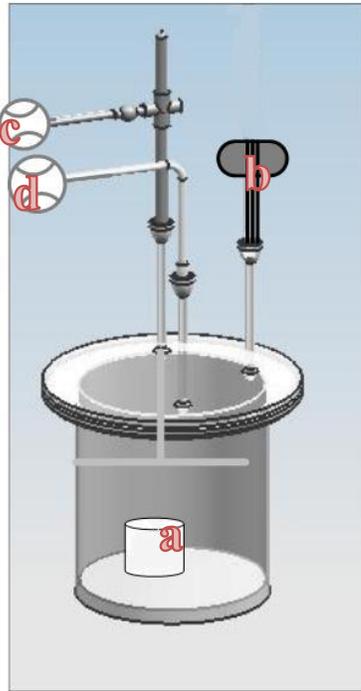


Figure 4-11; Schematic of the Blank Test

(“a” is the empty ITV, “b” is a sealed stem, “c” is nitrogen inlet stem with flow meter, and “d” is nitrogen outlet flow meter.)

#### 4.2.3.5.2.2 Evaluation of the Sealing Mechanism by monitoring the oxidation of materials (Oxidization tests)

The “oxidization” of a specimen was monitored to qualitatively determine the leakage of oxygen in the ITV. This indicated the performance of the sealing mechanism at high temperature. The “blank test” of the sealed vessel demonstrated that the nitrogen did not leak out from the vessel. There was still no guarantee that oxygen or water did not enter to the system from the atmosphere. An oxidization could occur due to the oxygen or water vapor leakage to the vessel.

In order to perform the “oxidization test”, initial weight of the sample should be measured and compared with final weight. Samples should be prepared in advance for the tests. All samples should be rinsed by distilled water and then polished with a sandpaper. The polishing should be done from the smaller grit numbers to the bigger and finally should be polished by the highest grit sandpaper (i.e. 600 grit) to clean the samples’ surface from steel oxidization. The polishing should occur in two perpendicular ways. Before running the experiments, initial weight should be measured three times by a close analytical balance. For each attempt the balance should be recalibrated. Tests should be run at different periods of time to ensure the sealing mechanism of the system. After running the tests, the final weight should be measured (three times with the initial measurement). After this procedure, samples should be kept in an isolated environment for more tests, in case of future use. All weights were measured by balance and error was  $\pm 0.0005$ . (**Figure 5-2**)

### **4.3. Immersion Test Apparatus Fault Analysis**

It was important to conduct a comprehensive fault analysis for all of the tests to ensure that the experiment could be performed in a safe manner without any undue risk to the laboratory and personnel working in it. The fault analysis was intended to predict all of the problems that might occur during an immersion experiment. There were several concerns that could cause accidents during an immersion test.

#### **4.3.1. Set up Hazard**

During the experiment set up, some risks could occur such as breakage of pipes and vessels. To prevent any danger during the set up, wearing Personal Protective Equipment (PPE or safety cloths, gloves and glasses) was suggested. The most fragile parts of the immersion test equipment were the vessel lids and joint pipe. The

ITV lid could be broken by the handling rod as these parts rub against each other. As the condenser lid could not be tightened to the condenser body (lack of space to tighten clamps), there were some possible risks when we had overpressure in the vessels. The joint pipe was fragile and could break due to overpressure in the system. However, this was controlled by the pressure relief valve.

#### **4.3.2. Pressure Hazard**

During a test, if there was an impediment between the joints, the flow of nitrogen gas might create pressure build-up inside the vessel. The tygon tubing connecting the tank with the immersion equipment might burst or become disconnected from the system.

The system required a pressure relief device. An inert gas like nitrogen flowed into the immersion vessel and pressure could develop in an unexpected situation, such as clog in one of the pipes or joints, and pressurize the immersion vessel. It was important to choose the right rating for pressure relief so that the release valve could bleed the purged gas before a high pressure build-up could compromise system safety. The threshold pressure of tygon tubing was rated around 16 psig, so when the pressure build-up exceeded the threshold amount, the condenser lid could be blown off first. In this case the tubing will burst since all the clamps holding the joints, other lids and the vessel have higher pressure ratings. A pressure relief device with a rating of 10 psig is installed in the system to relieve the overpressure and prevent an accident such as this.

However, there were some other possibilities of a pressure build-up within the system due to a clog/jam in one of the tubes or in the joint. This would create a

problem if one of the clamps holding the joint cannot withstand the pressure build-up. The clamp might be blown away and hit the operator working near the apparatus.

Clamps could not be fixed very well to the condenser body which does not have any designed lip as a space to tighten the condenser lid to the body, so this could be the only potential risk of the Immersion test experiment. However, it was better to seal it with low temperature glue.

#### **4.3.3. Temperature Hazard**

Once the system thermocouple was not working or it was unplugged, there was no temperature feedback from the heater to the controller. The controller would detect that the thermocouple was at a room temperature and would keep heating the vessel. The hazards caused by this failure and solutions to the problem include:

- ✓ The temperature inside the vessel would increase beyond a safe value and then chlorine gas could be generated which could cause pose toxicity hazard; A temperature controller with an automatic relay system has been designed. Once the temperature inside the ITV was higher than 650°C (The maximum temperature of the heater), the power source to the heating mantle was cut-off and the heater would shut off. When the thermocouple was not sending feedback, the controller had a warning light indicating that there was no signal being received. If this warning light occurs when the operator was present then the operator could check the thermocouple to make sure it works properly. If the operator was absent, a thermo cut-off was automatically used.
- ✓ The vessel could be cracked due to excessive heating; this problem should not be an issue because the vessel was made of quartz which was rated for 1000-1200°C operating temperature and the maximum temperature of the

heater was 650°C. The material of the vessel would be able to withstand during this condition.

✓ If the heater was overheating (it means controller did not work correctly), the bottom part of the vessel would be cracked and the crucible containing the CuCl would be cracked, then toxicity and temperature hazards would be created;

The probability of these three failures occurring simultaneously was small. However, if it occurred, the CuCl would be contained within the heating mantle. The over-temperature hazard would not be a danger to the operator because the heating mantle body could withstand temperatures >1000°C. The heating mantle interior was made of fiberglass cloth which had operating temperature >1000°C. [46]

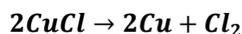
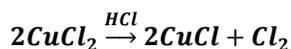
It was concluded that the temperature hazard was minimized because the system had a temperature controller with relay system that would cut-off the electrical power to the system, thereby preventing heater run-away or overheating to higher than the safe operating temperature.

#### **4.3.4. Toxicity Hazard-Chlorine Gas**

If there was a leak in the system, it was important that the any chlorine gas present in the system was within the safe limit established by the safety regulation for the building.

*“If the decomposition reaction is conducted in open atmosphere, a significant amount of chlorine would be released when above 380°C.”[61]* However, any generated chlorine gas would be minimal because cuprous chloride is stable, even

at elevated temperature. The chlorine gas that could be generated as a result of elevating the temperature can be estimated by the calculations presented in Appendix 1 [59] the Gibbs free energy change ( $\Delta G$ ) and investigating the equilibrium concentration of  $Cl_2$  for the reaction



$\Delta G^\circ$  at  $700^\circ C$  is greater than 0 for CuCl reaction which means the reaction is not spontaneous and will not proceed unless external energy is applied. The worst condition assumed is for a run-away heater at around  $700^\circ C$ , which is  $50^\circ C$  higher than the maximum heater temperature,  $650^\circ C$ . From the estimation, the equilibrium concentration of  $Cl_2$  for this reaction would be  $7.77 \times 10^{-27}$ . This concentration is so much lower than the limit of exposure given in the Chlorine MSDS sheet (10 ppm) [60] before eye-damage or irreversible health effect occurs.

The worst possible scenario that might occur is if there is a blockage in the immersion test apparatus, creating pressure build-up, and eventually a leak develops in the system. As a result, the exhaust gas escapes. At the same time, if the fume hood is not working, the exhaust gas covers up to the laboratory and the lab personnel were exposed. From the experiment estimation of the generated amount chlorine, it would be safe for the operator and other personnel working in the laboratory even if the scenario given above occurs. The possibility of a toxic hazard due to chlorine gas generation was deemed unlikely to occur.

#### 4.3.5. Explosion Hazard

As there were no explosive materials being used in this experiment, the risk of an explosion during the test was minimal.

The fume hood containing the system had a window which was kept closed during the experiment. However, an operator might work in the fume hood and may be exposed to the threat of a projectile (vessels and equipment could treat as a projectile). This problem was solved by placing a plexi-glass shield to protect the body of the operator while working near the system and by requiring the use of a face shield to protect the face of the operator.

Even though molten CuCl was expelled during the experiment, as the test was under the fume hood and also operator was worn with high-temperature PPE, molten CuCl risk could be negligible.

#### 4.3.6. Heating System Hazard

The heating system has an electrical safety device that will ensure the heater runs in a safe method with least supervision. The heating system used to heat the immersion vessel will run continuously to maintain the desired operating temperature for the length of the experiment. Since the immersion test run continuously for long time (i.e. 100 h), there were times that the apparatus was unattended. If a heating fault occurred, the apparatus could have been overheated and so that could crack the vessel. Regarding maximum temperature of the heater (650°C), as it was mentioned, if the cut-off system does not properly work, still we could be sure about safety of all other possible hazards. Cracking of the ITV and crucibles which are containing

the molten CuCl could allow molten CuCl and its other products escape in environment and create serious hazards.

#### **4.3.7. Handling Device Hazard**

One of the main risks that could occur during the immersion test was related to handling rod which was contacted at elevated temperature (around 500°C). Wearing high-temperature gloves was necessary to prevent skin burning. As there was a little space to hold the rod and as the lid holes did not have enough space to turn or lift the rod freely (it could break the lid as well) this troubleshooting seems important.

#### **4.4. Experiment Methodology**

This plan was provided for evaluating coatings performance at 500°C. Evaluation of sample is possible by visual examinations, weight change study, EIS tests, and SEM/EDX tests. Immersion tests are carried out using the methods reported in ASTM procedure ASTM-G-31-72, Standard Practice for Laboratory Immersion Corrosion Testing for Metals (ASTM 1998). Meanwhile, sealing mechanism should be evaluated by examining oxidation of a bare metal. It could help to evaluate whether the oxygen leaks to the system or residual oxygen causes diffusion on the samples in the vessel.

Each sample should be visually examined before and after the immersion test for CuCl attack (localized-uniformly) and a visual corrosion assessment should be reported. The samples are then photographed in the clean condition by a high-resolution camera and then by digital optical microscope. The visual comparison before and after the test could demonstrate some types of corrosion. Color change could help to distinguish the deposited materials. The sample could be evaluated

also by shape change if it is corroded severely or remaining deposits on the sample surface could demonstrate the quantity-form of corrosion. Some pits were identified by the visual examination or sometimes the pits were deep enough to characterize their depth by optical means.

Weight change measurements were carried out on mild steel blanks (bare specimens which was polished by sandpaper 600grit size) to determine weight change between samples before and after the immersion test from exposure to the solution and evaluating oxygen leakage to the system. ( $30\text{mm} \times 20\text{mm} \times 1\text{mm}$ ). The specimens were then cleaned and evaluated in accordance with ASTM-G-1-90 and ASTM-G-31-72, and the average uniform penetration rate could be calculated by weight change. This bare metal used as a sacrifice metal. Weight change could indicate the sealing mechanism and whether the oxygen enters the vessel or diffusion happens through the ITV.

SEM/EDS can be used to evaluate the characteristics of a surface material. SEM has some applications to provide a topographic image of the specimen surface. Using SEM and EDS, the surface condition before and after immersion testing can be evaluated.

Following steps should be performed in sequence on all samples. Initially, raw sample should be prepared for coating and future tests (Sec 4.4.1.). Some samples would be coated and some other should be kept uncoated (bare samples).

On coated samples, after cleaning the surface (which is represented in section 4.4.3.1) pre-SEM/EDX tests (sec 4.4.6) should be run. Then visual examination (sec 4.4.4) should be applied on them as well. At this moment, the immersion test (sec 4.4.3.2) should be run on samples. Meanwhile, another sample would be evaluated

at atmospheric condition. Once the immersion test was done, post-visual examinations (sec 4.4.4 and 4.4.5) and post SEM/EDX analysis (sec 4.4.6) had to be applied on coated samples, respectively.

At the same time with main experiment, a side experiment should be run to evaluate oxygen leakage. It should be evaluated based on weight change analysis (sec 4.4.5).

#### **4.4.1. Initial Raw Sample Preparation**

The initial preparation should be done before applying any coating onto the specimen. The initial preparation were two steps; sectioning and preparing (polish or sand blast). Raw material of the specimen are in the form of a metal rod that was cut into a bullet shape sample. The cut samples then were prepared before spraying the coating on the surface. The sectioning was done at UOIT and polishing was done at the University of Toronto.

#### **4.4.2. Sample Preparation**

Samples were rinsed with distilled water three times to ensure that the surface of the sample was cleaned and wet. The EIS cell with the 3.55 w/V% NaCl electrolyte was purged with argon for 5 minutes to remove oxygen before filling the cell with solution. The reference electrode which was maintained in saturated KCl should be placed in the luggin well. The sample was clamped by tightening the clamp holder. The O-ring was placed over the round tip of the sample and the sample aligned with the opening on the cell.

The counter electrode was attached to the other end of the cell. Once all the electrodes were attached to the cell was connected to the potentiostat by clipping the suitable alligator clip.

### 4.4.3. Immersion Test

#### 4.4.3.1. Preparation

##### 4.4.3.1.1. Washing the Vessel before Immersion Test

The ITV, vessels, and crucibles were cleaned before each immersion test to ensure that the cleaned vessel condition was maintained for every immersion test experiment. The CuCl deposit remaining on the ITV, vessels, and crucible were dissolved by using concentrated HCl. After this step the ITV, vessels and crucible were rinsed at least two times with distilled and tap water.

##### 4.4.3.1.2. Preparation before Immersion Test

The CuCl powder was placed in all the crucibles. The position of each crucible was marked and aligned for each specific sample. Therefore, when each sample was immersed it would not tip the crucible. The height of the CuCl powder should be approximately measured in order to have the value when it was melted. This is valuable because the molten CuCl should not have any contact with the sample holder. Since the volume of the CuCl powder will change once it is melted, the initial volume of the CuCl to be used was measured based on the mass of the CuCl powder and the density of molten CuCl. The density of molten CuCl is  $3.69\text{g/mL}$ . An observable mark was drawn on the outer layer of the crucible wall was one effective method to indicate how much CuCl powder was required.

On each of the holder pillars, two nuts were placed to act as stoppers in order to hang the specimen. Before each test, the nuts' and washers' placement were adjusted depending on the sample, the clamps, and the height of the molten CuCl estimated in the crucible.

#### *4.4.3.2. Immersion Experiment*

Once the preparation steps were done, the immersion test assembly should be prepared as well. The immersion test system had to be purged by inert gas (nitrogen gas) at 60 to 70ml/min for 30 minutes before running the main experiment. In order to check the sealing mechanism during the deaeration process, soapy water was sprayed over all connections and joints. Once the deaeration is over, the heating mantle should be at  $510 \pm 5^\circ\text{C}$ . The additional  $10^\circ\text{C}$  was based on ASTM and Fused quartz properties manual to compensate for thermal losses and gradient across the fused quartz immersion vessel body. Thermal losses could be controlled by wrapping insulating fiberglass cloth around the ITV.

When the temperature inside the ITV controlled at  $500.0 \pm 1.1^\circ\text{C}$  for 30-45 minutes (it could be recognised by the thermal cut-off thermocouple), the inert gas flow was decreased to around 20ml/min and maintained throughout the test. After 15 to 20 minutes of the last step, the CuCl powder had to be melted in the crucible. The samples were immersed by releasing the handling rod. The handling rod was safe to access by opening the cap of the top insertion of the connections to the immersion vessel. Once the samples were immersed in the ITV, the system should be closed and sealed by tightening the cap. The thermal cut-off system was set to  $550.0 \pm 1.1^\circ\text{C}$ .

The immersion test period which was chosen for this tests is around 5, 48, and 100 hours that was manageable during the week with initial experiment preparations and post steps and it was also appropriate if the results were confirmed to extend the test period. These periods were chosen to evaluate the corrosion rate and the period of corrosion development through the coatings.

Finally, once the immersion period was passed, the samples should be lifted from the crucible and left outside the crucible for 4 hours to allow the remaining CuCl on the surface to drip off while the inside temperature of ITV was still maintained at upper than CuCl melting point. The cooling process should be controlled by gradually reducing the temperature of the ITV. After 2 hours that the ITV was at room temperature, the lid of the ITV could be opened and the specimens were retrieved.

#### **4.4.4. Test Operation Method**

##### ***4.4.4.1. The Handling Device***

The handling device was installed, generally, in order to ensure sample contact with CuCl only during the immersion test operation at high temperature. The handling device functions were included; preventing sample contact with the CuCl during the pre-heating period; ensuring that holder did not have any contact with the molten CuCl; and allowing any remaining CuCl to drip off the sample at the end of the immersion period.

The samples were placed on a stainless steel plate which was controlled by a handling rod for lifting and turning the samples inside the immersion test vessel before and after running the test. The clamps were tightening on the top flat part of the sample, so round part of the sample was immersing in molten CuCl. All of the samples should be hung out of the CuCl during pre-heating. Once the CuCl reached to the molten state, the plate should be rotated on the pillars and allowed to slide down until the plate reached the stopper nuts to make samples immersing in the molten CuCl.

After the desired immersion period, the rod was lifted again and the top plate was placed on top of the three pillars. The sample hung inside the vessel, top of the crucibles, to drip off most of liquefied CuCl which remained on it.

#### *4.4.4.2. Pressure Relief Device*

A 10-psig pressure relief device (Figure 4-5) was installed for the immersion test. During the inert gas injection into the system, if the system pressure exceeded, the pressure relief valve would discharge the gas to reduce the pressure. This discharged gas would flow to the condenser through the hose that is attached to the discharge valve of the pressure relief. So, the discharged gas would remain in the immersion test apparatus and vent through the scrubber before releasing it to the fume hood.

#### *4.4.4.3. Thermal Cut-off System*

The heater controller mechanism was used in case the controller (Figure 4.6) did not receive any feedback signal from its own thermocouple during the immersion test. The controller will assume that the set temperature has not been achieved and will continue to heat the vessel until it reaches the maximum temperature (650°C).

Therefore, the thermal cut-off system was on-call. It means, if the thermal cut-off system received any feedback signal which indicated the system was achieved to the set temperature (this temperature (550°C) was set higher than the heater controller set temperature (500°C)) from the thermocouple which was used to monitor the ITV temperature of the heating mantel, the system (heating mantel and heater controller) that were supplied by thermal cut-off power supplier bar would be immediately shut-off. It would happen by a relay which would be switched off, cutting the system power, and turning the heating mantle off. When the inside temperature fell below

the cut-off temperature, the relay would be reset the condition again and this loop would continue, unremitting. The circuit diagram of the thermal cut-off system showed that this relay circuit was dependent on the feedback from the thermocouple. The thermal cut-off system would ensure that the immersion test could be run safely even during overnight without supervision.

#### ***4.4.4.4. Post Experiment Cleaning***

After the test, once the specimens were lifted from the ITV, there was usually some deposit CuCl remaining on the surface. The remaining deposit of CuCl on the surface should be removed to make the study on the surface of the sample possible. The solidified remaining CuCl was dissolved using saturated EDTA at around 80°C. All steps of the cleaning process was occurred on a heating plate and using a magnetic stirrer to accelerate the dissolution of the solidified CuCl. The saturated EDTA solution is colorless, therefore the solution color could be used to indicate if there was any solidified CuCl on the sample. Once the solution turned to a dark green-blue, the sample was removed, and the cleaning process was repeated by new solution.

After the cleaning process, the specimen were rinsed with distilled water and then drying them in the oven at 80°C for 20 minutes. After the rinsing and drying, the samples were placed in the insulated container.

#### **4.4.5. Visual Examination**

After each immersion test, it is considerable that the first evaluation is by visual examination. Any change in shape of the samples could be an indication to study. Delamination of coatings or major cracks are not good sign for coating resistance,

however delamination or cracks could be shallow and corrosion could be stopped before reaching to the underneath or bond layer. Pitting sometimes are also obvious during the visual examination.

Color change should be considered as an important evidence to study on samples. Green color is the sign of deposited copper on samples that was cleaned by EDTA, if it is on the coating it could be a good sign that coating resists in molten CuCl. Colorful surface is also considerable. This could be happened because of the coating material reactions with the environment materials either on the coating surface and CuCl or the base metal and CuCl and it needs further study. Red color could be the sign of corrosion on steel coatings or base metal (mild steel).

Optical microscope also could be appropriate equipment to determine the susceptible points in advance for SEM/EDX tests. All points had been chosen at this step could be marked and later that points can be evaluated by SEM/EDX. In this order, Model (KEYENCE VHX-1000) digital optical microscope was used. After the sample insertion under the microscope lens, microscope should manually adjusted gradually. It should be noted that optical point should be focused on the desired point of the sample. Once it was adjusted correctly, digital images had to be taken and save to a memory.

#### **4.4.6. Weight Change Analysis**

The “oxidation test” is an important experiment to evaluate and ensure that sealing mechanism performance at high temperature. After sealing the vessel and checking the leakage points by soapy water there was still no guarantee that oxidation did not occur in the system. The oxidation could happen by oxygen or water vapor entrance to the vessel.

#### ***4.4.6.1. Sample Treatment before Immersion***

According to the results of the “oxidation test”; initial weight of the bare specimen should be measured and compared with the final weight. Samples should be prepared in advance for the tests. Therefore initially, all samples should be rinsed three times by distilled water and then polished with a sandpaper. The polishing should be done from the coarsest to the finest sandpaper and finally should be polished with the softest sandpaper (i.e. 600 grit) to clean the samples’ surface from steel oxidation and eliminate the annoying film and coarse surface. The polishing should occur in two perpendicular ways. The specimen was held on a fix and flat table while it should be polished using sandpaper in one direction. Once, polishing lines got appeared on the specimen surface, the specimen should be rotated 90° and polished further.

#### ***4.4.6.2. Weight Change Analysis***

In advance, initial weight should be measured three times by a closed analytical balance. For each attempt the balance should be recalibrated and each attempt to contact the sample should occur with new plastic gloves. Tests should be run at different periods of time to ensure that sealing mechanism of the system. After running the tests, the final weight should be measured (three times). After this procedure samples should be kept in an isolated bag for more tests, in case of future use. All weights were measured by balance and error was  $\pm 0.0005$ .

It should be noted, the bare specimen was evaluated exactly after the immersion test. Once the immersion test is done and cell temperature drops to the room temperature, the bare specimen should be moved to the close analytical balance by new plastic

gloves. The specimen weight should be measured three times. After the measurement, specimens should be maintained in isolated bags.

One of the most effective methods to analyse the results of the mechanism is measuring the rate of weight change. Study on weight change could help to have a comprehensive analysis on the sealing mechanism.

#### **4.4.7. EIS and SEM/EDX**

##### ***4.4.7.1. Sample Preparation before SEM/EDX***

After the immersion test, samples had to be prepared for examination by SEM and EDX. The main preparation steps for SEM and EDX include: Sectioning, polishing, and mounting.

#### **Cutting and Polishing**

An automatic slow speed saw (Brilliant 221) was used to cut the specimen to obtain a cross-sectional sample. For cutting the coated sample, the lowest feed rate (0.1 mm/minute) was selected to minimize damage to the coating during the cutting process. Once they sectioned, the cross-sectional sample was placed in a 60 mm diameter plastic mold with the cross-section surface facing upward. An epoxy hardener was mixed with epoxy resin in a 1:5 ratio and then poured into the mold. The epoxy should be kept to solidify, usually taking 5 to 7 hours at room temperature 25°C or one hour at 80°C. Once, the epoxy mixture solidified, the sample was extracted from the mold.

The cross-sectional sample embedded in the epoxy mixture was polished to create a complete smooth surface before characterization. Different grit size sandpapers were usually used, starting from the coarsest (average 100 grit size) to the finest

(average 600 grit size). The coarsest paper was used to remove the major roughness from the surface. Water had to be used as a coolant while polishing the sample by wet sandpaper to get finer surface. In automatic machines, the sample was held in place by hand on the rotating sandpaper disk. Once, polishing lines appeared on the sample surface, the sample was rotated 90° and polished.

#### ***4.4.7.2. SEM and EDX Preparation***

The cross-sectional part of sample was mounted on a holder before inserting it to the microscope vacuum chamber. As the holder had a larger diameter than the sample, it was taped and glued to keep it and ensure that it would not fall off the holder while inside the vacuum chamber. A carbon tape should also be attached on the mounted sample to conduct the electrons on the sample (especially on the ceramic coatings which are non-conductive).

#### ***4.4.7.3. SEM and EDX Experiment***

The researcher could use different settings for micrographs of the instruments that have a wide range of adjustable variables and parameters. One of the considerable parameters is the accelerating voltage to modify the image resolution and quality. The best accelerating voltage for the materials examined was 15kV which provides an appropriate resolution and also allows enough time to acquire images of the non-conducting parts of the specimen. This accelerating voltage caused decrease in the charge build-up, even on the ceramic coated sample. The acceptable quality of SEM images was at 300-600X magnification.

The distance of the gun to the sample has effects on the image resolution. The higher resolution of the image if the specimen get closer to the electron gun and detectors.

Furthermore, the working distance is also essential to minimize losing signals of X-ray, secondary, and back scattered electron. The best effective way to adjust sample distance is using the holder patterns which are on the instruments. The shortest working distance was desired to accomplish a better quality microscopic image. Once the working distance was increased, the electron charges on the surface of the sample would be increased and the images would not be generated clear. The chosen optimal working distances were around 10mm and 15mm. Test operation with the selected working distances there was no room left between the electron gun, the detectors, and the holder for the sample to be moved, due to the size of sample. It was so easier to locate a carbon tape during SEM examination, as the tape has a tendency to keep a charge build-up on it. The tape was placed at a certain distance from the desired spot which was supposed to evaluate, hence the SEM/EDX examination process would be easier. When the spot was found, the EDX spectra and SEM image of that spot were recorded. The SEM image and EDX spectra were displayed on the monitor and meanwhile, image files could be saved on the memory.

[1]

## 5. RESULTS AND DISCUSSION

Based on earlier results, this project was started with modifying the sample geometry. Another critical part of this project was improving the system performance and ensuring that the experiments worked properly and in a safe manner. It was also decided that the focus of this study would be limited to the coatings at this stage without considering the substrate alloys. Therefore, all the coatings were applied on the substrate which was made from medium carbon steel.

### 5.1. New Geometry Performance

One of Edwin Siantar's conclusions was that the coatings delaminated due to improper coating application at the edges of the specimen, due to the nature of the thermal spray process.



Figure 5-1; (a) New Designed Samples and (b) Old Designed Samples

Therefore, a bullet shaped geometry (**Figure 5-1, a**) was chosen for the current project. Since this geometry was without the sharp edges, it allowed uniform deposition of the coatings on one of the specimen. This geometry should enable survival of the specimen when it is immersed in CuCl. Furthermore, new design provided an easy access to the immersed area cross-sections for characterization of the immersion results by using the SEM/EDX techniques.

## 5.2. Sealing Mechanism

An effective method to analyse the performance of the sealing mechanism which is explained in **Section 4.2.3.5**. is measuring the corrosion rate. A study of weight change of the specimen on exposure, which is indicative of corrosion rate, could help in evaluating the effectiveness of the sealing mechanism.

### 5.2.1. Pre-Oxidization Tests

In order to evaluate the vessel sealing mechanism before running main immersion test on coated samples, “Pre-oxidization tests” were performed. These tests were performed by suspending an uncoated specimen in the ITV and heating the apparatus to 500°C for different periods of time. The test was performed under the normal test conditions, without molten CuCl. The test schematic is shown in **Figure 5-2**.

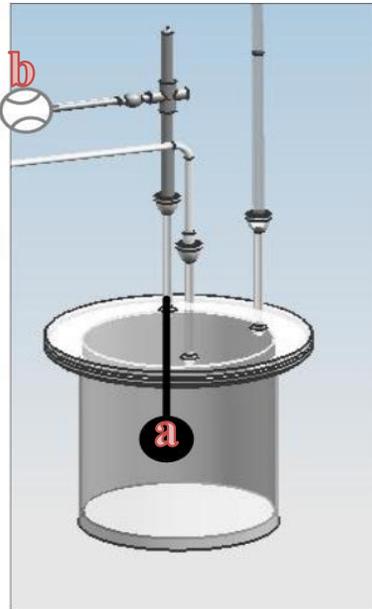


Figure 5-2; Schematic of Pre-Oxidation Test

(“a”, is the uncoated sample suspended at 500 °C, and “b” is the nitrogen pressure at the inlet entrance.)

Results of the pre-oxidization tests are shown in **Table 5-1**;

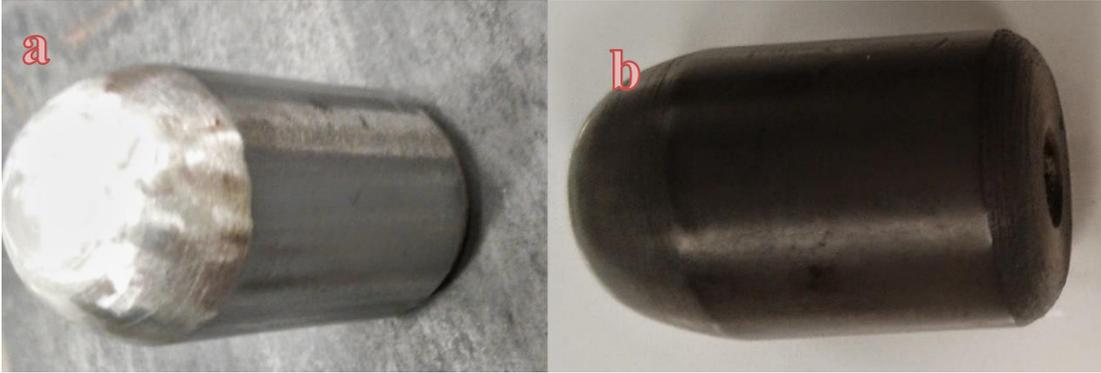
Table 5-1 ; weight change rate table of the pre-oxidization test

name	Period (hour)	Initial w (g)	Final w (g)	(Δ)Weight change (g)	Area (cm <sup>2</sup> )	Weight change/area (mg/cm <sup>2</sup> )
Blank sample 1	5	64.1235	64.1236	0.0001	21.9911	0.0045
Blank sample 2	48	65.1919	65.1921	0.0002	21.9911	0.0091
Blank sample 3	100	63.6851	63.6857	0.0006	23.1000	0.0260

The weight loss (in mg) over area (in cm<sup>2</sup>) of the specimen was calculated and is shown in the **Table 5-1**. The bullet shaped specimens have cylindrical part (this part

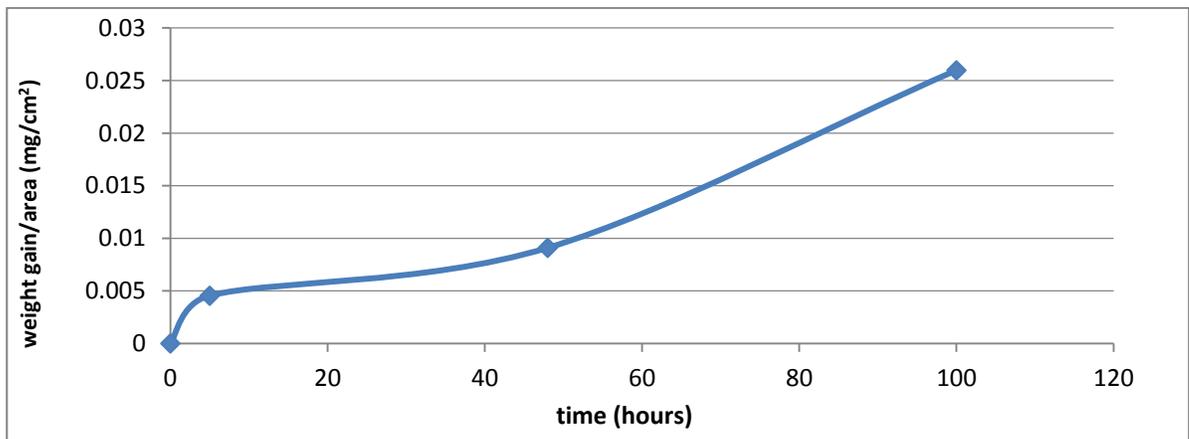
approximately has 1 cm diameter and 2 cm height) and an end which is a hemisphere (with approximately 1cm diameter).

**Figure 5-3** shows the specimen before and after the pre-oxidation test.



**Figure 5-3; Samples (a) Before and (b) After 100 Hours Pre-Oxidation Test**

**Figure 5-4** shows that, the corrosion rate did not increase or decrease monotonically with time. However, the regression and the corrosion rate demonstrated no significant fluctuation over time, therefore this behaviour could be anticipated for prolonged periods of time.



**Figure 5-4; Regression Plot of Pre-Oxidation Corrosion Rate**

The weight change, as shown in **Figure 5-4**, can indicate two possibilities;

- Weight change would steadily increase for long periods of time. This will indicate that oxygen continuously enters the apparatus during the experiment, or
- Weight change initially increases due to residual oxygen in the ITV. Once residual oxygen is consumed, weight change should stop and corrosion rate approaches to zero.

If the presence of oxygen is detected, it could be due to the reasons described earlier. In order to distinguish the two possibilities described above, a method was developed. In this method, a piece of uncoated metal should be used as a “sacrificial metal” to react with oxygen that enters the vessel during the immersion test or react with the residual oxygen which was trapped inside the immersion tests vessel. In case of the second possibility, since a fixed amount of oxygen reacts with more metal surfaces in the same period of time, weight increase would stop once all the residual oxygen is consumed and this would indicate that the sealing mechanism worked properly.

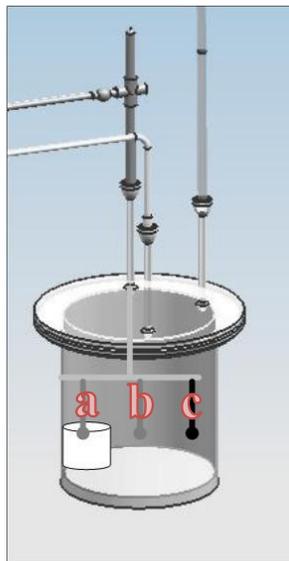
Furthermore, based on Uhlig’s handbook [46] and Revie [54], all corrosion rates which are less than 0.15 mm/y, are acceptable rate for the most critical applications.

The regression method demonstrated that the results were acceptable and could be used to predict the trend for longer periods.

### **5.2.2. Oxidization Test during the Immersion Test**

Once the sealing mechanism passed the pre-oxidation tests, new series of actual immersion tests were performed. This series of immersion test was performed in the

new sealing mechanism which is explained in **Section 4.2.3.5**. During new series of immersion tests, an additional “sacrificial metal” (‘c’ in **Figure 5-5**) was used to evaluate and monitor the sealing mechanism as explained previously in **Section 4.2.3.5.2.2**. The sacrificial metal has more affinity for oxygen compared to the coated samples being tested. Therefore, any oxygen present in the vessel is likely to corrode the “sacrificial metal” instead of reacting with the coatings being evaluated.



**Figure 5-5; Schematic of the Oxidization Test during the Immersion Test.**

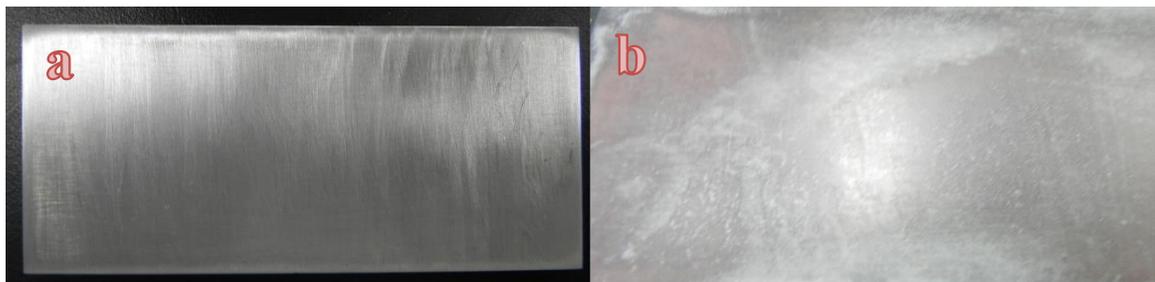
*(“a” is the coated specimen being evaluated in molten CuCl crucible , “b” is the coated specimen which is suspended in the ITV, and “c” is the suspended sacrificial metal.)*

All results were recorded based on ASTM procedures in detail in **Table 5-2**.

**Table 5-2; weight change rate table of the oxidization test**

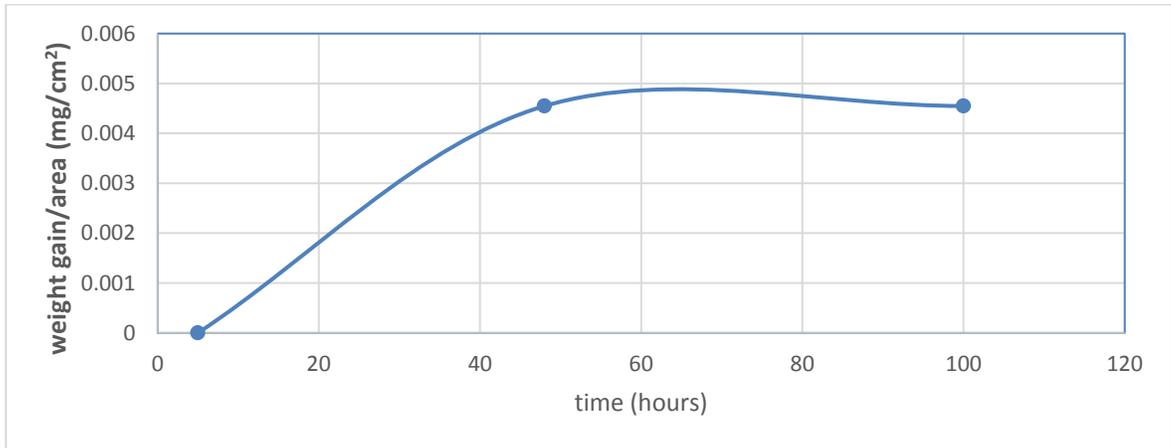
name	Period (hour)	Initial w (g)	Final w (g)	( $\Delta$ )Weight change (g)	Area ( $cm^2$ )	Weight change/area ( $mg/cm^2$ )
Blank sample 3	5	29.6889	29.6889	0	12.9991	0
Blank sample 4	48	27.588	27.5881	0.0001	12.9991	0.0077
Blank sample 5	100	29.3225	29.3226	0.0001	12.9991	0.0077

The “sacrificial metal” will also be helpful in determining if the oxidization occurred only due to the residual oxygen inside the vessel, or due to leakage in the sealing mechanism. If “sacrificial metal” weight increases, it would indicate that there was leakage in the ITV seals. If the oxidization rate or weight gain stopped after a while, this might indicate that the initial oxidization was based on residual oxygen inside the vessel, and there is no leakage in the system. **Figure 5-6** shows the conditions of the “sacrificial metal” before and after the test.



**Figure 5-6; Sacrificial Metal (a) Before and (b) After the Immersion Test for 48 Hours**

**Figure 5-7**, was plotted based on recorded weight changes of the sacrificial metal during the immersion tests for different periods could prove that the sealing mechanism worked properly. The weight change rate stopped after 50 hour experiment, demonstrating that the oxidization occurred from the initial stored amount of oxygen left in the vessel when the test was initiated.



**Figure 5-7; Regression Plot of Post-Oxidization Corrosion Rate**

### 5.3. Immersion Test Examination

There were six combinations of the samples which were evaluated; bare metal which was used for oxidation tests, metal coated with Diamalloy 4006 or SHS 9172 as a metallic coating, metal coated with YSZ as a ceramic coating, metal coated with YSZ and Diamalloy or SHS 9172.



Figure 5-8; Schematic Cross-Sections of Coatings on the Specimen which were Evaluated

( “a” is uncoated base metal only, “b” is metal coated with ceramic coating, “c” and “d” are metal coated with metallic coating, and “c” and “f” are metals which are coated with metallic and then ceramic coatings)

A list of all samples that were evaluated and tested during the immersion test, are provided bellow, in **Table 5-3**.

Table 5-3; The Samples List

Coating #	Sample name	Abbreviation
0	Bare (uncoated) medium carbon steel - 1045	Mild
1	Medium carbon steel (1045) coated with YSZ coating	YSZ
2	Medium carbon steel (1045) coated with Diamalloy 4006 and YSZ coatings	Dia+YSZ
3	Medium carbon steel (1045) coated with SHS 9172 coating	SHS
4	Medium carbon steel (1045) coated with Diamalloy 4006 coating	Dia
5	Medium carbon steel (1045) coated with SHS 9172 and YSZ coatings	SHS+YSZ

### 5.3.1. Immersion Tests Results

#### 5.3.1.1. Evaluation of Coating # 1 (YSZ):

First test was run for 5 hours on coating # 1 (as mentioned in **Table 5-3**). This sample was coated with YSZ coating on the mild steel without the bond coating.

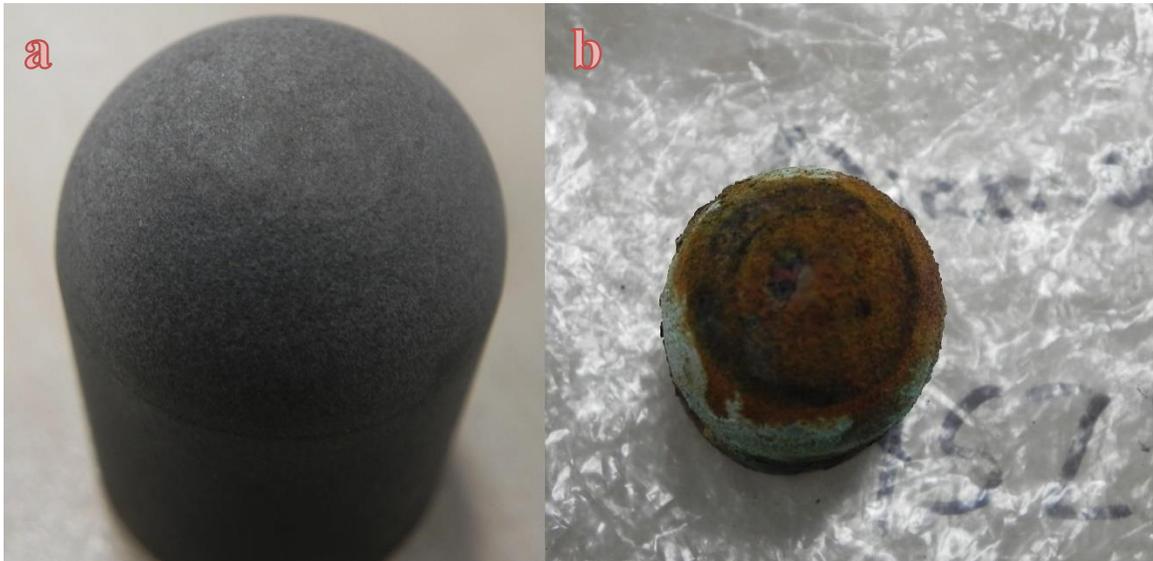


Figure 5-9; Picture of Sample with Coating #1, (a) before, and (b) after Post-Immersion Cleaning

**Figure 5-9** indicates YSZ corroded after 5 hours of immersion test. The SEM micrograph (**Figure 5-10**) shows only a thin layer of coating remained on the base metal. This coating corroded severely. This could be due to the fact that the coating did not have enough thickness to resist the molten CuCl attack. The other possible reason could be the lack of integrity between ceramic coating and the base metal, leading to faster degradation than usual.

After immersion test for 5 hours in CuCl and post-immersion cleaning, the specimen displayed green color which is copper deposits. This color became prominent once the sample was rinsed and cleaned with saturated EDTA. (**Figure 5-9**)

Furthermore, copper deposits could also be seen by EDX test (**Figure 5-10**). However, a thin layer of YSZ on the base metal and a layer of copper (chloride) deposits were also stuck on the base metal. It is shown by the compositions list from EDX results. Large amount of copper indicates severe corrosion occurred and copper diffused through the coating.

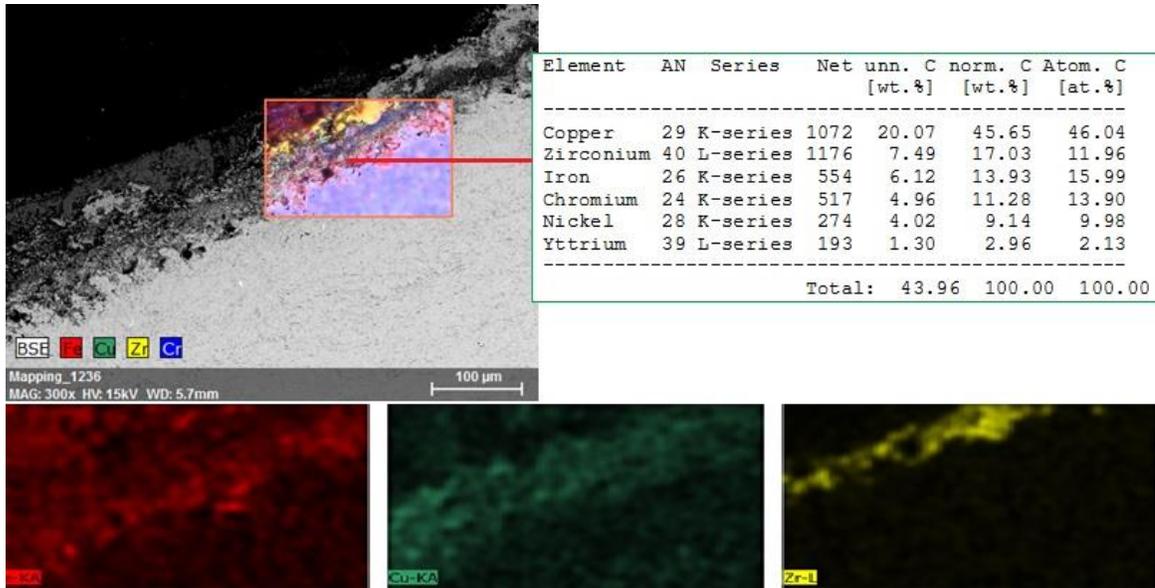


Figure 5-10; SEM/EDX of Sample with Coating #1 for 5 hours test

### 5.3.1.2. Evaluation of Coating # 2 (Diamalloy 4006 + YSZ):

Second test was performed on coating # 2 (as mentioned in **Table 5-3**). This sample was tested for 48 hours. This combination seemed more resistant in the molten CuCl solution. (**Figure 5-11**)

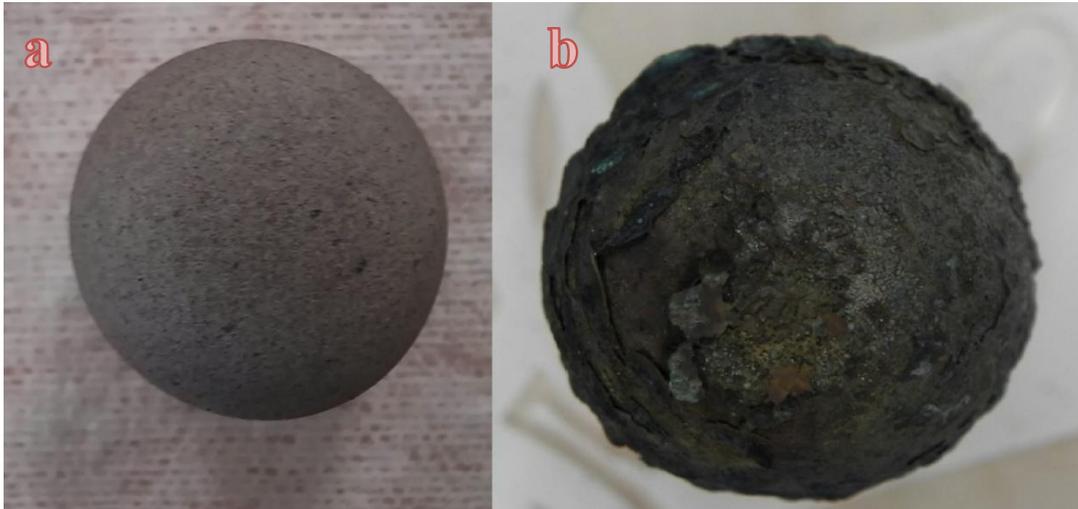


Figure 5-11; Picture of Coating # 2 (a) before and (b) after 48 h Immersion test

After the 48 hours test, the YSZ layer of coating was seen to have delaminated in some regions, as shown in **Figure 5-11**. In addition, SEM and EDX test was carried out to evaluate the depth and severity of the corrosion.

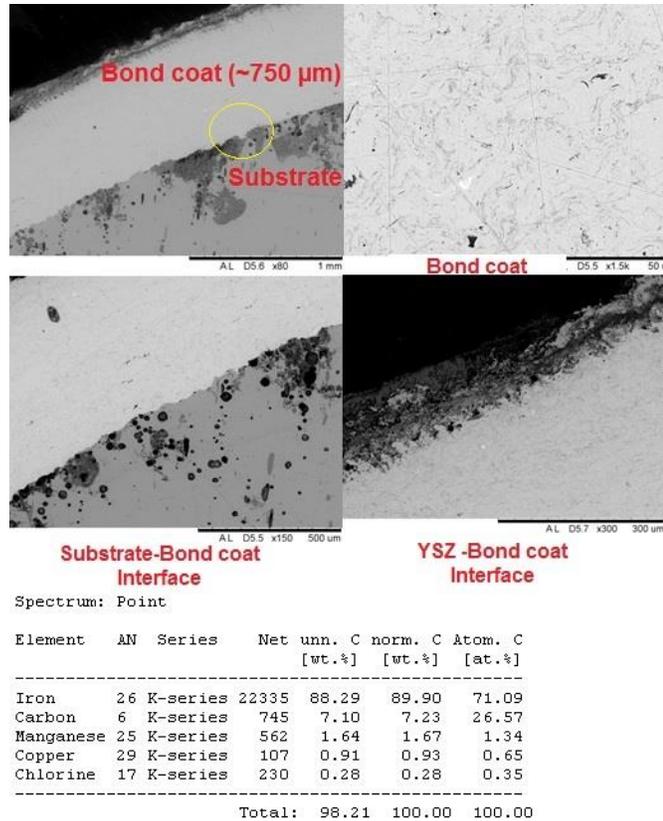


Figure 5-12; SEM and EDX Results of Coating # 2 after 48 hours Test

The top YSZ coat was dissolved in a manner similar to the first test for Coating # 1. However, Diamalloy coat looks intact, with good adhesion to the substrate. The most promising aspect was that the Diamalloy coating kept its integrity in molten CuCl environment for the tested duration. As **Figure 5-12** shows, the bond coating and the base metal look unaffected and intact, although EDX result shows small amount of chlorine and copper which were passed to the inner layers of the Diamalloy coating.

Coating # 2 was tested for a second time after the sealing mechanism was improved as described earlier in **Section 5.2.1.2**. This sample was evaluated in the similar conditions as it is shown in (**Figure 5-13**). On the initial inspection a few cracks on

the surface of this sample had were formed during the fabrication process. Since most of the cracks were appeared on the outer layer of the sample, it might indicate YSZ could not resist very well in the molten CuCl.

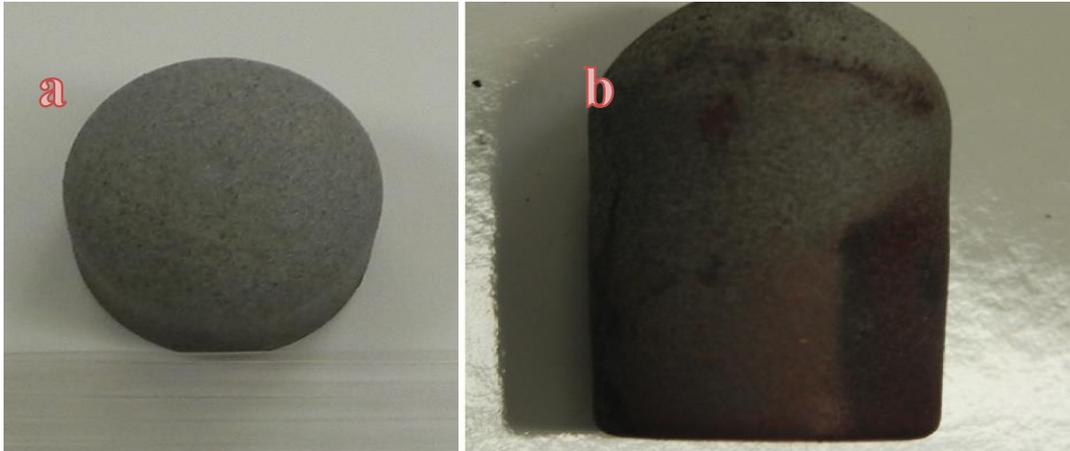


Figure 5-13; Coating # 2 which was immersed for 100 hours

The EDX indicates that in this sample, the coating was successful in preventing CuCl from reaching the base metal. Therefore, it seems that the sealing system was effective in preventing oxygen leakage into the ITV. However, the SEM images (**Figure 5-14**) indicate that the YSZ layer eroded and/or delaminated from the bond layer. The delamination could possibly have occurred during the cutting step while preparing the sample for SEM/EDX observation. Diamalloy exhibits good adhesion to the base metal.

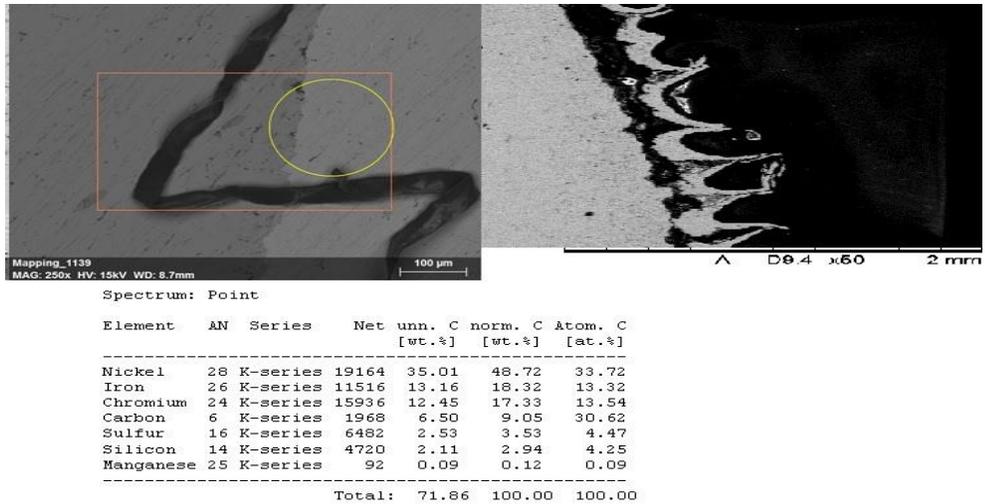


Figure 5-14; SEM/EDX Results of Coating # 2 which was Immersed for 100 h

### 5.3.1.3. Evaluation of Coating # 3 (SHS 9172):

One of the samples which was coated with coating # 3 was immersed in CuCl and a second sample was suspended in the ITV as shown in schematic **Figure 5-5** (without the sacrificial metal). **Figure 5-15** shows the sample which was suspended while a second sample was immersed in molten CuCl for 48 hours. It indicates that oxidization occurred in the ITV even when the sample was out of the molten salt. Few shallow cracks could be seen on the sample, however they were not considerable as the SHS coating is thick.

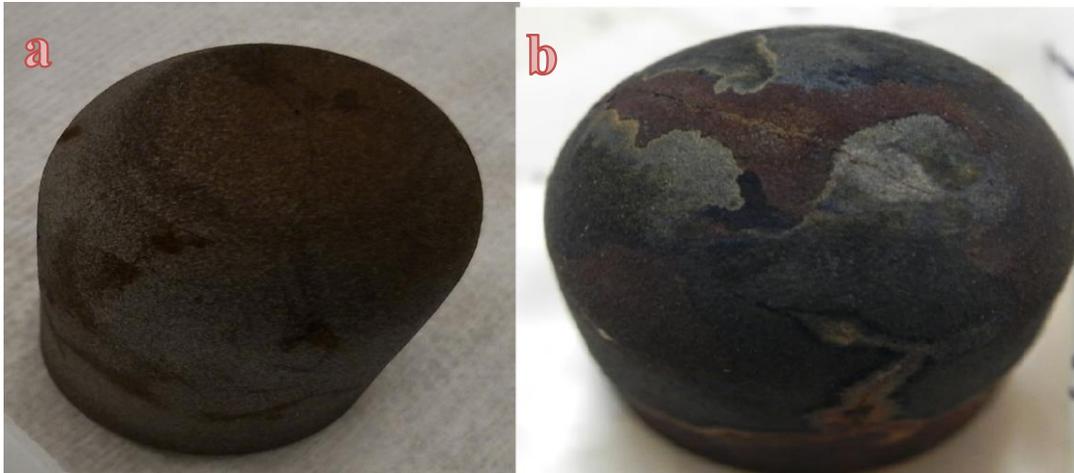


Figure 5-15; Pictures of Coating # 3 which was Suspended (a) before, and (b) after the Test

Since this bond coating had lower adhesion with the base metal which caused some difficulties during SEM/EDX preparation, the coating delaminated during the cutting operation. **Figure 5-16** shows that the SHS coating exhibited good corrosion resistance against CuCl as no trace of copper or chlorine was found in the inner regions of the coating.

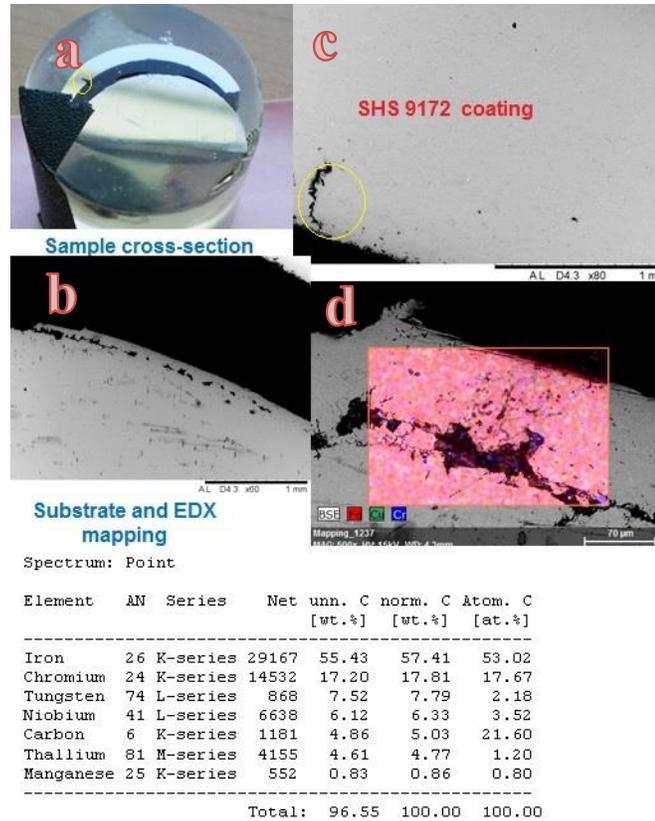


Figure 5-16; SEM/EDX of Suspended Coating # 3 for 48 hours

The second SHS coated sample was immersed in molten CuCl. However during the test, the clamp which was used to hold the sample corroded severely. This caused the sample to fall into the molten CuCl, and after cooling the sample was stuck in the solidified CuCl (**Figure 5-17, b**). The sample was cleaned first by gently removing the solidified CuCl and then by saturated EDTA solution, so that it could be evaluated by SEM/EDX.

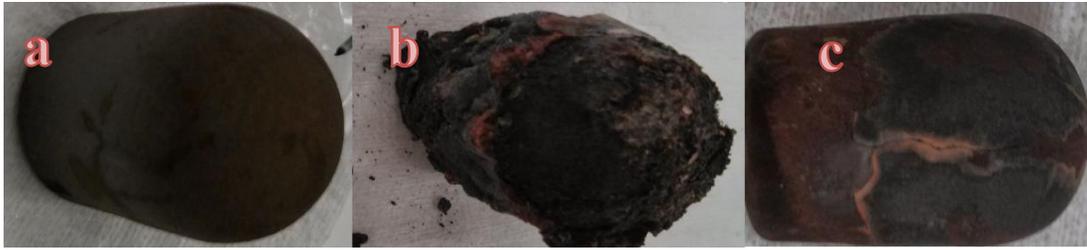


Figure 5-17; Pictures of Coating # 3 (a) before and (b) after Immersion Test and (c) after Post-Immersion Test Cleaning

Even this SHS coated sample, which was immersed for 48 hours demonstrated good resistance to corrosion in molten CuCl (**Figure 5-18**). EDX results indicate that during the immersion test only small amount of chlorine diffused to the substrate metal. The coating material delaminated during the cutting process for preparing the specimen for SEM/EDX.

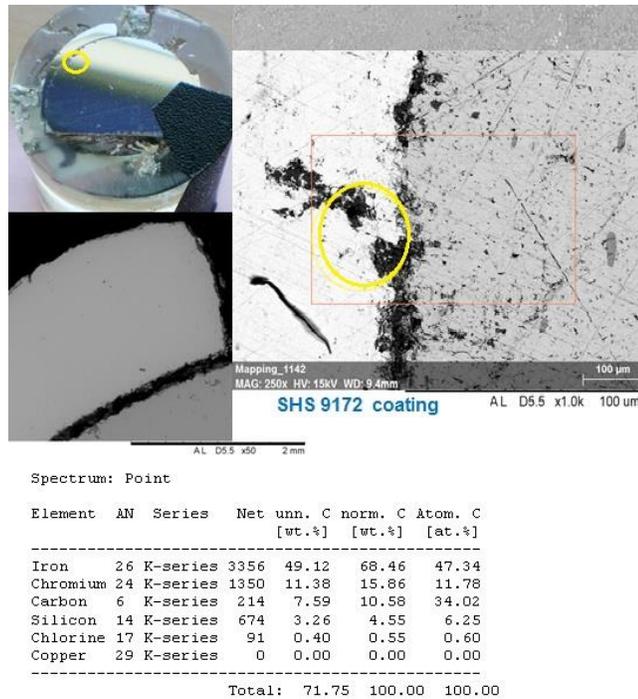
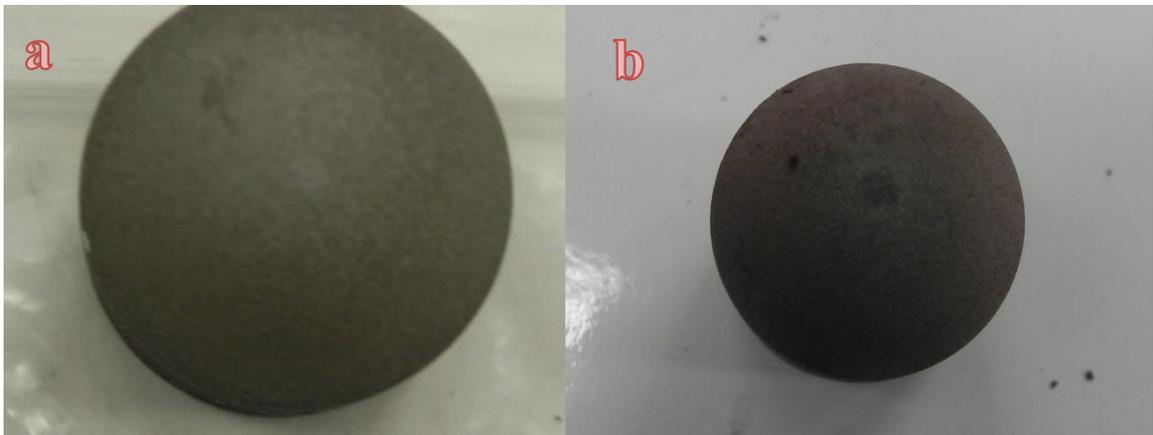


Figure 5-18; SEM/EDX of the Coating # 3 which was immersed for 48 hours

#### 5.3.1.4. Evaluation of Coating # 4 (Diamalloy 4006):

Diamalloy 4006 was evaluated after the sealing mechanism was improved (**Section 5.2.1.2**). The experiment was run for 100 hours with two samples. One of them was immersed inside the molten CuCl and the other one was suspended in the ITV, as shown in schematic **Figure 5.5**.

Both the Diamalloy 4006 coated specimens performed well in the experiment and did not show visual degradation after the test (**Figure 5-19** and **Figure 5-20**). They had good adhesion to the base metal during the experiment. There were no cracks on the samples, and after the post-immersion cleaning procedure the coatings looked intact with no visible damage or corrosion.



**Figure 5-19; Coating # 4 Suspended for 100 hours. (a) Before and (b) After the Test**

All deposits that made color change on the immersed sample (**Figure 5-19**) were cleaned during the post-immersion cleaning process.

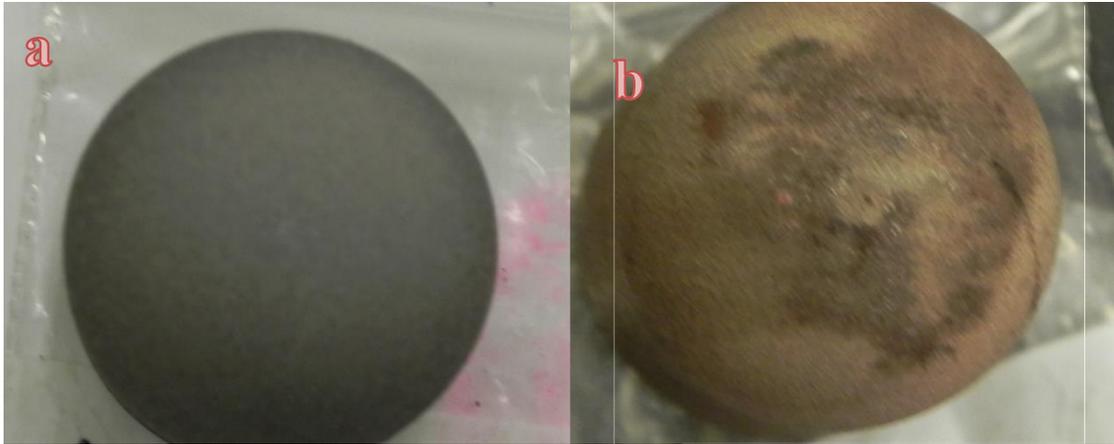


Figure 5-20; Coating # 4 Immersed in Molten CuCl for 100 hours. (a) Before and (b) After the Test.

EDX results indicate that no copper or chlorine reached the base metal after the 100 hours test. (Figure 5-21)

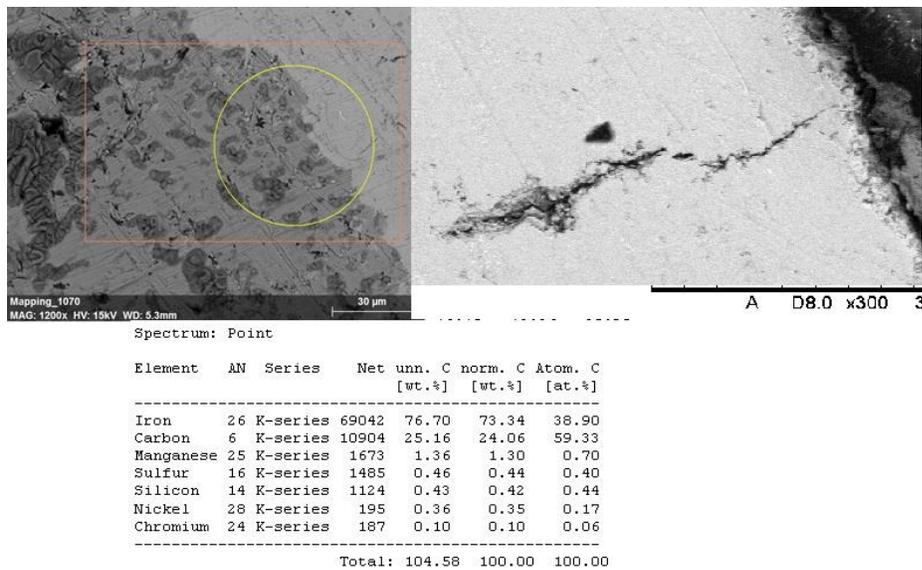
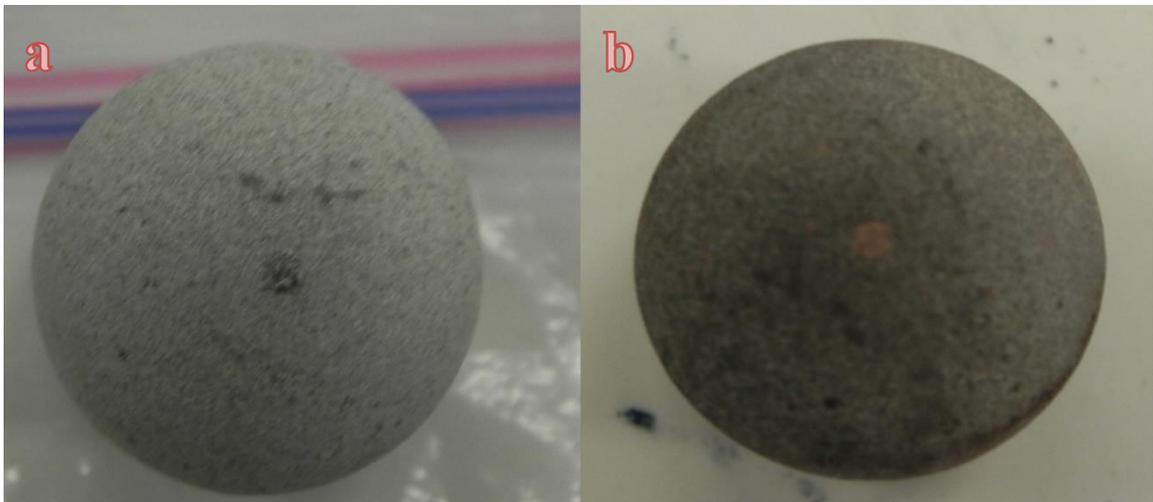


Figure 5-21; SEM and EDX Results of the coating # 4 which was Immersed for 100 hours

### 5.3.1.5. Evaluation of Coating # 5 (SHS + YSZ):

Two samples of coating # 5 were evaluated after the sealing mechanism was improved for 100 hours. One sample was suspended for 100 hours in the immersion test vessel (**Figure 5-22**) while the other sample was immersed in molten CuCl (**Figure 5-23**) as shown in schematic **Figure 5.5**.

The suspended sample (**Figure 5-22**) had an intact coating surface after the experiment. This sample even before post-cleaning procedure seemed clean.



**Figure 5-22; Coating # 5 which was Suspended for 100 hours**

The immersed sample (**Figure 5-23**) had some colorful deposited layers on the outer surface of coating. It looked intact during the visual examination.

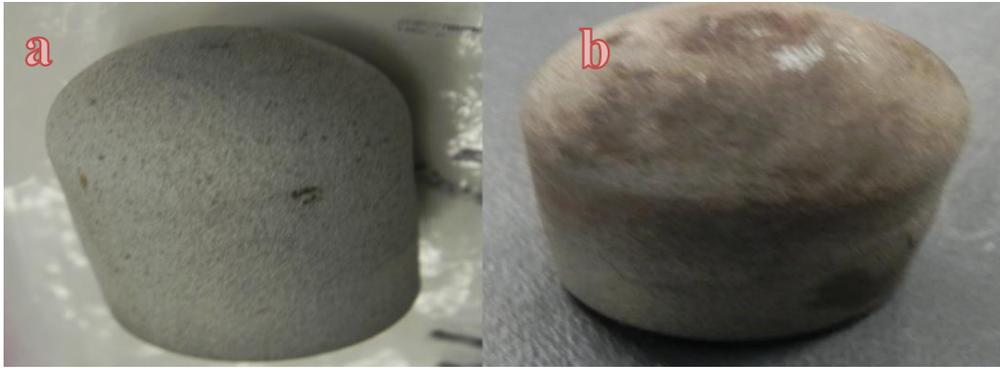
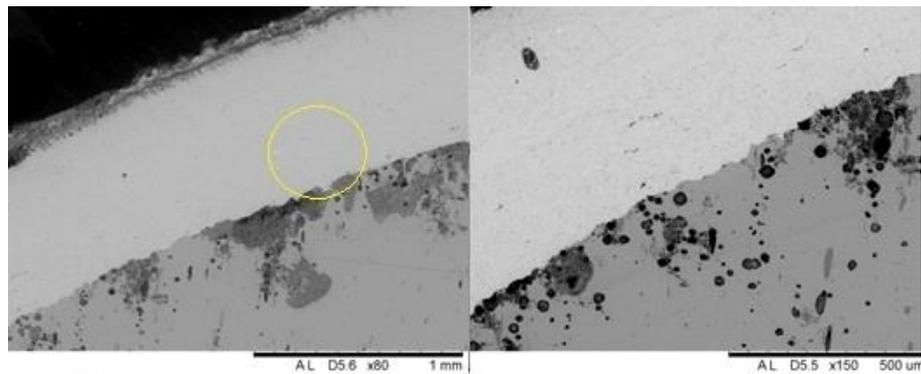


Figure 5-23; Coating # 5 which was Immersed in Molten CuCl for 100 hours

Based on SEM and EDX results shown in **Figure 5-24**, no copper or chlorine reached the surface of the base metal.



Spectrum: Point

Element	AN	Series	Net un.	C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Iron	26	K-series	11673	78.59	93.41	77.57
Carbon	6	K-series	281	4.44	5.28	20.38
Silicon	14	K-series	398	0.98	1.17	1.93
Chromium	24	K-series	29	0.11	0.14	0.12
Chlorine	17	K-series	0	0.00	0.00	0.00
Copper	29	K-series	0	0.00	0.00	0.00
Total:				84.13	100.00	100.00

Figure 5-24; SEM and EDX Results of Coating # 5 which was Immersed for 100 hours

### 5.3.2. Effectiveness of the Sealing Mechanism Developed

The immersion tests were performed after the initial modifications of the sample geometry, the ITV lid and the handling setup. Four main immersion tests were run on four different samples. All samples were tested and then evaluated based on the standard procedure as it is described in **Appendix 3**.

Out of the four samples tested, two coating candidates corroded severely and two of them survived. Since it was expected that new samples will perform significantly better due to changing geometry, these results could be attributed to other problems;

- One possibility could be, excessive leakage of oxygen into the ITV, and
- Delamination of samples could be due to corrosion seeping in from the other side of the sample which was not coated.

The sealing method was improved and verified by testing an uncoated sample as described in **Section 5.2.2**.

It was also decided to modify the specimen again to avoid sharp edge on the other end which was not immersed. The new shape enables uniform coating on the entire of the surface.

### 5.4. Coatings' Performance

The performance of both the bond coatings and the ceramic coatings were evaluated.

### 5.4.1. Bond Coating Performance

Some of the coatings fell off the surface of the samples, either during the experiments or during the examinations. Some possible causes of the coating disbonding can be:

- Differences between the thermal expansion coefficient of the coating and sample;
- Stress or attack from the molten CuCl; or
- The preparation process for SEM/EDX.

In previous study by Siantar, it was concluded that thermal expansion correction was not an important factor for the material that we are using.

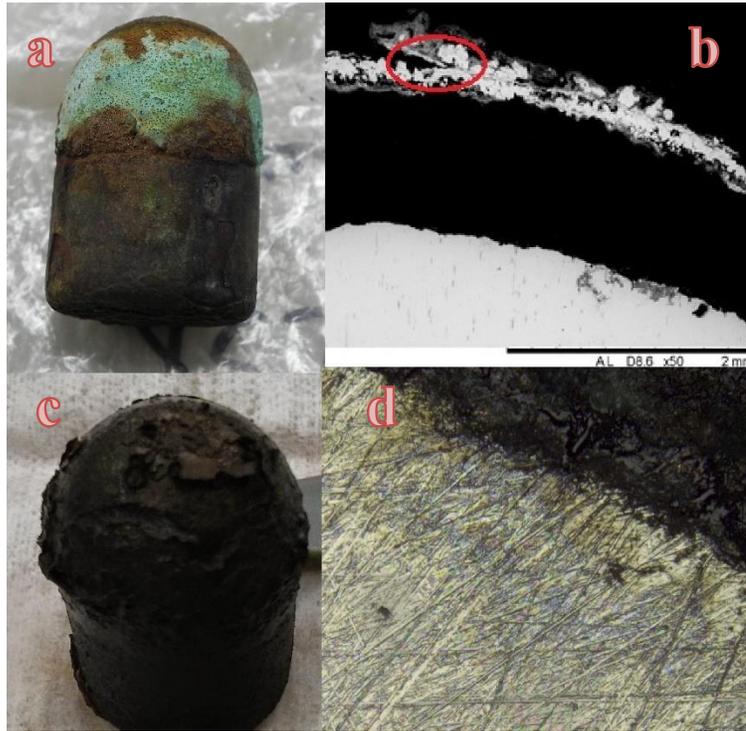
There were several samples where the coating remained on the surface after the post-immersion cleaning and rinsing. However, during the sample preparation steps involving cutting operation (for EIS and SEM), some of the ceramic coating fell off the surface. If the ceramic coatings were damaged during the immersion test, CuCl could be found on the underside of the coating and on the exposed metal which was originally under the ceramic coating. This means that during the immersion test, CuCl remained between the top layer of the sample (or metallic coating) and the underside of the ceramic coating, and might have acted as an adhesive layer between these two surfaces. After several times cleaning, rinsing and sample preparation, some of the CuCl deposits dissolved. Therefore, the ceramic coating fell off since there was not enough adhesion between the two surfaces.

### 5.4.2. Coatings Corrosion Resistance

The samples were only dipped halfway into the crucible containing the molten salt so that only the rounded tip was immersed in the salt. The remaining parts were

suspended over the molten CuCl and were exposed to CuCl vapor. CuCl could have different effects on the coating candidates.

YSZ coatings did not survive even short exposure of 5 hours. (**Figure 5-22**)



**Figure 5-25; Samples Performance which were Coated with YSZ**

YSZ corroded immediately on exposure to the molten CuCl (**Figure 5-25, a**). On EDX examination of this sample a thin layer of YSZ remained on the base metal which corroded uniformly and significant amounts of copper deposits were evident during evaluation and examination the underlying surface (**Figure 5-25, b**). YSZ performance was also analysed after other experiments such as a 48 hour immersion test (**Figure 5-25, c**), (**Figure 5-9**), or (**Figure 5-13**) and similar behaviour was observed.

Both bond coats demonstrated good corrosion resistance during the immersion tests. The Diamalloy coating exhibited high adhesion to the substrate metal, compared to SHS coating.

SHS also provided good corrosion resistance and remained completely intact when it was immersed in the molten CuCl. However, it did not have high adhesion to the base metal. If SHS adhesion could be improved, this coating might be acceptable as a final material candidate.

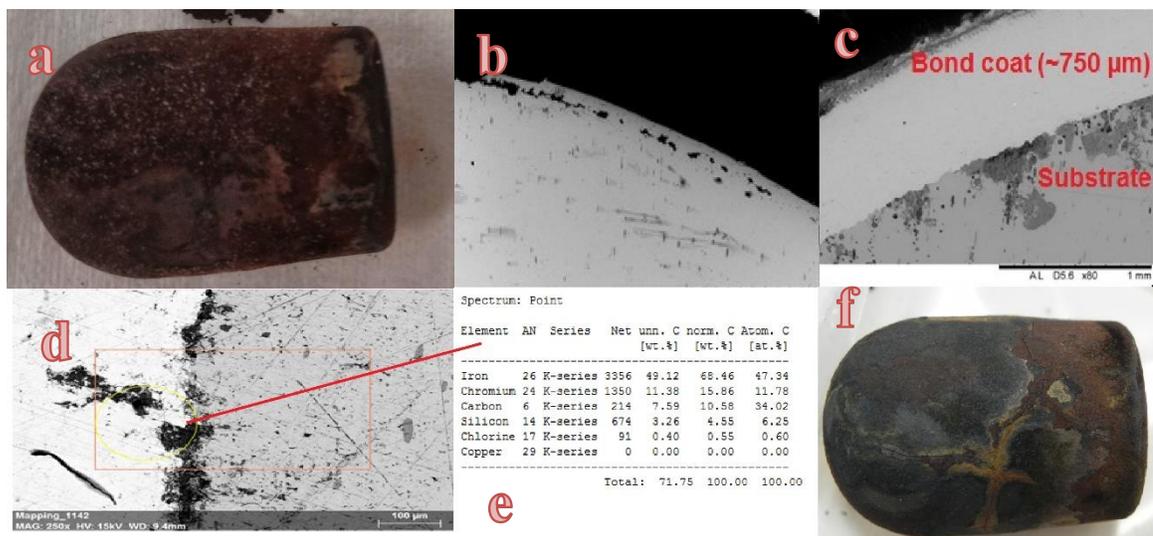


Figure 5-26; Intact Bond Coats in Different Tests

Bond coatings were expressed in (Figure 5-26). Diamalloy (and YSZ) looks intact after the 48 hour test (Figure 5-26, a) and the SEM image of this proved that the substrate metal stayed immune under the Diamalloy. SHS samples also performed well (Figure 5-26, f). However, there were serious issues about adhesion to the base metal (Figure 5-26, b) and (Figure 5-26, d). EDX results of the SHS coating surface and base metal indicated no copper on the base metal where cracks appeared on the sample.

## 6. CONCLUSION

Immersion apparatus was modified and improved as each problem was identified during the experimentation. The system is now expected to perform satisfactorily for prolonged times at the high temperature and corrosive conditions that the material is expected to experience in the proposed commercial hydrogen plant. Safety procedures and methods were developed and a new sample geometry was designed.

Immersion tests were performed to evaluate the corrosion performance of the selected candidate coatings in a molten CuCl environment similar to a proposed hydrogen plant. Medium carbon steel was selected as the base metal. For the coatings, five types of combination coatings were evaluated for their corrosion resistance during molten CuCl exposure.

The majority of coatings were intact and did not fall off. New sample geometry may have improved the integrity of the sprayed coatings, as there were no deep cracks or corrosions on the coated specimens. If the coating cracks, it could provide a pathway for the corrosive environment to go under the coating layer and react with the base metal.

The first coating to be evaluated was YSZ, applied directly onto the base metal. This coating did not survive even 5 hours of exposure to molten CuCl.

Both the bond coat materials, Diamalloy and SHS, performed well in inhibiting the molten CuCl from attacking the base metal. This was verified using SEM and EDX. SHS seemed to perform better than Diamalloy, at resisting molten CuCl penetration through it. SEM images showed a number of cracks on some samples in the coatings.

However, these could possibly have been generated during the cutting operation when the sample was being prepared for SEM/EDX, after the immersion test. These images also indicated that Diamalloy had better adhesion to medium carbon steel compared to SHS. Although SHS coatings survived during the immersion process, in terms of adhesion to the base metal, this coating could not withstand the forces generated during the cutting. Therefore, the coating delaminated from the substrate metal, which indicates weaker adhesion.

Finally, the ceramic coating (YSZ) was applied to the base metal with a bond coating, survived the immersion tests, however it showed corrosion and erosion within its layers.

These conclusions are based on limited experiments. Therefore, more experiments should be conducted for confirmation.

## 7. RECOMMENDATIONS FOR FUTURE WORKS

The recommended future works are as follows;

- All the candidate coatings have to be evaluated in detail on the new verified system with prolonged exposure time.
- More ceramic coating materials should be evaluated till at least three coating materials are identified which can withstand more than 100 hours of immersion in molten CuCl at 500°C. Few possible candidates are:
  1. Thicken layers of YSZ; 2. Al<sub>2</sub>O<sub>3</sub>; 3. Al<sub>2</sub>O<sub>3</sub>+15% YSZ; 4. Al<sub>2</sub>O<sub>3</sub>+50% YSZ; etc.
- Since Diamalloy had good adhesion to the base metal and SHS performed well as a corrosion resistant material, it would be interesting if Diamalloy is applied as a first bond coating for the base metal and SHS as the next layer, followed by a ceramic layer.
- Cobalt or Nickel should also be investigated for their performance as base coating materials.
- The successful coatings should be coated on the corrosion resistant alloys which were identified by the initial literature survey. This will yield different ceramic-alloys combinations. For all these combinations the performance should be evaluated in detail. The three most successful of these combinations should be selected for final study.
- The coating candidates should be re-analysed by subjecting them to thermal cycles in order to evaluate their capability to withstand thermal shocks.

## 8. REFERENCES

1. Siantar, Edwin. "Study of the Effect of Molten CuCl Immersion Test on Alloys with High Ni-Content with and without Surface Coatings.", Master's thesis, UOIT, 2012. Oshawa, Ont
2. G. Naterer, S. Suppiah, M. Lewis, K. Gabriel, I. Dincer, M.A. Rosen, M. Fowler, G. Rizvi, E.B. Easton, B.M. Ikeda, M.H. Kaye, L. Lu, I. Pioro, P. Spekkens, P. Tremaine, J. Mostaghimi, J. Avsec, J. Jiang, "Recent Canadian advances in nuclear-based hydrogen production and the thermochemical Cu-Cl cycle", *International Journal of Hydrogen Energy*, 34: 2901-2917, 2009
3. G. Naterer, S. Suppiah, L. Stolberg, M. Lewis, Z. Wang, V. Daggupati, K. Gabriel, I. Dincer, M.A. Rosen, P. Spekkens, S.N. Lvov, M. Fowler, P. Tremaine, J. Mostaghimi, E.B. Easton, L. Trevani, G. Rizvi, B.M. Ikeda, M.H. Kaye, L. Lu, I. Pioro, W.R. Smith, E. Secnik, J. Jiang, J. Avsec, "Canada's program on nuclear hydrogen production and thermochemical Cu-Cl cycle", *International Journal of Hydrogen Energy*, 35: 10905-10926, 2010
4. P.R. Roberge, *Designing, Planning, and Preparing Corrosion Tests, Corrosion: Fundamentals, Testing, and Protection, Vol 13A, ASM Handbook*, ASM International, 2003, p 420–424 R.A. & pp. 597-661, Chap. 14.
5. D. A. Jones (1996). *Principles and Prevention of Corrosion* (2nd Ed), Prentice Hall, New York, USA, pp. 43-73, Chap. 2
6. Schweitzer, Philip A. *Paint and Coatings: Applications and corrosion resistance*. CRC Press, 2005.
7. *Handbook of Chemistry and Physics* (71th Ed), CRC Press, 1991, Colorado, USA.

8. L. Pawlowski (2008). Science and Engineering of Thermal Spray Coatings (2nd Ed), John Wiley & Sons, Inc., Ohio, USA, pp. 67-98, Chap. 3
9. F.L. Toma, C.C. Stahr, L.M Berger, S. Saaro, M. Herrmann, D. Deska, G. Michael, "Corrosion Resistance of APS and HVOF Sprayed Coatings in the Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system", Journal of Thermal Spray Technology, 19: 1-2, 2010
10. J.Y. Kwon, J.H. Lee, Y.G Jung, U.Paik. "Effect of bond coat nature and thickness on mechanical characteristic and contact damage of zirconia-based thermal barrier coatings", Surface and Coating Technology, 201:3483-3490, 2006
11. A. S Khanna (2002). Introduction to high temperature oxidation and corrosion, ASM International, The Materials Information Society, California, USA, pp. 230-256, Chap. 12
12. D. Loveday, P. Peterson, B. Rodgers, "Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy: Application of EIS to Coatings", Journal of Coatings Technology 10: 88, 2004
13. N.D. Cogger, N.J. Evans. An Introduction to Electrochemical Impedance Measurement. Solartron Limited. Technical Report No.6. 1999, Allentown, USA.
14. D. Loveday, P. Peterson, B. Rodgers, "Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy: Fundamentals of Electrochemical Impedance Spectroscopy", Journal of Coatings Technology 8: 46, 2004
15. E. Barsoukov, J.R Macdonald (2005). Impedance Spectroscopy Theory, Experiment, and Applications (2nd Ed), John Wiley & Sons, Inc., Chicago, USA, pp. 1-20, Chap. 1
16. R.C. Dorf, J.A. Svoboda (2004). Electric Circuit (6th Ed), John Wiley & Sons, Inc., New York, USA, pp. 521-552, Chap. 12

17. J. Zhang, V. Desai, "Evaluation of thickness, porosity and pore shape of plasma sprayed TBC by electrochemical impedance spectroscopy", *Surface & Coatings Technology* 190: 98-109, 2005
18. J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer, J. Michael (2003). *Scanning electron microscopy and x-ray microanalysis* (3rd Ed), Springer Science, New York, USA, pp. 21-60, Chap. 2
19. M. Laflamme, J.D. Schiffbauer, S.Q. Dornbos (Ed), P.J. Orr., S.L. Kearns (2011). *X-ray Microanalysis of Burgess Shale and Similarly Preserved Fossils*, In *Topics in Geobiology*. Springer, New York, USA
20. J.E. Indacochea, J.L. Smith, K.R. Litko, E.J. Karell, "Corrosion performance of ferrous and refractory metals in molten salts under reducing conditions", *Journal of Materials Research* 15: 5, 1999
21. A.R. Shankar, U.K. Mudali, "Corrosion of type 316L stainless steel in molten LiCl-KCl salt" *Journal of Materials and Corrosion* 59: 878, 2008
22. M.A. Uusitalo, P.M.J. Vuoristo, T.A. Meantyl, "High temperature corrosion of coatings and boiler steels below chlorine-containing salt deposits, *Corrosion Science* 46: 1311-1331, 2004
23. C.A.C. Sequeira (Ed) 2003. "Fundamentals of Molten Salt Corrosion" In *High Temperature Corrosion in Molten Salts*, Vol. 7, Molten Salt Forum, pp. 3-40, Trans Tech Publications Ltd, Zurich, Swiss.
24. George Y.Lai (2007). *High temperature Corrosion and Materials Applications*, ASM International, The Materials Information Society, Ohio, USA, pp. 409-419, Chap. 15.
25. T.S. Sidhu, R.D. Agrawal, S. Prakash, "Hot corrosion of some superalloys and role of high-velocity oxy-fuel spray coatings—a review", *Journal of Surface and Coatings Technology* 198: 441-446, 2005

26. H. Singh, B. S. Sidhu, D. Puri, and S. Prakash, "Use of plasma spray technology for deposition of high temperature oxidation/corrosion resistant coatings – a review", *Materials and Corrosion* 58: 92, 2007
27. J.R. Davis (2000). "Nickel, cobalt, and their alloys", ASM International, The Materials Information Society, New York, USA, pp. 56-67, Chap. 1
28. J.L. Everhart (1971). "Engineering properties of nickel and nickel alloys", Plenum press, New York, USA, pp. 8-31, Chap. 2
29. W.A. Friend (1980). "Corrosion of Nickel and Nickel Base Alloys", John Wiley-Interscience Publication, New York, USA, pp.435-452, Chap. 11
30. A.R. Shankar, S. Mathiya, K. Thyagarajan, U.K. Mudali, "Corrosion and Microstructure correlation in Molten LiCl-KCl medium", *Metallurgical and Materials Transactions* 41: 1815-1825, 2010
31. J. E. Indacochea, J. L. Smith, K. R. Litko, E. J. Karell, and A. G. Raraz, "High-Temperature Oxidation and Corrosion of Structural Materials in Molten Chlorides", *Oxidation of Metals* 55: 1, 2001
32. S.Y. Parka, J.H. Kima, M.C. Kimb, H.S. Song, C.G. Park, "Microscopic observation of degradation behavior in yttria and ceria stabilized zirconia thermal barrier coatings under hot corrosion" *Surface & Coatings Technology* 190: 357– 365, 2005
33. A. R. Shankar, U. K. Mudali, R. Sole, H.S. Khatak, B. Raj, "Plasma-sprayed yttria-stabilized zirconia coatings on type 316L stainless steel for pyrochemical reprocessing plant", *Journal of Nuclear Materials* 372: 226– 232, 2008
34. Rolled alloys, "AL6XN material data sheet", rolled alloys (2011). <http://www.rolledalloys.ca/productline/alloyspecs.aspx?alloy=al6xn>. Web. 13 November 2011.

35. Rolled alloys, “Inconel 625 material data sheet”, rolled alloys (2011)  
<http://www.rolledalloys.ca/productline/alloyspecs.aspx?alloy=625>. Web. 13 November 2011.
36. Sulzermetco, “Thermal Spray Materials Guide”, Sulzer Metco (2006).  
[http://www.sulzermetco.com/en/Portaldata/13/Resources/2\\_Products\\_Services/Thermal\\_Spray\\_Materials\\_Guide\\_022006.pdf](http://www.sulzermetco.com/en/Portaldata/13/Resources/2_Products_Services/Thermal_Spray_Materials_Guide_022006.pdf). Web. 17 November 2011.
37. “ASTM G31-72 Standard Practice for Laboratory Immersion Corrosion Testing of Metals”, astm.org. ASTM International, n.d. Web. 11 November 2011.
38. W. D. Callister, (2008), Materials science and engineering: an introduction, (7th ed.), John Wiley & Sons., Utah, USA, Appendix B
39. Cambridge Glassblowing (2012), Glass properties. Retrieved January 04, 2012, from Cambridge glassblowing website:  
<http://www.camglassblowing.co.uk/gproperties.htm>. Web. 16 November 2011.
40. AdValue Technology LLC, “Fused Quartz Products”,  
<http://www.advaluetech.com>. Web. 19 November 2011.
41. B. Averill, P. Eldredge (2007). “Chemistry: Principles, Patterns, and Applications”, Prentice hall, New York, USA, pp.73-92, Chap. 3
42. I. Barin, Thermochemical Data of Pure Substances, Wiley-VCH, Third edition, 1997, New York, USA.
43. Chlorine; MSDS No. 7782-50-5 [Online]; Cleartech: Saskatoon, SK, November 8, 2010, <http://www.cleartech.ca/msds/chlorine.pdf>. Web. 12 November 2011.

44. H.B. Parizi, J. Mostaghimi, L. Pershin, H.S. Jazi, "Analysis of the Microstructure of Thermal Spray Coatings: A Modeling Approach, Journal of Thermal Spray Technology", 19: 737, 2010
45. J. R. Scully, D.C. Silverman, M.W. Kendig, (1993), Electrochemical impedance analysis and interpretation, American Society for Testing and Materials, Philadelphia, USA, pp. 154-170
46. S. Boccia, personal communication, University of Toronto.
47. Princeton Applied Research, "Potentiostat VersaSTAT 3 Specifications", <http://www.princetonappliedresearch.com/Our-Products/Potentiostats/VersaSTAT-3.aspx>. Web. 24 April 2012.
48. Uhlig, Herbert Henry, and R. Winston Revie. Uhlig's Corrosion Handbook. 51 Vol. John Wiley & Sons, 2011.
49. Kumar, Harish, and Vikas Yadav. "Corrosion Characteristics of Mild Steel Under Different Atmospheric Conditions by Vapour Phase Corrosion Inhibitors." American Journal of Materials Science and Engineering 1.3 (2013): 34-9.
50. <http://corrosion.ksc.nasa.gov/index.htm>
51. J.R. Davis, handbook of thermal spray technology, p 176
52. Tresder, R.S. NACE corrosion engineer's reference book. 3<sup>rd</sup> edition, National Association of Corrosion Engineers, 2002. 104,
53. Fontana, Mars Guy. Corrosion Engineering. 3<sup>rd</sup> edition. New York: McGraw-Hill, 1986.
54. Revie, R. Winston. Corrosion and corrosion control. John Wiley & Sons, 2008.

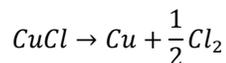
55. Valdez, B. "Corrosion Tests and Standards: Applications and Interpretation, Second Edition." Corrosion 62.3 (2006): 280.
56. Rapp, Corrosion by Molten Salts, Corrosion: Fundamentals, Testing, and Protection,, Vol 13A, ASM Handbook, ASM International, 2003, p 117–123
57. R.D. Kane, Molten Salt Corrosion, Corrosion: Fundamentals, Testing, and Protection, Vol 13A, ASM Handbook, ASM International, 2003, p 216–219
58. J. R. Scully, D.C. Silverman, M.W. Kendig, (1993), Electrochemical impedance analysis and interpretation, American Society for Testing and Materials, Philadelphia, USA, pp. 154-170
59. B. Averill, P. Eldredge (2007). "Chemistry: Principles, Patterns, and Applications", Prentice hall, New York, USA, pp.73-92, Chap. 3
60. Chlorine; MSDS No. 7782-50-5 [Online]; Cleartech: Saskatoon, SK, November 8, 2010, <http://www.cleartech.ca/msds/chlorine.pdf>. Web. 12 November 2011.
61. Gabriel D. Marin, "Kinetics and Transport Phenomena in the Chemical Decomposition of Copper Oxychloride in the Thermochemical Cu-Cl Cycle"
62. Tomashov, N. D. and Tugarinov, N. I., Zh. Prikl. Khim., 30, 1 681 (1957)
63. Edeleanu, C., Gibson, J. G. and Meredith, J. E., J. Iron St. Inst., 196, 59 (1960)
64. Shreir, Lionel Louis. Corrosion. Vol. I. Metal/environment reactions. No. Ed. 3. Butterworth & Co.(Publishers) Ltd., 1976.

## APPENDICES:

### Appendix 1: CuCl thermodynamic analysis

@ 800°K:

Element	H <sub>@ 800K</sub> (KJ/mol)	S <sub>@ 800K</sub> (J/K mol)
Cl <sub>2(g)</sub>	18.11	258.4
Cu <sub>(s)</sub>	13.13	58.75
CuCl <sub>(l)</sub>	-104.08	151.2
CuCl <sub>2(s)</sub>	-166.95	183.9



$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Products}} - (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Reactants}}$$

$$\Delta H_{CuCl}^\circ = \left(\frac{18.11}{2} + 13.13\right) - (-104.08) = 126.265 \text{ (KJ/mol)}$$

$$\Delta S_{CuCl}^\circ = \left(\frac{258.4}{2} + 58.75\right) - (151.2) = 36.75 \text{ (J/K)} = 0.03675 \text{ (KJ/K mol)}$$

$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_f$$

$$\Delta G^\circ = 126.265 - (800 \times 0.03675) = 96.865 \text{ (KJ/mol)}$$

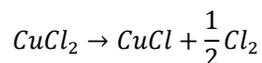
When  $\Delta G^\circ > 0$ , the reaction is not spontaneous in the forwarding.

$$\Delta G^\circ = -RT \ln k$$

$$\ln k = \frac{-\Delta G^\circ}{RT} = \frac{-(96.865 \times 10^3 \left(\frac{J}{mol}\right))}{8.31 \left(\frac{J}{K mol}\right) \times 800(K)} = -14.57$$

$$k = e^{-14.57} = 4.7 \times 10^{-7}$$

$$k = \frac{a_{Cu} \times P_{Cl_2}^{\frac{1}{2}}}{a_{CuCl}} = P_{Cl_2}^{\frac{1}{2}} x^2 \Rightarrow P_{Cl_2} = 2.21 \times 10^{-13}$$



$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Products}} - (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Reactants}}$$

$$\Delta H_{CuCl_2}^\circ = \left(\frac{18.11}{2} + -104.08\right) - (-166.95) = 71.925 \text{ (KJ/mol)}$$

$$\Delta S_{CuCl_2}^\circ = \left(\frac{258.4}{2} + 151.2\right) - (183.9) = 96.5 \text{ (J/K mol)} = 0.0965 \text{ (KJ/K mol)}$$

$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_f$$

$$\Delta G^\circ = 71.925 - (800 \times 0.0965) = -5.275 \text{ (KJ/mol)}$$

When  $\Delta G^\circ < 0$ , the reaction is spontaneous in the forwarding.

$$\Delta G^\circ = -RT \ln k$$

$$\ln k = -\Delta G^\circ / RT = \frac{-(-5.275 \times 10^3 \text{ (}\frac{J}{\text{mol}}\text{)})}{8.31 \text{ (}\frac{J}{\text{K mol}}\text{)} \times 800 \text{ (K)}} = 0.79$$

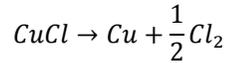
$$k = e^{0.79} = 2.21$$

$$k = \frac{a_{CuCl} \times P_{Cl_2}^{\frac{1}{2}}}{[CuCl_2]} = \frac{P_{Cl_2}^{\frac{1}{2}}}{[CuCl_2]} x^2 \Rightarrow \max[CuCl_2] = \frac{\sqrt{\max P_{Cl_2}(\text{threshold})}}{k} = \frac{\sqrt{10 \times 10^{-6}}}{2.21}$$

$$= 1.43 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

@ 1000°K:

Element	H <sub>@ 1000K</sub> (KJ/mol)	S <sub>@ 1000K</sub> (J/K mol)
Cl <sub>2(g)</sub>	25.56	266.8
Cu <sub>(s)</sub>	18.73	64.99
CuCl <sub>(l)</sub>	-84.2	174.8
CuCl <sub>2(s)</sub>	-150.61	202.1



$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Products}} - (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Reactants}}$$

$$\Delta H_{\text{CuCl}}^\circ = \left(\frac{25.56}{2} + 18.73\right) - (-84.2) = 115.71 \text{ (KJ/mol)}$$

$$\Delta S_{\text{CuCl}}^\circ = \left(\frac{266.8}{2} + 64.99\right) - (174.8) = 23.59 \text{ (J/K)} = 0.02359 \text{ (KJ/K mol)}$$

$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_f$$

$$\Delta G^\circ = 115.71 - (1000 \times 0.02359) = 92.12 \text{ (KJ/mol)}$$

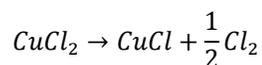
When  $\Delta G^\circ > 0$ , the reaction is not spontaneous in the forwarding.

$$\Delta G^\circ = -RT \ln k$$

$$\ln k = -\Delta G^\circ / RT = \frac{-(92.12 \times 10^3 \left(\frac{\text{J}}{\text{mol}}\right))}{8.31 \left(\frac{\text{J}}{\text{K mol}}\right) \times 1000(\text{K})} = -11.08$$

$$k = e^{-11.08} = 1.53 \times 10^{-5}$$

$$k = \frac{a_{\text{Cu}} \times P_{\text{Cl}_2}^{\frac{1}{2}}}{a_{\text{CuCl}}} = P_{\text{Cl}_2}^{\frac{1}{2}} \Rightarrow P_{\text{Cl}_2} = 2.35 \times 10^{-10}$$



$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Products}} - (\Delta H^\circ - T\Delta S^\circ)_{f \text{ Reactants}}$$

$$\Delta H^\circ_{\text{CuCl}_2} = \left(\frac{25.56}{2} + -84.2\right) - (-150.61) = 79.19 \text{ (KJ/mol)}$$

$$\Delta S^\circ_{\text{CuCl}_2} = \left(\frac{266.8}{2} + 174.8\right) - (202.1) = 106.1 \text{ (J/K mol)} = 0.1061 \text{ (KJ/K mol)}$$

$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ)_f$$

$$\Delta G^\circ = 79.19 - (1000 \times 0.1061) = -26.91 \text{ (KJ/mol)}$$

When  $\Delta G^\circ < 0$ , the reaction is spontaneous in the forwarding.

$$\Delta G^\circ = -RT \ln k$$

$$\ln k = -\Delta G^\circ / RT = \frac{-(-26.91 \times 10^3 \left(\frac{\text{J}}{\text{mol}}\right))}{8.31 \left(\frac{\text{J}}{\text{K mol}}\right) \times 1000 \text{ (K)}} = 3.24$$

$$k = e^{0.79} = 25.49$$

$$k = \frac{a_{\text{CuCl}} \times P_{\text{Cl}_2}^{\frac{1}{2}}}{[\text{CuCl}_2]} = \frac{P_{\text{Cl}_2}^{\frac{1}{2}}}{[\text{CuCl}_2]} \Rightarrow \max[\text{CuCl}_2] = \frac{\sqrt{\max P_{\text{Cl}_2}(\text{threshold})}}{k} = \frac{\sqrt{10 \times 10^{-6}}}{25.49}$$

$$= 1.24 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

## Appendix 2: EIS Test Experiment Procedure

1. Rinse the beaker and graduated cylinder with both tap and distilled water three times. Determine what type of solution is required as the electrolyte, and how many grams of a salt required. Weight carefully the mass and make the solution using de-aerated distilled water. Once the solution has been made, purge with argon gas for 5 minutes to remove all the oxygen in the solution.
2. Wash the cell with both tap and distilled water three times each and use a funnel to pour the solution into the cell. Make sure there are no bubbles formed in the tube inside of the reference electrode housing because it could disturb the stability of the potentiostat and create a false reading. If there is a bubble formed, press the top of the luggin well with your thumb to break the bubble. Shaking the flat cell could also help to break the bubble.
3. Rinse the reference electrode with distilled water and place it in the luggin well in the cell. Rinse the counter electrode and place it in the counter electrode compartment on the left of the cell. Purge the cell using argon gas for 5 minutes.
4. Rinse both sides of the sample and turn the flat cell 90° to the side so that the sample can be clamped into the cell. Place the o-ring on the desired area to be tested and then place it on top of the opening hole of the flat cell. Make sure that there are no bubbles within the cell and shake the flat cell upside down twice to remove any bubble build-up on the working electrode after clamping the sample. There is a possibility of a bubble trapped in the luggin capillary. This can be removed by pressing your thumb on the luggin well, allowing the bubble to be removed from the luggin capillary.

5. Turn on the potentiostat and wait for 5 minutes for the system could warm-up. Connect each alligator clip to the flat cell: green lead is for the working electrode; white lead is for the reference electrode; and red lead is for the counter electrode.
6. Run the OCP test for 5 minutes or wait until the potential (E) stabilizes. Start the Potentiostatic EIS experiment and set the parameters: frequency range of 30 kHz-0.1Hz, amplitude of 10 mV RMS, DC vs OCP, data quality of 5, and auto current range. Set up the display plot as Nyquist, Bode, and Phase angle plot.
7. Make sure that all the plots do not have irregular shape or spikes and the starting potential value is similar to the potential in OCP test. When the overload sign appear shut-down the experiment immediately and restart.
8. Look at the pre-selected spots on the sample and for every spot, takes three EIS readings in each spot to confirm the validity of the result. Once all the readings have been taken, make sure that the EIS experiment is off and remove all the connections (alligator clip) from the e-cell.
9. Change the position/removing the sample from the e-cell, clamp the inlet and outlet gas tubing, flip the cell 90° counter clockwise, remove the tested sample from the cell, rinse the new sample, and place it into the flat cell.
10. After clamping the sample, gently shake the flat cell to remove any bubbles formed on the electrode and sample, and press the luggin well with thumb so that any bubbles trapped in the luggin capillarity are removed.
11. When the whole set of EIS experiments are completed, rinse the sample with distilled water three times before putting it into the oven (80°C) for drying. Once dried, store the sample in a sealed container.

12. The reference electrode must be taken out of the cell, rinsed three times with distilled water, and stored into its filling solution. The flask filled with saturated KCl is used to store the reference electrode while it is not used.

### Appendix 3: Immersion Experiment Procedure

1. Wash all vessels, tubing, and samples using tap water, rinse three times with distilled water until there is no deposit/residual left in the vessel.
2. Measure the height of the crucible and mark the height to be filled with CuCl powder into the quartz crucible based on the height mark assigned in each crucible.
3. Place the crucibles on the bottom plate of the lifting and turning device and arranged them based on their assigned number to avoid mixing up the samples.
4. Caution is required to avoid tighten the clamp since it could crack or damage the coating. Wrap a stainless steel wire around the screws and tied it into the top part of sample holder based on the arrangement made.
5. Carefully place the lifting and turning device with the crucibles into the vessel. Place the lifting plate on top of the pillars and made sure that the position of each hole is close to the pillar.
6. Apply the high-temperature grease to the gasket and the lid of the ITV. Place the lid and gasket on the vessel body and clamp using the C-clamp. Make sure that the clamp is properly tightened to create a perfect seal around the immersion vessel.
7. Place the ITV in the heating mantle and connect the controller to the heater. Place the controller thermocouple between heating mantle and the ITV.
8. Insert the thermocouple into the fused glass tube thermo-well to ITV through one of the tubing. Make sure that the thermocouple does not contact the copper chloride since it could damage the thermocouple.
9. Wrap the teflon tape on the joint between steel tubing and the glass tube. Place the input gas tubing into the ITV and made sure that the clamp is tight

and secure so that the gas input tube does not come loose once the gas flow starts.

10. Wrap both ends of the tubing with teflon tape and attach the O-ring. Assemble the connecting tubing connecting the ITV to the condenser, clamped it properly, and check for leaks between the joint
11. Assemble the condenser and connect it to the scrubber. Attach the discharge tubing from the pressure relief device to one of the tubing on the lid.
12. Fill the scrubber with water (4.5 L) and sodium bicarbonate (390 g). Drop the plastic beads into the solution to reduce the size of bubble formed. Wrap a wire mesh to the end of the tube on the scrubber's lid that is going into the solution.
13. Place all the power cords for the system into the power bar that is connected into the thermal cut-off system and set the temperature limit to 550°C.
14. Wrap the top part of the main vessel ITV with a fibreglass cloth to reduce heat loss.
15. Purge the vessel using nitrogen gas for 30 minutes at 50-70 mL/min to purge oxygen or other gases from the immersion system before the preheating process.
16. Turn on the heating mantle and set the temperature to 520°C until the inside temperature has reached 500°C. Continue purging the nitrogen gas for another 15-20 minutes before reducing the nitrogen flow to 20 mL/min. This flow rate is kept for the entire length of the immersion test. Make sure when the nitrogen gas is being purged, the solution in the scrubber is bubbling to indicate that the exhaust gas flow is maintained by the immersion test system.
17. Open the opening cap and released the lifting rod to start immersing the samples. Close the opening cap and made sure there is no leak by spraying it with soapy water.

18. During the course of the immersion test, check for leaks and the bubble regularly, to ensure that the immersion system does not leak. Check the inside temperature of the ITV and make sure it stays at 500°C.
19. Once the immersion test period is reached, open the opening cap and lift the lifting rod, rotate it, and rest the plate on the three pillars. Leave the sample in lifting position for 4 hours with the heater turn-on to allow the molten CuCl to drip-off.
20. Gradually reduce the heater controller temperature to allow the immersion test to cool while maintain the nitrogen gas flow at 20 mL/min. Allow the inside of ITV to be cooled slowly and constantly check the handheld thermocouple thermometer until the temperature is at room temperature.
21. Once the ITV inside temperature is at room temperature, shut-off the nitrogen gas flow and open the lid of the ITV so that the sample can be retracted.

## Appendix 4: The Post-Immersion Cleaning Process

1. Cut the SS wire that is attached to the top plate of the lifting and turning device and bend the wire to make it shaped like a hook.
2. Prepare the saturated EDTA using 1 litre of distilled water and  $2 \pm 0.001$  g of EDTA. Firstly, heat the distilled water until it reaches  $80\text{ }^{\circ}\text{C}$  before adding the 2 g of EDTA. Place the solution into a 1.5 L beaker and place it on a hot plate magnetic stirrer ( $80^{\circ}\text{C}$ ) and set the stirrer at 75 rpm. Make sure that the solution is colourless.
3. Take the wire and hook it into the side of the beaker and ensure that the sample is not touching or close to the magnet strip that is rotating on the bottom of the beaker.
4. While the sample is being immersed, prepare another EDTA solution (repeat step 2) while observing the change of colour of the cleaning solution. Once the colour has changed into blue-green colour, retrieve the sample from the current solution and move it to the new solution.
5. Take the old solution and dispose it in the provided waste bucket.
6. Repeat step 4 until the colour of the solution remains colourless while the sample is being immersed inside the solution. Once there is no change in the solution colour, retrieve the sample and allow it to be air cooled for 10-15 minutes. Once the sample is cooled, rinse it with distilled water for several times.
7. Once the sample is cleaned, unclamped the sample holder carefully and rinse the sample with distilled water before placing it in the oven to be dried. When the sample is dried, store the sample in the sealed container.